EXHIBIT 5

03/16/02 JC658 U.S. PTO

25 Metro Drive
Suite 700

San Jose
California 95110

T: 408-453-9200
F: 408-453-7979

Austin, TX
Newport Beach, CA
San Francisco, CA

skjerven morrill
macpherson LLP

J1017 U.S. PTO
10/101863
03/16/02

Docket No.: M-12245 US

March 16, 2002

Box Patent Application
Commissioner For Patents
Washington, D. C. 20231

Enclosed herewith for filing is a patent application, as follows:

Inventor(s): Zhang, Hongmei; Narasimhan, Mukundan; Mullapudi, Ravi; and Demaray, Richard E.
Title: **Biased Pulse DC Reactive Sputtering of Oxide Films**

- X Return Receipt Postcard
- X This Transmittal Letter (in duplicate)
- 2 page(s) Declaration For Patent Application and Power of Attorney (unsigned)
- 34 page(s) Specification (not including claims)
- 4 page(s) Claims
- 1 page Abstract
- 27 Sheet(s) of Drawings
- ☒ **Applicant(s) assert(s) entitlement to small entity status for the attached patent application**

CLAIMS AS FILED (fees computed under 37 CFR §1.9(f))

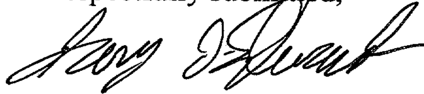
For	Number Filed			Number Extra		Rate			Basic Fee
								$	370.00
Total Claims	39	-20	=	9	x	$ 9.00	=	$	81.00
Independent Claims	5	-3	=	2	x	$42.00	=	$	84.00
☐ Fee of _____ for the first filing of one or more multiple dependent claims per application								$	
☐ Fee for Request for Extension of Time								$	

Please make the following charges to Deposit Account 19-2386:

☐ Total fee for filing the patent application in the amount of $ 525.00
☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account 19-2386.

EXPRESS MAIL LABEL NO:
EL 941 069 152 US

Respectfully submitted,



Gary J. Edwards
Attorney for Applicant(s)
Reg. No. 41,008

M-12245 US
852923 v1

Express Mail Label No.
EL 941069152 US

Biased Pulse DC Reactive Sputtering of Oxide Films

Hongmei Zhang
Mukundan Narasimhan
Ravi Mullapudi
Richard E. Demaray

Background

1. Field of the Invention

[0001] The present invention relates to deposition of oxide and oxynitride films and, in particular, to deposition of oxide and oxynitride films by pulsed DC reactive sputtering.

2. Discussion of Related Art

[0002] Deposition of insulating materials and especially optical materials is technologically important in several areas including production of optical devices and production of semiconductor devices. In semiconductor devices, doped alumina silicates can be utilized as high dielectric insulators.

[0003] The increasing prevalence of fiber optic communications systems has created an unprecedented demand for devices for processing optical signals. Planar devices such as optical waveguides, couplers, splitters, and amplifiers, fabricated on planar substrates, like those commonly used for integrated circuits, and configured to receive and process signals from optical fibers are highly desirable. Such devices hold promise for integrated optical and electronic signal processing on a single semiconductor-like substance.

[0004] The basic design of planar optical waveguides and amplifiers is well known, as described, for example, in U. S. Patent Nos. 5,119,460 and 5,563,979 to Bruce et al., 5,613,995 to Bhandarkar et al., 5,900,057 to Buchal et al., and 5,107,538 to Benton et al., to cite only a few. These devices, very generally, include a core region, typically bar shaped, of a certain refractive index surrounded by a cladding region of a lower refractive index. In the case of an optical amplifier, the core region includes a certain concentration of a dopant, typically a rare earth ion

such as an erbium or praseodymium ion which, when pumped by a laser, fluoresces, for example, in the 1550 nm and 1300 nm wavelength ranges used for optical communication, to amplify the optical signal passing through the core.

[0005] As described, for example in the patents by Bruce et al., Bhandarkar et al, and Buchal et al., planar optical devices may be fabricated by process sequences including forming a layer of cladding material on a substrate; forming a layer of core material on the layer of cladding mater; patterning the core layer using a photolighotgraphic mask and an etching process to form a core ridge; and covering the core ridge with an upper cladding layer.

[0006] The performance of these planar optical devices depends sensitively on the value and uniformity of the refractive index of the core region and of the cladding region, and particularly on the difference in refractive index, Δn, between the regions. Particularly for passive devices such as waveguides, couplers, and splitters, Δn should be carefully controlled, for example to values within about 1 %, and the refractive index of both core and cladding need to be highly uniform, for some applications at the fewer than parts per thousand level. In the case of doped materials forming the core region of planar optical amplifiers, it is important that the dopant be uniformly distributed so as to avoid non-radiative quenching or radiative quenching, for example by upconversion. The refractive index and other desirable properties of the core and cladding regions, such as physical and chemical uniformity, low stress, and high density, depend, of course, on the choice of materials for the devices and on the processes by which they are fabricated.

[0007] Because of their optical properties, silica and refractory oxides such as Al_2O_3, are good candidate materials for planar optical devices. Further, these oxides serve as suitable hosts for rare earth dopants used in optical amplifiers. A common material choice is so-called low temperature glasses, doped with alkali metals, boron, or phosphorous, which have the advantage of requiring lower processing temperatures. In addition, dopants are used to modify the refractive index. Methods such as flame hydrolysis, ion exchange for introducing alkali ions in glasses, sputtering, and various chemical vapor deposition processes (CVD) have been used to form films of doped glasses. However, dopants such as phosphorous and boron are hygroscopic, and alkalis are undesirable for integration with electronic devices. Control of uniformity of doping in CVD processes can be difficult and CVD deposited films can have structural defects

leading to scattering losses when used to guide light. In addition, doped low temperature glasses may require further processing after deposition. A method for eliminating bubbles in thin films of sodium-boro-silicate glass by high temperature sintering is described, for example, in the '995 patent to Bhandarkar et al.

[0008] Typically, RF sputtering has been utilized for deposition of oxide dielectric films. However, RF sputtering utilizes ceramic targets which are typically formed of multiple smaller tiles. Since the tiles can not be made very large, there may be a large problem of arcing between tiles and therefore contamination of the deposited film due to this arcing. Further, the reactors required for RF sputtering tend to be rather complicated. In particular, the engineering of low capacitance efficient RF power distribution to the cathode is difficult in RF systems. Routing of low capacitance forward and return power into a vacuum vessel of the reaction chamber often exposes the power path in such a way that diffuse plasma discharge is allowed under some conditions of impedance tuning of the matching networks.

[0009] Therefore, there is a need for new methods of depositing oxide and oxynitride films and for forming planar optical devices.

10141385.031402

Summary

[0010] In accordance with the present invention, a sputtering reactor apparatus for depositing oxide and oxynitride films is presented. Further, methods for depositing oxide and oxynitride films for optical waveguide devices are also presented. A sputtering reactor according to the present invention includes a pulsed DC power supply coupled through a filter to a target and a substrate electrode coupled to an RF power supply. A substrate mounted on the substrate electrode is therefore supplied with a bias from the RF power supply.

[0011] The target can be a metallic target made of a material to be deposited on the substrate. In some embodiments, the metallic target is formed from Al, Si and various rare-earth ions. A target with an erbium concentration, for example, can be utilized to deposit a film that can be formed into a waveguide optical amplifier.

[0012] A substrate can be any material and, in some embodiments, is a silicon wafer. In some

embodiments, RF power can be supplied to the wafer. In some embodiments, the wafer and the electrode can be separated by an insulating glass.

[0013] In some embodiments, up to about 10 kW of pulsed DC power at a frequency of between about 40 kHz and 350 kHz and a reverse pulse time of up to about 5 μs is supplied to the target. The wafer can be biased with up to about several hundred watts of RF power. The temperature of the substrate can be controlled to within about 10° C and can vary from about -50° C to several hundred degrees C. Process gasses can be fed into the reaction chamber of the reactor apparatus. In some embodiments, the process gasses can include combinations of Ar, N_2, O_2, C_2F_6, CO_2, CO and other process gasses.

[0014] Several material properties of the deposited layer can be modified by adjusting the composition of the target, the composition and flow rate of the process gasses, the power supplied to the target and the substrate, and the temperature of the substrate. For example, the index of refraction of the deposited layer depends on deposition parameters. Further, in some embodiments stress can be relieved on the substrate by depositing a thin film of material on a back side of the wafer. Films deposited according to the present invention can be utilized to form optical waveguide devices such as multiplexers and rare-earth doped amplifiers.

[0015] These and other embodiments, along with examples of material layers deposited according to the present invention, are further described below with respect to the following figures.

Brief Description of the Figures

[0016] Figures 1A and 1B show a pulsed DC sputtering reactor according to the present invention.

[0017] Figure 2 shows a planar view of target utilized in a reactor as shown in Figures 1A and 1B.

[0018] Figure 3 shows a cross-section view of an example target utilized in a reactor as shown in Figures 1A and 1B.

[0019] Figure 4 shows a flow chart of an embodiment of a process for depositing a film on a substrate according to the present invention.

[0020] Figure 5 shows a hysterises curve of target voltage versus oxygen flow rates for an example target in an embodiment of a reactor according to the present invention.

[0021] Figure 6 shows a photo-luminescence and lifetimes of a film deposited in a process according to the present invention as a function of after deposition anneal temperature.

[0022] Figure 7 shows the relationship between the index of refraction of a film as a function of deposited oxide layers according to the present invention and due to oxide build-up on the target.

[0023] Figure 8 shows a graph of the index of refraction of a film deposited according to the present invention as a function of the aluminum content in a composite Al/Si target.

[0024] Figure 9 shows a graph of typical indices of refraction of material layers deposited according to the present invention.

[0025] Figure 10 shows a table of indices of refraction for a silica layer deposited according to the present invention as a function of different process parameters.

[0026] Figure 11 shows the refractive indices as a function of O_2/Ar ratio utilized in an Alumina process according to the present invention.

[0027] Figure 12 shows the refractive indices as a function of DC pulsed power frequency for an Alumina layer deposited according to the present invention.

[0028] Figure 13 shows variation in the refractive index over time during repeated depositions from a single target.

[0029] Figure 14 shows variation in refractive index over time for repeated depositions from a target of another material layer according to the present invention.

[0030] Figure 15 shows the variation refractive index over time for repeated depositions from a target of another material layer according to the present invention.

[0031] Figure 16A through 16D shows a TEM film deposited according to the present invention.

[0032] Figure 17 shows the transparency of a film deposited according to the present invention.

[0033] Figure 18 shows an uppercladding layer deposited according to the present invention over a multiple-waveguide structure such that the deposited layer is substantially planarized.

[0034] Figure 19 illustrates the deposition of a film over a waveguide structure.

[0035] Figures 20 and 21 illustrate different etch and deposition rates for deposition of films as a function of the surface angle of the film.

[0036] Figure 22 illustrates calculation of the planarization time for a particular deposition process.

[0037] Figures 23 through 25 through illustrate adjustment of process parameters in order to achieve planarization of a film deposited over a waveguide structure according to the present invention.

[0038] Figure 26 shows the gain characteristics of an erbium doped waveguide amplifier formed of films depositions according to the present invention.

[0039] Figures 27 shows gain, insertion loss of a waveguide with an active core deposited according to the present invention.

[0040] Figure 28 shows up-conversion constants, and lifetimes of the active core layer of Figure 27 deposited according to the present invention.

[0041] Figure 29 shows drift in the index of refraction with subsequent depositions for films deposited from a target according to the present invention.

[0042] Figure 30 shows drift in the photoluminescence with subsequent depositions according to the present invention.

[0043] Figure 31 shows drift in the excited state lifetime with subsequent depositions according to the present invention.

[0044] Figure 32 shows stabilization of the index of refraction in subsequent depositions.

[0045] Figure 33 shows the index of refraction of a film formed from a pure silicon target as a

function of the ratio of O_2/N_2 in the process gas.

[0046] In the figures, elements having the same designation have the same or similar function.

Detailed Description

[0047] Reactive DC magnetron sputtering of nitrides and carbides is a widely practiced technique, but the reactive dc magnetron sputtering of nonconducting oxides is done rarely. Films such as aluminum oxide are almost impossible to deposit by conventional reactive DC magnetron sputtering due to rapid formation of insulating oxide layers on the target surface. The insulating surfaces charges up and result in arcing during process. This arcing can damage the power supply, produce particles and degrade the properties of deposited oxide films.

[0048] RF sputtering of oxide films is discussed in Application Serial No. 09/903,050 (the '050 application) by Demaray et al., entitled "Planar Optical Devices and Methods for Their Manufacture," assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, targets that can be utilized in a reactor according to the present invention are discussed in U.S. Application serial no. {Attorney Docket No. M-12247 US} (the '247 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. A gain-flattened amplifier formed of films deposited according to the present invention are described in U.S. Application serial no. {Attorney Docket No. M-12652 US} (the '652 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, a mode size converter formed with films deposited according to the present invention is described in U.S. Application serial no. {Attorney Docket No. M-12138 US} (the '138 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety.

[0049] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering of material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for

example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These Komatsu reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[0050] Apparatus 10 includes a target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. Magnet 20 is scanned across the top of target 12.

[0051] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering in apparatus 10.

[0052] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this example supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. The reverse voltage is 10% of the negative target voltage. Utilization of other power supplies will lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[0053] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 is a 2 MHz RF power supply, for example can be a Nova-25 power supply made by ENI, Colorado Springs, Co.

[0054] Therefore, filter 15 is a 2 MHz band rejection filter. In some embodiments, the band

width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[0055] However, both RF and pulsed DC deposited films are not fully dense and most likely have columnar structures. These columnar structures are detrimental for optical wave guide applications due to the scattering loss caused by the structure. By applying a RF bias on wafer 16 during deposition, the deposited film can be dandified by energetic ion bombardment and the columnar structure can be substantially eliminated.

[0056] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimension about 150 mm by 600 mm.

[0057] A top down view of magnet 20 and wide area target 12 is shown in Figure 2. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, where physical and chemical uniformity provide refractive index uniformity, for example. Figure 2 indicates that region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

[0058] In some embodiments, magnet 20 extends beyond area 52 in one direction, the Y direction in Figure 2, so that scanning is necessary in only one direction, the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform

sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[0059] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission or absorptivity.

[0060] Target 12 can be formed of any materials, but is typically metallic materials such as, for example, combinations of Al and Si. Therefore, in some embodiments, target 12 includes a metallic target material formed from intermetalic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetalics. *See* the '247 application.

[0061] In several embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. Figure 3A shows an embodiment of target 12 formed with individual tiles 30 mounted on a cooled backplate 25. In order to form a wide area target of an alloy target material, the consolidated material of individual tiles 30 should first be uniform to the grain size of the powder from which it is formed. It also should be formed into a structural material capable of forming and finishing to a tile shape having a surface roughness on the order of the powder size from which it is consolidated. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles 30, for example between 2 to 20 individual tiles 30. Tiles 30 are finished to a size so as to provide a margin of non-contact, tile to tile, 29 in Figure 3A, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes between adjacent ones of tiles 30. The distance between tiles 30 of target 12 and the dark space anode or ground shield 19, in Figure 1B can be somewhat larger so as to provide non contact assembly or provide for thermal expansion tolerance during process chamber conditioning or

operation.

[0062] Several useful examples of target 12 that can be utilized in apparatus 10 according to the present invention include the following targets compositions: (Si/Al/Er/Yb) being about (57.0/41.4/0.8/0.8), (48.9/49/1.6/0.5), (92/8/0/0), (60/40/0/0), (50/50/0/0), (65/35/0/0), (70/30/0,0), and (50,48.5/1.5/0) cat. %, to list only a few. These targets can be referred to as the 0.8/0.8 target, the 1.6/.5 target, the 92-8 target, the 60-40 target, the 50-50 target, the 65-35 target, the 70-30 target, and the 1.5/0 target, respectively. The 0.8/0.8, 1.6/0.5, and 1.5/0 targets can be made by pre-alloyed targets formed from an atomization and hot-isostatic pressing (HIPing) process as described in the '247 application. The remaining targets can be formed, for example, by HIPing. Targets formed from Si, Al, Er and Yb can have any composition. In some embodiments, the rare earth content can be up to 10 cat. % of the total ion content in the target. Rare earth ions are added to form active layers for amplification. Targets utilized in apparatus 10 can have any composition and can include ions other than Si, Al, Er and Yb, including: Zn, Ga, Ge, P, As, Sn, Sb, Pb, Ag, Au, and rare earths: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy Ho, Er, Tm Yb and Lu.

[0063] Optically useful materials to be deposited onto substrate 16 include oxides, fluorides, sulfides, nitrides, phosphates, sulfates, and carbonates, as well as other wide band gap semiconductor materials. To achieve uniform deposition, target 12, itself can be chemically uniform and of uniform thickness over an extended area.

[0064] Target 12 can be a composite target fabricated from individual tiles, precisely bonded together on a backing plate with minimal separation, as is discussed further with respect to Figure 3. In some embodiments, the mixed intermetalllics can be plasma sprayed directly onto a backing plate to form target 12. The complete target assembly can also includes structures for cooling the target, embodiments of which have been described in U. S. Patent No. 5,565,071 to Demaray et al, and incorporated herein by reference.

[0065] Substrate 16 can be a solid, smooth surface. Typically, substrate 16 can be a silicon wafer or a silicon wafer coated with a layer of silicon oxide formed by a chemical vapor deposition process or by a thermal oxidation process. Alternatively, substrate 16 can be a glass, such as Corning 1737 (Corning Inc., Elmira, NY), a glass-like material, quartz, a metal, a metal oxide, or a plastic material. Substrate 16 can be supported on a holder or carrier sheet that may

be larger than substrate 16. Substrate 16 can be electrically biased by power supply 18.

[0066] In some embodiments, the area of wide area target 12 can be greater than the area on the carrier sheet on which physically and chemically uniform deposition is accomplished. Secondly, in some embodiments a central region on target 12, overlying substrate 16, can be provided with a very uniform condition of sputter erosion of the target material. Uniform target erosion is a consequence of a uniform plasma condition. In the following discussion, all mention of uniform condition of target erosion is taken to be equivalent to uniform plasma condition. Uniform target erosion is evidenced by the persistence of film uniformity throughout an extended target life. A uniformly deposited film can be defined as a film having a nonuniformity in thickness, when measured at representative points on the entire surface of a substrate wafer, of less than about 5 % or 10%. Thickness nonuniformity is defined, by convention, as the difference between the minimum and maximum thickness divided by twice the average thickness. If films deposited from a target from which more than about 20 % of the weight of the target has been removed continue to exhibit thickness uniformity, then the sputtering process is judged to be in a condition of uniform target erosion for all films deposited during the target life.

[0067] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12, can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations).

[0068] In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0069] Other approaches to providing a uniform condition of sputter erosion rely on creating a large uniform magnetic field or a scanning magnetic field that produces a time-averaged,

uniform magnetic field. For example, rotating magnets or electromagnets can be utilized to provide wide areas of substantially uniform target erosion. For magnetically enhanced sputter deposition, a scanning magnet magnetron source can be used to provide a uniform, wide area condition of target erosion.

[0070] As illustrated in FIG. 1A, apparatus 10 can include a scanning magnet magnetron source 20 positioned above target 12. An embodiment of a scanning magnetron source used for dc sputtering of metallic films is described in U. S. Patent No. 5,855,744 to Halsey, et. al., (hereafter '744), which is incorporated herein by reference in its entirety. The '744 patent demonstrates the improvement in thickness uniformity that is achieved by reducing local target erosion due to magnetic effects in the sputtering of a wide area rectangular target. As described in the '744 patent, by reducing the magnetic field intensity at these positions, the local target erosion was decreased and the resulting film thickness nonuniformity was improved from 8%, to 4%, over a rectangular substrate of 400 x 500 mm.

[0071] The process gas utilized in reactor 10 includes an inert gas, typically argon, used as the background sputtering gas. Additionally, with some embodiments of target 12, reactive components such as, for example, oxygen may be added to the sputtering gas. Other gasses such as N_2, NH_3, CO, NO, CO_2, halide containing gasses other gas-phase reactants can also be utilized. The deposition chamber can be operated at low pressure, often between about .5 millitorr and 8-10 millitorr. Typical process pressure is below about 3-5millitorr where there are very few collisions in the gas phase, resulting in a condition of uniform "free molecular" flow. This ensures that the gas phase concentration of a gaseous component is uniform throughout the process chamber. For example, background gas flow rates in the range of up to about 200 sccm, used with a pump operated at a fixed pumping speed of about 50 liters/second, result in free molecular flow conditions.

[0072] The distance d, in Figure 1A, between target 12 and substrate 16 can, in some embodiments, be varied between about 4 cm and about 9 cm. A typical target to substrate distance d is about 6 cm. The target to substrate distance can be chosen to optimize the thickness uniformity of the film. At large source to substrate distances the film thickness distribution is dome shaped with the thickest region of the film at the center of the substrate. At close source to substrate distance the film thickness is dish shaped with the thickest film formed at the edge of the substrate. The substrate temperature can be held constant in the range of about -40 °C to

10140785.031502

about 550°C and can be maintained at a chosen temperature to within about 10 °C by means of preheating substrate 16 and the substrate holder prior to deposition. During the course of deposition, the heat energy impressed upon the substrate by the process can be conducted away from substrate 16 by cooling the table on which substrate 16 is positioned during the process, as known to those skilled in the art. The process is performed under conditions of uniform gas introduction, uniform pumping speed, and uniform application of power to the periphery of the target as known to skilled practitioners.

[0073] The speed at which a scanning magnet 20 can be swept over the entire target can be determined such that a layer thickness less than about 5 to 10 Å, corresponding roughly to two to four monolayers of material, is deposited on each scan. Magnet 20 can be moved at rates up to about 30 sec/one-way scan and typically is moved at a rate of about 4 sec/one-way scan. The rate at which material is deposited depends on the applied power and on the distance d, in Figure 1A, between the target 12 and the substrate 16. For deposition of optical oxide materials, for example scanning speeds between about 2 sec/one-way scan across the target to 20-30 sec/scan provide a beneficial layer thickness. Limiting the amount of material deposited in each pass promotes chemical and physical uniformity of the deposited layer.

[0074] Substrate bias has been used previously to planarize RF sputtered deposited quartz films. A theoretical model of the mechanism by which substrate bias operates, has been put forward by Ting et al. (J. Vac. Sci. Technol. 15, 1105 (1978)). When power is applied to the substrate, a so-called plasma sheath is formed about the substrate and ions are coupled from the plasma. The sheath serves to accelerate ions from the plasma so that they bombard the film as it is deposited, sputtering the film, and forward scattering surface atoms, densifying the film and eliminating columnar structure. The effects of adding substrate bias are akin to, but more dramatic than, the effects of adding the low frequency RF component to the sputter source.

[0075] Biasing substrate 16 results in the deposited film being simultaneously deposited and etched. The net accumulation of film at any point on a surface depends on the relative rates of deposition and etching, which depend respectively, on the power applied to the target and to the substrate, and to the angle that the surface makes with the horizontal. The rate of etching is greatest for intermediate angles, on the order of 45 degrees, that is between about 30 and 60 degrees.

[0076] Powers to target 12 and substrate 16 can be adjusted such that the rates of deposition and etching are approximately the same for a range of intermediate angles. In this case, films deposited with bias sputtering have the following characteristics. At a step where a horizontal surface meets a vertical surface, the deposited film makes an intermediate angle with the horizontal. On a surface at an intermediate angle, there will be no net deposition since the deposition rate and etch rate are approximately equal. There is net deposition on a vertical surface.

[0077] Target 12 can have an active size of about 675.70 X 582.48 by 4 mm, for example, in a AKT-1600 based system in order to deposit films on a substrate 16 that is about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C. The distance between target 12 and substrate 16 can be between 3 and 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate of between about 30 to about 100 sccm while the pressure in the chamber of apparatus 10 can be held at below about 2 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan.

[0078] Therefore, any given process utilizing apparatus 10 can be characterized by providing the power supplied to target 12, the power supplied to substrate 16, the temperature of substrate 16, the characteristics and constituents of the reactive gasses, the speed of the magnet, and the spacing between substrate 16 and target 12.

[0079] Sputtered oxide films according to some embodiments of the present invention can be deposited onto a Si wafer or thermal oxide wafers at pressure of between about 3 and about 6 mTorr. The ratio of O_2/Ar gas flow can be set at a value to ensure that target 12 is operating within a poison mode. The poison mode is defined as the ratio where the oxide is etched from the surface of target 12 as fast as the oxide layer is formed. Operating in the poison mode results in the stoichiometric film. Sub-stoichiometric oxides may not be optically transparent. The pulsing frequency range for power supply 14 can be from about up to about 250 KHz. The frequency 40 KHz is approximately the lowest frequency at which no arcing will occur during deposition in, for example, the AKT 1600 based system. The reverse pulsing time is determined by the amount of arcing generated during the process. Longer reverse time means longer discharge time and thus less arcs. However, if the reverse time is too long, the deposition rate will decrease. Power supply 18 is a 2 MHz RF power supply operated at powers up to several

hundred Watts.

[0080] Figure 4 shows an embodiment of a process procedure 400 performed on apparatus 10. In step 401, the target is prepared for the deposition. In some embodiments, target 12 can be cleaned by pure Ar sputtering. In other words, apparatus 10 is operated with pure Ar gas only (referred to as the metal mode) in order to sputter away a surface layer of target 12.

[0081] Figure 7 shows the typical drift in the index of refraction with deposition of oxide layers for several different targets over different runs for each target. In Figure 7, the compositions of the target materials utilized in target 12 for the depositions shown are as follows: Si: 60 cat. % and Al: 40 cat. %; Si: 50 cat. % and Al: 50 cat. %; Si: 85 cat. % and Al: 15 cat. %; Si: 35 cat. % and Al: 65 cat. %; and Si: 92 cat. % and 8 cat. %. Each deposition was operated under the same process parameters: 4.5 kW of pulsed DC power at 200 kHz with a reverse time of 2.3 μs applied to target 12, O_2 flow at 44 sccm, Ar flow at 30 sccm introduced to apparatus 10, 100 W of bias power at 2 MHz applied to substrate 16, the temperature of substrate 16 held at 200° C, and the distance between substrate 16 and target 12 being set at 6 cm. For each target measured, the index drifted up during repeated utilization.

[0082] Figure 8 shows the relationship between the index of refraction of a film deposited according to the present invention and the amount of aluminum in the composite target. As can be seen from Figure 8, the index of refraction of the deposited film depends strongly on the aluminum content. Therefore, as the aluminum in a metal target is depleted, the index of refraction drifts. In some embodiments, the ratio of Ar and O_2 utilized in the process can be maintained to provide films of uniform index over a large number of depositions on the target.

[0083] Reactive sputtering from a metal or metallic alloy target 12 can be characterized by two modes of operation. In the first mode, which is sometimes referred to as the 'metallic mode' the surface of target 12 is substantially metallic. This mode is characterized by a small addition of reactive gas to the inert gas flow of apparatus 10 as well as a higher impedance magnetron discharge. It is also characterized by incomplete oxidation of film deposited on substrate 16 and therefore higher index films. As the proportion of reactive to inert gas is increased, the sputter voltage at target 12 begins to fall at constant power.

[0084] Figure 5 shows the voltage on target 12 of an embodiment of apparatus 10 according to

the present invention as a function of process gas constitution. In the example illustrated in Figure 5, for example, a metallic target with composition .8 cat. % Er, .8 cat. % Yb, 57.4 cat. % Si and 41 cat. % Si, which can be formed as described in the '247 application, was sputtered in an embodiment of apparatus 10 based on the AKT-1600 PVD system with 6 kW of pulsed DC power at a frequency of 120 kHz and a reverse time of 2.3 micro seconds. The Argon gas flow was set at 60 sccm and the Oxygen gas flow was varied from zero up to 40 sccm. For more details regarding this deposition, see Example 1 below.

[0085] As shown in Figure 5, the voltage on target 12 during deposition (the "target voltage") was constant at about 420 Volts for oxygen flow rates up to about 20 sccm. This is clearly the metallic mode of operation for this embodiment of target 12. Films deposited in this range of oxygen flow are characterized as metallic with an oxygen content that increases with oxygen flow rate during deposition. As the oxygen flow is increased up to about 26 sccm, the voltage on target 12 begins to decrease, indicating that the surface of target 12 is beginning to form an oxide layer. The oxide layer on the surface of target 12 has a higher secondary electron yield under the influence of the Argon ion flux. The additional electron flux to the magnetron electron trap increases the ion production in the plasma, which, in turn, decreases the impedance of the plasma discharge in apparatus 10.

[0086] At slightly higher oxygen flow during deposition, the oxide layer on target 12 forms a continuous layer and the voltage of target 12 during deposition falls rapidly to the range of about 190 to about 270 Volts, indicating complete coverage of the surface of target 12 with an oxide that is at least as thick as the material removed during one scan of the magnetron. Under this condition, the rate of oxide formation on the surface of target 12 equals or exceeds the rate of sputter removal of the surface of target 12 by the moving magnetron 20. This condition is sometimes referred to as the 'poisoned mode'.

[0087] Under steady state DC voltage conditions, the oxide layer on target 12 soon charges up, leading to reduced rate of sputtering and increased micro-arc discharging in apparatus 10. This discharging leads to particulation of the oxide layer on target 12, which degrades the quality of a film deposited on substrate 16. In the example shown with Figure 5, the negative going DC Voltage is reduced at a frequency of 120 kHz to a positive value for a period of about 2.3 micro seconds per cycle, allowing charge neutralization of the surface of target 12, increasing the steady state sputter and deposition rates as well as decreasing the rate of micro-arcing.

[0088] In the case of a magnetron configuration of magnet 20 having a significant deep local target erosion (rather than a configuration of magnet 20 described above which yields uniform target erosion), the change in the target voltage of target 12 is more gradual with increasing oxygen flow since it is more difficult to establish an oxide condition at the center of an intense region of local erosion. The resulting deposited film, however, will be rich in metallic sputtered flux to the substrate in the region of higher sputter erosion, leading to non uniform stoicheometry and non-uniform indices of refraction in a film deposited on substrate 16. In the case of a scanning magnetron 20 with uniform target erosion, the change in the surface condition from metallic to poisoned is more abrupt, as the formation rate of the oxide increases to equal the sputter removal of the oxide over a wide area of the target. In this case, there is uniform distribution of sputtered oxide from the target. Uniform stoicheometry and uniform indices of refraction result for the film deposited on substrate 16.

10105863.051502

[0089] Figure 8 shows the range of indices of refraction of films deposited for targets of differing silica and alumina compositions, as deposited and after a subsequent anneal step. In the case of a pure silicon target, the as-deposited index of refraction can be as high as 3.4 for pure amorphous silicon. In Figure 8, pure silica films (zero Al%) can be deposited with a reactive pulsed DC and substrate bias deposition according to the present invention with substantially complete oxygen stoicheometry, so as to approximate monolithic amorphous silica. The index of refraction of such films decreases with a subsequent heat treatment of between about 700-900° C, indicating somewhat more complete oxidation reaction of the material of the film together with some degree of stress relaxation of the film deposited on substrate 16.

[0090] At the opposite extreme, a pure aluminum embodiment of target 12 (100% Al) can be utilized to deposit films on substrate 16 under similar process conditions as is utilized to deposit pure silica films on substrate 16. In the case of the pure aluminum reactive deposition, the dependence of the index of refraction of the film deposited on substrate 16 on oxygen flow as well as on the frequency of the pulsed DC process can be examined. As a result, a larger range of effective index of refraction is achieved together with a reduced or zero dependence of the index on the subsequent anneal process. Six targets having differing aluminum composition were utilized to evaluate the index of refraction of sputtered films on substrate 16 of related composition. The largest change of index with the sputtering conditions is achieved for composition near the middle of the Al/Si composition range (about 50% Al and 50% Si).

[0091] Figure 7 shows the change in film index for oxide films for several embodiments of target 12 and processes with an initial 30 minutes of Argon only sputtering, followed by continuous deposition with an oxygen flow rate sufficient for operation in the poisonous mode. Note that the rate of increase in the index of refraction of a resulting film deposited on substrate 16 with continuous poisoned mode deposition is proportional to the concentration of aluminum in the composition of target 12. This result is due to the depletion of the aluminum from the target surface during the metallic sputtering or pre-condition process. The aluminum in target 12 is preferentially sputtered over the silicon in target 12, leaving the surface of target 12 rich in silicon. At the onset of poisoned mode sputtering, the film deposited on substrate 16 is rich in silica and demonstrates a systematic and reproducible decrease in index of refraction. During continuous poisoned mode deposition, the silicon rich surface of target 12 can be sputtered away and the aluminum portion substantially returned to the bulk composition of target 12. Consequently, a metallic pre-condition step can be utilized to achieve a subsequent process for the deposition of a film having an increasing index of refraction under conditions of oxide/metal stoicheometry.

10951075 .031701

[0092] In step 402 of Figure 4, substrate 16 is prepared. Substrate 16 can be mounted on carrier sheet 17 and placed in apparatus 10. In step 403, gas flow parameters are adjusted for the particular deposition to be performed. The constituency and flow rates of the process gas are fixed. In some embodiments, the ratio of Ar and O_2, for example, can be set and the flow rate of each gas set. Further, the combination of flow rate and vacuum system of apparatus 10 determines the pressure during deposition in apparatus 10.

[0093] In step 404, the substrate temperature is set. Substrate 16 may be brought to temperature over a period of time. In step 405, the scan characteristics of magnet 20 are fixed. In step 406, the power setting for power supply 18 is set. Finally, in step 407, the parameters of pulsed DC power supply 14 is set, including the power, frequency, and reverse pulsing time. In step 408, then, a film that depends on the parameters of reactor apparatus 10 is deposited on substrate 16. In some embodiments, films deposited by procedure 400 are thermally annealed after deposition.

[0094] Figure 4 illustrates an example deposition process only. Embodiments of deposition processes according to the present invention can be performed in various different orders.

[0095] Figure 9 shows a chart of various deposition parameters according to the present invention for various embodiments of target 12 and the indices of refraction, both before and after an anneal step, for the resulting deposited film on substrate 16. Each deposition was accomplished with an embodiment of apparatus 10 based on the AKT 1600 PVD reactor. Anneals were accomplished at 725° C for 30 min. Specific examples of particular depositions and characteristics of the resulting films deposited on substrate 16 are further discussed below.

[0096] Figure 10 shows the dependence of the index of refraction of silica layers deposited according to the present invention with process conditions. Figure 11 shows the dependence of index of refraction on the O2/Ar flow ratio for the deposition of pure alumina according to the present invention. Figure 12 shows the dependence of index for pure alumina films on the frequency of the pulsed DC power applied to target 12. Both parameters can be utilized to reliably control the index of refraction of films deposited on substrate 16 over a range of index values without the use of an additional cationic species, a so called 'dopant'. A third process parameter that can be utilized to adjust the index of refraction of a film deposited on substrate 16 is the bias power applied to substrate 16. Increasing the oxygen flow ratio, the frequency of the pulsed DC power applied to target 12 or the bias power applied to substrate 16 will systematically increase the index of refraction of the alumina film deposited on substrate 16. In the case of pure alumina films, minor to no change in the index occurs due to a subsequent anneal process.

[0097] Figure 13 shows the index of refraction of a film deposited on substrate 16 from an embodiment of target 12 with about 92 cat. % of Si and about 8 cat. % of Al for a series of sequential depositions in an embodiment of apparatus 10 based on the AKT 4300 PVD reactor, each following a metallic process condition. For constant high oxygen flow conditions, a small upward trend in the index of refraction is observed. As is generally true, the index of films deposited with higher substrate bias power is systematically lower than films deposited without substrate bias.

[0098] Figure 14 shows the upward trend of the index of refraction after metallic mode precondition of an embodiment of target 12 having composition of about 83 cat. % Si and about 17 cat. % Al for a series of depositions in an embodiment of apparatus 10 based on the AKT 1600 PVD reaction. As is shown in Figure 14, longer metallic preconditioning of target 12 results in the index of refraction of the films deposited on substrate 16 having a higher rate of

10101863.031502

increase than for cases with less prolonged metallic preconditioning of target 12. The vertical lines on Figure 14 indicate places where target 12 was preconditioned with only Ar for the indicated periods of time. Figure 15 shows a decrease in the change in index for sequential films with this embodiment of target 12 deposited with reduced oxygen flow rates at a constant total pressure. A flow rate for oxygen was determined so that the run to run variation for the index of refraction of the film deposited on substrate 16 from this target was about .0001 (see the circled data points on the graph of Figure 15) which is similar to the variance of the index over the entire wafer of substrate 16, which is about 70 parts per million.

[0099] In some embodiments, films deposited by a pulsed DC biased method according to the present invention are uniformly amorphous throughout their thickness. As has been discussed above, biasing of substrate 16 leads to densification and uniformity in the deposited film. Figures 16A through 16D show a TEM photograph of a film 1601 deposited according to the present invention. Further, diffraction patterns shown in Figures 16B, 16C and 16D at points a, b and c, respectively, in deposited film 1601 show that the film is ammorphous through the thickness of the film. The diffraction patterns of Figures 16B, 16C and 16D show no effects of crystallization. Further, the smoothness of the surface of film 1601 indicates a defect free film. The film deposited in Figure 16A is deposited with an 0.8/0.8 target (i.e., a target having the composition 52.0 cat. % of Si, 41.0 cat. % of Al, 0.8 cat. % of Er and 0.8 cat. % of Yb). The film is deposited at 6 kW of 120 kHz pulsed DC power with a reverse time of 2.3 μs. The Argon and Oxygen flow rates are 60 sccm and 28 sccm, respectively. Substrate 16 is biased with 100 W of power.

[0100] Figure 17 shows the optical loss per centimeter, measured at 1310 nm, using a three prism coupling to the so called slab mode of the film on a 10 micron oxide, silicon wafer. As deposited the biased, pulsed DC film from a 60 cat. % Si and 40 cat. %Al film demonstrated about .1dB/cm loss. After an 800° C anneal in air, the loss was less than the measurement sensitivity of the prism coupling method. This data clearly demonstrates that films deposited according to embodiments of the present invention can be used for the purpose of constructing low loss planar light wave circuits.

[0101] Deposition of films according to the present invention can be utilized to deposit cladding layers, active core layers, and passive core layers of an optical amplifier structure or optical

waveguide structure. In some applications, for example multiplexer structures, the separation between adjacent waveguides can be small, for example about 8 μm. In some embodiments, the deposition parameters of the upper cladding layer can be adjusted to not only adjust the index of refraction of the layer, but also to insure that the spacing between adjacent waveguides is small.

[0102] Figure 18 shows an example planarization deposition over a multiplexer structure. In the particular example of upper cladding layer 1803 shown in Figure 18, the deposition parameters from a 92 cat. % Si and 8 cat. % Al is: 5.5 Kw of Pulsed DC power applied at 200 KHz with 2.2 μs of reverse time, gas flow of 75 sccm Ar and 100 sccm O_2, a substrate bias of 650 W (at 2 MHz), and a substrate temperature of 200 °C. Layer 1803 was deposited with an AKT 4300 based embodiment of apparatus 10. As shown in Figure 18, the layer thickness in areas other than over waveguide structures 1801 and 1802 is 11.4 μm. Waveguide structures 1801 and 1802 are 8.20 μm high waveguides and separated by 6.09 μm at the base and by 8.40 μm at their top. In Figure 18, the undercladding layer 1804 is about 1.98 μm thick.

[0103] Figure 19 illustrates deposition of material over a structure. Upper cladding layer 1803, in region 1901, will be angled from the horizontal by an angle θ. The deposition and etching rates of a deposited layer depends on the angle θ. Figures 20 and 21 illustrate different cases of deposition and etch rates as a function of the angle θ. The relationship between the rate of deposition and the etch rates can be adjusted by adjusting the deposition parameters. For example, the bias power to substrate 16 can be adjusted to control the relationship between the etch rates and deposition rates of material.

[0104] Figure 22 illustrates deposition rates over a structure 2201 as a function of time. In Figure 2201, h is the thickness deposited over structure 2201. The planarization when layer 1803 becomes flat.

[0105] The time for planarization can be estimated as

$$t_p = \frac{\frac{W}{2}\tan\alpha + H}{a_{flat} - \frac{a_{\min}}{\cos\alpha}},$$

where W is the width of structure 2201, H is the height of structure 2201, a_{flat} refers to the

accumulation rate on the flat surface, a_{min} refers to the accumulation rate on the minimum accumulation slope, and α is the surface angle from the horizontal plane of the minimum accumulation slope.

[0106] Figure 23 shows a deposited film 1803 as shown in Figure 18, except that the bias power to substrate 16 is set to 400 W instead of 650 W. As can be seen in Figure 23, a keyhole 2301 is formed with an incomplete filling of uppercladding layer 1803 between structures 1801 and 1802. Deposition of uppercladding layer 1803 substantially follows the trends illustrated in Figures 19 through 22.

[0107] Figure 24 shows deposition as shown in Figure 18, except that the bias power to substrate 16 is set to 600 W instead of 650 W. As can be seen in Figure 24, keyhole 2301 has closed leaving a small line defect 2401 in the fill.

[0108] Figure 28 shows deposition as shown in Figure 18, except that the bias power to substrate 16 is set to 900 W instead of 650 W. As can be seen in Figure 28, the etch rate has been increased to such an extent that the corners of structures 1801 and 1802 have been etched to form slopes 2501 and 2502, respectively.

[0109] Therefore, as illustrated in figures 18 through 25, an uppercladding layer can be deposited in accordance with the present invention such that it fills the space between adjacently placed waveguides. In general, the parameters can be optimized for index control and the bias power to substrate 16 can be adjusted for fill. In some embodiments, other parameters (e.g., the constituency of process gas, frequency and power of pulsed DC power source 14, and other parameters) in order to adjust the deposition and etch rates and thereby effectively planarize the structure as described.

[0110] Therefore, depositions of various films in embodiments of apparatus 10 according to the present invention with several embodiments of target 12 and the effects on index of refraction, uniformity of films, and fill characteristics of varying several of the process parameters has been discussed above. In some embodiments, stress effects due to wafer bowing of substrate 16 can also be reduced. Wafer bowing of substrate 16 can be reduced, reducing the stress in a film deposited on substrate 16, by, for example, depositing a film on the backside of substrate 16 before deposition of a film on substrate 16. In some embodiments, a film having a similar

10140186.031502

thickness of a similar layer of material can be deposited on backside of substrate 16 prior to deposition of the film on substrate 16 according to the present invention. The wafer bowing resulting from differing thermal expansions of the film and substrate 16 is therefore countered by a similar stress from another film deposited on the backside of substrate 16.

[0111] Several specific examples film depositions utilizing apparatus 10 are discussed below. Further, examples of optical amplifiers produced utilizing the ceramic tiles according to the present invention are presented. These examples are provided for illustrative purposes only and are not intended to be limiting. Unless otherwise specified, apparatus 10 utilized in the following examples was based on the AKT 1600 reactor. Further, unless otherwise specified, the temperature of substrate 16 was held at about 200° C and the distance between substrate 16 and target 12 was 4 s/scan. The separation between substrate 16 and target 12 is about 6 cm.

10101653.031502

EXAMPLE 1

[0112] An AKT 1600 based reactor can be utilized to deposit a film. In this example, a wide area metallic target of dimension 550X 650 mm with composition (Si/Al/Er/Yb) being about 57.0 cat. % Si, 41.4 cat. % Al, 0.8 cat. % Er, and 0.8 cat. % Yb (a ".8/.8" target) was fabricated as described in the '247 patent.

[0113] In step 402, a 150 mm P-type silicon wafer substrate was placed in the center of a 400x500 mm glass carrier sheet 17. Power supply 14 was set to supply 6000 watts of pulse DC power at a frequency of 120KHz with a reverse pulsing time of about 2.3us. Magnet 20, which is a race-track shaped magnet of approximate dimension 150mmx600mm, was swept over the backside of the target at a rate of about 4 seconds per one-way scan. The temperature of substrate 16 was held at 200C and 100W of 2 MHz RF power was applied to substrate 16. The target 12 to substrate 16 distance was about 6.5 cm. The sputtering gas was a mixture of Argon and Oxygen. Substrate 16 and carrier 17 was preheated to 350° C for at least 30min prior to deposition. The active film was deposited in the poison mode. Deposition efficiency was approximately 1um/hr.

[0114] Figure 5 shows the hysteresis curve of this particular embodiment of target 12. When target 12 under goes the transition from metallic to poison mode, the target voltage drops from

an average of about 420V to an average of about 260V. Before each film deposition, in step 401, target 12 is cleaned by pure Argon sputtering in the metallic mode. Then target is then conditioned in poison mode with the oxygen flow much higher than the flow required at the transition region.

[0115] Tables 1A through 1C shows some effects on the deposited films of depositions with the 0.8/0.8 target under different operating conditions. Table 1A includes photoluminescence (pumped at 532 nm) and index of refraction for films deposited on substrate 16 with different Ar/O_2 gas flow ratios with no bias power applied to substrate 16.

10169563 .031502

Table 1A

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
6	30/42	200	2.3	0	1973	1.5142
6	30/36	200	2.3	0	2358	1.5215
6	60/30	200	2.3	0	3157	1.5229
6	60/28	200	2.3	0	3421	1.5229

[0116] Table 1B shows the variation in photoluminescence (pumped at 532 nm) and index of refraction of the film deposited on substrate 16 with deposition processes having with the same Ar/O_2 ratios but different pulsed DC power frequencies from power supply 14.

Table 1B

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
3	60/28	100	2.3	100	1472	1.5146
4	60/28	75	3.5	100	2340	1.5189
6	60/28	120	2.3	100	5178	1.5220

[0117] Table 1C shows the photoluinescence and index as deposited where the bias power to substrate 16 is varied.

Table 1C

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
6	60/28	200	2.3	0	3657	1.5230
6	60/28	200	2.3	100	2187	1.5244
6	60/28	200	2.3	200	3952	1.5229
6	60/28	200	2.3	300	5000	1.5280

[0118] The photoluminescence values can be measured with a Phillips PL-100. The deposited film can be pumped with a 532 nm laser and the luminescence at 980 is measured. The index is the index of refraction. Typically, films deposited are annealed in order to activate the erbium. Figure 6 shows the photoluminescence and lifetime versus anneal temperature for a typical film deposited as described in this example.

10106963 . 031502

EXAMPLE 2

[0119] A waveguide amplifier can be deposited according to the present invention. An embodiment of target 12 having composition 57.4 cat. % Si, 41.0 cat. % Al, 0.8 cat. % Er 0.8 cat. % Yb (the ".8/.8 target") can be formed as disclosed in the '245 application. The Er-Yb (0.8/0.8) co-doped Alumino-Silicate film was deposited onto a 6 inch wafer of substrate 16 which includes a 10 μm thick thermal oxide substrate, which can be purchased from companies such as Silicon Quest International, Santa Clara, CA. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The power supplied to target 12 during conditioning was kept at about 6 kW.

[0120] An active core film was then deposited on substrate 16. The thickness of the deposited film is approximately 1.2 μm. The deposition parameters are shown in Table 2.

Table 2.

. Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)
6	60/28	120	100	2.3

[0121] A straight waveguide pattern can then formed by standard photolithography techniques. The active core was etched using reactive ion etch followed by striping and cleaning. Next, a 10 µm top cladding layer is deposited using a similar deposition process according to the present invention. An embodiment of target 12 with composition 92 cat. % Si and 8 cat. % Al as shown in Figure 9 to form the top cladding layer. The index difference between the top cladding layer and the active layer is about 3.7%. The amplifier is then annealed at 725° C for about 30 min (see Figure 6, for example).

[0122] The erbium excited-state lifetime and the up-conversion coefficient were measured to be 3ms and 4.5 x 10^{-18} cm^3/s, respectively. A net gain of about 4dB for small signal (about –20 dBm) with fiber to waveguide and to fiber coupling was obtained. Waveguide length was 10cm and the width was about 1.5 to 8 µm. The coupling loss between the fiber and the waveguide is 3-4 dB/facet, and passive excess loss is 0.1-0.2 dB/cm for 3um waveguide. The waveguide was both co- and counter pumped with 150 mW 980nm laser per facet.

10108593.031502

EXAMPLE 3

[0123] This example describes production of a dual core Erbium/Yttrbium co-doped amplifier according to the present invention. In one example, substrate 16 is a silicon substrate with an undercladding layer of thermally oxidized SiO_2 of about 15 µm thick. Substrate 16 with the thermal oxide layer can be purchased from companies such as Silicon Quest International, Santa Clara, CA. A layer of active core material is then deposited on substrate 16 with a Shadow Mask as described in the '138 application. Use of a shadow mask results in a vertical taper on each side of a finished waveguide which greatly enhances the coupling of light into and out of the waveguide.

[0124] Active core layer is deposited from a 0.8/0.8 target as described in the '247 application having composition 57.4 cat. % Si, 41.0 cat. % Al, 0.8 cat. % Er, and 0.8 cat. % Yb. The deposition parameters are identical to that of Example 2 described above. The active layer is deposited to a thickness of about 1.2 μm.

[0125] A passive layer of aluminasilicate is then deposited over the active layer. A passive layer of about 4.25 μm thickness can be deposited with an embodiment of target 12 having composition of Si/Al of about 87 cat. % Si and about 13 cat. % Al. The passive layer and active layer are then patterned by standard lithography techniques to form a core that has a width of about 5.0 μm for the active core and tapering to about 3.5 μm at the top of the passive core with an effective length of about 9.3 cm.

[0126] Upper cladding layer is then deposited from a Si/Al target of 92 cat. % Si and 8 cat. % Al. Deposition of the upper cladding layer is shown in Figure 9. In some embodiments, the upper cladding layer can be deposited with a non-biased process. The thickness of the upper cladding layer can be about 10 μm. The amplifier formed by this process is then annealed at 725° C for about 30 min.

[0127] The as-deposited Erbium and Ytterbium concentrations in the active layer of core 303 is 2.3×10^{20} cm^{-3} Erbium concentration and 2.3×10^{20} cm^{-3} Ytterbium concentration. The index of the core is 1.508 and the index of cladding layers are 1.4458 for undercladding layer 302 and 1.452 for uppercladding layer 304. The parameter $\Delta n/n$ is therefore about 5.0%.

[0128] A reverse taper mode size converter, *see* the '138 application, is utilized for coupling light into waveguide amplifier 300. The insertion loss at 1310 nm is about 2 dB. Figure 26 shows the amplifier performance of this example. In Figure 26, amplifier 300 is pumped with 150 mW from one side pumping with 984 nm light. Gain flattening is achieved within about 1 dB in the range 1528 nm to 1562 nm for small input signals (-20 dBm). For large input signals (0 dBm), gain flattening is also achieved within about 1 dB.

<u>EXAMPLE 4</u>

10110185.030902

[0129] Another example of production of a waveguide amplifier is described here. Again, substrate 16 can be a Si wafer with about a 15 μm thick thermal oxide as can be purchased from Silicon Quest International, Santa Clara, CA. The embodiment of target 12 for the deposition of the active core can have a composition of about 50 cat. % Si, 48.5 cat. % Al, 1.5 cat. % Er (the "1.5/0" target), which can be fabricated as discussed in the '138 application. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively.

[0130] The pulsed DC power supplied to target 12 was about 6 kW. Whenever a brand new target was used or when the target has been expose to atmosphere, a long time of condition (for example more than 30hrs of conditioning) may be necessary to ensure films with the best active core property (longest life time and highest photoluminescence) are deposited. Substrate 16 is then preheat at about 350° C for about 30min before deposition.

[0131] The active core film was deposited onto a 6 inch thermal oxide wafer, which has been previously discussed, from the 1.5/0 target. The thermal oxide thickness was about 10 μm as described in previous examples. The active core is deposited to a thickness of about 1.2 μm with a deposition time of approximately 1 hr. The process condition are as listed in Table 4 below.

Table 3

Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)
6	60/28	120	100	2.3

[0132] A straight waveguide pattern can then be formed by a standard photolithography procedure. The active core was etched using reactive ion etch followed by striping and cleaning. Finally, a 10 μm top cladding layer is deposited using a similar process. A target having composition 92 cat. % Si and 8 cat. % Al with deposition parameters as described in Figure 9 was used to deposit the top cladding. The difference between the index of refraction between the core and the cladding is then about 3.7%.

[0133] In this example, annealing of the amplifier structure was performed at various anneal temperatures. The results of the various anneals are shown graphically in Figures 27 and 28. Figure 27 shows both internal gain in the C-band and insertion loss at 1310 nm of a 2.5μm wide, 10.1 cm long waveguide as deposited in this example as a function of annealing temperature. The life time in ms and up-conversion constants in cm^{-3}/s measurements for the deposited active core film at different annealing temperature are shown in Figure 28.

10140186.031502

EXAMPLE 5

[0134] One of the problems encountered during the reactive sputtering from an alloy metallic target is that the film composition drifts from run to run due to the difference in sputtering yields from the elements that forms the target alloy. For example, with Ar as a sputtering gas, the sputtering yield of Aluminum is about 3-4 times that of Silicon, while sputtering yield of Alumina is only about 50% that of Silica. Therefore, during the metal burn in, more Aluminum is sputtered from the target, resulting in a Si rich target surface. When sputtering in the poison mode, more Silica will be removed from target. Thus, as deposition goes on, the composition of the film deposited on substrate 16 will drift from lower Alumina concentration to higher Alumina concentration. This results in the index of refraction of a film drifting up with subsequent depositions from a target 12, as is shown for the deposition described in Example 4 in Figure 29. Figure 30 shows the drift in photoluminescence pumped at 532 nm with subsequent depositions. Figure 31 shows drift in the excited state lifetime with subsequent depositions from a target. The embodiment of target 12 utilized in Figures 29 through 31 is the 1.5/0 target and the deposition parameters are as described above in Example 4.

[0135] The drift can be stabilized by recondition target 12 prior to deposition. The recondition process (or burn in) consists of both sputtering in metallic mode and then sputtering in poison mode to condition target 12. The burn in time in metallic mode needs to be as short as possible and at the same time insure no arcing during the poison mode deposition. Figure 32 shows the

much improved drift in the index of refraction and the photoluminescence when target 12 is reconditioned between subsequent depositions.

EXAMPLE 6

[0136] This example describes the fabrication of another Er-Yb codoped waveguide amplifier according to the present invention. The active core is deposited with an embodiment of target 12 with composition about **49 cat. % Si, 48 cat. % Al, 1.6 cat. % Er and 0.5 cat. % Yb**, which can be fabricated as described in the '247 application. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The pulsed DC power supplied to target 12 was kept at 5 kW. Table 4 shows photoluminescence and index of refraction of as-deposited films from this example at some typical process conditions. The units for photoluminescence are the number of counts per micron. Lifetime and photoluminescence measured after annealing at various different temperatures are shown in Table 5.

Target 4

Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)	532 nm PL/um	Index
5	60/34	120	100	2.3	3367	1.5333
5	60/30	120	100	2.3	3719	1.5334

Table 5

Anneal Temperature °C	Life Time (ms)	PL (532nm)/um
725	3	7000
775	3	7000
800	4	7500
825	4.7	8560
850	5.8	10000
900	6.9	17000

[0137] A waveguide amplifier was fabricated using this material in the similar fashion as described in examples 2-4. The active core was first deposited on substrate 16, which includes a

10um thermal oxide layer, using the following deposition parameters: target power 5KW, pulsing frequency 120KHz, bias 100W, reverse time 2.3us, Argon and Oxygen flow are 60 sccm and 30sccm respectively. The active core thickness is deposited to a thickness about 1.2μm, which takes approximately 1 hr. All wafers are preheated at about 350° C for 30min before deposition. A straight waveguide pattern is then formed by standard photolithography procedure. The active core was etched using reactive ion etch following by striping and cleaning. Next, a 10μm top cladding layer is deposited using similar process. The "92/8" (92 cat. % Si and 8 cat. % Al) metallic target was used to deposit top clad according to deposition parameters shown in Figure 9, resulting in a 4 % index difference between active core and cladding. The wave guide was then annealed at 800° C for about 30 min.

[0138] This waveguide was tested for gain using the method described in previous examples. However no net gain was observed from this waveguide since the passive loss was too high.

EXAMPLE 7

[0139] In addition to active material layers (i.e., layers having rare-earth ion concentrations), passive layers can also be deposited. Figure 9 shows deposition parameters for several target compositions, including some targets for deposition of passive (i.e., alloys of Al and Si with no rare earth ion concentration) layers. In this example, an embodiment of target 12 with a material composition of pure silicon is utilized.

[0140] Apparatus 10 can be based on an AKT 1600 reactor and deposited with about 1 to 3 kW of pulsed DC target power supplied to target 12. Particular depositions have been accomplished at 2.5 kW and 1.5 kW. The frequency of the pulsed DC power is between about 100 and 200 Khz. Some depositions were performed at 200 kHz while others were performed at 100 kHz. The reverse time was varied between about 2 μs and about 4 μs with particular depositions performed at 2.3 μs and 3.5 μs. The bias power to substrate 16 was set to zero.

[0141] Index variation of SiO2 films with bias to substrate 16 and deposition rates as a function of bias power to substrate 16 is shown in Figure 10.

10101965.031502

[0142] The process gas included a mixture of Ar, N_2 and O_2. The Ar flow rates was set at 20 sccm while the O_2 flow rate was varied between about 5 and about 20 sccm and the N_2 flow rate was varied from about 2 to about 35 sccm. Figure 33 shows the variation in the index of refraction of a film deposition on substrate 16 as the O_2/N_2 ratio is varied.

EXAMPLE 8

[0143] Alternatively, films can be deposited on substrate 16 from a pure alumina target. In an example deposition with an embodiment of target 12 of alumina in an embodiment of apparatus 10 based on the AKT 1600 reactor, the pulsed DC target power was set at 3 kW and the frequency was varied between about 60 kHz and 200 kHz. The reverse time was set at 2.5 μs. Again, no bias power was supplied to substrate 16. The O_2 flow rate was varied from about 20 to about 35 sccm, with particular depositions performed at 22 and 35 sccm. The Ar flow rate was set at 26 sccm. A post deposition anneal of substrate 16 at 800° C for 30 min. was performed.

[0144] Figure 12 shows the variation of refractive index of the film deposited on substrate 16 with varying frequency of the pulsed DC power supplied to target 12. Figure 11 shows the variation in refractive index of a film deposited on substrate 16 with varying O_2/Ar ratio. As can be seen from Figures 33, 34 and 35, the index of refraction of films deposited from alumina can be adjusted by adjusting the process gas constituents or by adjusting the frequency of the pulsed DC power supplied to target 12 during deposition.

EXAMPLE 9

[0145] Additionally, passive films can be deposited from targets having a composition of Si and Al. For example, layers have been deposited from embodiments of target 12 with composition 83 % Si and 17 % Al. About 4.5 kW of pulsed DC power at about 200 kHz frequency was supplied to target 12. The reverse time was about 2.2 μs. A bias power of about 150 W was

supplied to substrate 16 during deposition. Figures 14 and 15 show variation of the index of refraction for subsequent runs from this target.

[0146] The examples and embodiments discussed above are exemplary only and are not intended to be limiting. One skilled in the art can vary the processes specifically described here in various ways. Further, the theories and discussions of mechanisms presented above are for discussion only. The invention disclosed herein is not intended to be bound by any particular theory set forth by the inventors to explain the results obtained. As such, the invention is limited only by the following claims.

10170963.031602

Claims

We claim:

1. A method of depositing a film on a substrate, comprising:

   providing pulsed DC power through a filter to a target;

   providing bias power to a substrate positioned opposite the target;

   providing process gas between the target and the substrate,

   wherein the filter protects a pulsed DC power supply from the bias power.

2. The method of Claim 1, further including holding the temperature of the substrate substantially constant.

3. The method of Claim 1, wherein providing pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. The method of Claim 1, wherein providing bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. The method of Claim 4, wherein the filter is a band reject filter at the frequency of the bias power.

6. The method of claim 4, wherein the bias power is zero.

7. The method of Claim 1, wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

8. The method of Claim 1, wherein the process gas includes a mixture of Oxygen and Argon.

9. The method of Claim 9, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

10. The method of Claim 8, wherein the process gas further includes nitrogen.

11. The method of Claim 1, wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate.

12. The method of Claim 1, further including uniformly sweeping the target with a magnetic field.

13. The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. The method of Claim 1, further including depositing a film on the backside of target 12.

15. A reactor according to the present invention, comprising:

a target area for receiving a target;

a substrate area opposite the target area for receiving a substrate;

a pulsed DC power supply; and

a bias power supply coupled to the substrate.

16. The reactor of Claim 15, wherein the target has a surface area greater than the surface area of the substrate.

17. The reactor of Claim 15, further including a scanning magnet which provides uniform erosion of the target.

18. The reactor of Claim 17, wherein the scanning magnet scans across the target in a first direction and extends in a second direction perpendicular to the first direction.

19. The reactor of Claim 18, wherein the magnet extends beyond the target in the second direction.

20. A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting the bias power to the substrate;

setting the process gas flow; and

applying pulsed DC power to the target to deposit the film.

21. The method of Claim 20, wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25. A method of forming a waveguide amplifier, comprising:

providing a substrate with an undercladding layer;

providing a target having a concentration of rare-earth ions opposite the substrate;

supplying process gas between the target and the substrate;

applying pulsed DC power through a filter to the target to deposit a film;

patterning the film to form a core;

depositing an uppercladding layer over the core.

26. The method of Claim 25, wherein providing a substrate includes providing a silicon substrate with a thermal oxide layer.

27. The method of Claim 25, wherein providing a target includes providing a target having a concentration of up to about 5 cat. % of rare earth ions.

10103563.031502

28. The method of Claim 27, wherein providing a target includes providing a target of Al and Si.

29. The method of claim 25, wherein providing a target includes providing a target with a concentration of Al.

30. The method of Claim 29, wherein providing a target includes providing a target with a concentration of Si.

31. The method of Claim 29, wherein providing a target includes providing a target with a concentration of rare earth ions.

32. The method of Claim 25, further including providing bias power to the substrate.

33. The method of Claim 25, further including scanning a magnet over the target.

34. The method of Claim 25, wherein scanning the magnet over the target includes moving the magnet in a first direction.

35. The method of Claim 34, wherein the magnet extends beyond the target in a second direction perpendicular to the first direction.

36. The method of Claim 25, wherein the target has a surface area greater than the surface area of the substrate.

37. The method of Claim 32, wherein the filter rejects power at a frequency of the bias power.

38. A sputtering apparatus, comprising:

means for providing pulsed DC power to a target; and

means for providing bias power to a substrate.

39. The apparatus of Claim 38, further including

means for providing process gas between the target and the substrate.

M-12245 US
852923 v1

Biased Pulse DC Reactive Sputtering of Oxide Films

Hongmei Zhang
Mukundan Narasimhan
Ravi Mullapudi
Richard E. Demaray

Abstract

A biased pulse DC reactor for sputtering of oxide films is presented. The biased pulse DC reactor couples pulsed DC at a particular frequency to the target through a filter which filters out the effects of a bias power applied to the substrate, protecting the pulsed DC power supply. Films deposited utilizing the reactor have controllable material properties such as the index of refraction. Optical components such as waveguide amplifiers and multiplexers can be fabricated using processes performed on a reactor according to the present inention.

M-12245 US
1/27

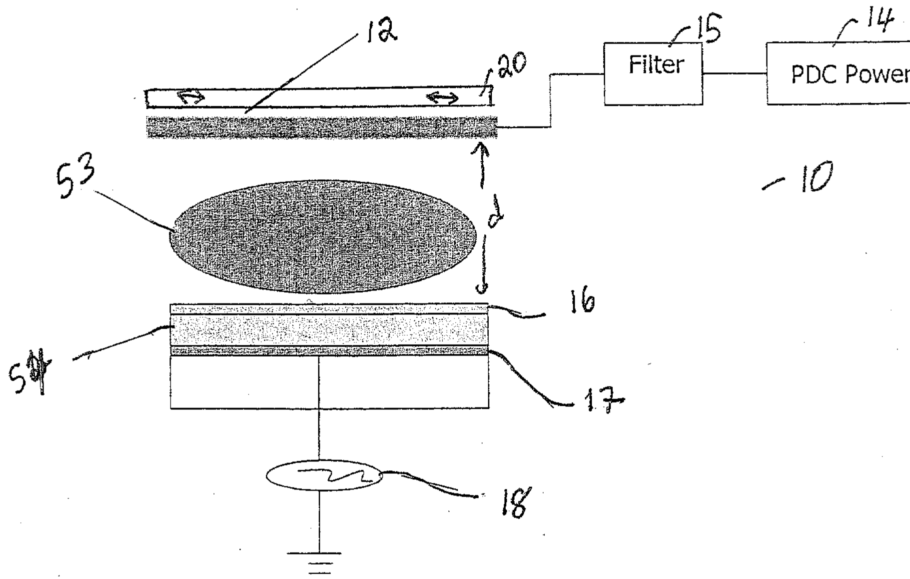


Figure 1A

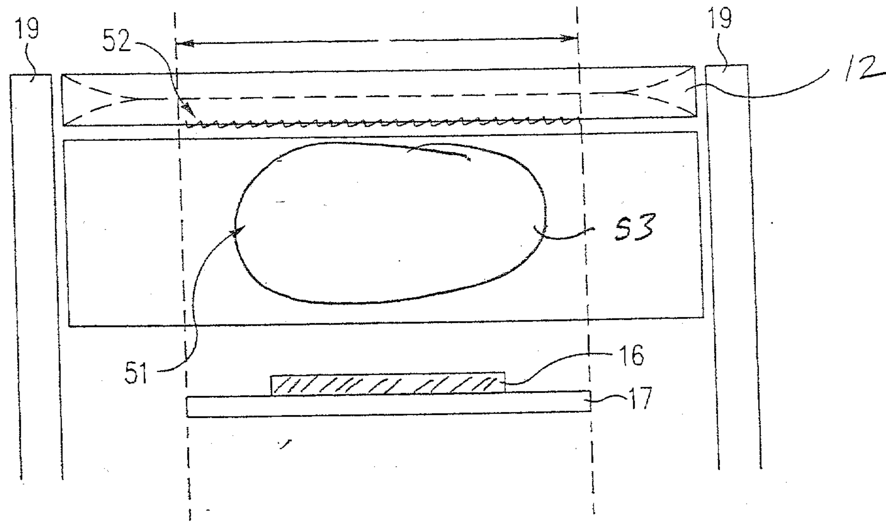


FIG. 1B

M- 12245 US
2/27

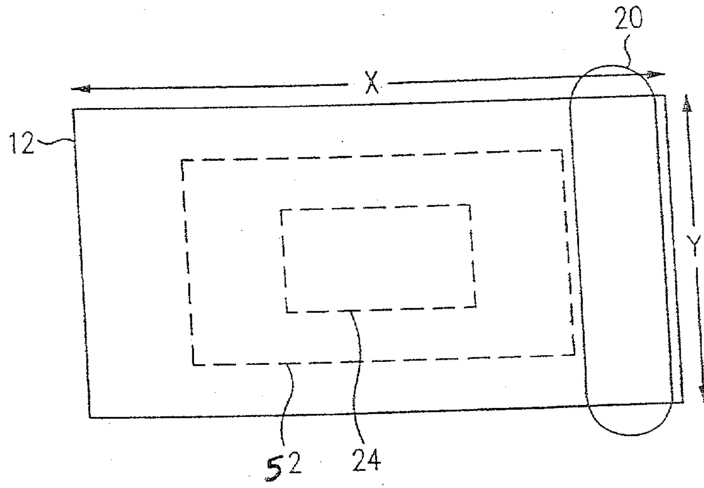


FIG. 2

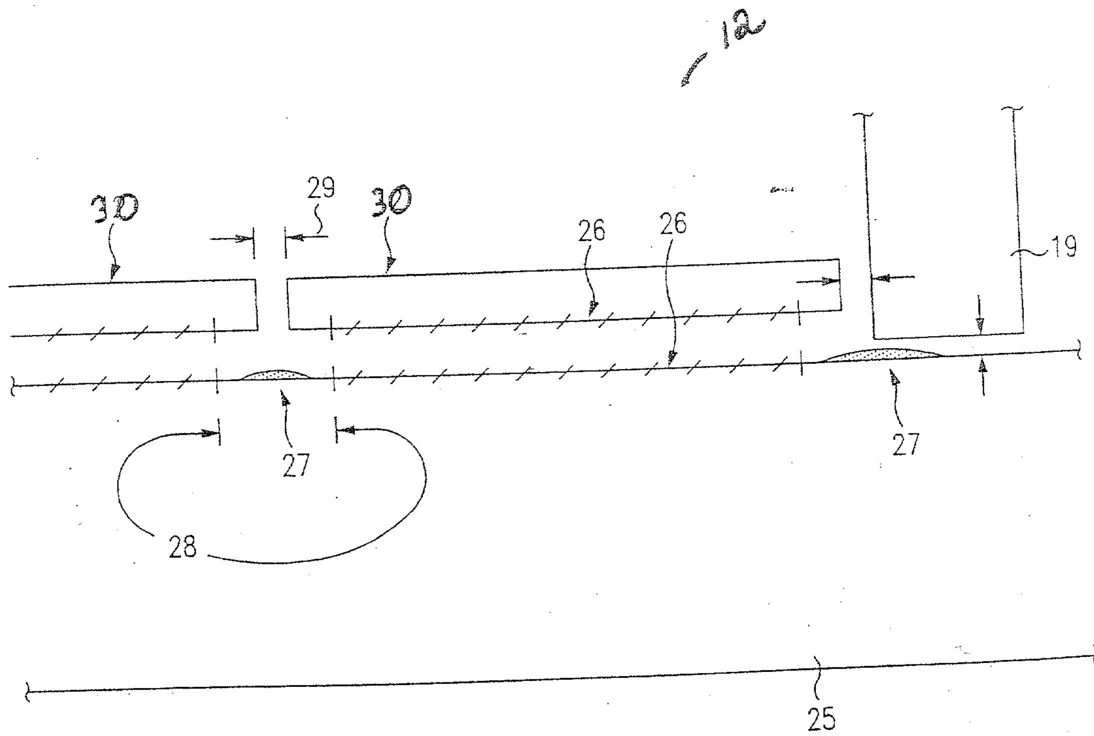


FIG. 3

m- 12245 US
3/27

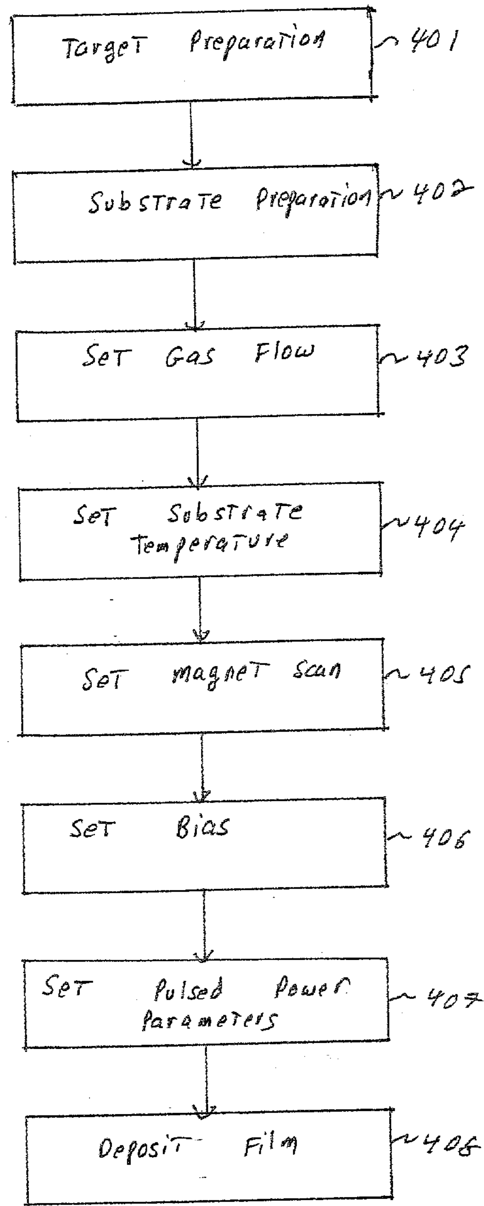


Figure 4

M-12245 US
4/27

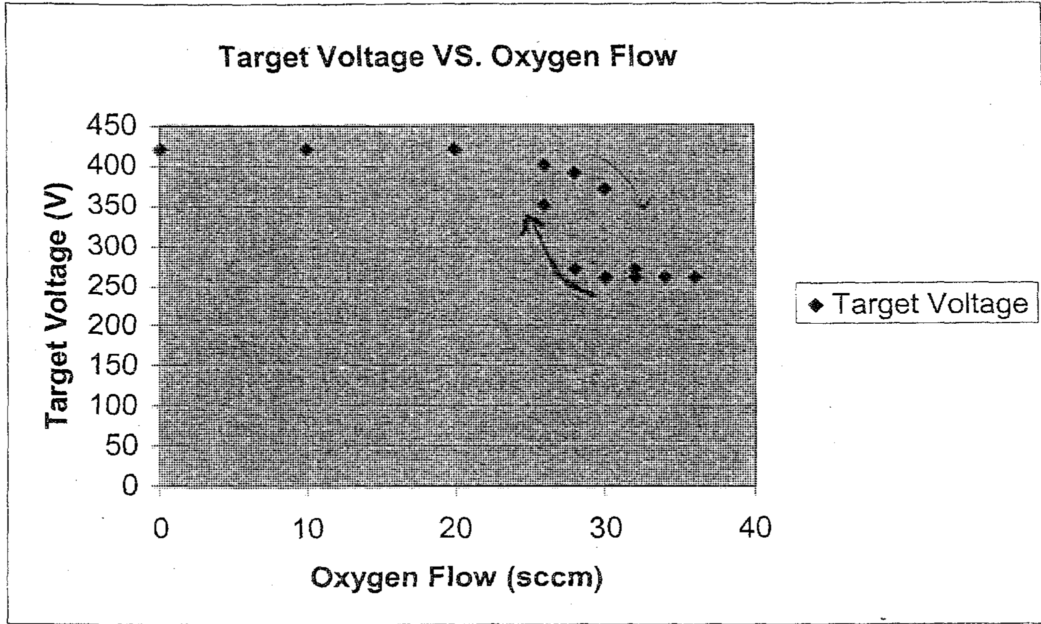


Figure 5

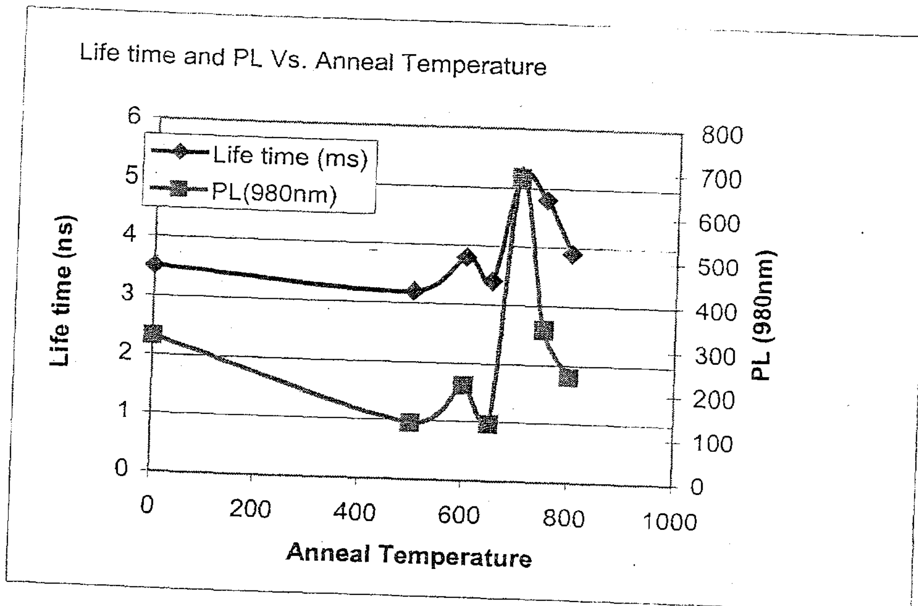


Figure 6

20961023.052602

209TE0"E98T0T0T

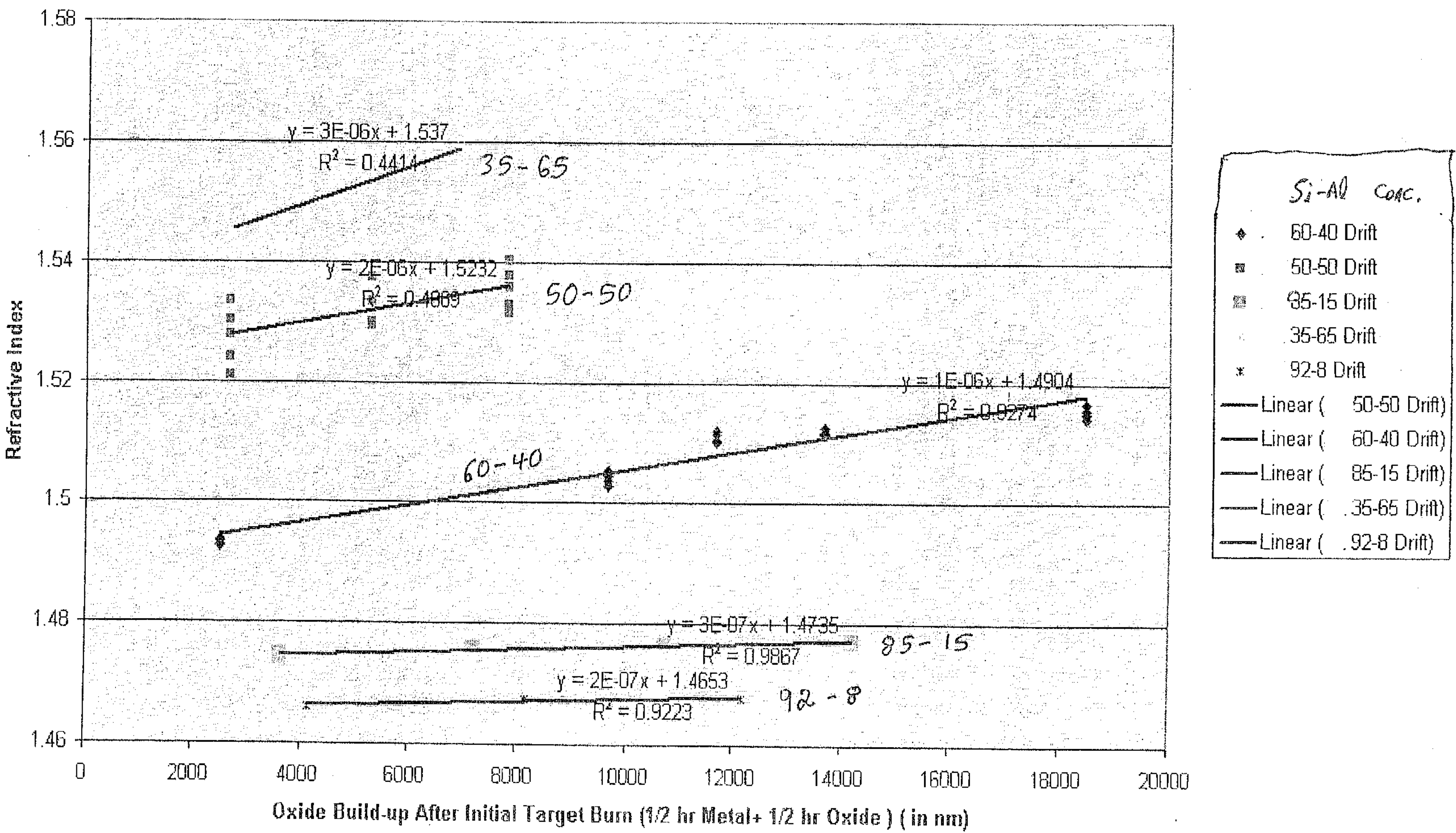


Figure 7

M-12245 US
5/27

20913630 " E9310101

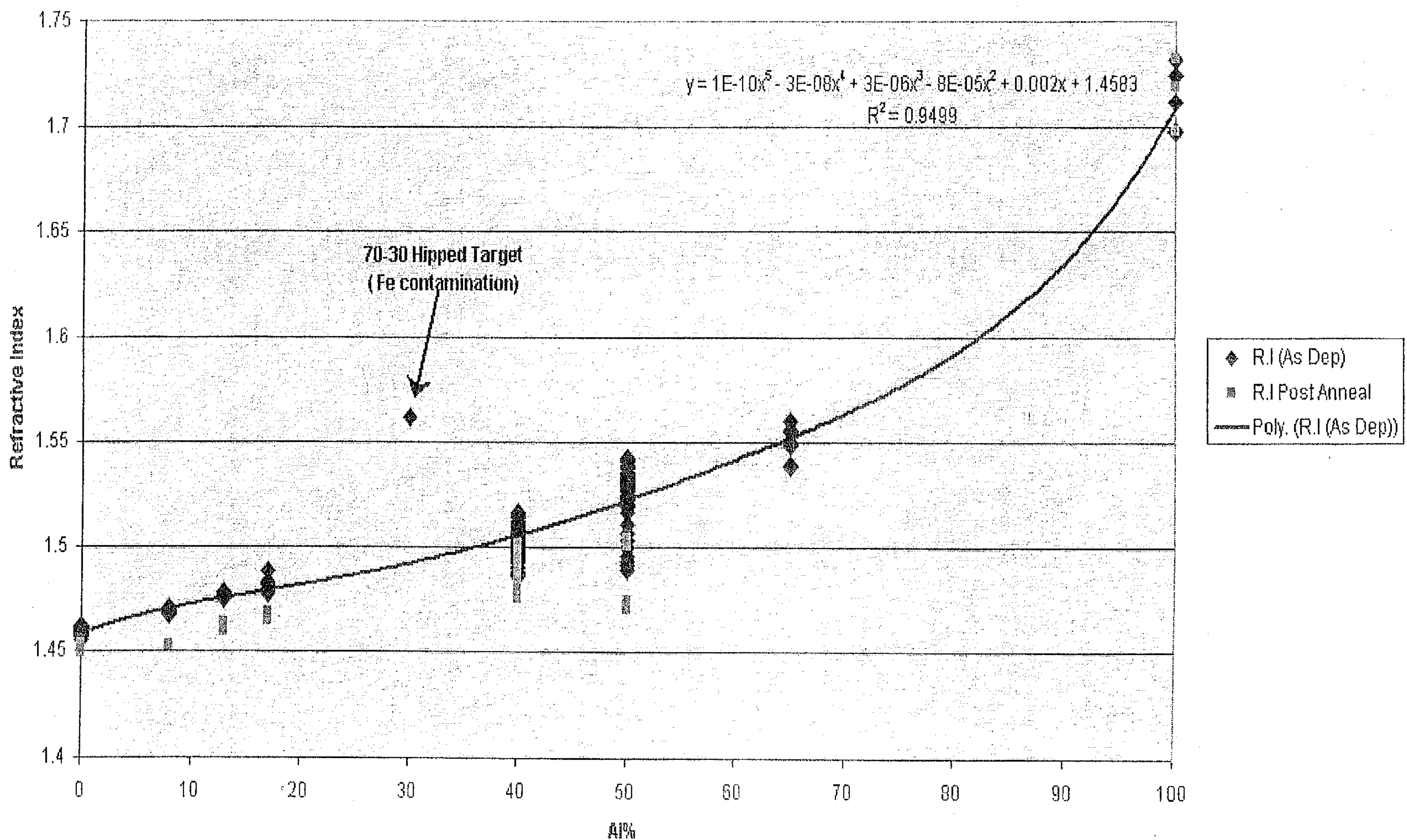


Figure 8

m- 12845 US
6/27

209TEO"E98T0T0T

Material (Er/Yb/Al/Si)	Expected index (Post anneal)	Actual index (Post anneal)	Process Conditions (Annealed 725c 30min)
0.8/0.8/41.4/57	1.506	1.510	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.6/0.5/49/48.9	1.526	1.528	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/8/92	1.452	1.456-1.459	4.5KW, Ar-30-60,O2-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/40/60	1.504	1.486-1.501	3.0-4.5KW, Ar-30,O2-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/50/50	1.520	1.491-1.503	4.0-4.5KW, Ar-30,O2-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/65/35	1.544	1.545-1.560	4.5-5.5KW, Ar75-90, O285-100, 200Khz,2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/30/70	1.490	1.562 (high Fe content)	5.0KW, Ar75, O2-100, 200Khz,2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.5/0/48.5/50	1.523	1.509-1.513	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias

Figure 9

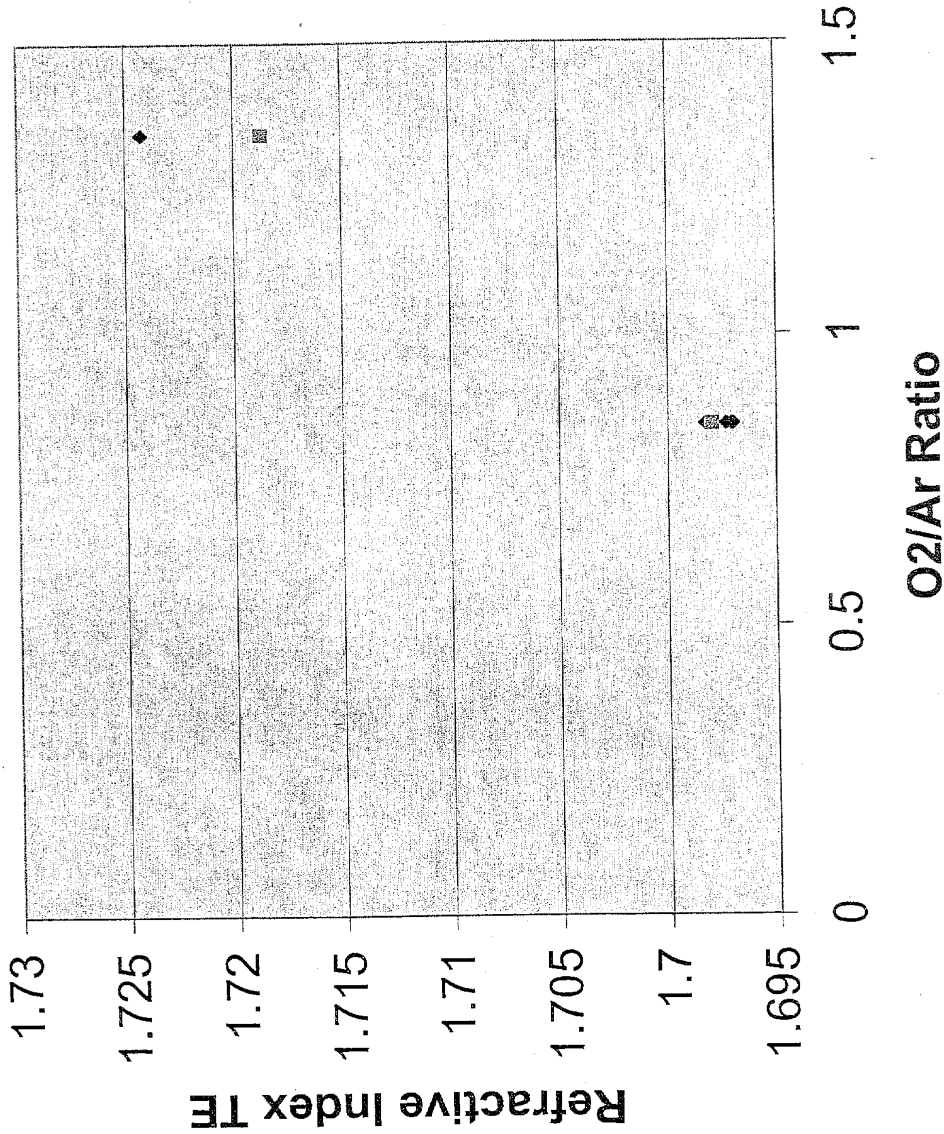
M-12245 US
7/27

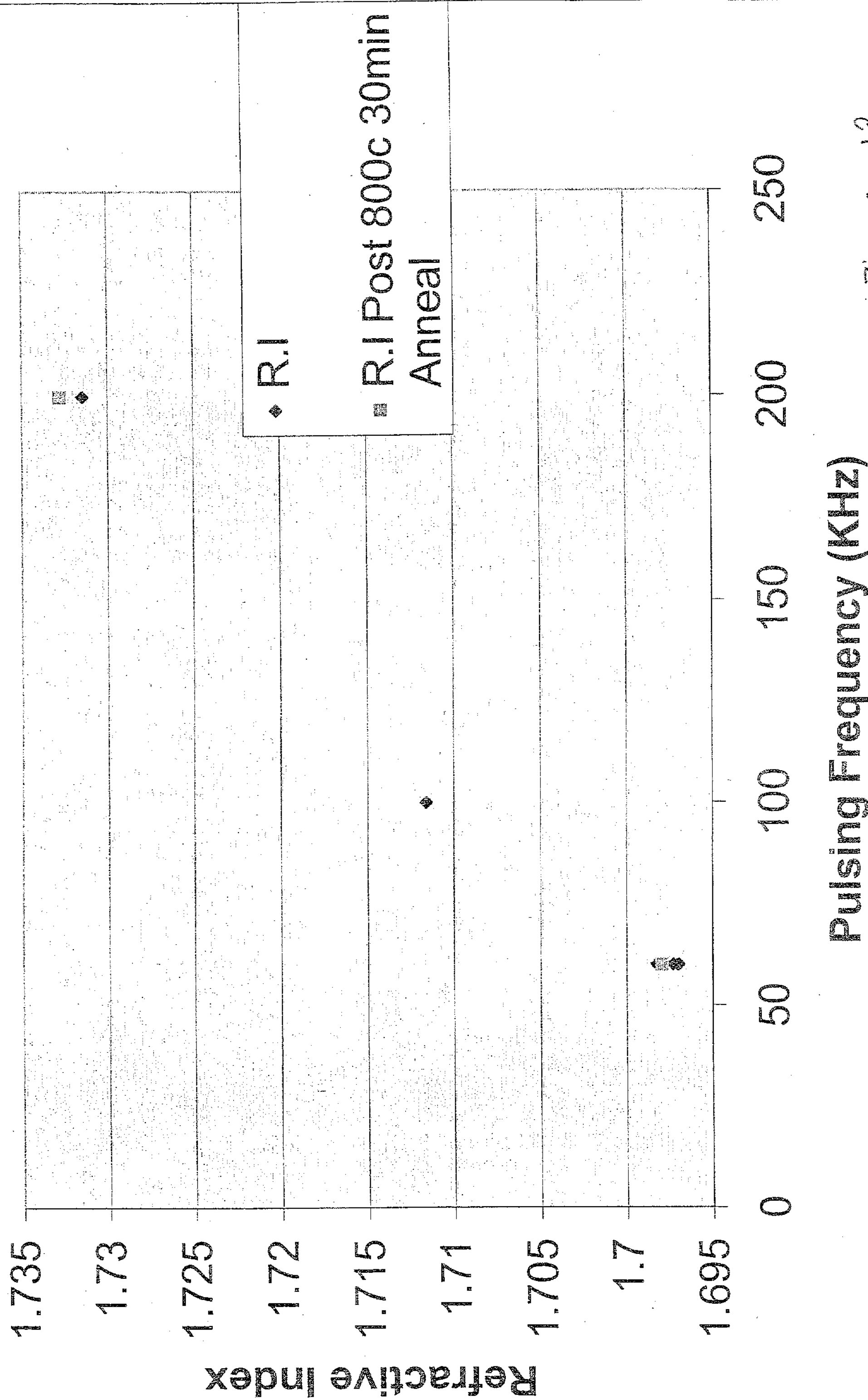
20951503 . 053101018

Bias Power (Watts)	DC Power (KW)	Pulsing Freq (KHz)	Reverse Time (μs)	Ar Flow (sccms)	O2 Flow (sccms)	Wafer Position	Target To Wafer Spacing (mm)	Refractive Index Avg (@1550nm)	Refractive Index STD (@1550nm)	Dep Rate (um/Hr)
150	4.5	200	2.2	100	100	1	55	1.461508	0.000535	0.957654
150	4.5	200	2.2	100	100	2	55	1.462329	0.000376	0.962581
400	4.5	200	2.2	100	100	1	55	1.462774	0.000103	0.814007
400	4.5	200	2.2	100	100	2	55	1.463583	0.000095	0.824566

Figure 10

m-12 2~~8~~5 US
8/27


R.I. vs O2/Ar Ratio
Refractive Index TE
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
0.5
1
1.5
O2/Ar Ratio
R.I. Vs O2/Ar Ratio
R.I Post Anneal Vs O2/Ar Ratio
Figure 11


R.I. vs Pulsing Frequency for Alumina
Refractive Index
1.735
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
50
100
150
200
250
Pulsing Frequency (KHz)
R.I
R.I Post 800c 30min Anneal
Figure 12

209FE0"E98T0T0T

Target 92-8
AKT 4300 Based Reactor

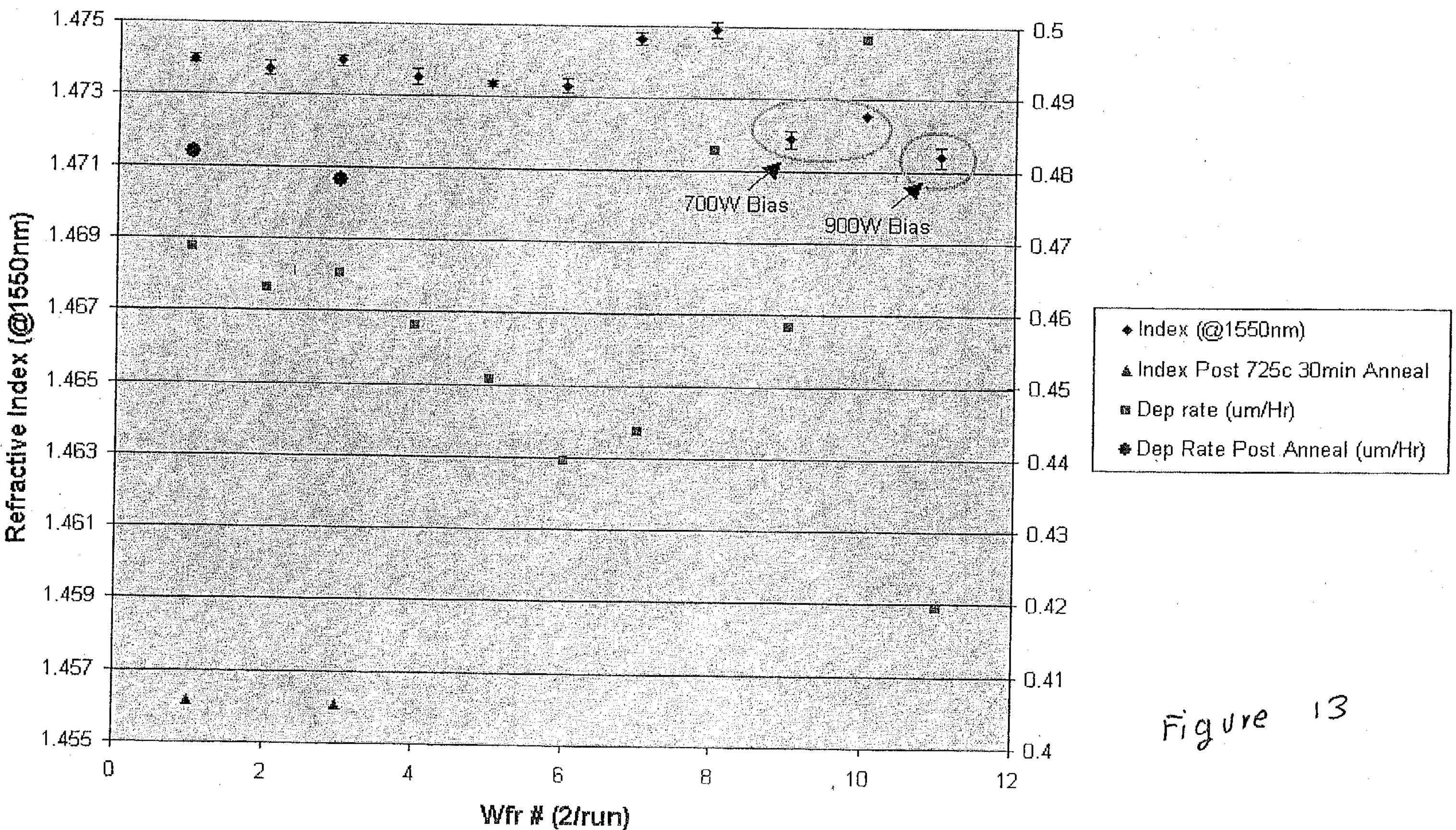


Figure 13

m- 12 245 US
11/27

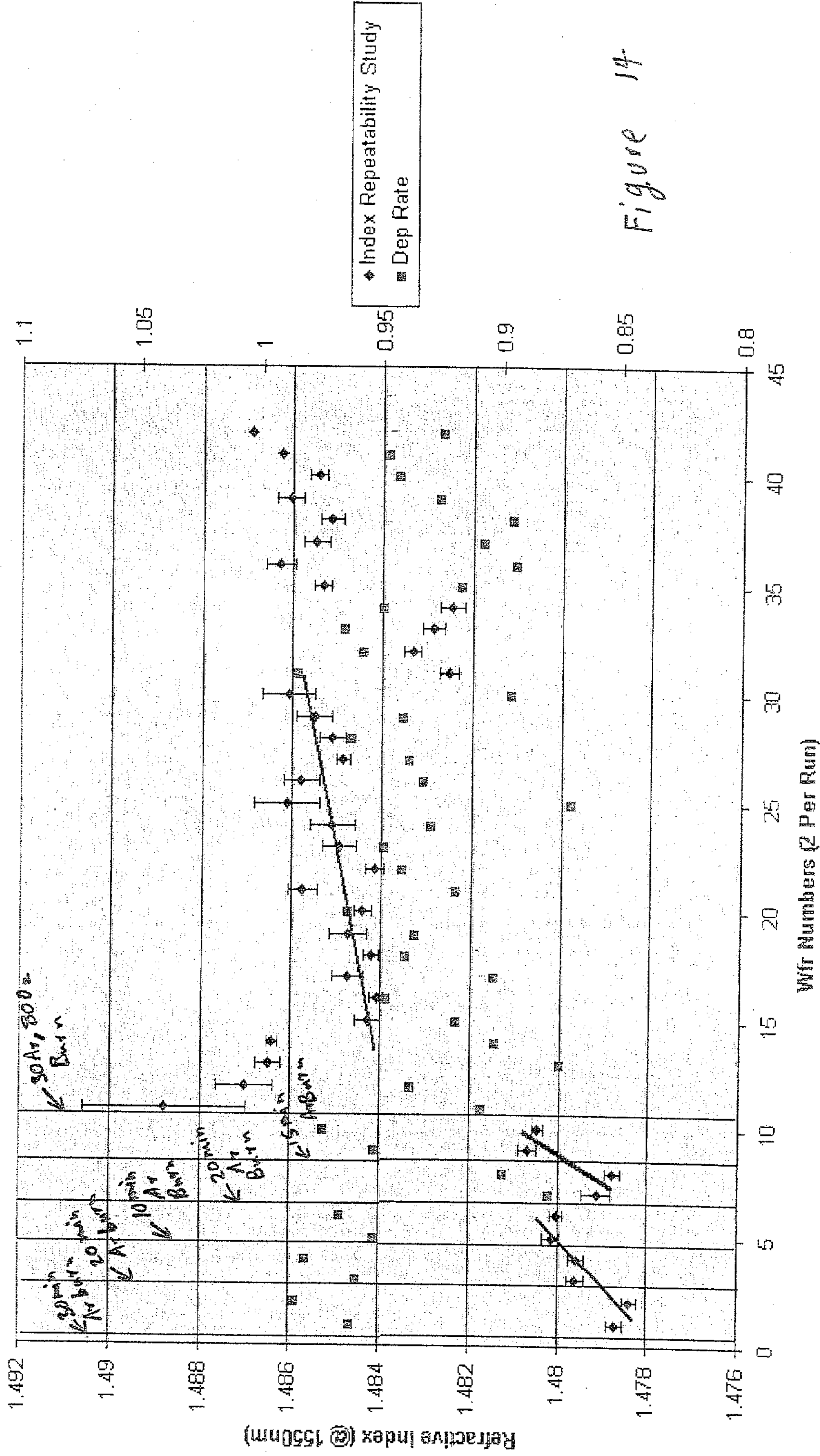


Figure 14

12/27
m-12845 US

209TE0"E98T0T0T

83-17 Target / AKT 1600 based reactor.

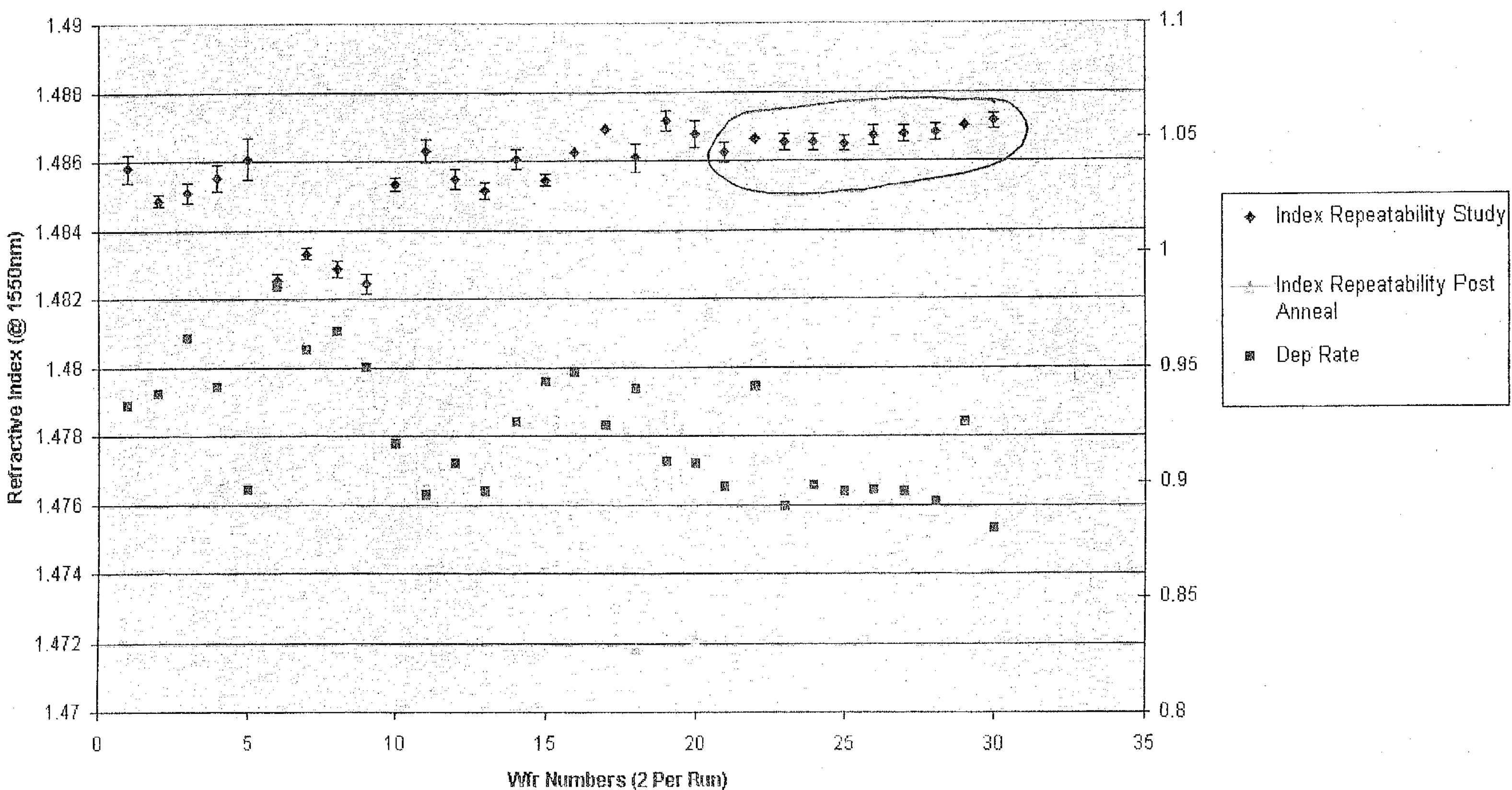
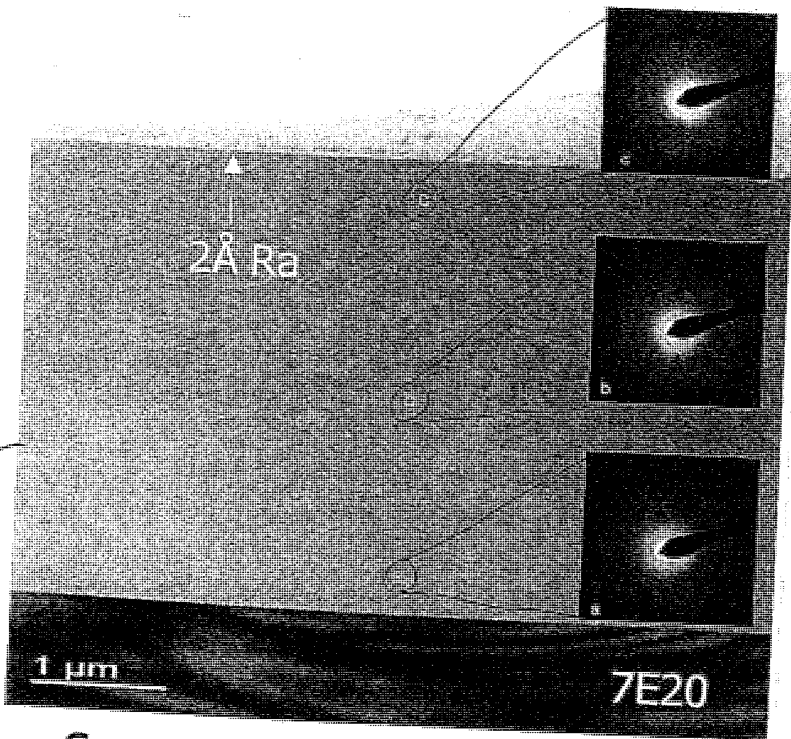


Figure 15

M- 12245 US
13/27

M- 12245 US
14/27



Symmorphix PVD aluminosilicate

Figure 16A

20963288.031402

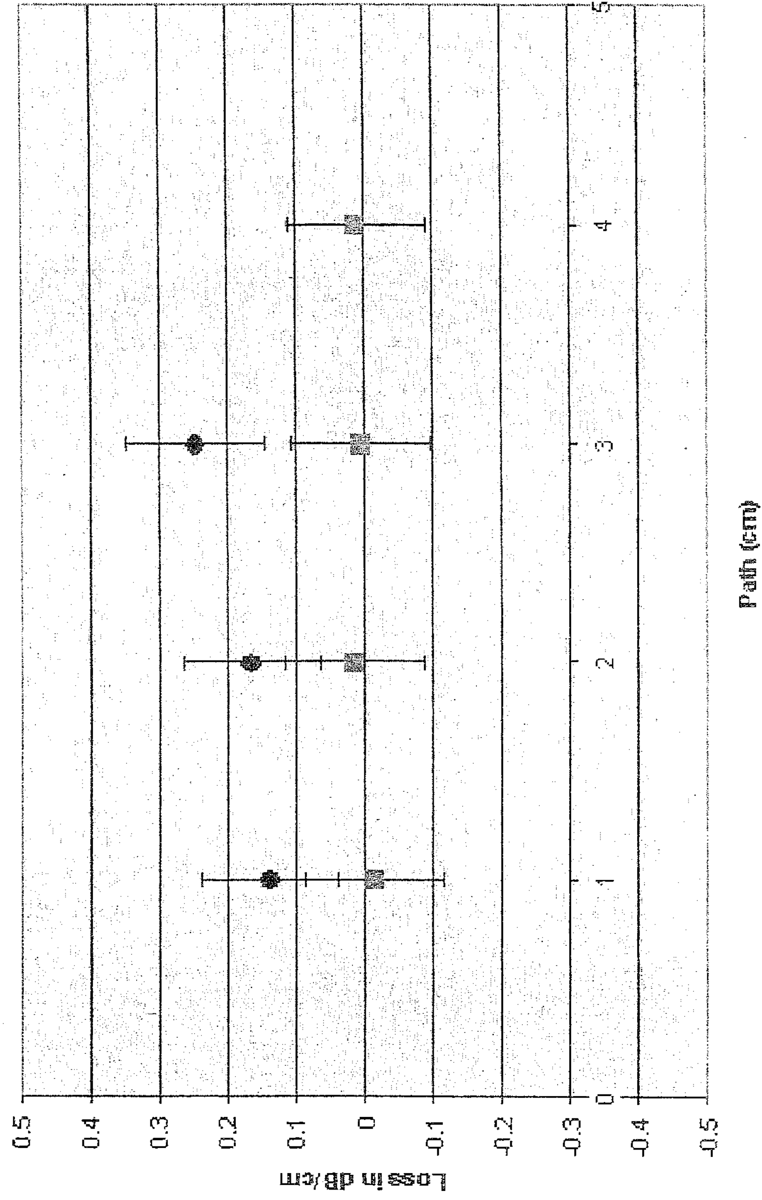


Figure 17

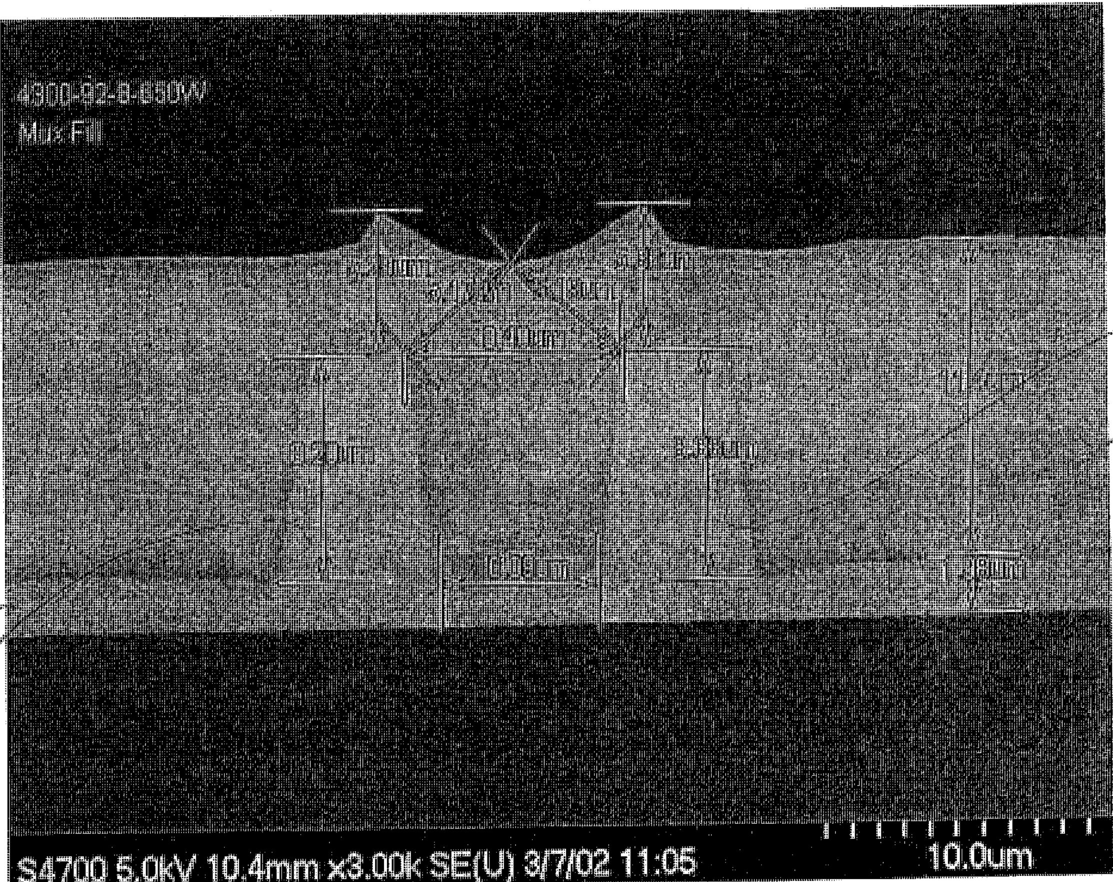


Figure 18

m-12245 US
16/27

m-12245 US
17/27

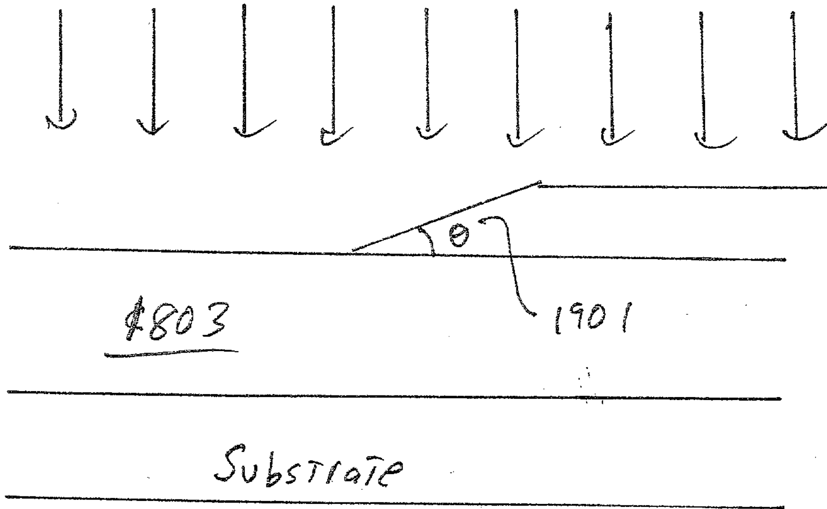


Figure 19

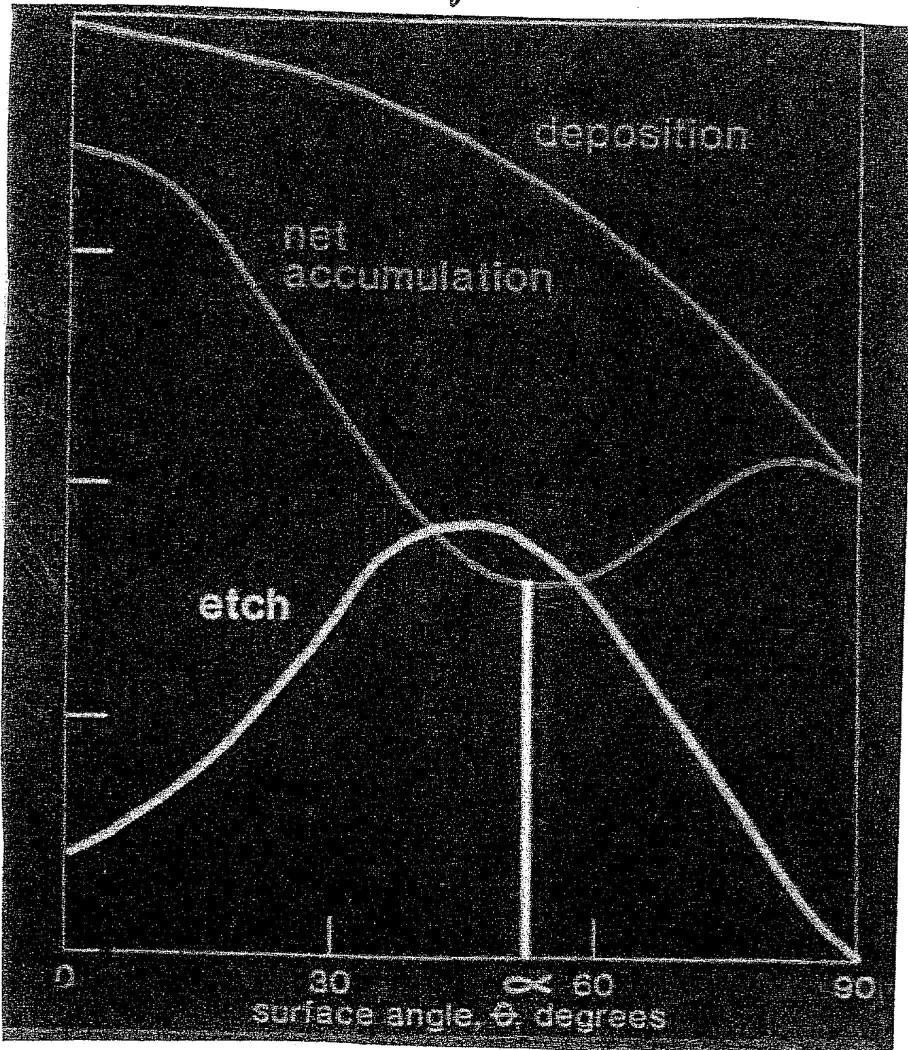


Figure 20

20951059 .031701

m-12245 US
18/27

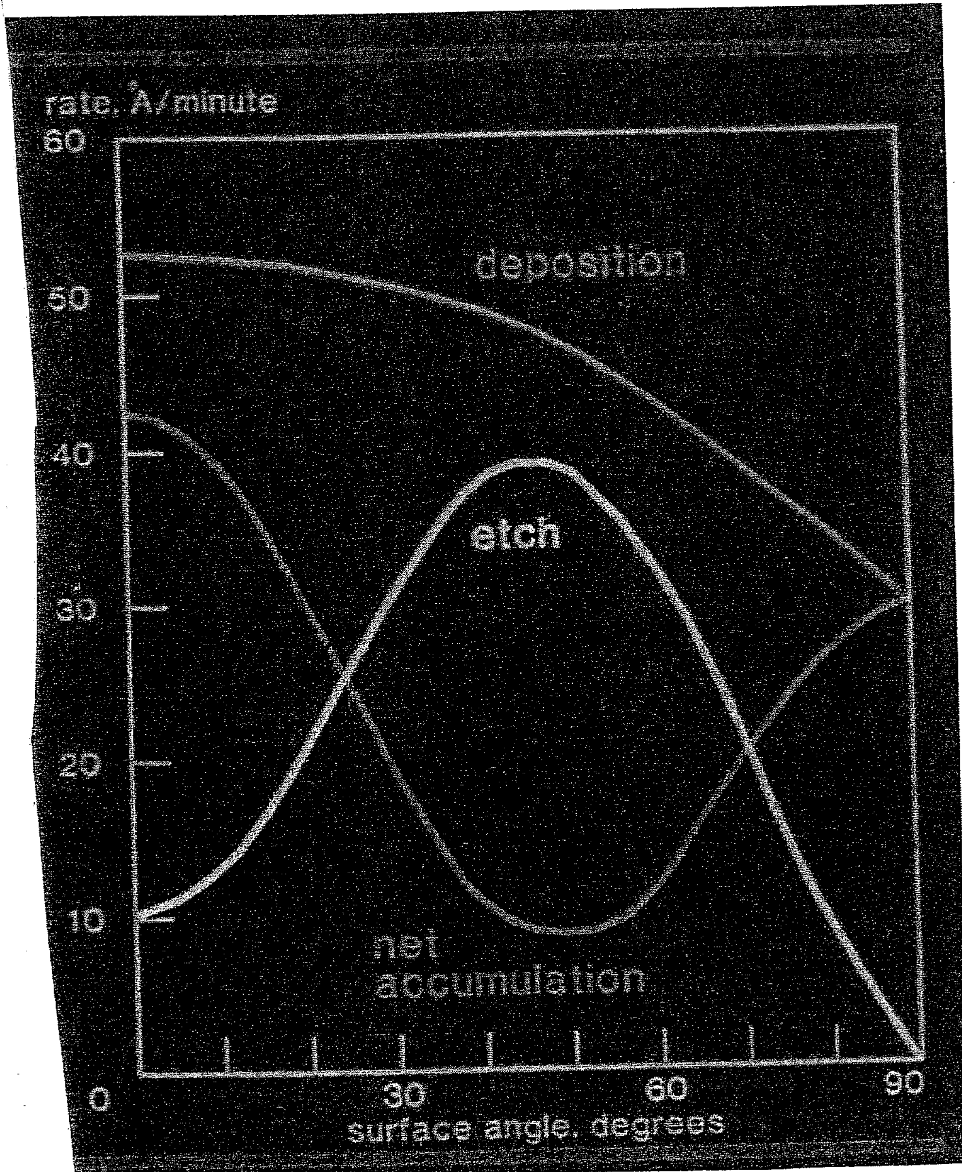


Figure 21

20573063 .122601

m-12245 US
19/27

20916851 .030702

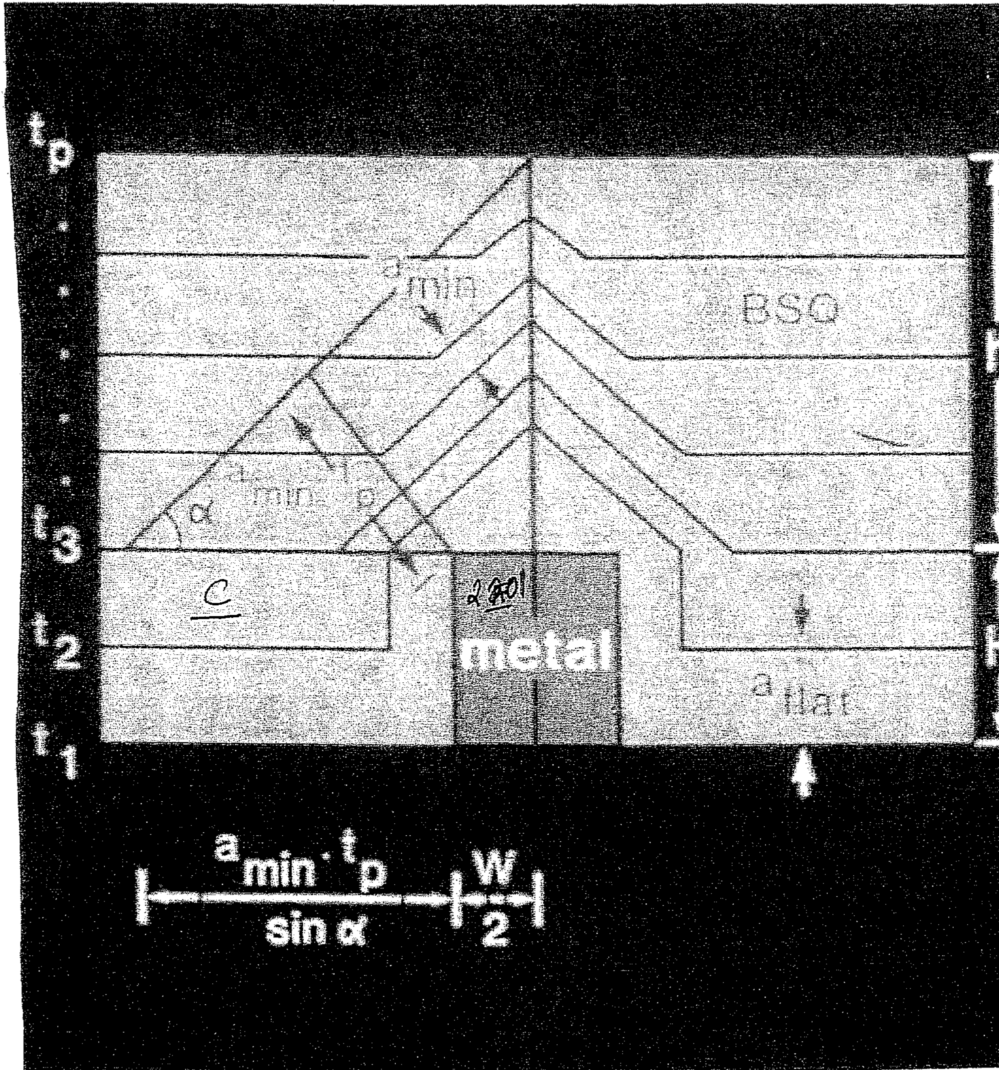


Figure 22

m-12 245 US
20/27

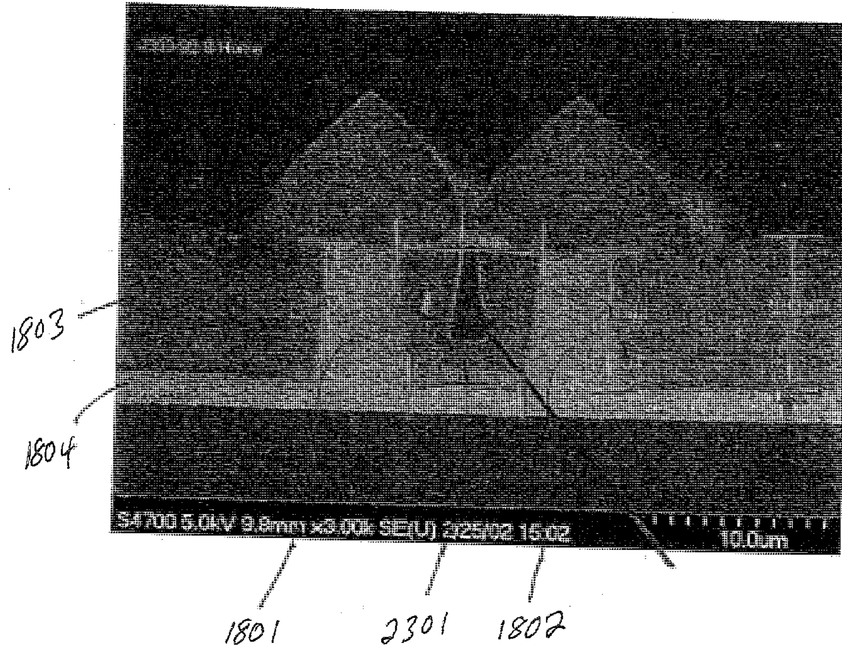


Figure 23

20071203 02210

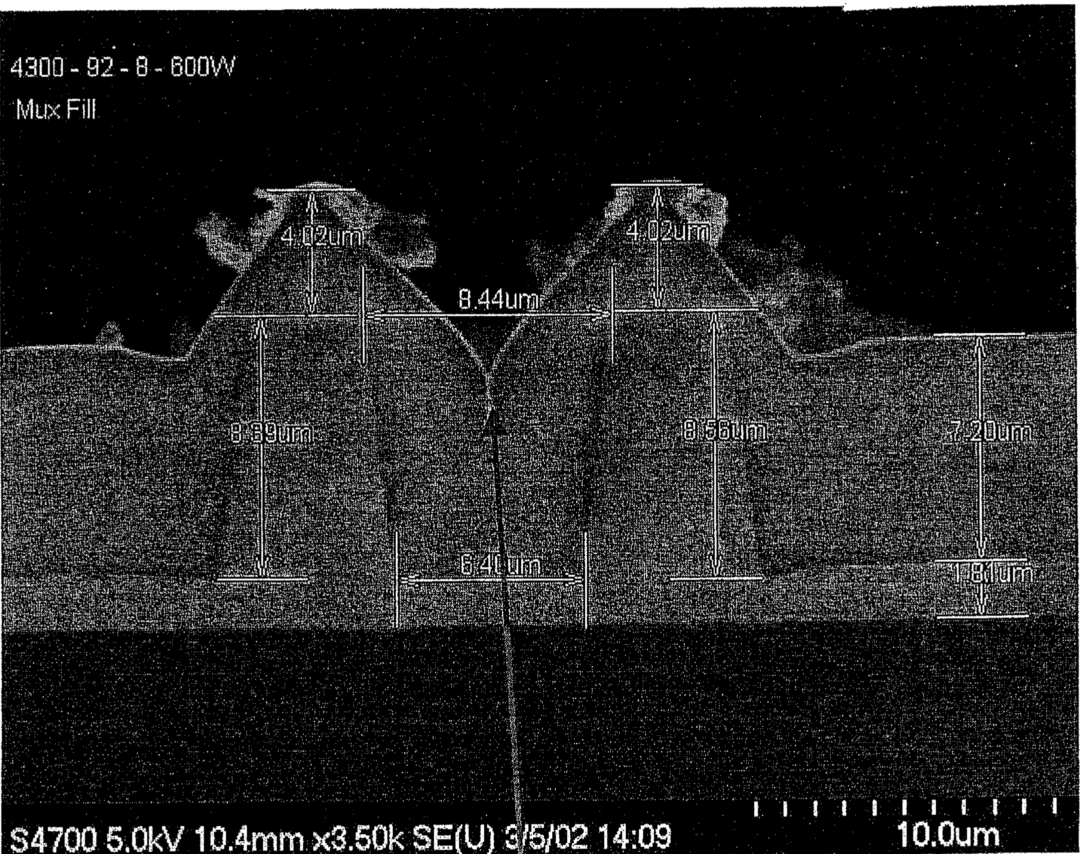


Figure 24

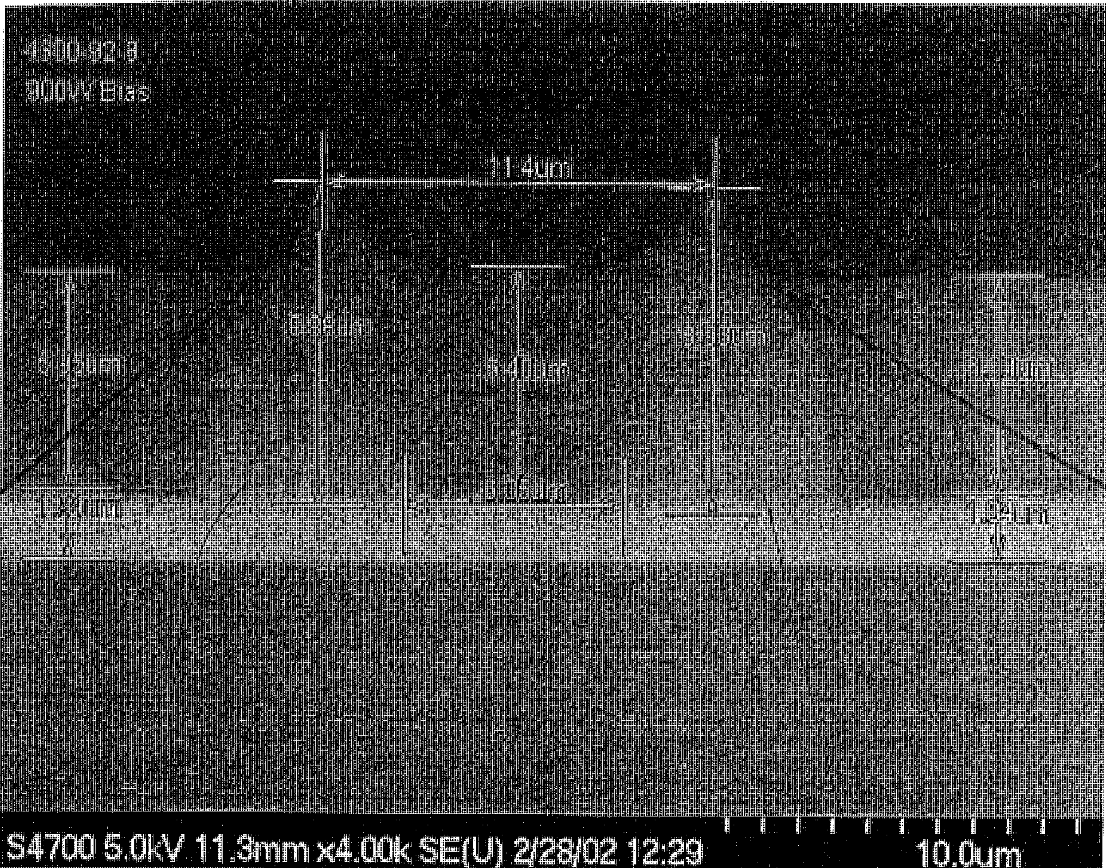


Figure 25

m- 12245 US
23/27

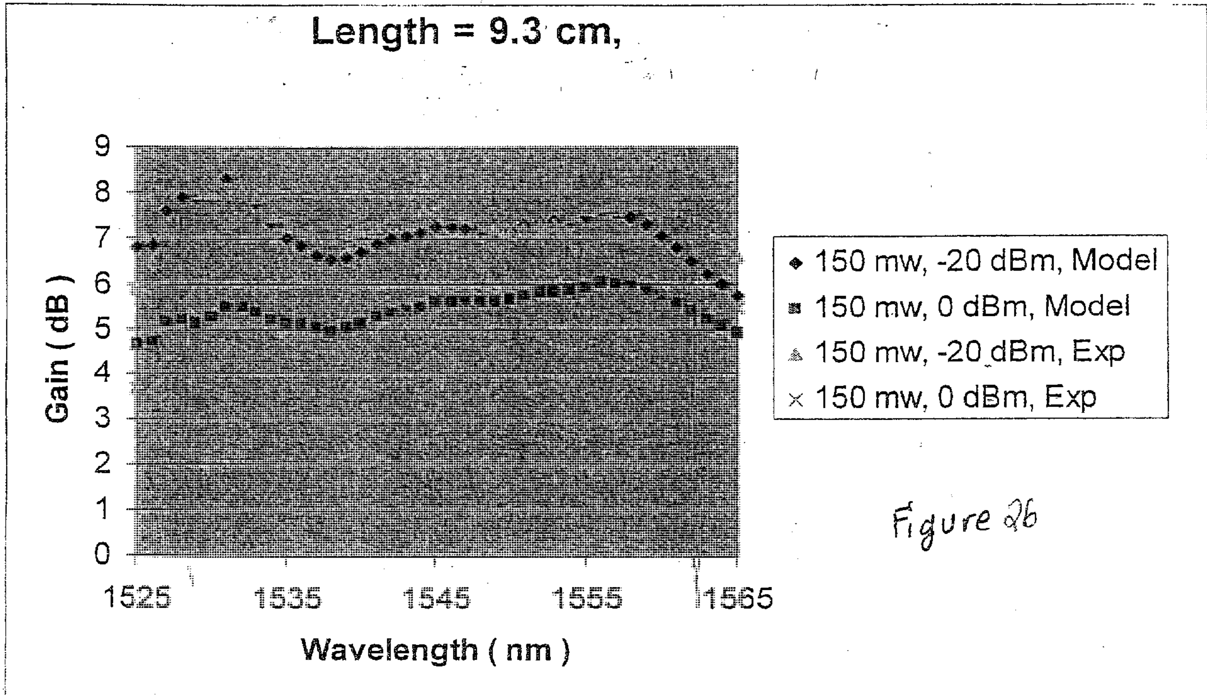


Figure 26

m- 12 245 US
24/27

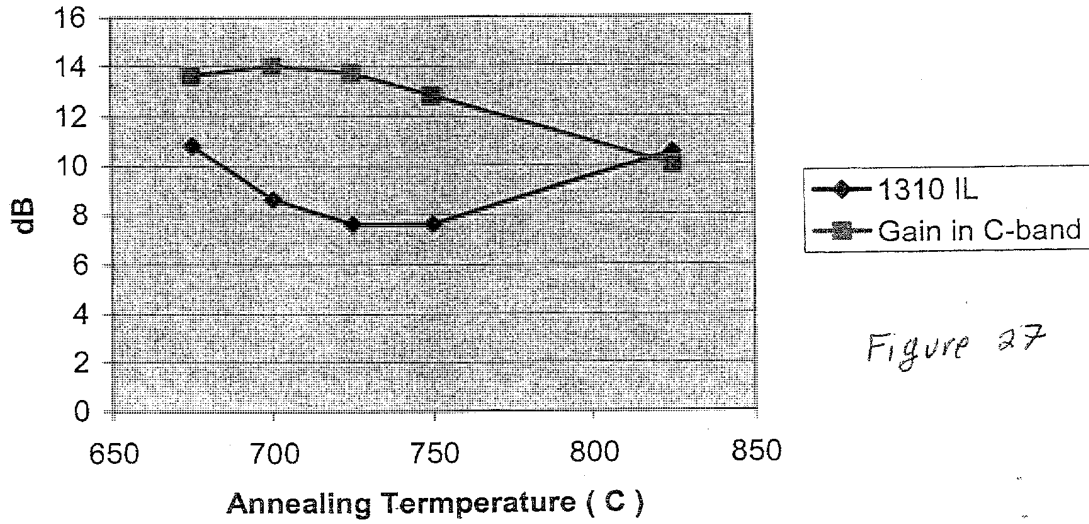
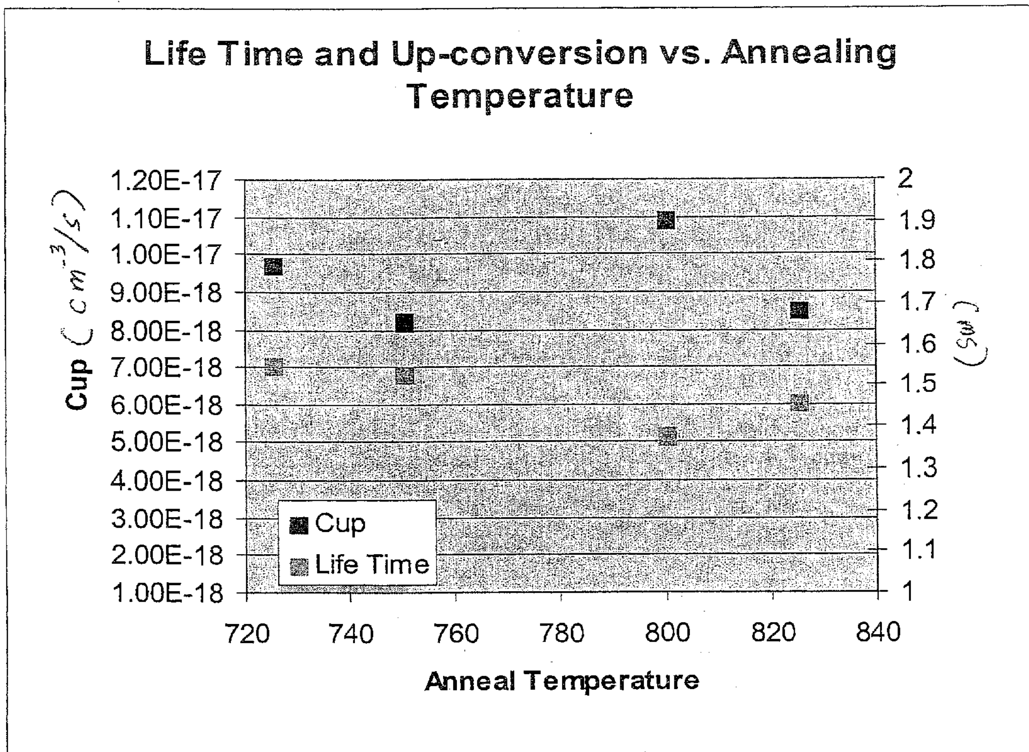


Figure 27

Figure 28



20951263.031501

M-12245 US
25/27

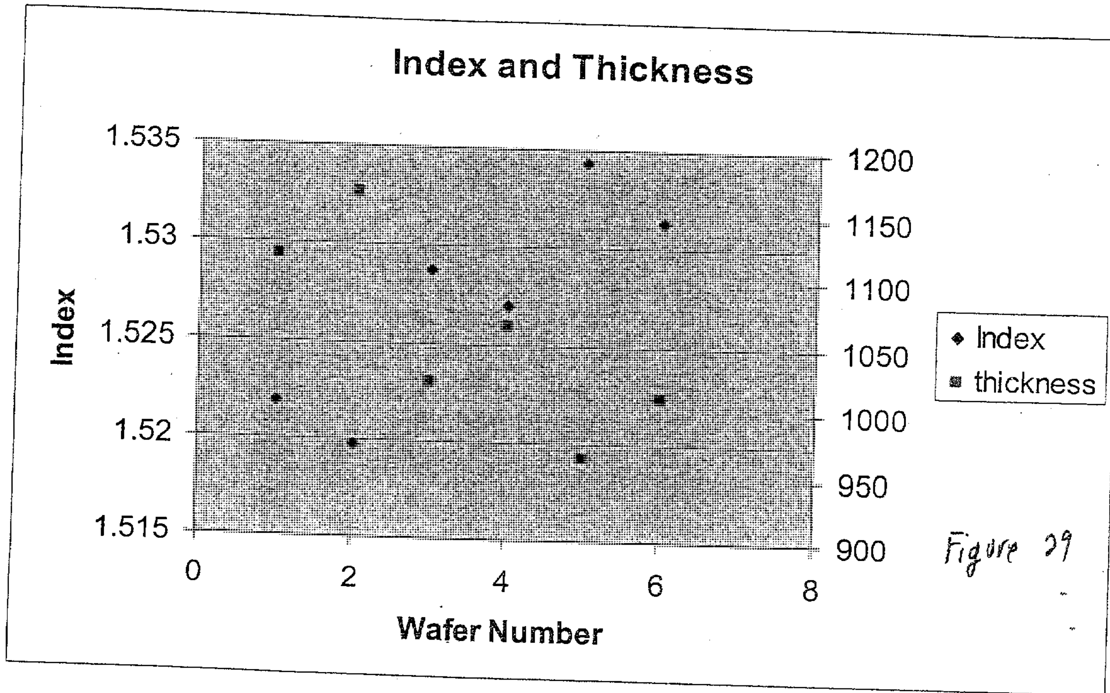


Figure 29

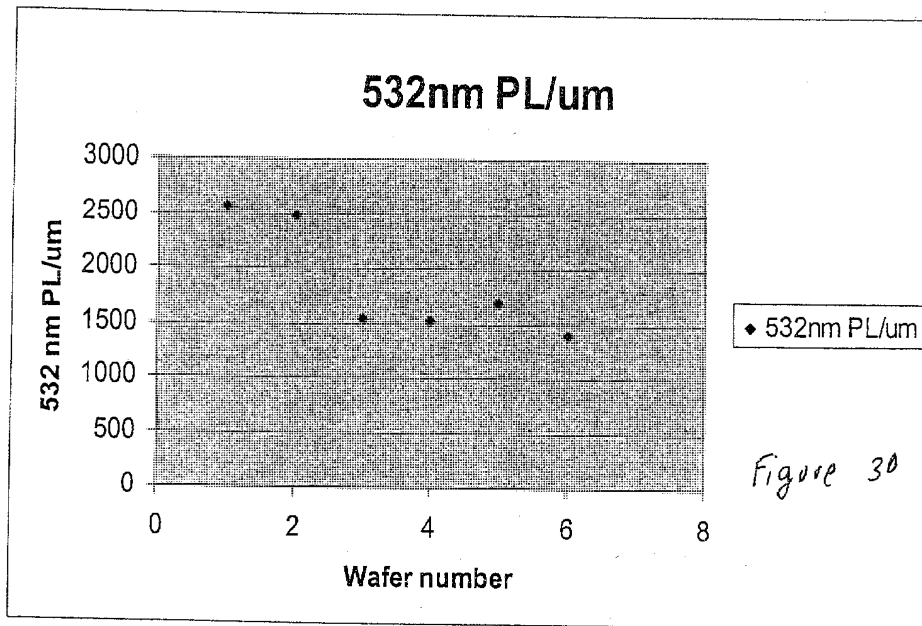


Figure 30

20974033.052501

m- 12245 US
26/27

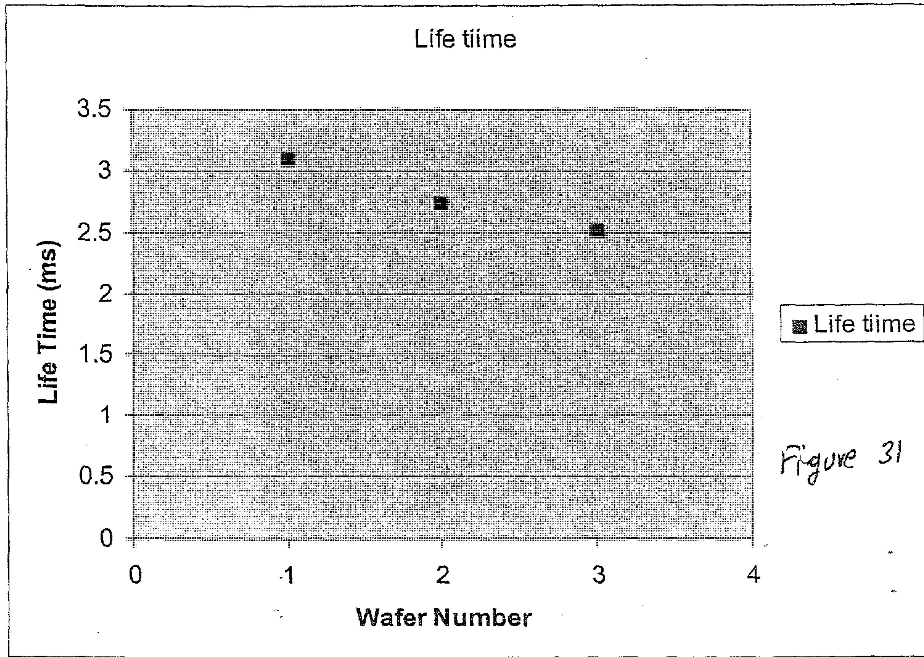


Figure 31

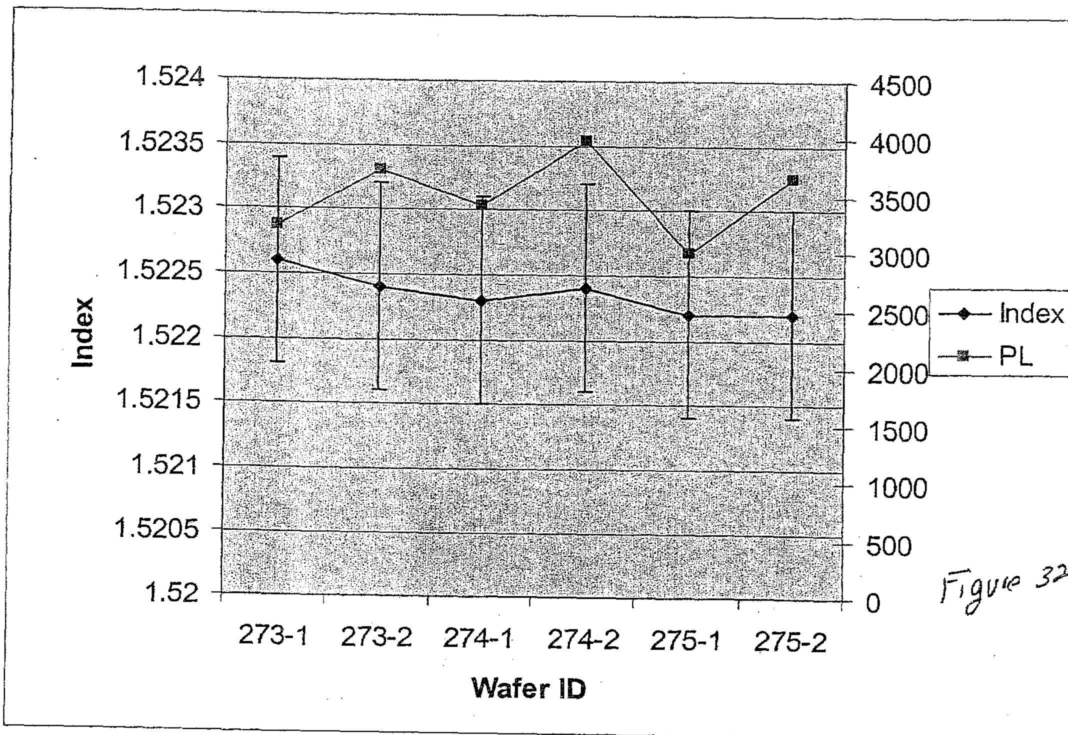


Figure 32

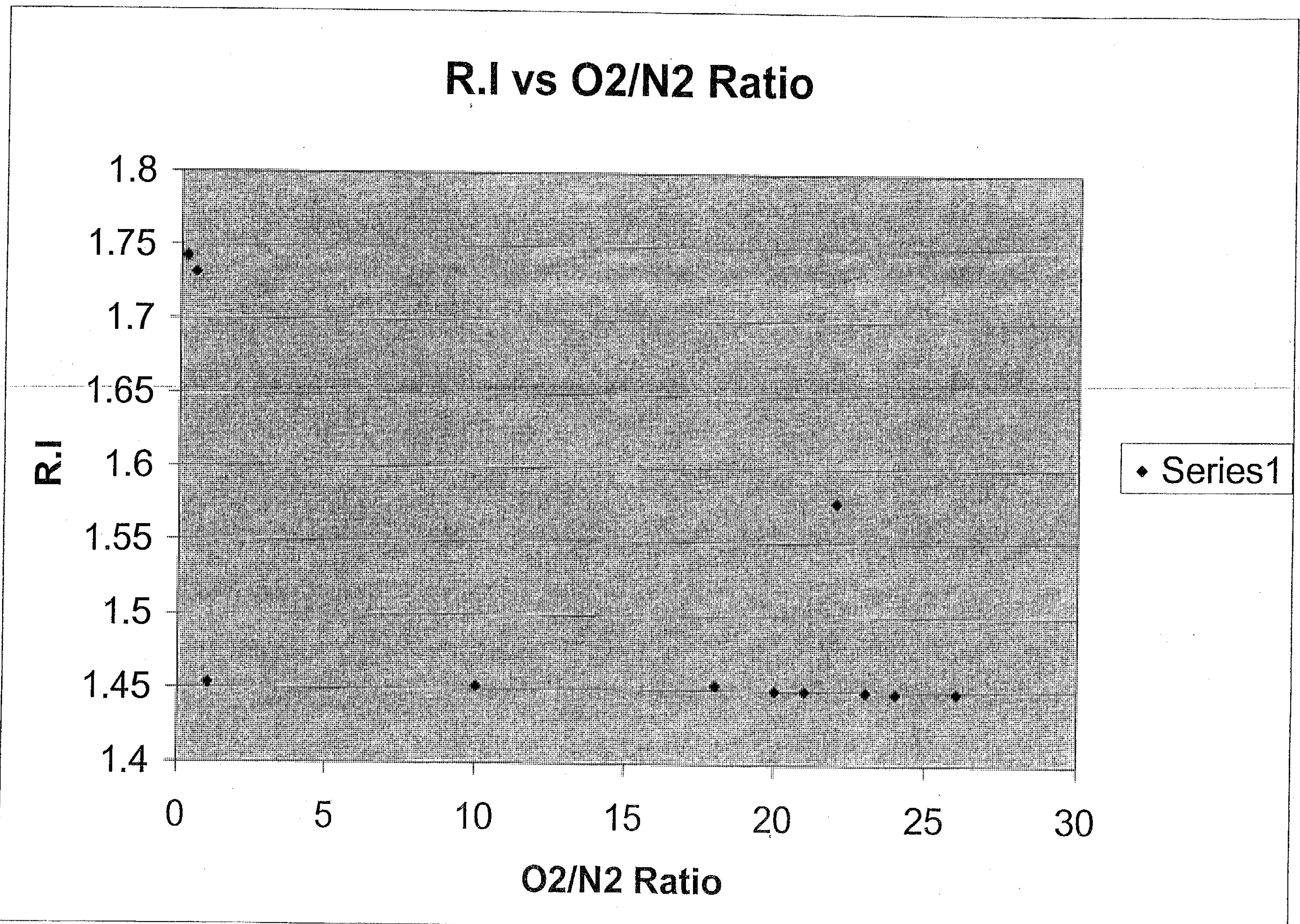


Figure 33

**DECLARATION FOR PATENT APPLICATION
AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of subject matter (process, machine, manufacture, or composition of matter, or an improvement thereof) which is claimed and for which a patent is sought by way of the application entitled

Biased Pulse DC Reactive Sputtering of Oxide Films

which (check) ☒ is attached hereto.

☐ and is amended by the Preliminary Amendment attached hereto.

☐ was filed on as Application Serial No.

☐ and was amended on (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
Number	Country	Day/Month/Year Filed	Yes	No
N/A			☐	☐

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date
N/A	

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)
N/A		

I hereby appoint the following practitioners to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith:

Customer Number 24251

Please direct all telephone calls to:

Gary J. Edwards

Telephone: 408-453-9200

I declare that all statements made herein of my own knowledge are true, all statements made herein on information and belief are believed to be true, and all statements made herein are made with the knowledge that whoever, in any matter within the jurisdiction of the Patent and Trademark Office, knowingly and willfully falsifies, conceals, or covers up by any trick, scheme, or device a material fact, or makes any false, fictitious or fraudulent statements or representations, or makes or uses any false writing or document knowing the same to contain any false, fictitious or fraudulent statement or entry, shall be subject to the penalties including fine or imprisonment or both as set forth under 18 U.S.C. 1001, and that violations of this paragraph may jeopardize the validity of the application or this document, or the validity or enforceability of any patent, trademark registration, or certificate resulting therefrom.

Full name of **first** joint inventor: Hongmei Zhang
Inventor's Signature: ______________________ Date: ______________
Residence:
Post Office Address: Citizenship:

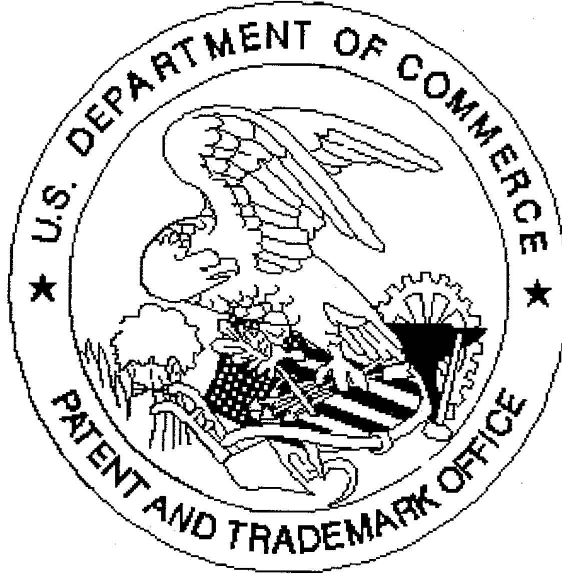
Full name of **third** joint inventor: Mukundan Narasimhan
Inventor's Signature: ______________________ Date: ______________
Residence:
Post Office Address: Citizenship:

Full name of **second** joint inventor: Ravi B. Mullapudi
Inventor's Signature: ______________________ Date: ______________
Residence: San Jose, California
Post Office Address: 2117 Shiangzone Court
San Jose, California 95121
Citizenship: India

Full name of **fourth** joint inventor: Richard E. Demaray
Inventor's Signature: ______________________ Date: ______________
Residence: Portola Valley, California
Post Office Address: 190 Fawn Lane
Portola Valley, California 94028
Citizenship: USA

United States Patent & Trademark Office

Office of Initial Patent Examination -- Scanning Division



Application deficiencies found during scanning:

☐ Page(s)____________ of ________________________________ were not present for scanning. (Document title)

☐ Page(s)____________ of ________________________________ were not present for scanning. (Document title)

☒ ***Scanned copy is best available.*** Drawing are dark.

BEST AVAILABLE COPY

10/101863 U.S. PTO 03/16/02

PATENT NUMBER and ISSUE DATE

U.S. UTILITY Patent Application

APPL NUM	FILING DATE	CLASS	SUBCLASS	GAU	EXAMINER
10101863	03/16/2002	~~230~~		~~2817~~	ESTRADA

**APPLICANTS: Zhang Hongmei; Narasimhan Mukundan; Mullapudi Ravi; Demaray Richard;

**CONTINUING DATA VERIFIED:

** FOREIGN APPLICATIONS VERIFIED:

PG-PUB	DO NOT PUBLISH ☐	RESCIND ☐	

Foreign priority claimed ☐ yes ☐ no
35 USC 119 conditions met ☐ yes ☐ no
Verified and Acknowledged Examiners's intials

ATTORNEY DOCKET NO
M-12245 US

TITLE : Biased pulse DC reactive sputtering of oxide films

U.S.DEPT. OF COMM./PAT.& TM-PTO-436L(Rev. 12-94)

NOTICE OF ALLOWANCE MAILED	Assistant Examiner	CLAIMS ALLOWED: Total Claims / Print Claim for O.G
ISSUE FEE: Amount Due / Date Paid	Primary Examiner	DRAWING: Sheets Drwg. / Figs.Drwg. / Print Fig.
☐ TERMINAL DISCLAMER	PREPARED FOR ISSUE	Application Examiner

WARNING: The information disclosed herein may be restricted. Unauthorized disclosure may be prohibited by the United States Code Title 35, Sections 122, 181 and 368, Possession outside the U.S. Patent & Trademark Office is restricted to authorized employees and contractors only.

FILED WITH: ☐ DISK (CRF) ☐ CD-ROM
(Attached in pocket on right inside flap)

BEST AVAILABLE COPY

SEARCH

Class	Sub.	Date	Exmr.

SEARCH NOTES

(List databases searched. Attach search strategy inside.)

	Date	Exmr.

INTERFERENCE SEARCHED

Class	Sub.	Date	Exmr.

BEST AVAILABLE COPY

Date Received (incl. C. of M.)

EET

APERS

ISSUE SLIP STAPLE AREA (for additional cross-references)

ISSUING CLASSIFICATION

ORIGINAL		CROSS REFERENCE(S)						
CLASS	SUBCLASS	CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					
INTERNATIONAL CLASSIFICATION								
/								
/								
/								
/								
/								

^ Continued on Issue Slip Inside File Jacket

BEST AVAILABLE COPY

INDEX OF CLAIMS

✓ .... Rejected
= .... Allowed
– (Through numeral) ... Canceled
+ .... Restricted
N .... Non-elected
I .... Interference
A .... Appeal
O .... Objected

Claim Final	Claim Original	Date	Claim Final	Claim Original	Date	Claim Final	Claim Original	Date
	1			51			101	
	2			52			102	
	3			53			103	
	4			54			104	
	5			55			105	
	6			56			106	
	7			57			107	
	8			58			108	
	9			59			109	
	10			60			110	
	11			61			111	
	12			62			112	
	13			63			113	
	14			64			114	
	15			65			115	
	16			66			116	
	17			67			117	
	18			68			118	
	19			69			119	
	20			70			120	
	21			71			121	
	22			72			122	
	23			73			123	
	24			74			124	
	25			75			125	
	26			76			126	
	27			77			127	
	28			78			128	
	29			79			129	
	30			80			130	
	31			81			131	
	32			82			132	
	33			83			133	
	34			84			134	
	35			85			135	
	36			86			136	
	37			87			137	
	38			88			138	
	39			89			139	
	40			90			140	
	41			91			141	
	42			92			142	
	43			93			143	
	44			94			144	
	45			95			145	
	46			96			146	
	47			97			147	
	48			98			148	
	49			99			149	
	50			100			150	

If more than 150 claims or 9 actions staple additional sheet here

BEST AVAILABLE COPY

JC658 U.S. PTO
03/16/02

25 Metro Drive
Suite 700
San Jose
California 95110
T: 408-453-9200
F: 408-453-7979
Austin, TX
Newport Beach, CA
San Francisco, CA

skjerven morrill macpherson LLP

Docket No.: M-12245 US

J1017 U.S. PTO
10/101863
03/16/02

March 16, 2002

Box Patent Application
Commissioner For Patents
Washington, D. C. 20231

Enclosed herewith for filing is a patent application, as follows:

Inventor(s): Zhang, Hongmei; Narasimhan, Mukundan; Mullapudi, Ravi; and Demaray, Richard E.

Title: **Biased Pulse DC Reactive Sputtering of Oxide Films**

X Return Receipt Postcard
X This Transmittal Letter (in duplicate)
2 page(s) Declaration For Patent Application and Power of Attorney (unsigned)
34 page(s) Specification (not including claims)
4 page(s) Claims
1 page Abstract
27 Sheet(s) of Drawings
☒ **Applicant(s) assert(s) entitlement to small entity status for the attached patent application**

10101863 031602

CLAIMS AS FILED (fees computed under 37 CFR §1.9(f))

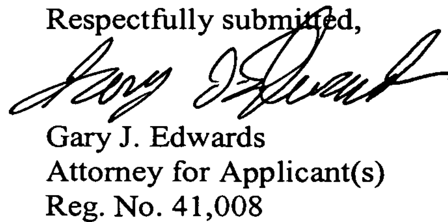
For	Number Filed			Number Extra		Rate			Basic Fee
								$	370.00
Total Claims	39	-20	=	9	x	$ 9.00	=	$	81.00
Independent Claims	5	-3	=	2	x	$42.00	=	$	84.00
☐ Fee of _____ for the first filing of one or more multiple dependent claims per application								$	
☐ Fee for Request for Extension of Time								$	

Please make the following charges to Deposit Account 19-2386:

☐ Total fee for filing the patent application in the amount of $ 525.00
☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account 19-2386.

EXPRESS MAIL LABEL NO:
EL 941 069 152 US

Respectfully submitted,



Gary J. Edwards
Attorney for Applicant(s)
Reg. No. 41,008

M-12245 US
1/27

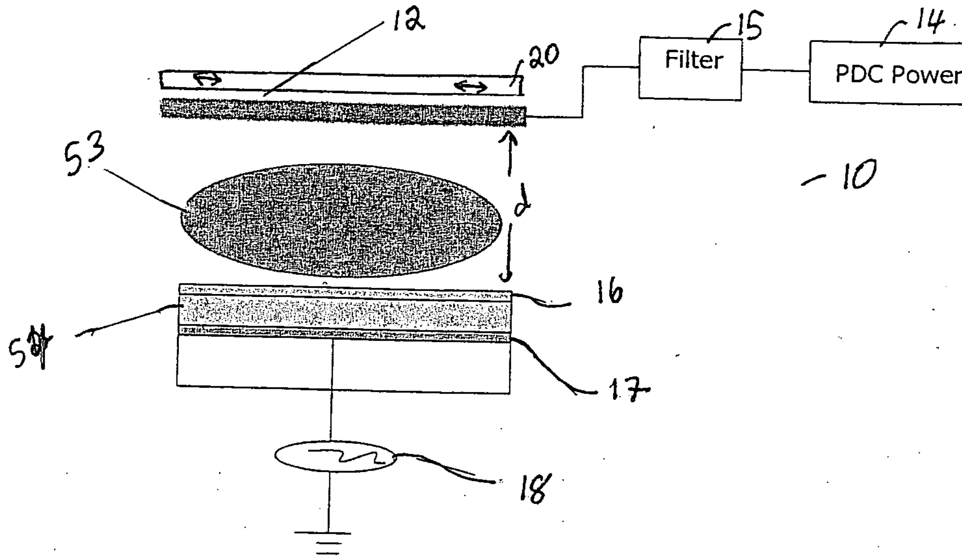


Figure 1A

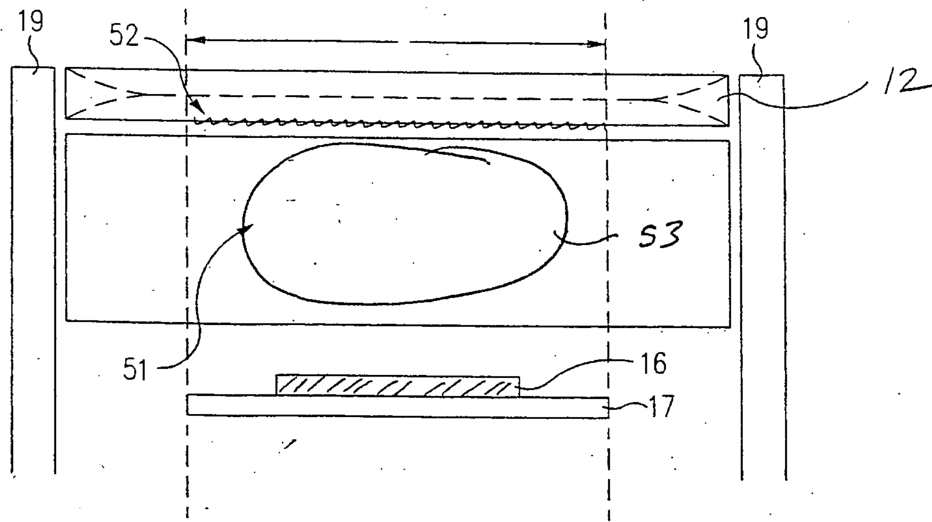


FIG. 1B

10101653.031602

M- 12245 US
2/27

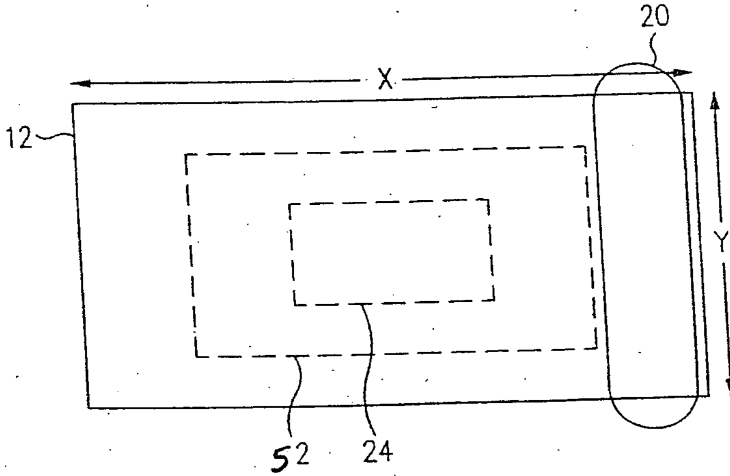


FIG. 2

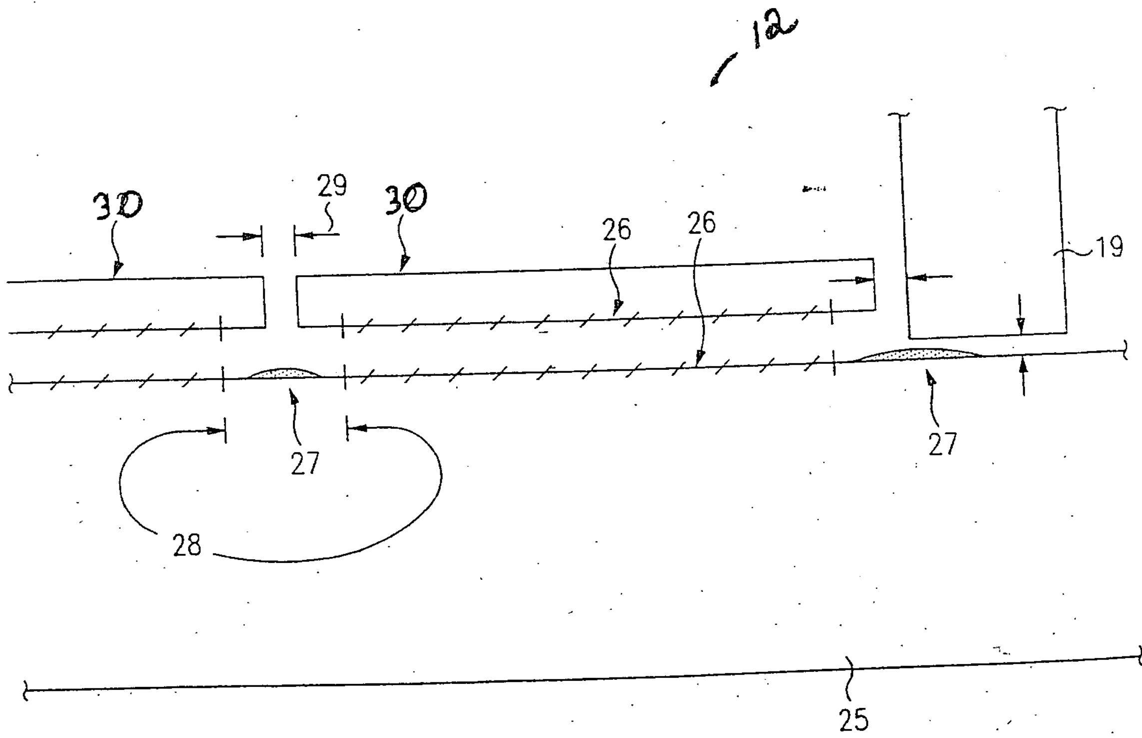


FIG. 3

10101853.031602

M- 12245 US
3/27

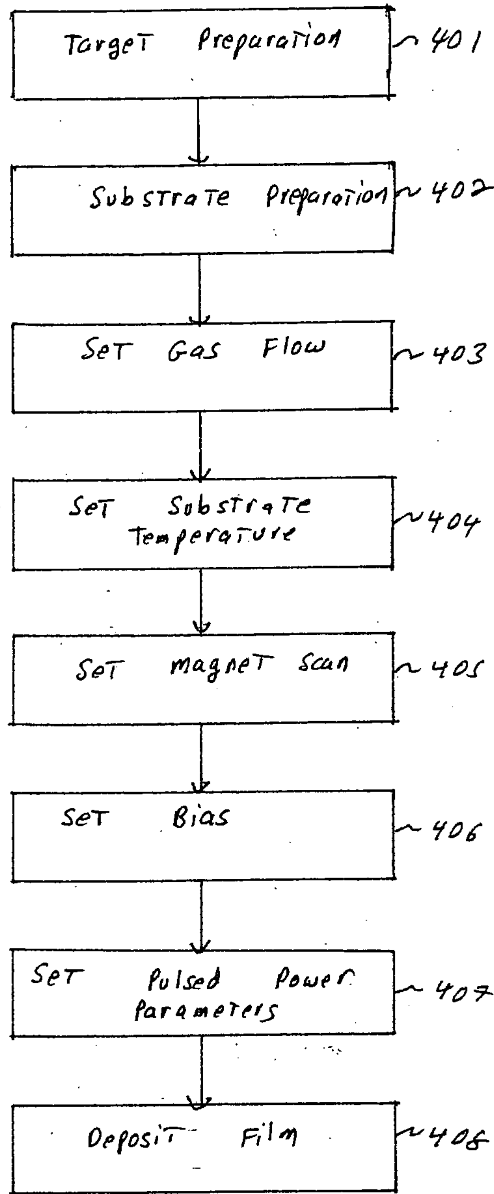


Figure 4

20091203.031501

m- 12245 US
4/27

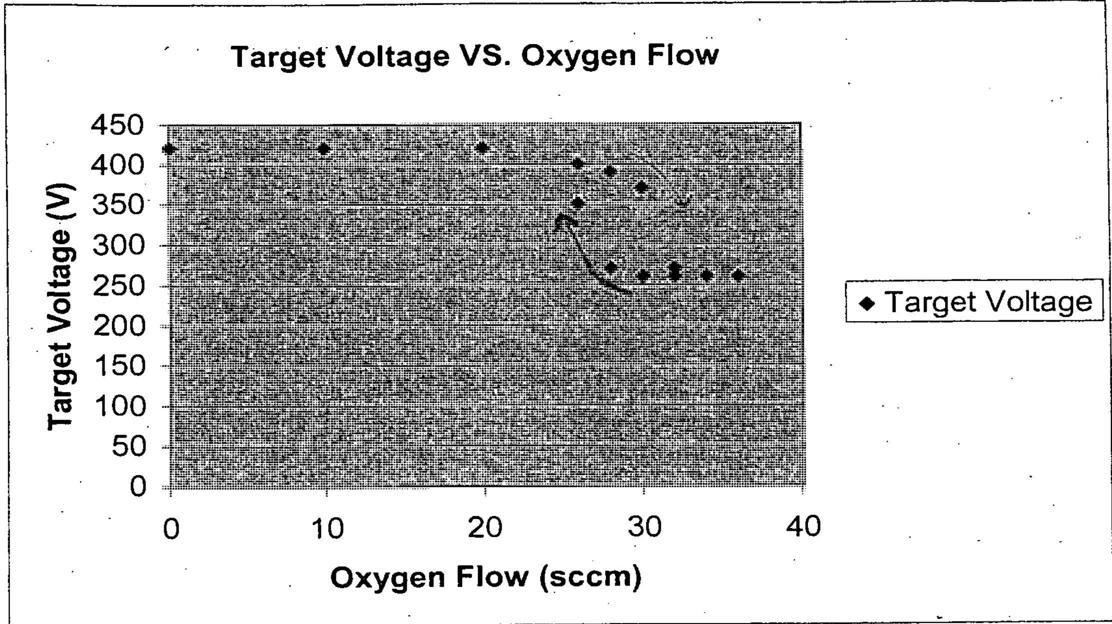


Figure 5

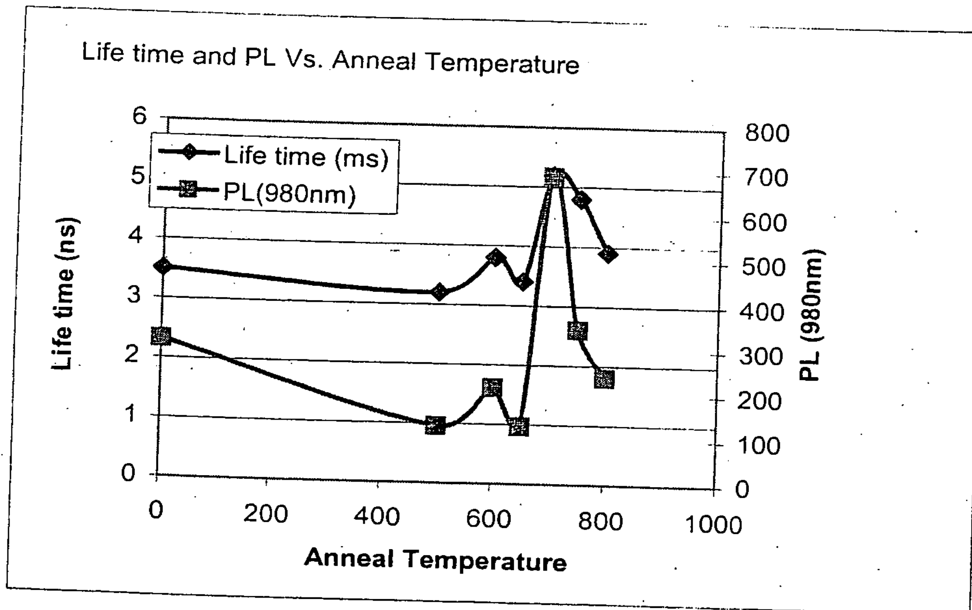


Figure 6

20951E03.010101

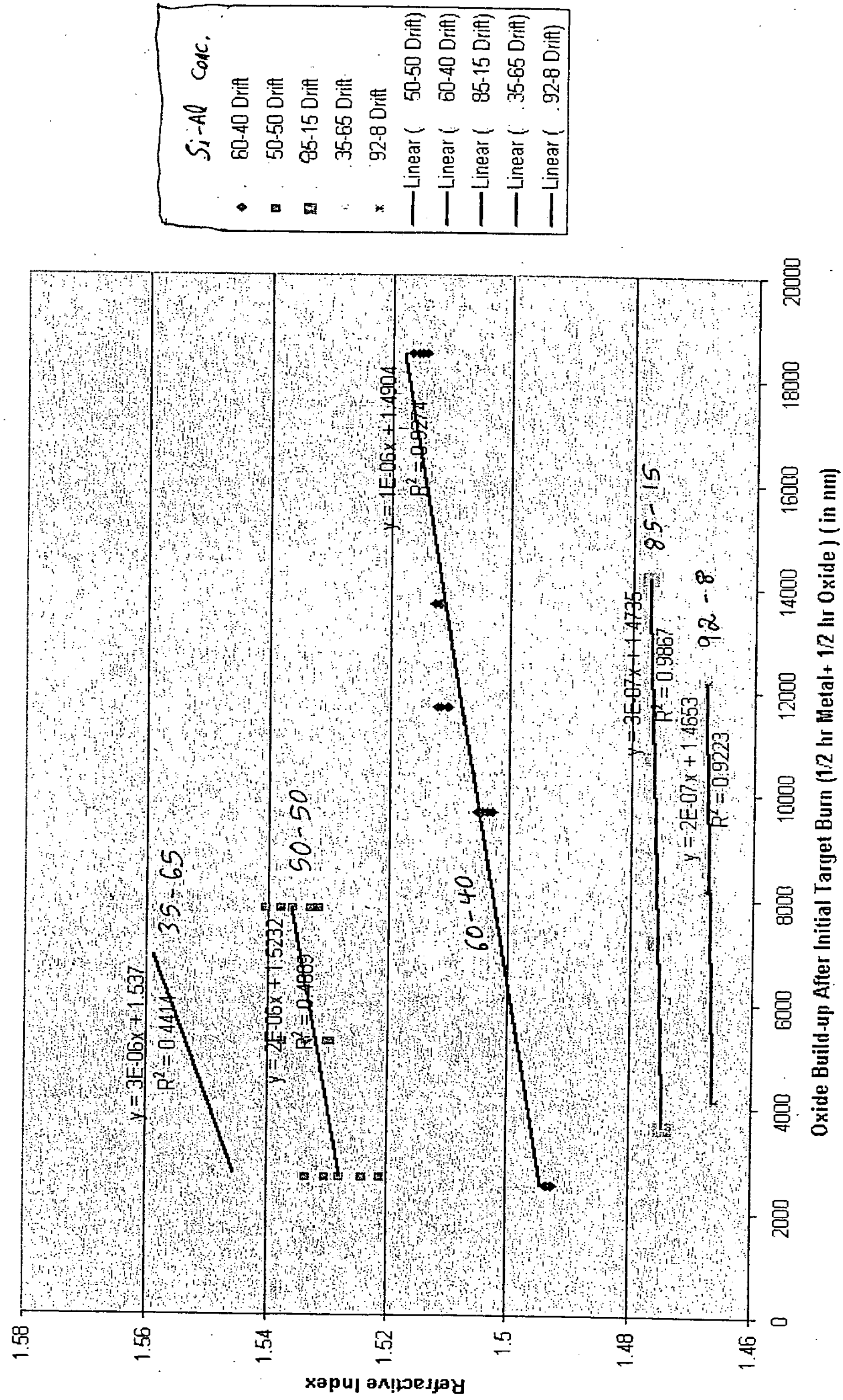


Figure 7

Refractive Index as a function of Al% in Aluminosilicates

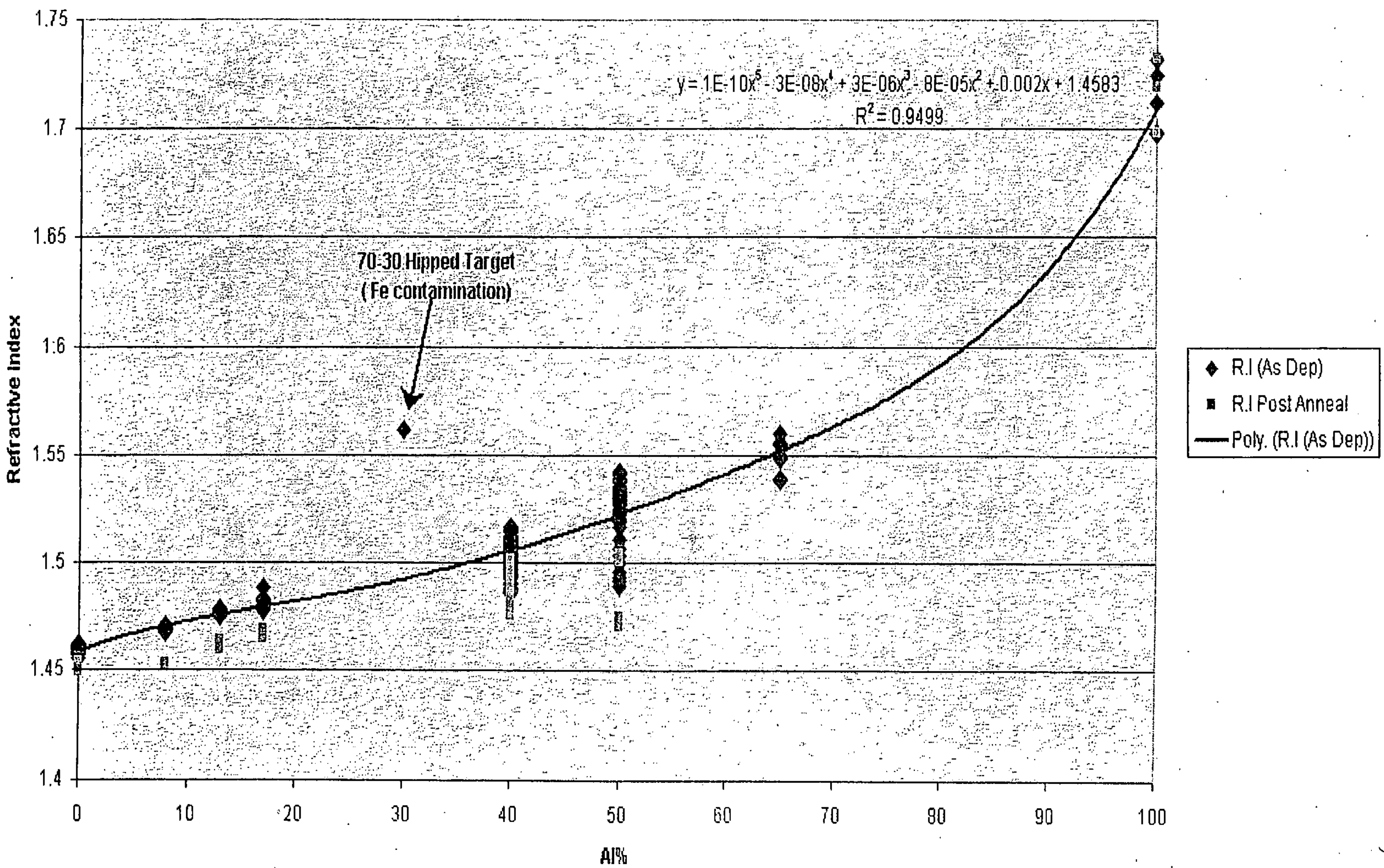


Figure 8

m- 12245 US
6/27

209TEO" E98TOTOT

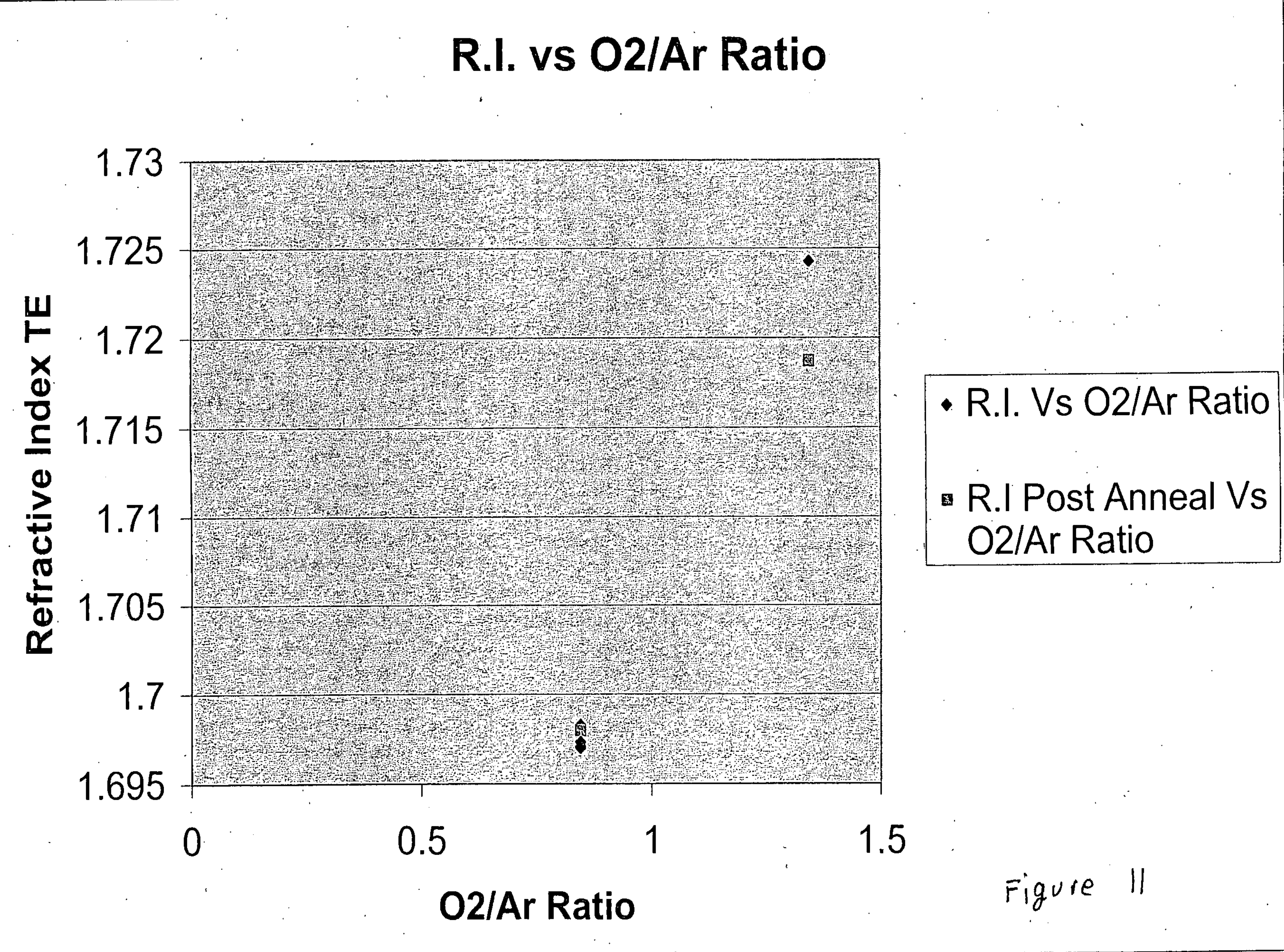
Material (Er/Yb/Al/Si)	Expected index (Post anneal)	Actual index (Post anneal)	Process Conditions (Annealed 725c 30min)
0.8/0.8/41.4/57	1.506	1.510	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.6/0.5/49/48.9	1.526	1.528	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/8/92	1.452	1.456-1.459	4.5KW, Ar-30-60,O2-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/40/60	1.504	1.486-1.501	3.0-4.5KW, Ar-30,O2-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/50/50	1.520	1.491-1.503	4.0-4.5KW, Ar-30,O2-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/65/35	1.544	1.545-1.560	4.5-5.5KW, Ar75-90, O285-100, 200Khz,2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/30/70	1.490	1.562 (high Fe content)	5.0KW, Ar75, O2-100, 200Khz,2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.5/0/48.5/50	1.523	1.509-1.513	6KW, Ar-60,O2-28sccm, 120KHz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias

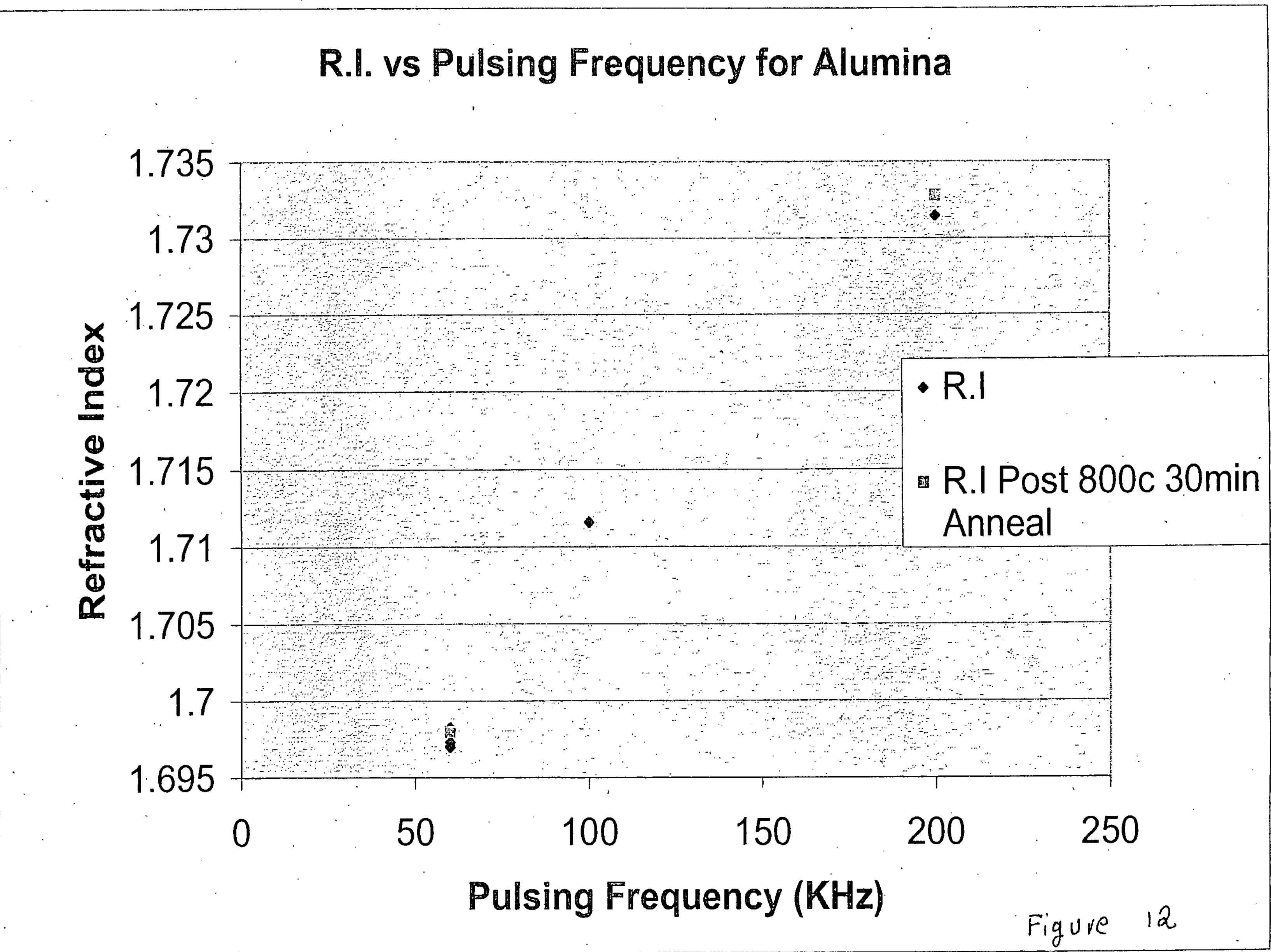
Figure 9

m - 12245 US
7/27

Bias P wer (Watts)	DC Power (KW)	Pulsing Freq (KHz)	Reverse Time (µs)	Ar Flow (sccms)	O2 Flow (sccms)	Wafer Position	Target To Wafer Spacing (mm)	Refractive Index Avg (@1550nm)	Refractive Index STD (@1550nm)	Dep Rate (um/Hr)
150	4.5	200	2.2	100	100	1	55	1.461508	0.000535	0.957654
150	4.5	200	2.2	100	100	2	55	1.462329	0.000376	0.962581
400	4.5	200	2.2	100	100	1	55	1.462774	0.000103	0.814007
400	4.5	200	2.2	100	100	2	55	1.463583	0.000095	0.824566

Figure 10


R.I. vs O2/Ar Ratio
Refractive Index TE
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
0.5
1
1.5
O2/Ar Ratio
R.I. Vs O2/Ar Ratio
R.I Post Anneal Vs O2/Ar Ratio
Figure 11


R.I. vs Pulsing Frequency for Alumina
Refractive Index
1.735
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
50
100
150
200
250
Pulsing Frequency (KHz)
R.I
R.I Post 800c 30min Anneal
Figure 12

209TE0"E98T0T0T

Target 92-8
AKT 4300 Based Reactor

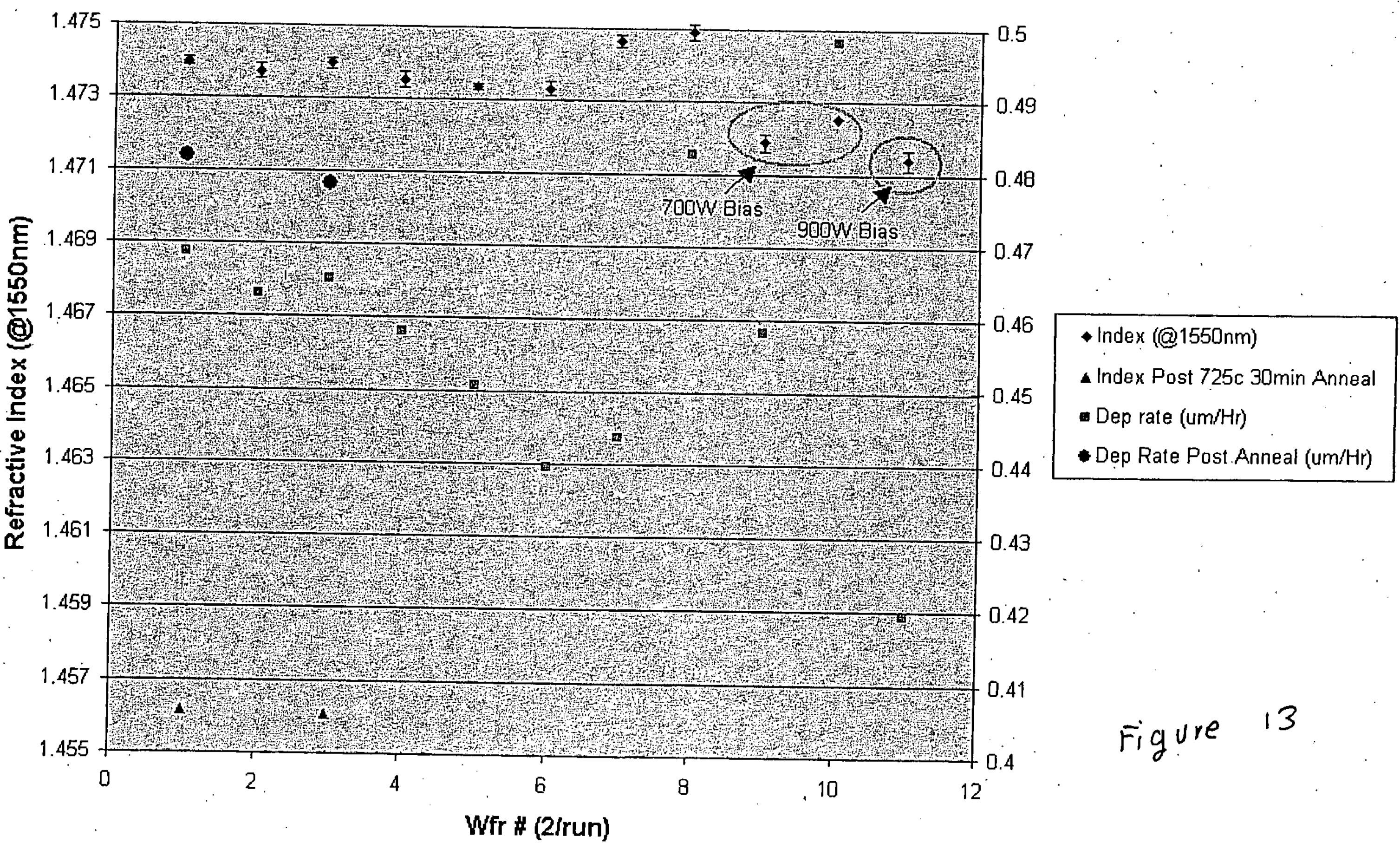
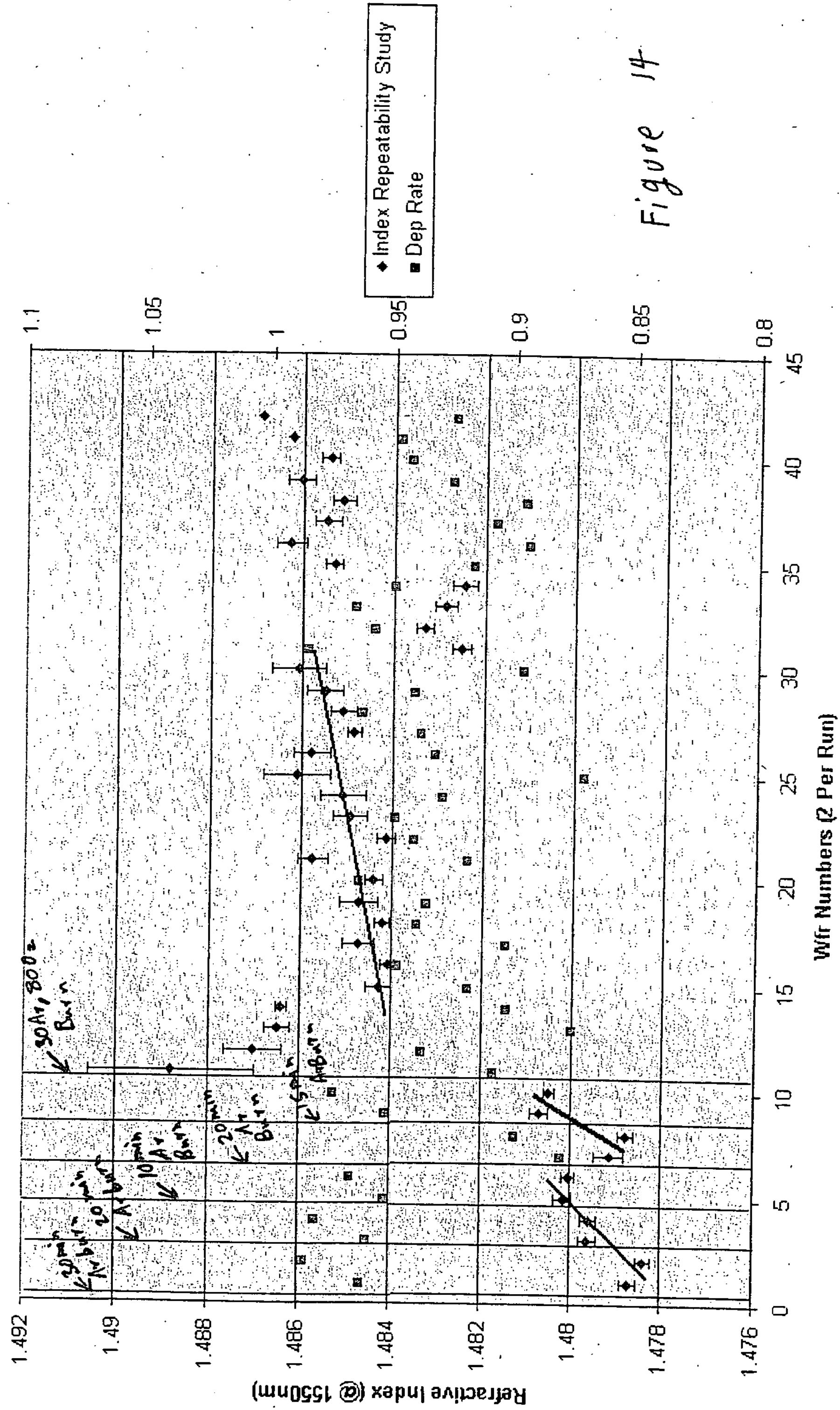


Figure 13

m-12 245 US
11/27


Index Drift Control
Target Comp. 83-17
(AKT-1600 based reactor)
Index Repeatability Study
Dep Rate
Refractive Index (@ 1550nm)
Wfr Numbers (2 Per Run)
1.492
1.49
1.488
1.486
1.484
1.482
1.48
1.478
1.476
1.1
1.05
1
0.95
0.9
0.85
0.8
0
5
10
15
20
25
30
35
40
45
Figure 14

83-17 TargeT / AKT 1600 based reactor

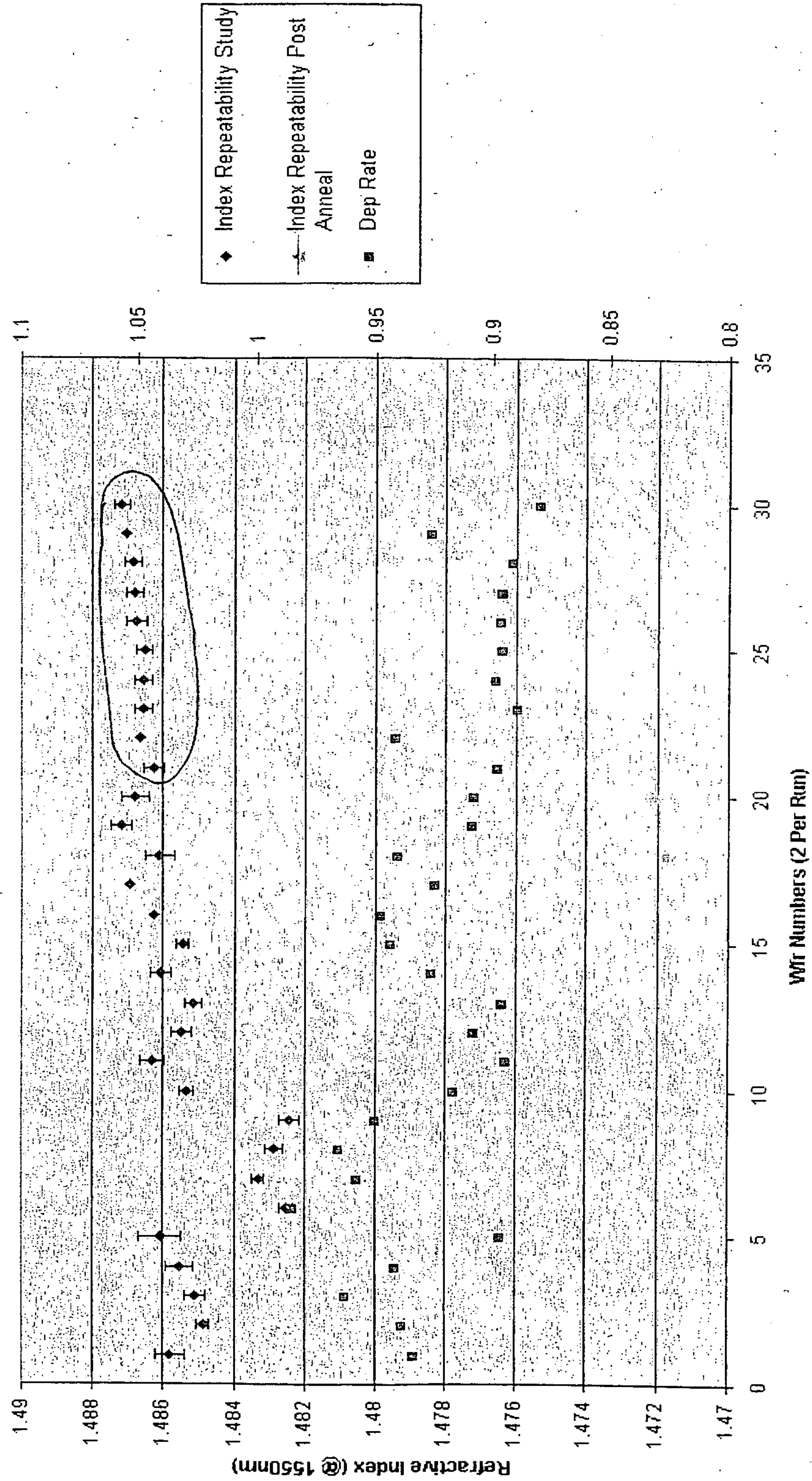
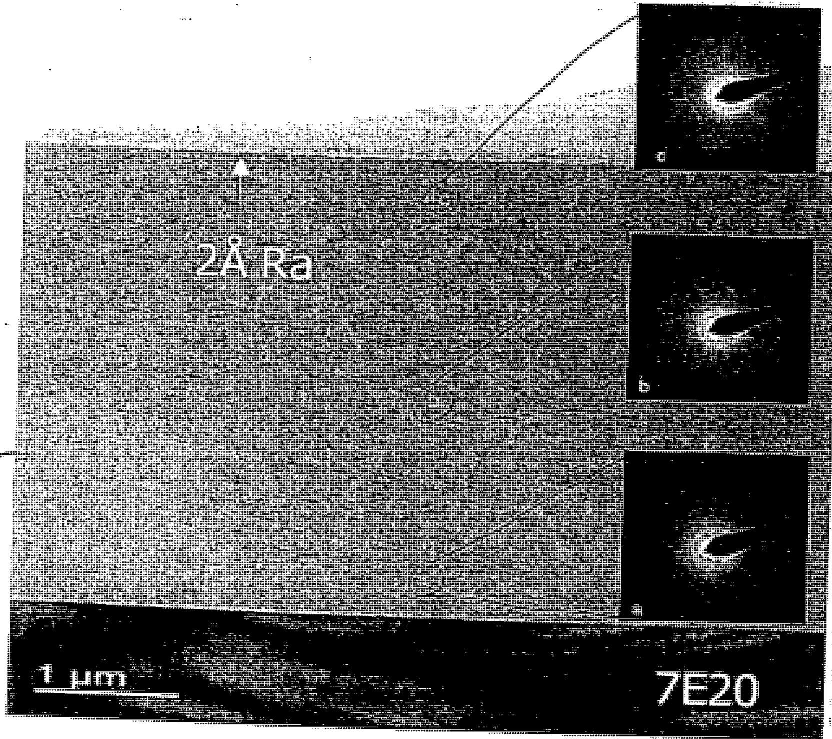


Figure 15

m- 12245 US
14/27

20910031.031801



Symmorphix PVD aluminosilicate

Figure 16 A

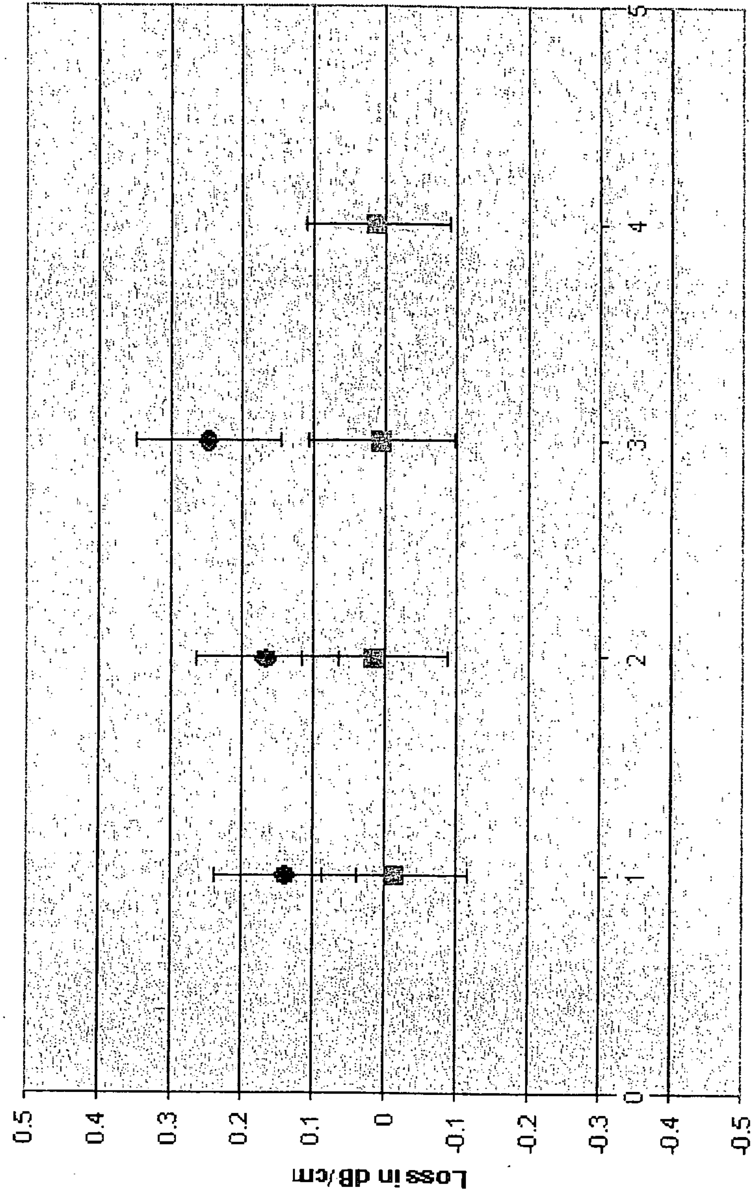


Figure 17

m- 12245 US
15/27

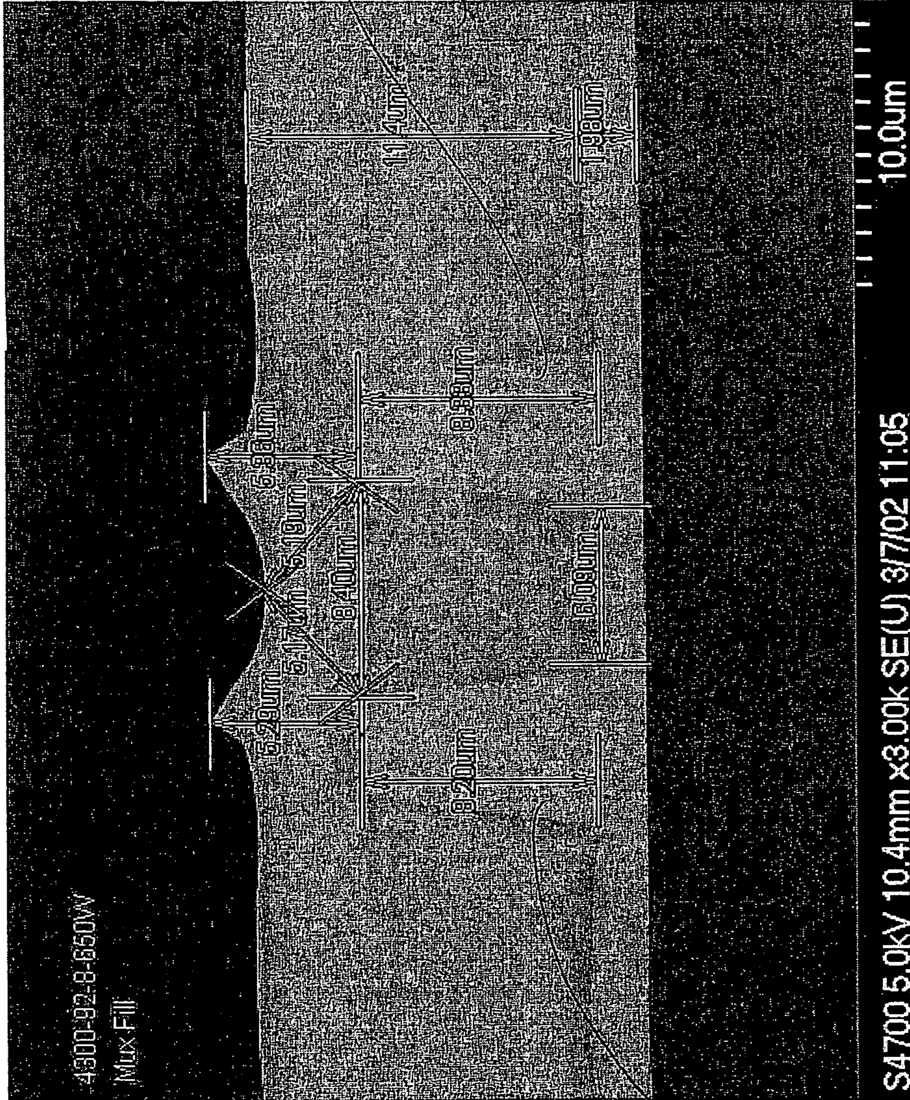


Figure 18

m-12245 US
16/32

M-12245 US
17/27

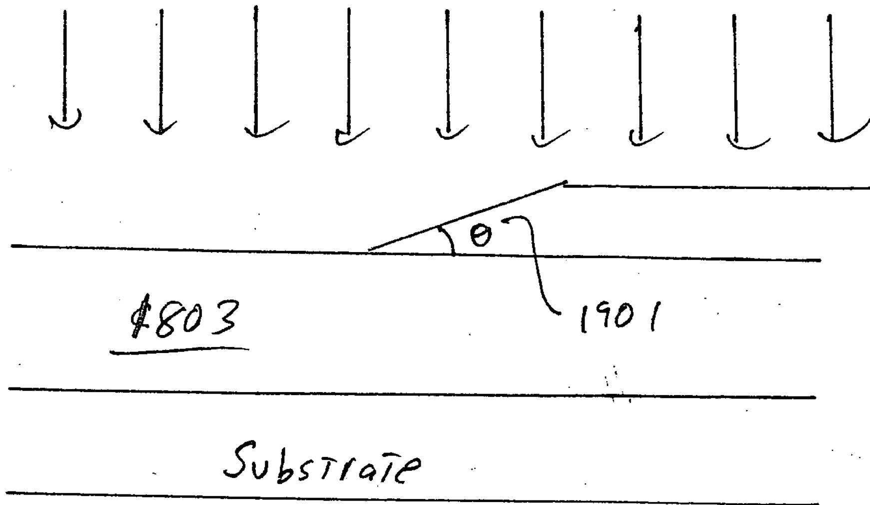


Figure 19

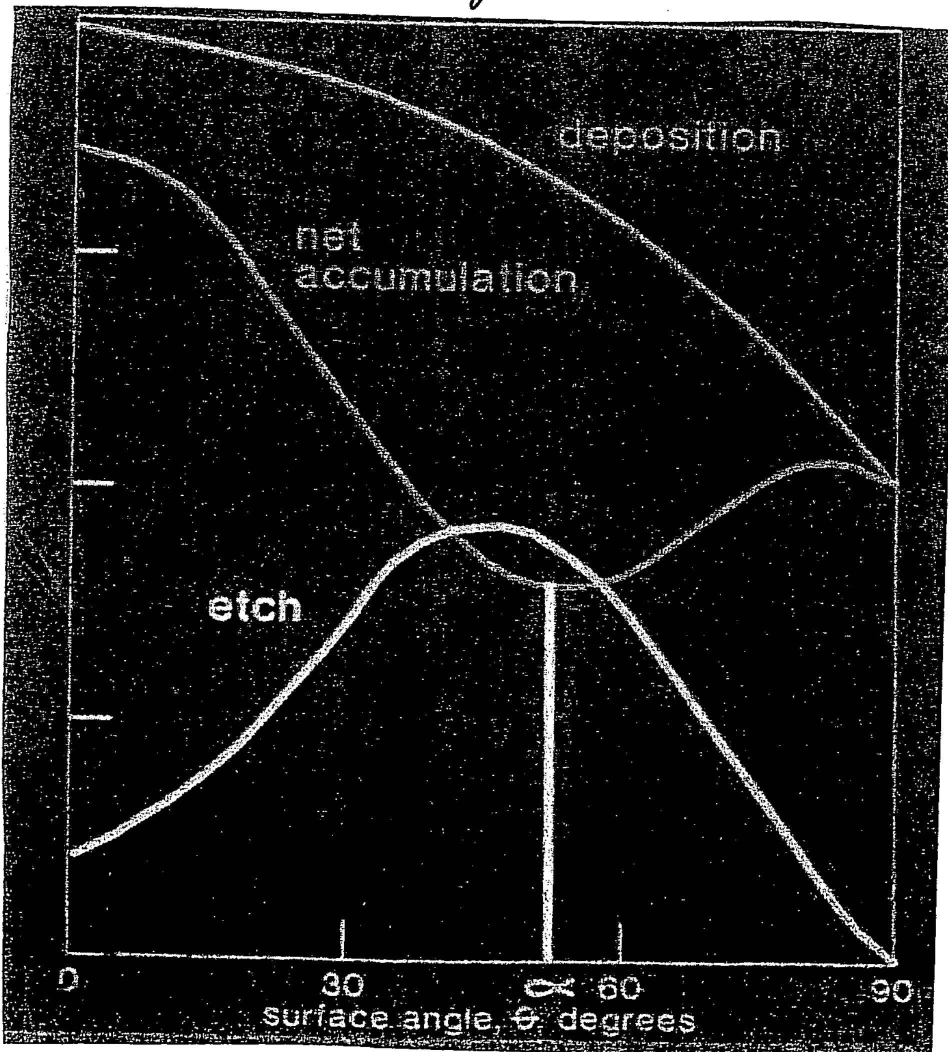


Figure 20

20915023.031502

m-12245 US
18/27

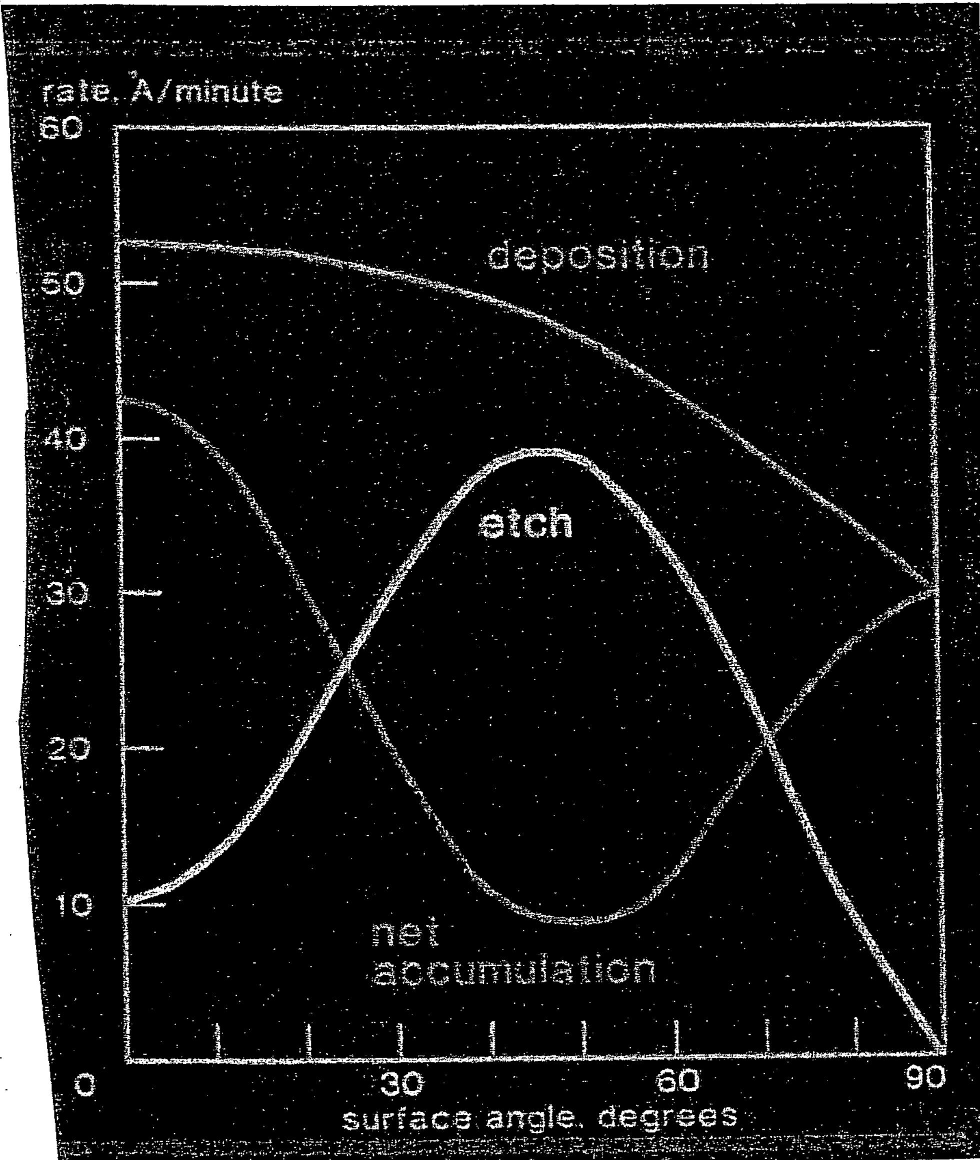


Figure 21

20916303.298101
01

m-12245 US
19/27

10101863.031502

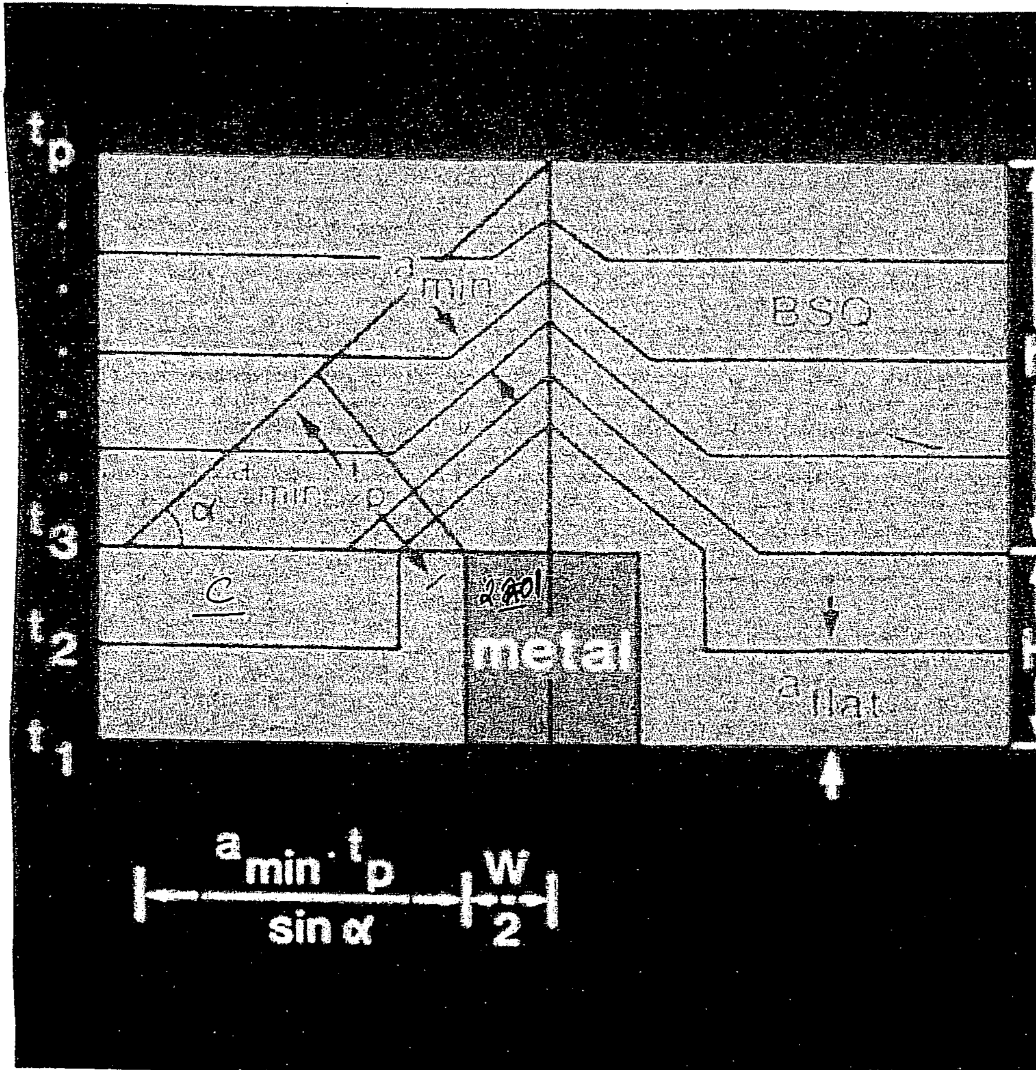


Figure 22

m-12 245 US
20/27

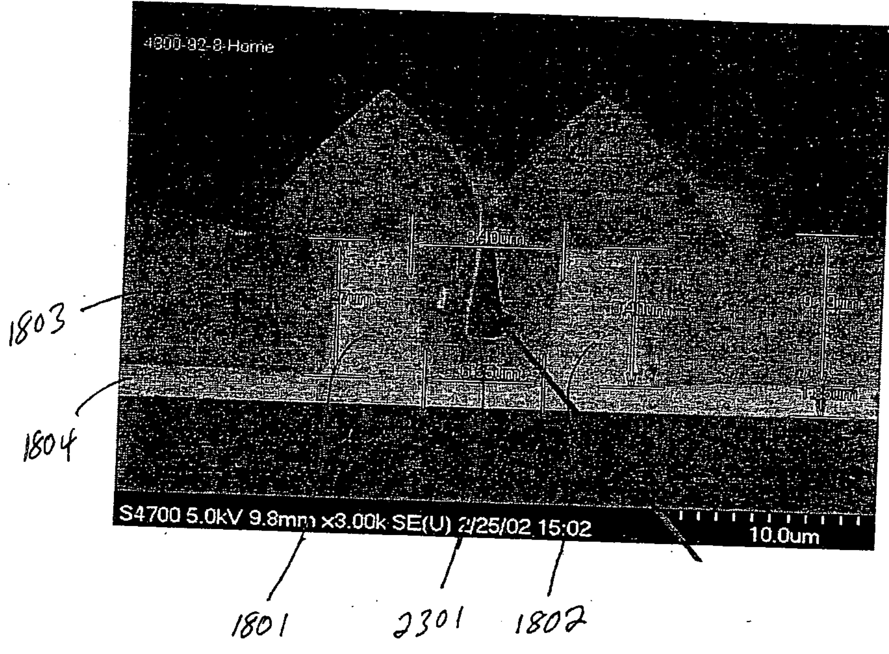
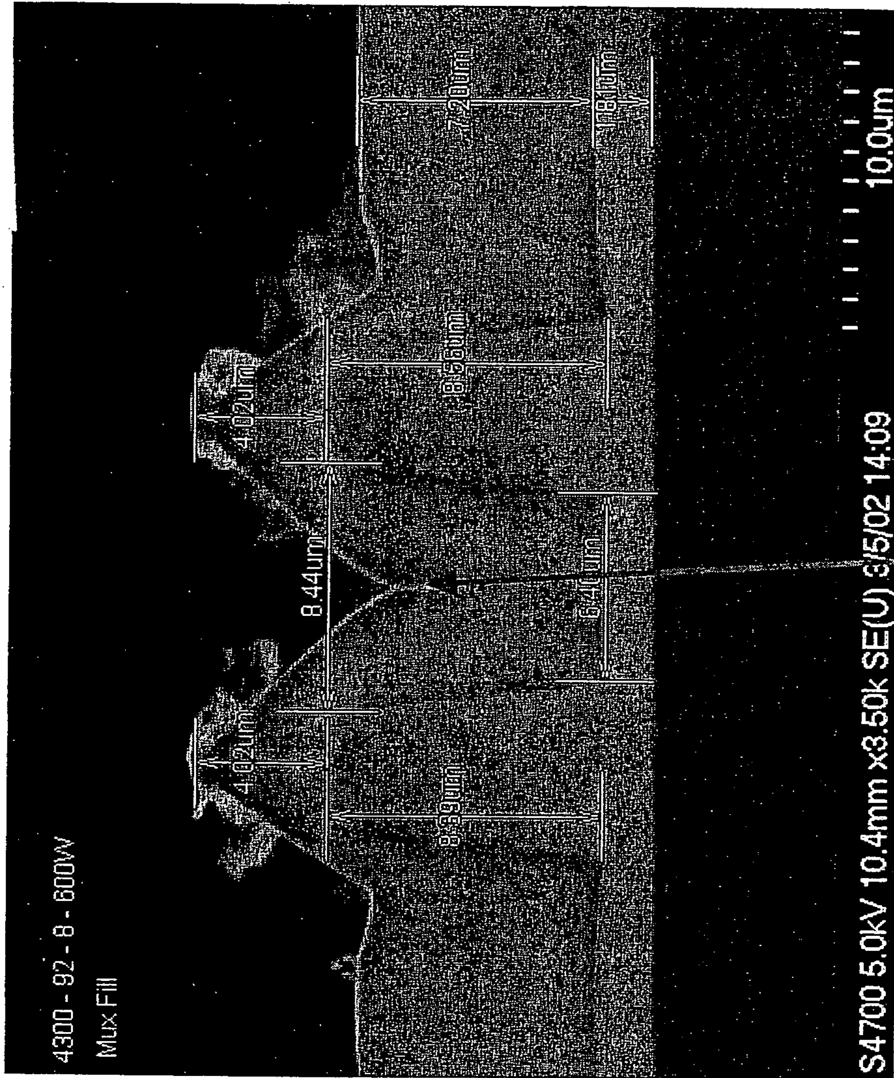


Figure 23



2401

Figure 24

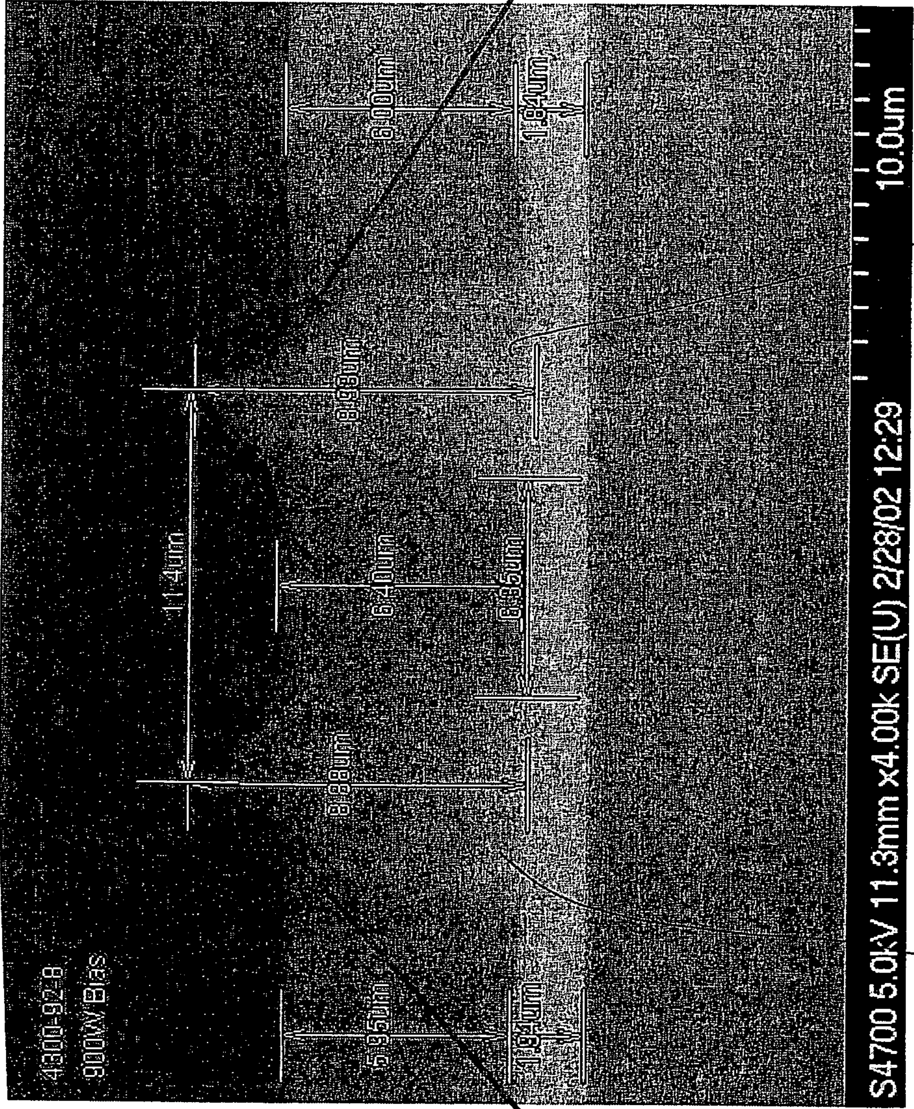


Figure 25

m- 12245 US
23/27

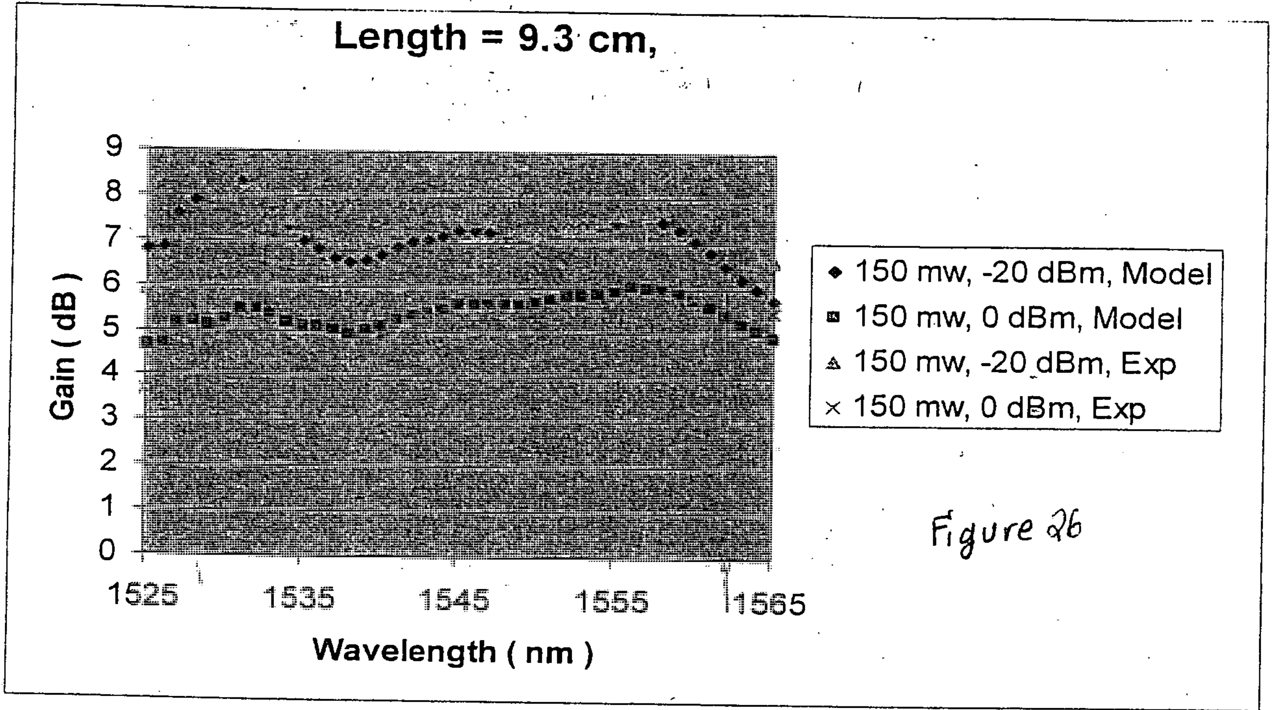


Figure 26

20916563.010101

m- 12 245 US
24/27

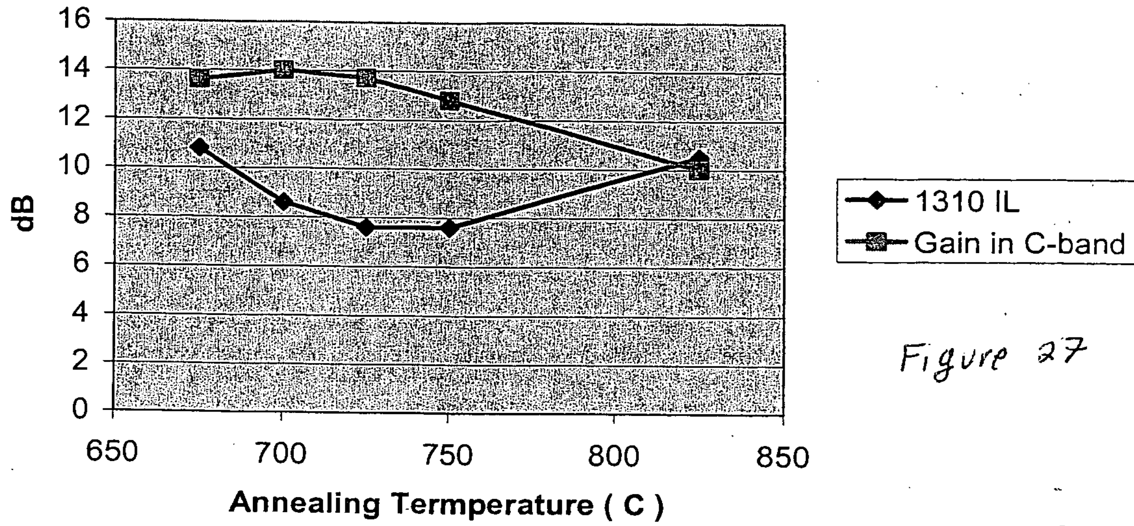
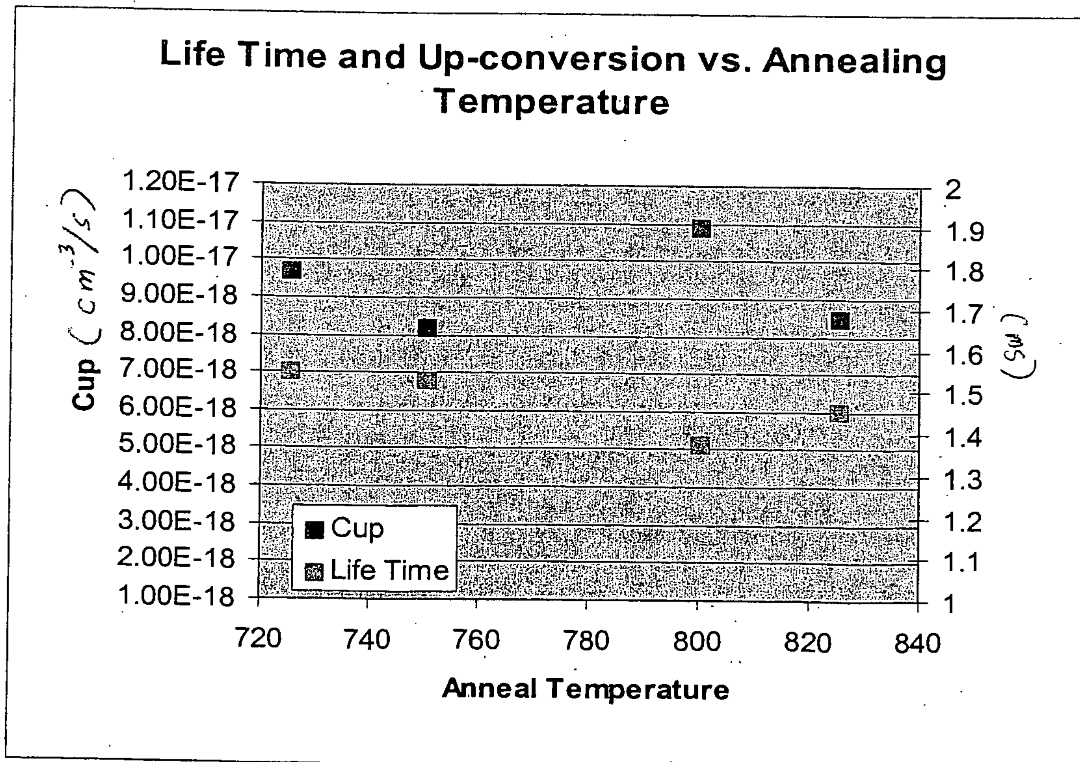


Figure 27

Figure 28



20910863.031601

m-12245 US
25/27

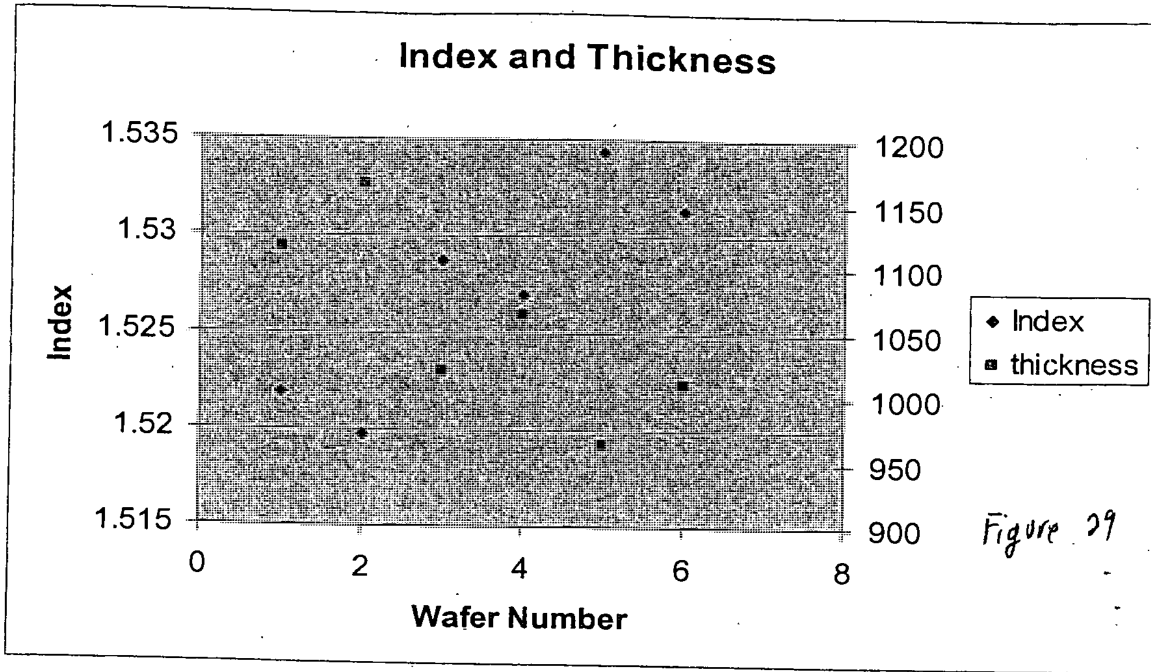


Figure 29

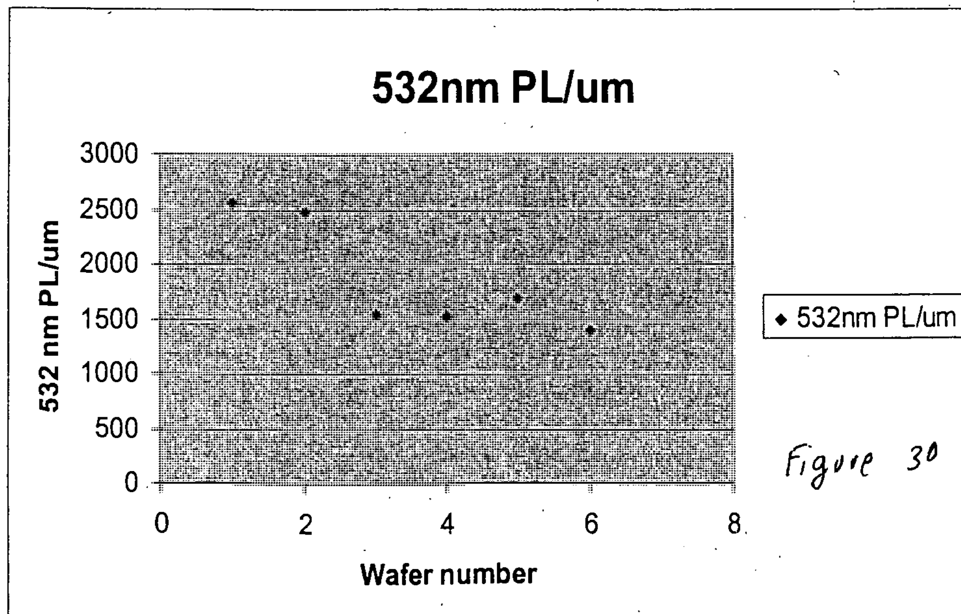


Figure 30

2091503 .03386140101

m- 12245 US
26/27

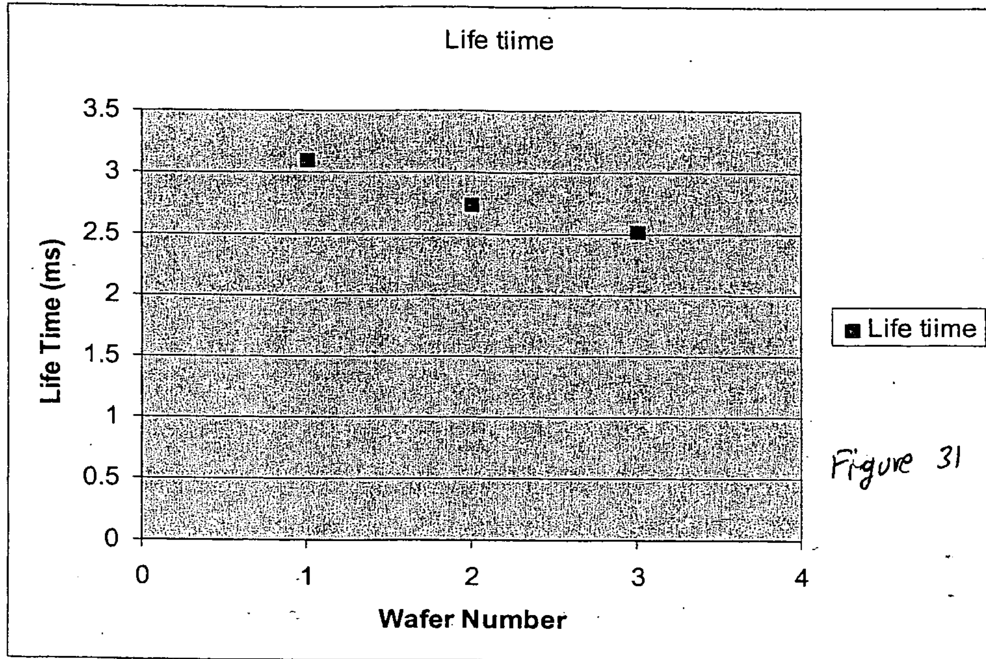


Figure 31

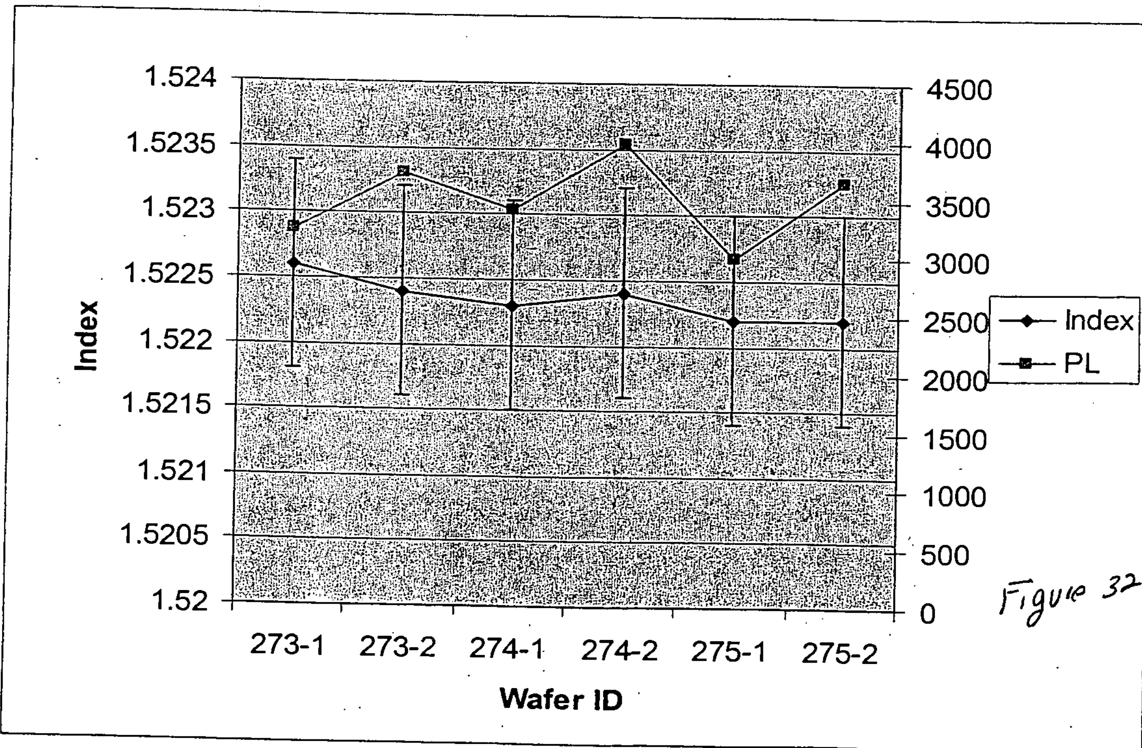


Figure 32

10101863 .031602

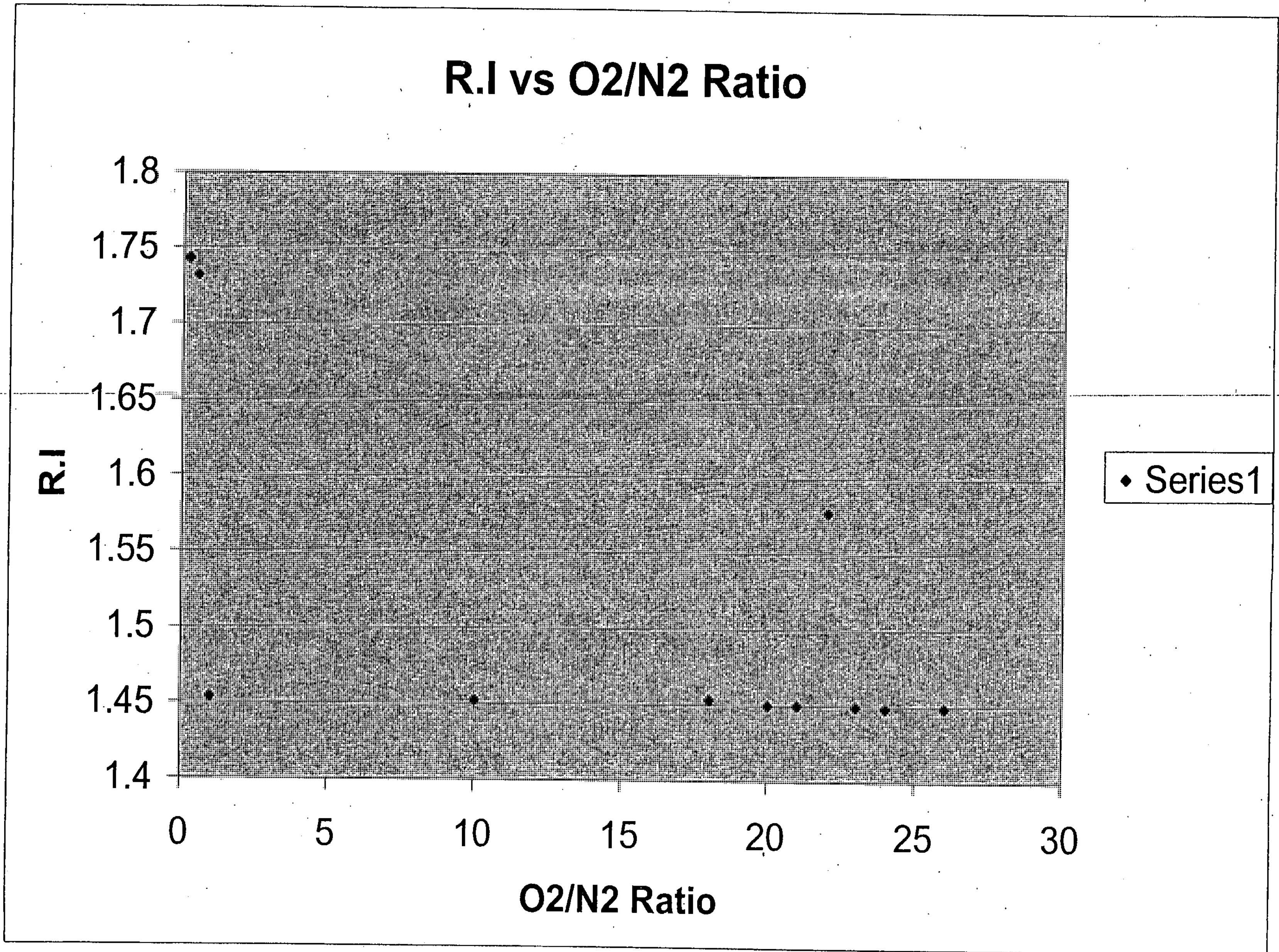


Figure 33

M-12245 US
852923 v1

Express Mail Label No.
EL 941069152 US

Biased Pulse DC Reactive Sputtering of Oxide Films

Hongmei Zhang
Mukundan Narasimhan
Ravi Mullapudi
Richard E. Demaray

Background

1. Field of the Invention

[0001] The present invention relates to deposition of oxide and oxynitride films and, in particular, to deposition of oxide and oxynitride films by pulsed DC reactive sputtering.

2. Discussion of Related Art

[0002] Deposition of insulating materials and especially optical materials is technologically important in several areas including production of optical devices and production of semiconductor devices. In semiconductor devices, doped alumina silicates can be utilized as high dielectric insulators.

[0003] The increasing prevalence of fiber optic communications systems has created an unprecedented demand for devices for processing optical signals. Planar devices such as optical waveguides, couplers, splitters, and amplifiers, fabricated on planar substrates, like those commonly used for integrated circuits, and configured to receive and process signals from optical fibers are highly desirable. Such devices hold promise for integrated optical and electronic signal processing on a single semiconductor-like substance.

[0004] The basic design of planar optical waveguides and amplifiers is well known, as described, for example, in U. S. Patent Nos. 5,119,460 and 5,563,979 to Bruce et al., 5,613,995 to Bhandarkar et al., 5,900,057 to Buchal et al., and 5,107,538 to Benton et al., to cite only a few. These devices, very generally, include a core region, typically bar shaped, of a certain refractive index surrounded by a cladding region of a lower refractive index. In the case of an optical amplifier, the core region includes a certain concentration of a dopant, typically a rare earth ion

such as an erbium or praseodymium ion which, when pumped by a laser, fluoresces, for example, in the 1550 nm and 1300 nm wavelength ranges used for optical communication, to amplify the optical signal passing through the core.

[0005] As described, for example in the patents by Bruce et al., Bhandarkar et al, and Buchal et al., planar optical devices may be fabricated by process sequences including forming a layer of cladding material on a substrate; forming a layer of core material on the layer of cladding mater; patterning the core layer using a photolighotgraphic mask and an etching process to form a core ridge; and covering the core ridge with an upper cladding layer.

[0006] The performance of these planar optical devices depends sensitively on the value and uniformity of the refractive index of the core region and of the cladding region, and particularly on the difference in refractive index, Δn, between the regions. Particularly for passive devices such as waveguides, couplers, and splitters, Δn should be carefully controlled, for example to values within about 1 %, and the refractive index of both core and cladding need to be highly uniform, for some applications at the fewer than parts per thousand level. In the case of doped materials forming the core region of planar optical amplifiers, it is important that the dopant be uniformly distributed so as to avoid non-radiative quenching or radiative quenching, for example by upconversion. The refractive index and other desirable properties of the core and cladding regions, such as physical and chemical uniformity, low stress, and high density, depend, of course, on the choice of materials for the devices and on the processes by which they are fabricated.

[0007] Because of their optical properties, silica and refractory oxides such as Al_2O_3, are good candidate materials for planar optical devices. Further, these oxides serve as suitable hosts for rare earth dopants used in optical amplifiers. A common material choice is so-called low temperature glasses, doped with alkali metals, boron, or phosphorous, which have the advantage of requiring lower processing temperatures. In addition, dopants are used to modify the refractive index. Methods such as flame hydrolysis, ion exchange for introducing alkali ions in glasses, sputtering, and various chemical vapor deposition processes (CVD) have been used to form films of doped glasses. However, dopants such as phosphorous and boron are hygroscopic, and alkalis are undesirable for integration with electronic devices. Control of uniformity of doping in CVD processes can be difficult and CVD deposited films can have structural defects

leading to scattering losses when used to guide light. In addition, doped low temperature glasses may require further processing after deposition. A method for eliminating bubbles in thin films of sodium-boro-silicate glass by high temperature sintering is described, for example, in the '995 patent to Bhandarkar et al.

[0008] Typically, RF sputtering has been utilized for deposition of oxide dielectric films. However, RF sputtering utilizes ceramic targets which are typically formed of multiple smaller tiles. Since the tiles can not be made very large, there may be a large problem of arcing between tiles and therefore contamination of the deposited film due to this arcing. Further, the reactors required for RF sputtering tend to be rather complicated. In particular, the engineering of low capacitance efficient RF power distribution to the cathode is difficult in RF systems. Routing of low capacitance forward and return power into a vacuum vessel of the reaction chamber often exposes the power path in such a way that diffuse plasma discharge is allowed under some conditions of impedance tuning of the matching networks.

[0009] Therefore, there is a need for new methods of depositing oxide and oxynitride films and for forming planar optical devices.

Summary

[0010] In accordance with the present invention, a sputtering reactor apparatus for depositing oxide and oxynitride films is presented. Further, methods for depositing oxide and oxynitride films for optical waveguide devices are also presented. A sputtering reactor according to the present invention includes a pulsed DC power supply coupled through a filter to a target and a substrate electrode coupled to an RF power supply. A substrate mounted on the substrate electrode is therefore supplied with a bias from the RF power supply.

[0011] The target can be a metallic target made of a material to be deposited on the substrate. In some embodiments, the metallic target is formed from Al, Si and various rare-earth ions. A target with an erbium concentration, for example, can be utilized to deposit a film that can be formed into a waveguide optical amplifier.

[0012] A substrate can be any material and, in some embodiments, is a silicon wafer. In some

embodiments, RF power can be supplied to the wafer. In some embodiments, the wafer and the electrode can be separated by an insulating glass.

[0013] In some embodiments, up to about 10 kW of pulsed DC power at a frequency of between about 40 kHz and 350 kHz and a reverse pulse time of up to about 5 μs is supplied to the target. The wafer can be biased with up to about several hundred watts of RF power. The temperature of the substrate can be controlled to within about 10° C and can vary from about -50° C to several hundred degrees C. Process gasses can be fed into the reaction chamber of the reactor apparatus. In some embodiments, the process gasses can include combinations of Ar, N_2, O_2, C_2F_6, CO_2, CO and other process gasses.

[0014] Several material properties of the deposited layer can be modified by adjusting the composition of the target, the composition and flow rate of the process gasses, the power supplied to the target and the substrate, and the temperature of the substrate. For example, the index of refraction of the deposited layer depends on deposition parameters. Further, in some embodiments stress can be relieved on the substrate by depositing a thin film of material on a back side of the wafer. Films deposited according to the present invention can be utilized to form optical waveguide devices such as multiplexers and rare-earth doped amplifiers.

10108965.030602

[0015] These and other embodiments, along with examples of material layers deposited according to the present invention, are further described below with respect to the following figures.

Brief Description of the Figures

[0016] Figures 1A and 1B show a pulsed DC sputtering reactor according to the present invention.

[0017] Figure 2 shows a planar view of target utilized in a reactor as shown in Figures 1A and 1B.

[0018] Figure 3 shows a cross-section view of an example target utilized in a reactor as shown in Figures 1A and 1B.

[0019] Figure 4 shows a flow chart of an embodiment of a process for depositing a film on a substrate according to the present invention.

[0020] Figure 5 shows a hysterises curve of target voltage versus oxygen flow rates for an example target in an embodiment of a reactor according to the present invention.

[0021] Figure 6 shows a photo-luminescence and lifetimes of a film deposited in a process according to the present invention as a function of after deposition anneal temperature.

[0022] Figure 7 shows the relationship between the index of refraction of a film as a function of deposited oxide layers according to the present invention and due to oxide build-up on the target.

[0023] Figure 8 shows a graph of the index of refraction of a film deposited according to the present invention as a function of the aluminum content in a composite Al/Si target.

[0024] Figure 9 shows a graph of typical indices of refraction of material layers deposited according to the present invention.

[0025] Figure 10 shows a table of indices of refraction for a silica layer deposited according to the present invention as a function of different process parameters.

[0026] Figure 11 shows the refractive indices as a function of O_2/Ar ratio utilized in an Alumina process according to the present invention.

[0027] Figure 12 shows the refractive indices as a function of DC pulsed power frequency for an Alumina layer deposited according to the present invention.

[0028] Figure 13 shows variation in the refractive index over time during repeated depositions from a single target.

[0029] Figure 14 shows variation in refractive index over time for repeated depositions from a target of another material layer according to the present invention.

[0030] Figure 15 shows the variation refractive index over time for repeated depositions from a target of another material layer according to the present invention.

[0031] Figure 16A through 16D shows a TEM film deposited according to the present invention.

10101835.031502

[0032] Figure 17 shows the transparency of a film deposited according to the present invention.

[0033] Figure 18 shows an uppercladding layer deposited according to the present invention over a multiple-waveguide structure such that the deposited layer is substantially planarized.

[0034] Figure 19 illustrates the deposition of a film over a waveguide structure.

[0035] Figures 20 and 21 illustrate different etch and deposition rates for deposition of films as a function of the surface angle of the film.

[0036] Figure 22 illustrates calculation of the planarization time for a particular deposition process.

[0037] Figures 23 through 25 through illustrate adjustment of process parameters in order to achieve planarization of a film deposited over a waveguide structure according to the present invention.

[0038] Figure 26 shows the gain characteristics of an erbium doped waveguide amplifier formed of films depositions according to the present invention.

[0039] Figures 27 shows gain, insertion loss of a waveguide with an active core deposited according to the present invention.

[0040] Figure 28 shows up-conversion constants, and lifetimes of the active core layer of Figure 27 deposited according to the present invention.

[0041] Figure 29 shows drift in the index of refraction with subsequent depositions for films deposited from a target according to the present invention.

[0042] Figure 30 shows drift in the photoluminescence with subsequent depositions according to the present invention.

[0043] Figure 31 shows drift in the excited state lifetime with subsequent depositions according to the present invention.

[0044] Figure 32 shows stabilization of the index of refraction in subsequent depositions.

[0045] Figure 33 shows the index of refraction of a film formed from a pure silicon target as a

function of the ratio of O_2/N_2 in the process gas.

[0046] In the figures, elements having the same designation have the same or similar function.

Detailed Description

[0047] Reactive DC magnetron sputtering of nitrides and carbides is a widely practiced technique, but the reactive dc magnetron sputtering of nonconducting oxides is done rarely. Films such as aluminum oxide are almost impossible to deposit by conventional reactive DC magnetron sputtering due to rapid formation of insulating oxide layers on the target surface. The insulating surfaces charges up and result in arcing during process. This arcing can damage the power supply, produce particles and degrade the properties of deposited oxide films.

[0048] RF sputtering of oxide films is discussed in Application Serial No. 09/903,050 (the '050 application) by Demaray et al., entitled "Planar Optical Devices and Methods for Their Manufacture," assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, targets that can be utilized in a reactor according to the present invention are discussed in U.S. Application serial no. {Attorney Docket No. M-12247 US} (the '247 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. A gain-flattened amplifier formed of films deposited according to the present invention are described in U.S. Application serial no. {Attorney Docket No. M-12652 US} (the '652 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, a mode size converter formed with films deposited according to the present invention is described in U.S. Application serial no. {Attorney Docket No. M-12138 US} (the '138 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety.

[0049] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering of material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for

example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These Komatsu reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[0050] Apparatus 10 includes a target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. Magnet 20 is scanned across the top of target 12.

[0051] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering in apparatus 10.

[0052] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this example supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. The reverse voltage is 10% of the negative target voltage. Utilization of other power supplies will lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[0053] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 is a 2 MHz RF power supply, for example can be a Nova-25 power supply made by ENI, Colorado Springs, Co.

[0054] Therefore, filter 15 is a 2 MHz band rejection filter. In some embodiments, the band

width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[0055] However, both RF and pulsed DC deposited films are not fully dense and most likely have columnar structures. These columnar structures are detrimental for optical wave guide applications due to the scattering loss caused by the structure. By applying a RF bias on wafer 16 during deposition, the deposited film can be dandified by energetic ion bombardment and the columnar structure can be substantially eliminated.

[0056] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimension about 150 mm by 600 mm.

10108573 031502

[0057] A top down view of magnet 20 and wide area target 12 is shown in Figure 2. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, where physical and chemical uniformity provide refractive index uniformity, for example. Figure 2 indicates that region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

[0058] In some embodiments, magnet 20 extends beyond area 52 in one direction, the Y direction in Figure 2, so that scanning is necessary in only one direction, the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform

sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[0059] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission or absorptivity.

10101895.031502

[0060] Target 12 can be formed of any materials, but is typically metallic materials such as, for example, combinations of Al and Si. Therefore, in some embodiments, target 12 includes a metallic target material formed from intermetalic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetalics. *See* the '247 application.

[0061] In several embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. Figure 3A shows an embodiment of target 12 formed with individual tiles 30 mounted on a cooled backplate 25. In order to form a wide area target of an alloy target material, the consolidated material of individual tiles 30 should first be uniform to the grain size of the powder from which it is formed. It also should be formed into a structural material capable of forming and finishing to a tile shape having a surface roughness on the order of the powder size from which it is consolidated. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles 30, for example between 2 to 20 individual tiles 30. Tiles 30 are finished to a size so as to provide a margin of non-contact, tile to tile, 29 in Figure 3A, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes between adjacent ones of tiles 30. The distance between tiles 30 of target 12 and the dark space anode or ground shield 19, in Figure 1B can be somewhat larger so as to provide non contact assembly or provide for thermal expansion tolerance during process chamber conditioning or

operation.

[0062] Several useful examples of target 12 that can be utilized in apparatus 10 according to the present invention include the following targets compositions: (Si/Al/Er/Yb) being about (57.0/41.4/0.8/0.8), (48.9/49/1.6/0.5), (92/8/0/0), (60/40/0/0), (50/50/0/0), (65/35/0/0), (70/30/0,0), and (50,48.5/1.5/0) cat. %, to list only a few. These targets can be referred to as the 0.8/0.8 target, the 1.6/.5 target, the 92-8 target, the 60-40 target, the 50-50 target, the 65-35 target, the 70-30 target, and the 1.5/0 target, respectively. The 0.8/0.8, 1.6/0.5, and 1.5/0 targets can be made by pre-alloyed targets formed from an atomization and hot-isostatic pressing (HIPing) process as described in the '247 application. The remaining targets can be formed, for example, by HIPing. Targets formed from Si, Al, Er and Yb can have any composition. In some embodiments, the rare earth content can be up to 10 cat. % of the total ion content in the target. Rare earth ions are added to form active layers for amplification. Targets utilized in apparatus 10 can have any composition and can include ions other than Si, Al, Er and Yb, including: Zn, Ga, Ge, P, As, Sn, Sb, Pb, Ag, Au, and rare earths: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy Ho, Er, Tm Yb and Lu.

[0063] Optically useful materials to be deposited onto substrate 16 include oxides, fluorides, sulfides, nitrides, phosphates, sulfates, and carbonates, as well as other wide band gap semiconductor materials. To achieve uniform deposition, target 12, itself can be chemically uniform and of uniform thickness over an extended area.

[0064] Target 12 can be a composite target fabricated from individual tiles, precisely bonded together on a backing plate with minimal separation, as is discussed further with respect to Figure 3. In some embodiments, the mixed intermetalllics can be plasma sprayed directly onto a backing plate to form target 12. The complete target assembly can also includes structures for cooling the target, embodiments of which have been described in U. S. Patent No. 5,565,071 to Demaray et al, and incorporated herein by reference.

[0065] Substrate 16 can be a solid, smooth surface. Typically, substrate 16 can be a silicon wafer or a silicon wafer coated with a layer of silicon oxide formed by a chemical vapor deposition process or by a thermal oxidation process. Alternatively, substrate 16 can be a glass, such as Corning 1737 (Corning Inc., Elmira, NY), a glass-like material, quartz, a metal, a metal oxide, or a plastic material. Substrate 16 can be supported on a holder or carrier sheet that may

be larger than substrate 16. Substrate 16 can be electrically biased by power supply 18.

[0066] In some embodiments, the area of wide area target 12 can be greater than the area on the carrier sheet on which physically and chemically uniform deposition is accomplished. Secondly, in some embodiments a central region on target 12, overlying substrate 16, can be provided with a very uniform condition of sputter erosion of the target material. Uniform target erosion is a consequence of a uniform plasma condition. In the following discussion, all mention of uniform condition of target erosion is taken to be equivalent to uniform plasma condition. Uniform target erosion is evidenced by the persistence of film uniformity throughout an extended target life. A uniformly deposited film can be defined as a film having a nonuniformity in thickness, when measured at representative points on the entire surface of a substrate wafer, of less than about 5 % or 10%. Thickness nonuniformity is defined, by convention, as the difference between the minimum and maximum thickness divided by twice the average thickness. If films deposited from a target from which more than about 20 % of the weight of the target has been removed continue to exhibit thickness uniformity, then the sputtering process is judged to be in a condition of uniform target erosion for all films deposited during the target life.

10101895 . 031502

[0067] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12, can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations).

[0068] In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0069] Other approaches to providing a uniform condition of sputter erosion rely on creating a large uniform magnetic field or a scanning magnetic field that produces a time-averaged,

uniform magnetic field. For example, rotating magnets or electromagnets can be utilized to provide wide areas of substantially uniform target erosion. For magnetically enhanced sputter deposition, a scanning magnet magnetron source can be used to provide a uniform, wide area condition of target erosion.

[0070] As illustrated in FIG. 1A, apparatus 10 can include a scanning magnet magnetron source 20 positioned above target 12. An embodiment of a scanning magnetron source used for dc sputtering of metallic films is described in U. S. Patent No. 5,855,744 to Halsey, et. al., (hereafter '744), which is incorporated herein by reference in its entirety. The '744 patent demonstrates the improvement in thickness uniformity that is achieved by reducing local target erosion due to magnetic effects in the sputtering of a wide area rectangular target. As described in the '744 patent, by reducing the magnetic field intensity at these positions, the local target erosion was decreased and the resulting film thickness nonuniformity was improved from 8%, to 4%, over a rectangular substrate of 400 x 500 mm.

10108583.031902

[0071] The process gas utilized in reactor 10 includes an inert gas, typically argon, used as the background sputtering gas. Additionally, with some embodiments of target 12, reactive components such as, for example, oxygen may be added to the sputtering gas. Other gasses such as N_2, NH_3, CO, NO, CO_2, halide containing gasses other gas-phase reactants can also be utilized. The deposition chamber can be operated at low pressure, often between about .5 millitorr and 8-10 millitorr. Typical process pressure is below about 3-5millitorr where there are very few collisions in the gas phase, resulting in a condition of uniform "free molecular" flow. This ensures that the gas phase concentration of a gaseous component is uniform throughout the process chamber. For example, background gas flow rates in the range of up to about 200 sccm, used with a pump operated at a fixed pumping speed of about 50 liters/second, result in free molecular flow conditions.

[0072] The distance d, in Figure 1A, between target 12 and substrate 16 can, in some embodiments, be varied between about 4 cm and about 9 cm. A typical target to substrate distance d is about 6 cm. The target to substrate distance can be chosen to optimize the thickness uniformity of the film. At large source to substrate distances the film thickness distribution is dome shaped with the thickest region of the film at the center of the substrate. At close source to substrate distance the film thickness is dish shaped with the thickest film formed at the edge of the substrate. The substrate temperature can be held constant in the range of about -40 °C to

about 550°C and can be maintained at a chosen temperature to within about 10 °C by means of preheating substrate 16 and the substrate holder prior to deposition. During the course of deposition, the heat energy impressed upon the substrate by the process can be conducted away from substrate 16 by cooling the table on which substrate 16 is positioned during the process, as known to those skilled in the art. The process is performed under conditions of uniform gas introduction, uniform pumping speed, and uniform application of power to the periphery of the target as known to skilled practitioners.

[0073] The speed at which a scanning magnet 20 can be swept over the entire target can be determined such that a layer thickness less than about 5 to 10 Å, corresponding roughly to two to four monolayers of material, is deposited on each scan. Magnet 20 can be moved at rates up to about 30 sec/one-way scan and typically is moved at a rate of about 4 sec/one-way scan. The rate at which material is deposited depends on the applied power and on the distance d, in Figure 1A, between the target 12 and the substrate 16. For deposition of optical oxide materials, for example scanning speeds between about 2 sec/one-way scan across the target to 20-30 sec/scan provide a beneficial layer thickness. Limiting the amount of material deposited in each pass promotes chemical and physical uniformity of the deposited layer.

10101859.031602

[0074] Substrate bias has been used previously to planarize RF sputtered deposited quartz films. A theoretical model of the mechanism by which substrate bias operates, has been put forward by Ting et al. (J. Vac. Sci. Technol. 15, 1105 (1978)). When power is applied to the substrate, a so-called plasma sheath is formed about the substrate and ions are coupled from the plasma. The sheath serves to accelerate ions from the plasma so that they bombard the film as it is deposited, sputtering the film, and forward scattering surface atoms, densifying the film and eliminating columnar structure. The effects of adding substrate bias are akin to, but more dramatic than, the effects of adding the low frequency RF component to the sputter source.

[0075] Biasing substrate 16 results in the deposited film being simultaneously deposited and etched. The net accumulation of film at any point on a surface depends on the relative rates of deposition and etching, which depend respectively, on the power applied to the target and to the substrate, and to the angle that the surface makes with the horizontal. The rate of etching is greatest for intermediate angles, on the order of 45 degrees, that is between about 30 and 60 degrees.

[0076] Powers to target 12 and substrate 16 can be adjusted such that the rates of deposition and etching are approximately the same for a range of intermediate angles. In this case, films deposited with bias sputtering have the following characteristics. At a step where a horizontal surface meets a vertical surface, the deposited film makes an intermediate angle with the horizontal. On a surface at an intermediate angle, there will be no net deposition since the deposition rate and etch rate are approximately equal. There is net deposition on a vertical surface.

[0077] Target 12 can have an active size of about 675.70 X 582.48 by 4 mm, for example, in a AKT-1600 based system in order to deposit films on a substrate 16 that is about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C. The distance between target 12 and substrate 16 can be between 3 and 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate of between about 30 to about 100 sccm while the pressure in the chamber of apparatus 10 can be held at below about 2 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan.

[0078] Therefore, any given process utilizing apparatus 10 can be characterized by providing the power supplied to target 12, the power supplied to substrate 16, the temperature of substrate 16, the characteristics and constituents of the reactive gasses, the speed of the magnet, and the spacing between substrate 16 and target 12.

[0079] Sputtered oxide films according to some embodiments of the present invention can be deposited onto a Si wafer or thermal oxide wafers at pressure of between about 3 and about 6 mTorr. The ratio of O_2/Ar gas flow can be set at a value to ensure that target 12 is operating within a poison mode. The poison mode is defined as the ratio where the oxide is etched from the surface of target 12 as fast as the oxide layer is formed. Operating in the poison mode results in the stoichiometric film. Sub-stoichiometric oxides may not be optically transparent. The pulsing frequency range for power supply 14 can be from about up to about 250 KHz. The frequency 40 KHz is approximately the lowest frequency at which no arcing will occur during deposition in, for example, the AKT 1600 based system. The reverse pulsing time is determined by the amount of arcing generated during the process. Longer reverse time means longer discharge time and thus less arcs. However, if the reverse time is too long, the deposition rate will decrease. Power supply 18 is a 2 MHz RF power supply operated at powers up to several

hundred Watts.

[0080] Figure 4 shows an embodiment of a process procedure 400 performed on apparatus 10. In step 401, the target is prepared for the deposition. In some embodiments, target 12 can be cleaned by pure Ar sputtering. In other words, apparatus 10 is operated with pure Ar gas only (referred to as the metal mode) in order to sputter away a surface layer of target 12.

[0081] Figure 7 shows the typical drift in the index of refraction with deposition of oxide layers for several different targets over different runs for each target. In Figure 7, the compositions of the target materials utilized in target 12 for the depositions shown are as follows: Si: 60 cat. % and Al: 40 cat. %; Si: 50 cat. % and Al: 50 cat. %; Si: 85 cat. % and Al: 15 cat. %; Si: 35 cat. % and Al: 65 cat. %; and Si: 92 cat. % and 8 cat. %. Each deposition was operated under the same process parameters: 4.5 kW of pulsed DC power at 200 kHz with a reverse time of 2.3 μs applied to target 12, O_2 flow at 44 sccm, Ar flow at 30 sccm introduced to apparatus 10, 100 W of bias power at 2 MHz applied to substrate 16, the temperature of substrate 16 held at 200° C, and the distance between substrate 16 and target 12 being set at 6 cm. For each target measured, the index drifted up during repeated utilization.

10103583.031502

[0082] Figure 8 shows the relationship between the index of refraction of a film deposited according to the present invention and the amount of aluminum in the composite target. As can be seen from Figure 8, the index of refraction of the deposited film depends strongly on the aluminum content. Therefore, as the aluminum in a metal target is depleted, the index of refraction drifts. In some embodiments, the ratio of Ar and O_2 utilized in the process can be maintained to provide films of uniform index over a large number of depositions on the target.

[0083] Reactive sputtering from a metal or metallic alloy target 12 can be characterized by two modes of operation. In the first mode, which is sometimes referred to as the 'metallic mode' the surface of target 12 is substantially metallic. This mode is characterized by a small addition of reactive gas to the inert gas flow of apparatus 10 as well as a higher impedance magnetron discharge. It is also characterized by incomplete oxidation of film deposited on substrate 16 and therefore higher index films. As the proportion of reactive to inert gas is increased, the sputter voltage at target 12 begins to fall at constant power.

[0084] Figure 5 shows the voltage on target 12 of an embodiment of apparatus 10 according to

the present invention as a function of process gas constitution. In the example illustrated in Figure 5, for example, a metallic target with composition .8 cat. % Er, .8 cat. % Yb, 57.4 cat. % Si and 41 cat. % Si, which can be formed as described in the '247 application, was sputtered in an embodiment of apparatus 10 based on the AKT-1600 PVD system with 6 kW of pulsed DC power at a frequency of 120 kHz and a reverse time of 2.3 micro seconds. The Argon gas flow was set at 60 sccm and the Oxygen gas flow was varied from zero up to 40 sccm. For more details regarding this deposition, see Example 1 below.

[0085] As shown in Figure 5, the voltage on target 12 during deposition (the "target voltage") was constant at about 420 Volts for oxygen flow rates up to about 20 sccm. This is clearly the metallic mode of operation for this embodiment of target 12. Films deposited in this range of oxygen flow are characterized as metallic with an oxygen content that increases with oxygen flow rate during deposition. As the oxygen flow is increased up to about 26 sccm, the voltage on target 12 begins to decrease, indicating that the surface of target 12 is beginning to form an oxide layer. The oxide layer on the surface of target 12 has a higher secondary electron yield under the influence of the Argon ion flux. The additional electron flux to the magnetron electron trap increases the ion production in the plasma, which, in turn, decreases the impedance of the plasma discharge in apparatus 10.

[0086] At slightly higher oxygen flow during deposition, the oxide layer on target 12 forms a continuous layer and the voltage of target 12 during deposition falls rapidly to the range of about 190 to about 270 Volts, indicating complete coverage of the surface of target 12 with an oxide that is at least as thick as the material removed during one scan of the magnetron. Under this condition, the rate of oxide formation on the surface of target 12 equals or exceeds the rate of sputter removal of the surface of target 12 by the moving magnetron 20. This condition is sometimes referred to as the 'poisoned mode'.

[0087] Under steady state DC voltage conditions, the oxide layer on target 12 soon charges up, leading to reduced rate of sputtering and increased micro-arc discharging in apparatus 10. This discharging leads to particulation of the oxide layer on target 12, which degrades the quality of a film deposited on substrate 16. In the example shown with Figure 5, the negative going DC Voltage is reduced at a frequency of 120 kHz to a positive value for a period of about 2.3 micro seconds per cycle, allowing charge neutralization of the surface of target 12, increasing the steady state sputter and deposition rates as well as decreasing the rate of micro-arcing.

[0088] In the case of a magnetron configuration of magnet 20 having a significant deep local target erosion (rather than a configuration of magnet 20 described above which yields uniform target erosion), the change in the target voltage of target 12 is more gradual with increasing oxygen flow since it is more difficult to establish an oxide condition at the center of an intense region of local erosion. The resulting deposited film, however, will be rich in metallic sputtered flux to the substrate in the region of higher sputter erosion, leading to non uniform stoicheometry and non-uniform indices of refraction in a film deposited on substrate 16. In the case of a scanning magnetron 20 with uniform target erosion, the change in the surface condition from metallic to poisoned is more abrupt, as the formation rate of the oxide increases to equal the sputter removal of the oxide over a wide area of the target. In this case, there is uniform distribution of sputtered oxide from the target. Uniform stoicheometry and uniform indices of refraction result for the film deposited on substrate 16.

10101865 031502

[0089] Figure 8 shows the range of indices of refraction of films deposited for targets of differing silica and alumina compositions, as deposited and after a subsequent anneal step. In the case of a pure silicon target, the as-deposited index of refraction can be as high as 3.4 for pure amorphous silicon. In Figure 8, pure silica films (zero Al%) can be deposited with a reactive pulsed DC and substrate bias deposition according to the present invention with substantially complete oxygen stoicheometry, so as to approximate monolithic amorphous silica. The index of refraction of such films decreases with a subsequent heat treatment of between about 700-900° C, indicating somewhat more complete oxidation reaction of the material of the film together with some degree of stress relaxation of the film deposited on substrate 16.

[0090] At the opposite extreme, a pure aluminum embodiment of target 12 (100% Al) can be utilized to deposit films on substrate 16 under similar process conditions as is utilized to deposit pure silica films on substrate 16. In the case of the pure aluminum reactive deposition, the dependence of the index of refraction of the film deposited on substrate 16 on oxygen flow as well as on the frequency of the pulsed DC process can be examined. As a result, a larger range of effective index of refraction is achieved together with a reduced or zero dependence of the index on the subsequent anneal process. Six targets having differing aluminum composition were utilized to evaluate the index of refraction of sputtered films on substrate 16 of related composition. The largest change of index with the sputtering conditions is achieved for composition near the middle of the Al/Si composition range (about 50% Al and 50% Si).

[0091] Figure 7 shows the change in film index for oxide films for several embodiments of target 12 and processes with an initial 30 minutes of Argon only sputtering, followed by continuous deposition with an oxygen flow rate sufficient for operation in the poisonous mode. Note that the rate of increase in the index of refraction of a resulting film deposited on substrate 16 with continuous poisoned mode deposition is proportional to the concentration of aluminum in the composition of target 12. This result is due to the depletion of the aluminum from the target surface during the metallic sputtering or pre-condition process. The aluminum in target 12 is preferentially sputtered over the silicon in target 12, leaving the surface of target 12 rich in silicon. At the onset of poisoned mode sputtering, the film deposited on substrate 16 is rich in silica and demonstrates a systematic and reproducible decrease in index of refraction. During continuous poisoned mode deposition, the silicon rich surface of target 12 can be sputtered away and the aluminum portion substantially returned to the bulk composition of target 12. Consequently, a metallic pre-condition step can be utilized to achieve a subsequent process for the deposition of a film having an increasing index of refraction under conditions of oxide/metal stoicheometry.

[0092] In step 402 of Figure 4, substrate 16 is prepared. Substrate 16 can be mounted on carrier sheet 17 and placed in apparatus 10. In step 403, gas flow parameters are adjusted for the particular deposition to be performed. The constituency and flow rates of the process gas are fixed. In some embodiments, the ratio of Ar and O_2, for example, can be set and the flow rate of each gas set. Further, the combination of flow rate and vacuum system of apparatus 10 determines the pressure during deposition in apparatus 10.

[0093] In step 404, the substrate temperature is set. Substrate 16 may be brought to temperature over a period of time. In step 405, the scan characteristics of magnet 20 are fixed. In step 406, the power setting for power supply 18 is set. Finally, in step 407, the parameters of pulsed DC power supply 14 is set, including the power, frequency, and reverse pulsing time. In step 408, then, a film that depends on the parameters of reactor apparatus 10 is deposited on substrate 16. In some embodiments, films deposited by procedure 400 are thermally annealed after deposition.

[0094] Figure 4 illustrates an example deposition process only. Embodiments of deposition processes according to the present invention can be performed in various different orders.

10101835.031502

[0095] Figure 9 shows a chart of various deposition parameters according to the present invention for various embodiments of target 12 and the indices of refraction, both before and after an anneal step, for the resulting deposited film on substrate 16. Each deposition was accomplished with an embodiment of apparatus 10 based on the AKT 1600 PVD reactor. Anneals were accomplished at 725° C for 30 min. Specific examples of particular depositions and characteristics of the resulting films deposited on substrate 16 are further discussed below.

[0096] Figure 10 shows the dependence of the index of refraction of silica layers deposited according to the present invention with process conditions. Figure 11 shows the dependence of index of refraction on the O2/Ar flow ratio for the deposition of pure alumina according to the present invention. Figure 12 shows the dependence of index for pure alumina films on the frequency of the pulsed DC power applied to target 12. Both parameters can be utilized to reliably control the index of refraction of films deposited on substrate 16 over a range of index values without the use of an additional cationic species, a so called 'dopant'. A third process parameter that can be utilized to adjust the index of refraction of a film deposited on substrate 16 is the bias power applied to substrate 16. Increasing the oxygen flow ratio, the frequency of the pulsed DC power applied to target 12 or the bias power applied to substrate 16 will systematically increase the index of refraction of the alumina film deposited on substrate 16. In the case of pure alumina films, minor to no change in the index occurs due to a subsequent anneal process.

10101853.031502

[0097] Figure 13 shows the index of refraction of a film deposited on substrate 16 from an embodiment of target 12 with about 92 cat. % of Si and about 8 cat. % of Al for a series of sequential depositions in an embodiment of apparatus 10 based on the AKT 4300 PVD reactor, each following a metallic process condition. For constant high oxygen flow conditions, a small upward trend in the index of refraction is observed. As is generally true, the index of films deposited with higher substrate bias power is systematically lower than films deposited without substrate bias.

[0098] Figure 14 shows the upward trend of the index of refraction after metallic mode precondition of an embodiment of target 12 having composition of about 83 cat. % Si and about 17 cat. % Al for a series of depositions in an embodiment of apparatus 10 based on the AKT 1600 PVD reaction. As is shown in Figure 14, longer metallic preconditioning of target 12 results in the index of refraction of the films deposited on substrate 16 having a higher rate of

increase than for cases with less prolonged metallic preconditioning of target 12. The vertical lines on Figure 14 indicate places where target 12 was preconditioned with only Ar for the indicated periods of time. Figure 15 shows a decrease in the change in index for sequential films with this embodiment of target 12 deposited with reduced oxygen flow rates at a constant total pressure. A flow rate for oxygen was determined so that the run to run variation for the index of refraction of the film deposited on substrate 16 from this target was about .0001 (see the circled data points on the graph of Figure 15) which is similar to the variance of the index over the entire wafer of substrate 16, which is about 70 parts per million.

[0099] In some embodiments, films deposited by a pulsed DC biased method according to the present invention are uniformly amorphous throughout their thickness. As has been discussed above, biasing of substrate 16 leads to densification and uniformity in the deposited film. Figures 16A through 16D show a TEM photograph of a film 1601 deposited according to the present invention. Further, diffraction patterns shown in Figures 16B, 16C and 16D at points a, b and c, respectively, in deposited film 1601 show that the film is ammorphous through the thickness of the film. The diffraction patterns of Figures 16B, 16C and 16D show no effects of crystallization. Further, the smoothness of the surface of film 1601 indicates a defect free film. The film deposited in Figure 16A is deposited with an 0.8/0.8 target (i.e., a target having the composition 52.0 cat. % of Si, 41.0 cat. % of Al, 0.8 cat. % of Er and 0.8 cat. % of Yb). The film is deposited at 6 kW of 120 kHz pulsed DC power with a reverse time of 2.3 μs. The Argon and Oxygen flow rates are 60 sccm and 28 sccm, respectively. Substrate 16 is biased with 100 W of power.

[0100] Figure 17 shows the optical loss per centimeter, measured at 1310 nm, using a three prism coupling to the so called slab mode of the film on a 10 micron oxide, silicon wafer. As deposited the biased, pulsed DC film from a 60 cat. % Si and 40 cat. %Al film demonstrated about .1dB/cm loss. After an 800° C anneal in air, the loss was less than the measurement sensitivity of the prism coupling method. This data clearly demonstrates that films deposited according to embodiments of the present invention can be used for the purpose of constructing low loss planar light wave circuits.

[0101] Deposition of films according to the present invention can be utilized to deposit cladding layers, active core layers, and passive core layers of an optical amplifier structure or optical

10108513.031502

waveguide structure. In some applications, for example multiplexer structures, the separation between adjacent waveguides can be small, for example about 8 μm. In some embodiments, the deposition parameters of the upper cladding layer can be adjusted to not only adjust the index of refraction of the layer, but also to insure that the spacing between adjacent waveguides is small.

[0102] Figure 18 shows an example planarization deposition over a multiplexer structure. In the particular example of upper cladding layer 1803 shown in Figure 18, the deposition parameters from a 92 cat. % Si and 8 cat. % Al is: 5.5 Kw of Pulsed DC power applied at 200 KHz with 2.2 μs of reverse time, gas flow of 75 sccm Ar and 100 sccm O_2, a substrate bias of 650 W (at 2 MHz), and a substrate temperature of 200 °C. Layer 1803 was deposited with an AKT 4300 based embodiment of apparatus 10. As shown in Figure 18, the layer thickness in areas other than over waveguide structures 1801 and 1802 is 11.4 μm. Waveguide structures 1801 and 1802 are 8.20 μm high waveguides and separated by 6.09 μm at the base and by 8.40 μm at their top. In Figure 18, the undercladding layer 1804 is about 1.98 μm thick.

[0103] Figure 19 illustrates deposition of material over a structure. Upper cladding layer 1803, in region 1901, will be angled from the horizontal by an angle θ. The deposition and etching rates of a deposited layer depends on the angle θ. Figures 20 and 21 illustrate different cases of deposition and etch rates as a function of the angle θ. The relationship between the rate of deposition and the etch rates can be adjusted by adjusting the deposition parameters. For example, the bias power to substrate 16 can be adjusted to control the relationship between the etch rates and deposition rates of material.

[0104] Figure 22 illustrates deposition rates over a structure 2201 as a function of time. In Figure 2201, h is the thickness deposited over structure 2201. The planarization when layer 1803 becomes flat.

[0105] The time for planarization can be estimated as

$$t_p = \frac{\frac{W}{2}\tan\alpha + H}{a_{flat} - \frac{a_{\min}}{\cos\alpha}},$$

where W is the width of structure 2201, H is the height of structure 2201, a_{flat} refers to the

accumulation rate on the flat surface, a_{min} refers to the accumulation rate on the minimum accumulation slope, and α is the surface angle from the horizontal plane of the minimum accumulation slope.

[0106] Figure 23 shows a deposited film 1803 as shown in Figure 18, except that the bias power to substrate 16 is set to 400 W instead of 650 W. As can be seen in Figure 23, a keyhole 2301 is formed with an incomplete filling of uppercladding layer 1803 between structures 1801 and 1802. Deposition of uppercladding layer 1803 substantially follows the trends illustrated in Figures 19 through 22.

[0107] Figure 24 shows deposition as shown in Figure 18, except that the bias power to substrate 16 is set to 600 W instead of 650 W. As can be seen in Figure 24, keyhole 2301 has closed leaving a small line defect 2401 in the fill.

[0108] Figure 28 shows deposition as shown in Figure 18, except that the bias power to substrate 16 is set to 900 W instead of 650 W. As can be seen in Figure 28, the etch rate has been increased to such an extent that the corners of structures 1801 and 1802 have been etched to form slopes 2501 and 2502, respectively.

10101865 031502

[0109] Therefore, as illustrated in figures 18 through 25, an uppercladding layer can be deposited in accordance with the present invention such that it fills the space between adjacently placed waveguides. In general, the parameters can be optimized for index control and the bias power to substrate 16 can be adjusted for fill. In some embodiments, other parameters (e.g., the constituency of process gas, frequency and power of pulsed DC power source 14, and other parameters) in order to adjust the deposition and etch rates and thereby effectively planarize the structure as described.

[0110] Therefore, depositions of various films in embodiments of apparatus 10 according to the present invention with several embodiments of target 12 and the effects on index of refraction, uniformity of films, and fill characteristics of varying several of the process parameters has been discussed above. In some embodiments, stress effects due to wafer bowing of substrate 16 can also be reduced. Wafer bowing of substrate 16 can be reduced, reducing the stress in a film deposited on substrate 16, by, for example, depositing a film on the backside of substrate 16 before deposition of a film on substrate 16. In some embodiments, a film having a similar

thickness of a similar layer of material can be deposited on backside of substrate 16 prior to deposition of the film on substrate 16 according to the present invention. The wafer bowing resulting from differing thermal expansions of the film and substrate 16 is therefore countered by a similar stress from another film deposited on the backside of substrate 16.

[0111] Several specific examples film depositions utilizing apparatus 10 are discussed below. Further, examples of optical amplifiers produced utilizing the ceramic tiles according to the present invention are presented. These examples are provided for illustrative purposes only and are not intended to be limiting. Unless otherwise specified, apparatus 10 utilized in the following examples was based on the AKT 1600 reactor. Further, unless otherwise specified, the temperature of substrate 16 was held at about 200° C and the distance between substrate 16 and target 12 was 4 s/scan. The separation between substrate 16 and target 12 is about 6 cm.

10101856 031502

EXAMPLE 1

[0112] An AKT 1600 based reactor can be utilized to deposit a film. In this example, a wide area metallic target of dimension 550X 650 mm with composition (Si/Al/Er/Yb) being about 57.0 cat. % Si, 41.4 cat. % Al, 0.8 cat. % Er, and 0.8 cat. % Yb (a ".8/.8" target) was fabricated as described in the '247 patent.

[0113] In step 402, a 150 mm P-type silicon wafer substrate was placed in the center of a 400x500 mm glass carrier sheet 17. Power supply 14 was set to supply 6000 watts of pulse DC power at a frequency of 120KHz with a reverse pulsing time of about 2.3us. Magnet 20, which is a race-track shaped magnet of approximate dimension 150mmx600mm, was swept over the backside of the target at a rate of about 4 seconds per one-way scan. The temperature of substrate 16 was held at 200C and 100W of 2 MHz RF power was applied to substrate 16. The target 12 to substrate 16 distance was about 6.5 cm. The sputtering gas was a mixture of Argon and Oxygen. Substrate 16 and carrier 17 was preheated to 350° C for at least 30min prior to deposition. The active film was deposited in the poison mode. Deposition efficiency was approximately 1um/hr.

[0114] Figure 5 shows the hysteresis curve of this particular embodiment of target 12. When target 12 under goes the transition from metallic to poison mode, the target voltage drops from

an average of about 420V to an average of about 260V. Before each film deposition, in step 401, target 12 is cleaned by pure Argon sputtering in the metallic mode. Then target is then conditioned in poison mode with the oxygen flow much higher than the flow required at the transition region.

[0115] Tables 1A through 1C shows some effects on the deposited films of depositions with the 0.8/0.8 target under different operating conditions. Table 1A includes photoluminescence (pumped at 532 nm) and index of refraction for films deposited on substrate 16 with different Ar/O_2 gas flow ratios with no bias power applied to substrate 16.

10170385.031502

Table 1A

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
6	30/42	200	2.3	0	1973	1.5142
6	30/36	200	2.3	0	2358	1.5215
6	60/30	200	2.3	0	3157	1.5229
6	60/28	200	2.3	0	3421	1.5229

[0116] Table 1B shows the variation in photoluminescence (pumped at 532 nm) and index of refraction of the film deposited on substrate 16 with deposition processes having with the same Ar/O_2 ratios but different pulsed DC power frequencies from power supply 14.

Table 1B

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
3	60/28	100	2.3	100	1472	1.5146
4	60/28	75	3.5	100	2340	1.5189
6	60/28	120	2.3	100	5178	1.5220

[0117] Table 1C shows the photoluinescence and index as deposited where the bias power to substrate 16 is varied.

Table 1C

Target Power (KW)	Ar/O2	Frequency (KHz)	Reverse Pulsing Time (us)	Bias (W)	PL/um (532nm)	Index
6	60/28	200	2.3	0	3657	1.5230
6	60/28	200	2.3	100	2187	1.5244
6	60/28	200	2.3	200	3952	1.5229
6	60/28	200	2.3	300	5000	1.5280

[0118] The photoluminescence values can be measured with a Phillips PL-100. The deposited film can be pumped with a 532 nm laser and the luminescence at 980 is measured. The index is the index of refraction. Typically, films deposited are annealed in order to activate the erbium. Figure 6 shows the photoluminescence and lifetime versus anneal temperature for a typical film deposited as described in this example.

10103963.031602

EXAMPLE 2

[0119] A waveguide amplifier can be deposited according to the present invention. An embodiment of target 12 having composition 57.4 cat. % Si, 41.0 cat. % Al, 0.8 cat. % Er 0.8 cat. % Yb (the ".8/.8 target") can be formed as disclosed in the '245 application. The Er-Yb (0.8/0.8) co-doped Alumino-Silicate film was deposited onto a 6 inch wafer of substrate 16 which includes a 10 μm thick thermal oxide substrate, which can be purchased from companies such as Silicon Quest International, Santa Clara, CA. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The power supplied to target 12 during conditioning was kept at about 6 kW.

[0120] An active core film was then deposited on substrate 16. The thickness of the deposited film is approximately 1.2 μm. The deposition parameters are shown in Table 2.

Table 2.

. Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)
6	60/28	120	100	2.3

[0121] A straight waveguide pattern can then formed by standard photolithography techniques. The active core was etched using reactive ion etch followed by striping and cleaning. Next, a 10 μm top cladding layer is deposited using a similar deposition process according to the present invention. An embodiment of target 12 with composition 92 cat. % Si and 8 cat. % Al as shown in Figure 9 to form the top cladding layer. The index difference between the top cladding layer and the active layer is about 3.7%. The amplifier is then annealed at 725° C for about 30 min (see Figure 6, for example).

[0122] The erbium excited-state lifetime and the up-conversion coefficient were measured to be 3ms and 4.5 x 10^{-18} cm^3/s, respectively. A net gain of about 4dB for small signal (about –20 dBm) with fiber to waveguide and to fiber coupling was obtained. Waveguide length was 10cm and the width was about 1.5 to 8 μm. The coupling loss between the fiber and the waveguide is 3-4 dB/facet, and passive excess loss is 0.1-0.2 dB/cm for 3um waveguide. The waveguide was both co- and counter pumped with 150 mW 980nm laser per facet.

EXAMPLE 3

[0123] This example describes production of a dual core Erbium/Yttrbium co-doped amplifier according to the present invention. In one example, substrate 16 is a silicon substrate with an undercladding layer of thermally oxidized SiO_2 of about 15 μm thick. Substrate 16 with the thermal oxide layer can be purchased from companies such as Silicon Quest International, Santa Clara, CA. A layer of active core material is then deposited on substrate 16 with a Shadow Mask as described in the '138 application. Use of a shadow mask results in a vertical taper on each side of a finished waveguide which greatly enhances the coupling of light into and out of the waveguide.

[0124] Active core layer is deposited from a 0.8/0.8 target as described in the '247 application having composition 57.4 cat. % Si, 41.0 cat. % Al, 0.8 cat. % Er, and 0.8 cat. % Yb. The deposition parameters are identical to that of Example 2 described above. The active layer is deposited to a thickness of about 1.2 μm.

[0125] A passive layer of aluminasilicate is then deposited over the active layer. A passive layer of about 4.25 μm thickness can be deposited with an embodiment of target 12 having composition of Si/Al of about 87 cat. % Si and about 13 cat. % Al. The passive layer and active layer are then patterned by standard lithography techniques to form a core that has a width of about 5.0 μm for the active core and tapering to about 3.5 μm at the top of the passive core with an effective length of about 9.3 cm.

[0126] Upper cladding layer is then deposited from a Si/Al target of 92 cat. % Si and 8 cat. % Al. Deposition of the upper cladding layer is shown in Figure 9. In some embodiments, the upper cladding layer can be deposited with a non-biased process. The thickness of the upper cladding layer can be about 10 μm. The amplifier formed by this process is then annealed at 725° C for about 30 min.

10104853.031602

[0127] The as-deposited Erbium and Ytterbium concentrations in the active layer of core 303 is 2.3×10^{20} cm^{-3} Erbium concentration and 2.3×10^{20} cm^{-3} Ytterbium concentration. The index of the core is 1.508 and the index of cladding layers are 1.4458 for undercladding layer 302 and 1.452 for uppercladding layer 304. The parameter $\Delta n/n$ is therefore about 5.0%.

[0128] A reverse taper mode size converter, *see* the '138 application, is utilized for coupling light into waveguide amplifier 300. The insertion loss at 1310 nm is about 2 dB. Figure 26 shows the amplifier performance of this example. In Figure 26, amplifier 300 is pumped with 150 mW from one side pumping with 984 nm light. Gain flattening is achieved within about 1 dB in the range 1528 nm to 1562 nm for small input signals (-20 dBm). For large input signals (0 dBm), gain flattening is also achieved within about 1 dB.

<u>EXAMPLE 4</u>

[0129] Another example of production of a waveguide amplifier is described here. Again, substrate 16 can be a Si wafer with about a 15 μm thick thermal oxide as can be purchased from Silicon Quest International, Santa Clara, CA. The embodiment of target 12 for the deposition of the active core can have a composition of about 50 cat. % Si, 48.5 cat. % Al, 1.5 cat. % Er (the "1.5/0" target), which can be fabricated as discussed in the '138 application. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively.

[0130] The pulsed DC power supplied to target 12 was about 6 kW. Whenever a brand new target was used or when the target has been expose to atmosphere, a long time of condition (for example more than 30hrs of conditioning) may be necessary to ensure films with the best active core property (longest life time and highest photoluminescence) are deposited. Substrate 16 is then preheat at about 350° C for about 30min before deposition.

[0131] The active core film was deposited onto a 6 inch thermal oxide wafer, which has been previously discussed, from the 1.5/0 target. The thermal oxide thickness was about 10 μm as described in previous examples. The active core is deposited to a thickness of about 1.2 μm with a deposition time of approximately 1 hr. The process condition are as listed in Table 4 below.

Table 3

Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)
6	60/28	120	100	2.3

[0132] A straight waveguide pattern can then be formed by a standard photolithography procedure. The active core was etched using reactive ion etch followed by striping and cleaning. Finally, a 10 μm top cladding layer is deposited using a similar process. A target having composition 92 cat. % Si and 8 cat. % Al with deposition parameters as described in Figure 9 was used to deposit the top cladding. The difference between the index of refraction between the core and the cladding is then about 3.7%.

[0133] In this example, annealing of the amplifier structure was performed at various anneal temperatures. The results of the various anneals are shown graphically in Figures 27 and 28. Figure 27 shows both internal gain in the C-band and insertion loss at 1310 nm of a 2.5μm wide, 10.1 cm long waveguide as deposited in this example as a function of annealing temperature. The life time in ms and up-conversion constants in cm^{-3}/s measurements for the deposited active core film at different annealing temperature are shown in Figure 28.

10101853 . 031502

EXAMPLE 5

[0134] One of the problems encountered during the reactive sputtering from an alloy metallic target is that the film composition drifts from run to run due to the difference in sputtering yields from the elements that forms the target alloy. For example, with Ar as a sputtering gas, the sputtering yield of Aluminum is about 3-4 times that of Silicon, while sputtering yield of Alumina is only about 50% that of Silica. Therefore, during the metal burn in, more Aluminum is sputtered from the target, resulting in a Si rich target surface. When sputtering in the poison mode, more Silica will be removed from target. Thus, as deposition goes on, the composition of the film deposited on substrate 16 will drift from lower Alumina concentration to higher Alumina concentration. This results in the index of refraction of a film drifting up with subsequent depositions from a target 12, as is shown for the deposition described in Example 4 in Figure 29. Figure 30 shows the drift in photoluminescence pumped at 532 nm with subsequent depositions. Figure 31 shows drift in the excited state lifetime with subsequent depositions from a target. The embodiment of target 12 utilized in Figures 29 through 31 is the 1.5/0 target and the deposition parameters are as described above in Example 4.

[0135] The drift can be stabilized by recondition target 12 prior to deposition. The recondition process (or burn in) consists of both sputtering in metallic mode and then sputtering in poison mode to condition target 12. The burn in time in metallic mode needs to be as short as possible and at the same time insure no arcing during the poison mode deposition. Figure 32 shows the

much improved drift in the index of refraction and the photoluminescence when target 12 is reconditioned between subsequent depositions.

EXAMPLE 6

[0136] This example describes the fabrication of another Er-Yb codoped waveguide amplifier according to the present invention. The active core is deposited with an embodiment of target 12 with composition about **49 cat. % Si, 48 cat. % Al, 1.6 cat. % Er and 0.5 cat. % Yb**, which can be fabricated as described in the '247 application. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The pulsed DC power supplied to target 12 was kept at 5 kW. Table 4 shows photoluminescence and index of refraction of as-deposited films from this example at some typical process conditions. The units for photoluminescence are the number of counts per micron. Lifetime and photoluminescence measured after annealing at various different temperatures are shown in Table 5.

Target 4

Target Power (KW)	Ar/O2 (sccm)	Pulsing Frequency (KHz)	Bias (W)	Reverse pulsing time (us)	532 nm PL/um	Index
5	60/34	120	100	2.3	3367	1.5333
5	60/30	120	100	2.3	3719	1.5334

Table 5

Anneal Temperature °C	Life Time (ms)	PL (532nm)/um
725	3	7000
775	3	7000
800	4	7500
825	4.7	8560
850	5.8	10000
900	6.9	17000

[0137] A waveguide amplifier was fabricated using this material in the similar fashion as described in examples 2-4. The active core was first deposited on substrate 16, which includes a

10um thermal oxide layer, using the following deposition parameters: target power 5KW, pulsing frequency 120KHz, bias 100W, reverse time 2.3us, Argon and Oxygen flow are 60 sccm and 30sccm respectively. The active core thickness is deposited to a thickness about 1.2μm, which takes approximately 1 hr. All wafers are preheated at about 350° C for 30min before deposition. A straight waveguide pattern is then formed by standard photolithography procedure. The active core was etched using reactive ion etch following by striping and cleaning. Next, a 10μm top cladding layer is deposited using similar process. The "92/8" (92 cat. % Si and 8 cat. % Al) metallic target was used to deposit top clad according to deposition parameters shown in Figure 9, resulting in a 4 % index difference between active core and cladding. The wave guide was then annealed at 800° C for about 30 min.

[0138] This waveguide was tested for gain using the method described in previous examples. However no net gain was observed from this waveguide since the passive loss was too high.

EXAMPLE 7

[0139] In addition to active material layers (i.e., layers having rare-earth ion concentrations), passive layers can also be deposited. Figure 9 shows deposition parameters for several target compositions, including some targets for deposition of passive (i.e., alloys of Al and Si with no rare earth ion concentration) layers. In this example, an embodiment of target 12 with a material composition of pure silicon is utilized.

[0140] Apparatus 10 can be based on an AKT 1600 reactor and deposited with about 1 to 3 kW of pulsed DC target power supplied to target 12. Particular depositions have been accomplished at 2.5 kW and 1.5 kW. The frequency of the pulsed DC power is between about 100 and 200 Khz. Some depositions were performed at 200 kHz while others were performed at 100 kHz. The reverse time was varied between about 2 μs and about 4 μs with particular depositions performed at 2.3 μs and 3.5 μs. The bias power to substrate 16 was set to zero.

[0141] Index variation of SiO2 films with bias to substrate 16 and deposition rates as a function of bias power to substrate 16 is shown in Figure 10.

[0142] The process gas included a mixture of Ar, N_2 and O_2. The Ar flow rates was set at 20 sccm while the O_2 flow rate was varied between about 5 and about 20 sccm and the N_2 flow rate was varied from about 2 to about 35 sccm. Figure 33 shows the variation in the index of refraction of a film deposition on substrate 16 as the O_2/N_2 ratio is varied.

EXAMPLE 8

[0143] Alternatively, films can be deposited on substrate 16 from a pure alumina target. In an example deposition with an embodiment of target 12 of alumina in an embodiment of apparatus 10 based on the AKT 1600 reactor, the pulsed DC target power was set at 3 kW and the frequency was varied between about 60 kHz and 200 kHz. The reverse time was set at 2.5 μs. Again, no bias power was supplied to substrate 16. The O_2 flow rate was varied from about 20 to about 35 sccm, with particular depositions performed at 22 and 35 sccm. The Ar flow rate was set at 26 sccm. A post deposition anneal of substrate 16 at 800° C for 30 min. was performed.

[0144] Figure 12 shows the variation of refractive index of the film deposited on substrate 16 with varying frequency of the pulsed DC power supplied to target 12. Figure 11 shows the variation in refractive index of a film deposited on substrate 16 with varying O_2/Ar ratio. As can be seen from Figures 33, 34 and 35, the index of refraction of films deposited from alumina can be adjusted by adjusting the process gas constituents or by adjusting the frequency of the pulsed DC power supplied to target 12 during deposition.

EXAMPLE 9

[0145] Additionally, passive films can be deposited from targets having a composition of Si and Al. For example, layers have been deposited from embodiments of target 12 with composition 83 % Si and 17 % Al. About 4.5 kW of pulsed DC power at about 200 kHz frequency was supplied to target 12. The reverse time was about 2.2 μs. A bias power of about 150 W was

supplied to substrate 16 during deposition. Figures 14 and 15 show variation of the index of refraction for subsequent runs from this target.

[0146] The examples and embodiments discussed above are exemplary only and are not intended to be limiting. One skilled in the art can vary the processes specifically described here in various ways. Further, the theories and discussions of mechanisms presented above are for discussion only. The invention disclosed herein is not intended to be bound by any particular theory set forth by the inventors to explain the results obtained. As such, the invention is limited only by the following claims.

10101863 .031602

Claims

We claim:

1. A method of depositing a film on a substrate, comprising:

    providing pulsed DC power through a filter to a target;

    providing bias power to a substrate positioned opposite the target;

    providing process gas between the target and the substrate,

    wherein the filter protects a pulsed DC power supply from the bias power.

2. The method of Claim 1, further including holding the temperature of the substrate substantially constant.

3. The method of Claim 1, wherein providing pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. The method of Claim 1, wherein providing bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. The method of Claim 4, wherein the filter is a band reject filter at the frequency of the bias power.

6. The method of claim 4, wherein the bias power is zero.

7. The method of Claim 1, wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

8. The method of Claim 1, wherein the process gas includes a mixture of Oxygen and Argon.

9. The method of Claim 9, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

10. The method of Claim 8, wherein the process gas further includes nitrogen.

10141835.031502

11. The method of Claim 1, wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate.

12. The method of Claim 1, further including uniformly sweeping the target with a magnetic field.

13. The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. The method of Claim 1, further including depositing a film on the backside of target 12.

15. A reactor according to the present invention, comprising:

a target area for receiving a target;

a substrate area opposite the target area for receiving a substrate;

a pulsed DC power supply; and

a bias power supply coupled to the substrate.

16. The reactor of Claim 15, wherein the target has a surface area greater than the surface area of the substrate.

17. The reactor of Claim 15, further including a scanning magnet which provides uniform erosion of the target.

18. The reactor of Claim 17, wherein the scanning magnet scans across the target in a first direction and extends in a second direction perpendicular to the first direction.

19. The reactor of Claim 18, wherein the magnet extends beyond the target in the second direction.

20. A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting the bias power to the substrate;

setting the process gas flow; and

applying pulsed DC power to the target to deposit the film.

21. The method of Claim 20, wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25. A method of forming a waveguide amplifier, comprising:

providing a substrate with an undercladding layer;

providing a target having a concentration of rare-earth ions opposite the substrate;

supplying process gas between the target and the substrate;

applying pulsed DC power through a filter to the target to deposit a film;

patterning the film to form a core;

depositing an uppercladding layer over the core.

26. The method of Claim 25, wherein providing a substrate includes providing a silicon substrate with a thermal oxide layer.

27. The method of Claim 25, wherein providing a target includes providing a target having a concentration of up to about 5 cat. % of rare earth ions.

10101863.031502

28. The method of Claim 27, wherein providing a target includes providing a target of Al and Si.

29. The method of claim 25, wherein providing a target includes providing a target with a concentration of Al.

30. The method of Claim 29, wherein providing a target includes providing a target with a concentration of Si.

31. The method of Claim 29, wherein providing a target includes providing a target with a concentration of rare earth ions.

32. The method of Claim 25, further including providing bias power to the substrate.

33. The method of Claim 25, further including scanning a magnet over the target.

34. The method of Claim 25, wherein scanning the magnet over the target includes moving the magnet in a first direction.

35. The method of Claim 34, wherein the magnet extends beyond the target in a second direction perpendicular to the first direction.

36. The method of Claim 25, wherein the target has a surface area greater than the surface area of the substrate.

37. The method of Claim 32, wherein the filter rejects power at a frequency of the bias power.

38. A sputtering apparatus, comprising:

means for providing pulsed DC power to a target; and

means for providing bias power to a substrate.

39. The apparatus of Claim 38, further including

means for providing process gas between the target and the substrate.

10103835.031502

M-12245 US
852923 v1

Biased Pulse DC Reactive Sputtering of Oxide Films

Hongmei Zhang
Mukundan Narasimhan
Ravi Mullapudi
Richard E. Demaray

Abstract

A biased pulse DC reactor for sputtering of oxide films is presented. The biased pulse DC reactor couples pulsed DC at a particular frequency to the target through a filter which filters out the effects of a bias power applied to the substrate, protecting the pulsed DC power supply. Films deposited utilizing the reactor have controllable material properties such as the index of refraction. Optical components such as waveguide amplifiers and multiplexers can be fabricated using processes performed on a reactor according to the present inention.

10101865.031502

Atto Docket No.: M-12245 US

**DECLARATION FOR PATENT APPLICATION
AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of subject matter (process, machine, manufacture, or composition of matter, or an improvement thereof) which is claimed and for which a patent is sought by way of the application entitled

Biased Pulse DC Reactive Sputtering of Oxide Films

which (check) ☒ is attached hereto.
☐ and is amended by the Preliminary Amendment attached hereto.
☐ was filed on as Application Serial No.
☐ and was amended on (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
Number	Country	Day/Month/Year Filed	Yes	No
N/A			☐	☐

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date
N/A	

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)
N/A		

I hereby appoint the following practitioners to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith:

Customer Number 24251

Please direct all telephone calls to:

Gary J. Edwards

Telephone: 408-453-9200

I declare that all statements made herein of my own knowledge are true, all statements made herein on information and belief are believed to be true, and all statements made herein are made with the knowledge that whoever, in any matter within the jurisdiction of the Patent and Trademark Office, knowingly and willfully falsifies, conceals, or covers up by any trick, scheme, or device a material fact, or makes any false, fictitious or fraudulent statements or representations, or makes or uses any false writing or document knowing the same to contain any false, fictitious or fraudulent statement or entry, shall be subject to the penalties including fine or imprisonment or both as set forth under 18 U.S.C. 1001, and that violations of this paragraph may jeopardize the validity of the application or this document, or the validity or enforceability of any patent, trademark registration, or certificate resulting therefrom.

Full name of **first** joint inventor: Hongmei Zhang
Inventor's Signature: ______________________ Date: ______________
Residence:
Post Office Address: Citizenship:

Full name of **third** joint inventor: Mukundan Narasimhan
Inventor's Signature: ______________________ Date: ______________
Residence:
Post Office Address: Citizenship:

Full name of **second** joint inventor: Ravi B. Mullapudi
Inventor's Signature: ______________________ Date: ______________
Residence: San Jose, California
Post Office Address: 2117 Shiangzone Court
San Jose, California 95121
Citizenship: India

Full name of **fourth** joint inventor: Richard E. Demaray
Inventor's Signature: ______________________ Date: ______________
Residence: Portola Valley, California
Post Office Address: 190 Fawn Lane
Portola Valley, California 94028
Citizenship: USA

CLAIMS ONLY

SERIAL NO. | FILING DATE

APPLICANT(S)

CLAIMS

	AS FILED		AFTER 1st AMENDMENT		AFTER 2nd AMENDMENT			*		*		*	
	IND.	DEP.	IND.	DEP.	IND.	DEP.		IND.	DEP.	IND.	DEP.	IND.	DEP.
1	/						51						
2		/					52						
3		/					53						
4		/					54						
5		/					55						
6		/					56						
7		/					57						
8		/					58						
9		/					59						
10		/					60						
11		/					61						
12		/					62						
13		/					63						
14		/					64						
15	/						65						
16		/					66						
17		/					67						
18		/					68						
19		/					69						
20	/						70						
21		/					71						
22		/					72						
23		/					73						
24		/					74						
25	/						75						
26		/					76						
27		/					77						
28		/					78						
29		/					79						
30		/					80						
31		/					81						
32		/					82						
33		/					83						
34		/					84						
35		/					85						
36		/					86						
37		/					87						
38	/						88						
39		/					89						
40							90						
41							91						
42							92						
43							93						
44							94						
45							95						
46							96						
47							97						
48							98						
49							99						
50							100						
TOTAL IND.	5						TOTAL IND.						
TOTAL DEP.	34						TOTAL DEP.						
TOTAL CLAIMS	39						TOTAL CLAIMS						

* MAY BE USED FOR ADDITIONAL CLAIMS OR ADMENDMENTS

FORM PTO-2022 (1-98)

U.S.DEPARTMENT OF COMMERCE
Patent and Trademark Office

*U.S. Government Printing Office: 1998 - 433-214/70303

BEST AVAILABLE COPY

PATENT APPLICATION FEE DETERMINATION RECORD
Effective October 1, 2001

Application or Docket Number

CLAIMS AS FILED - PART I

	(Column 1)	(Column 2)
TOTAL CLAIMS	39	
FOR	NUMBER FILED	NUMBER EXTRA
TOTAL CHARGEABLE CLAIMS	39 minus 20=	* 19
INDEPENDENT CLAIMS	5 minus 3 =	* 2
MULTIPLE DEPENDENT CLAIM PRESENT	☐	

* If the difference in column 1 is less than zero, enter "0" in column 2

SMALL ENTITY TYPE ☐ RATE	FEE	OR	OTHER THAN SMALL ENTITY RATE	FEE
BASIC FEE	370.00	OR	BASIC FEE	740.00
19 X$ 9=	171	OR	X$18=	
2 X42=	84	OR	X84=	
+140=		OR	+280=	
TOTAL	625	OR	TOTAL	

CLAIMS AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

SMALL ENTITY RATE	ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	ADDITIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT C

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."
***If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
☆U.S GPO:2001 482-124 / 59197

BEST AVAILABLE COPY

UNITED STATES PATENT AND TRADEMARK OFFICE

COMMISSIONER FOR PATENTS
UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. 20231
www.uspto.gov

APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NUMBER
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

FORMALITIES LETTER

OC000000008148448

Date Mailed: 05/17/2002

NOTICE TO FILE MISSING PARTS OF NONPROVISIONAL APPLICATION

FILED UNDER 37 CFR 1.53(b)

Filing Date Granted

Items Required To Avoid Abandonment:

An application number and filing date have been accorded to this application. The item(s) indicated below, however, are missing. Applicant is given **TWO MONTHS** from the date of this Notice within which to file all required items and pay any fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

- The statutory basic filing fee is missing.
  Applicant must submit $ **370** *to complete the basic filing fee for a small entity.*
- The oath or declaration is unsigned.
- To avoid abandonment, a late filing fee or oath or declaration surcharge as set forth in 37 CFR 1.16(l) of $65 for a small entity in compliance with 37 CFR 1.27, must be submitted with the missing items identified in this letter.

Items Required To Avoid Processing Delays:

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- Additional claim fees of $**255** as a small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.

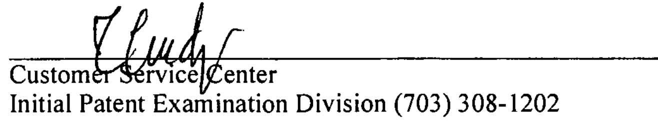
SUMMARY OF FEES DUE:

Total additional fee(s) required for this application is $**690** for a Small Entity

- $**370** Statutory basic filing fee.
- $**65** Late oath or declaration Surcharge.
- Total additional claim fee(s) for this application is $**255**
  - $**171** for **19** total claims over 20.

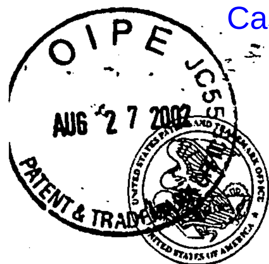
- $**84** for **2** independent claims over 3.

A copy of this notice <u>MUST</u> be returned with the reply.



Customer Service Center
Initial Patent Examination Division (703) 308-1202

PART 3 - OFFICE COPY



COPY OF PAPERS ORIGINALLY FILED

#3

UNITED STATES PATENT AND TRADEMARK OFFICE

COMMISSIONER FOR PATENTS
UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. 20231
www.uspto.gov

APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NUMBER
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938

FORMALITIES LETTER

OC000000008148448

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

Date Mailed: 05/17/2002

BEST AVAILABLE COPY

NOTICE TO FILE MISSING PARTS OF NONPROVISIONAL APPLICATION

FILED UNDER 37 CFR 1.53(b)

Filing Date Granted

Items Required To Avoid Abandonment:

An application number and filing date have been accorded to this application. The item(s) indicated below, however, are missing. Applicant is given **TWO MONTHS** from the date of this Notice within which to file all required items and pay any fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

- The statutory basic filing fee is missing.
  Applicant must submit $ **370** *to complete the basic filing fee for a small entity.*
- The oath or declaration is unsigned.
- To avoid abandonment, a late filing fee or oath or declaration surcharge as set forth in 37 CFR 1.16(l) of $65 for a small entity in compliance with 37 CFR 1.27, must be submitted with the missing items identified in this letter.

Items Required To Avoid Processing Delays:

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- Additional claim fees of **$255** as a small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.

08/28/2002 MAHMED1 00000073 192386 10101863
01 FC:201 370.00 CH
02 FC:202 84.00 CH
03 FC:203 171.00 CH
04 FC:205 65.00 CH

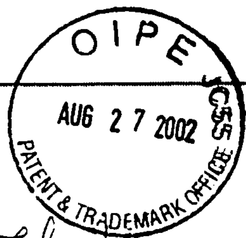
SUMMARY OF FEES DUE:

Total additional fee(s) required for this application is **$690** for a Small Entity

- **$370** Statutory basic filing fee.
- **$65** Late oath or declaration Surcharge.
- Total additional claim fee(s) for this application is **$255**
  - **$171** for **19** total claims over 20.

COPY OF PAPERS ORIGINALLY FILED

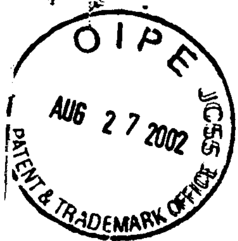
- **$84** for **2** independent claims over 3.



A copy of this notice <u>MUST</u> be returned with the reply.

Customer Service Center
Initial Patent Examination Division (703) 308-1202

PART 2 - COPY TO BE RETURNED WITH RESPONSE



COPY OF PAPERS ORIGINALLY FILED

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Hongmei Zhang, Mukundan Narasimhan, Ravi B. Mullapudi and Richard E. Demaray		
Assignee:	Symmorphix, Inc.		
Title:	Biased Pulse DC Reactive Sputtering Of Oxide Films		
Serial No.:	10/101,863	Filing Date:	March 16, 2002
Examiner:	Unknown	Group Art Unit:	Unknown
Docket No.:	M-12245 US		

San Jose, California
August 19, 2002

BOX MISSING PARTS
COMMISSIONER FOR PATENTS
Washington, D.C. 20231

RESPONSE TO NOTICE TO FILE MISSING PARTS OF NON-PROVISIONAL APPLICATION - FILING DATE GRANTED

Dear Sir:

In response to the "Notice to File Missing Parts of Non-Provisional Application - Filing Date Granted" mailed by the United States Patent and Trademark Office on May 17, 2002, the following documents are enclosed to complete the filing of the above-identified patent application:

1. A declaration signed by the inventors in compliance with 37 CFR 1.63;

2. Copy of Notice to File Missing Parts of Non-Provisional Application - Filing Date Granted; and

3. Petition for Extension of Time.

The United States Patent and Trademark Office is hereby authorized to charge the following fees to Deposit Account No. 19-2386:

1.	Surcharge for filing declaration on a date later than the filing date of the application.	$65.00

LAW OFFICES OF
SKJERVEN MORRILL LLP
25 METRO DRIVE
SUITE 700
SAN JOSE, CA 95110
(408) 453-9200
FAX (408) 453-7979

COPY OF PAPERS ORIGINALLY FILED

2.	Statutory basic filing fee	$370.00
3.	19 extra claims at $9.00 each	$171.00
4.	2 extra independent claims at $42.00 each	$84.00
5.	Petition for Extension of Time	$55.00
6.	TOTAL FEES:	$745.00

The Commissioner is hereby authorized to charge any additional fees, which may be required, or credit any overpayment to Deposit Account No. 19-2386.

It is hereby respectfully submitted that the enclosed documents complete the filing of the above patent application and justify the filing date of March 16, 2002. Please telephone the undersigned at (408) 453-9200, if there are any questions. This form is being submitted in duplicate.

I hereby certify that this correspondence is being deposited with the United States Postal Service as First Class Mail in an envelope addressed to: Box Missing Parts, Commissioner for Patents, Washington, D.C. 20231, on August 19, 2002.

Gary J. Edwards 8/19/02
Attorney for Applicants Date of Signature

Respectfully submitted,

Gary J. Edwards
Gary J. Edwards
Attorney for Applicant
Reg. No. 41,008

LAW OFFICES OF
SKJERVEN MORRILL LLP
25 METRO DRIVE
SUITE 700
SAN JOSE, CA 95110
(408) 453-9200
FAX (408) 453-7979

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 152 of 1543

#3

COPY OF PAPERS ORIGINALLY FILED

Attorney Docket No.: M-12245 US

BEST AVAILABLE COPY

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of subject matter (process, machine, manufacture, or composition of matter, or an improvement thereof) which is claimed and for which a patent is sought by way of the application entitled

Biased Pulse DC Reactive Sputtering of Oxide Films

which (check) ☐ is attached hereto.
☐ and is amended by the Preliminary Amendment attached hereto.
☒ was filed on March 16, 2002 as Application Serial No. 10/101,863.
☐ and was amended on (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
Number	Country	Day/Month/Year Filed	Yes	No
N/A			☐	☐

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date
N/A	

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information, which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)
N/A		

Attorney Docket No.: M-12245 US

I hereby appoint the following practitioners to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith:

Customer Number 24251

COPY OF PAPERS ORIGINALLY FILED

Please direct all telephone calls to:

Gary J. Edwards

Telephone: 408-453-9200

I declare that all statements made herein of my own knowledge are true, all statements made herein on information and belief are believed to be true, and all statements made herein are made with the knowledge that whoever, in any matter within the jurisdiction of the Patent and Trademark Office, knowingly and willfully falsifies, conceals, or covers up by any trick, scheme, or device a material fact, or makes any false, fictitious or fraudulent statements or representations, or makes or uses any false writing or document knowing the same to contain any false, fictitious or fraudulent statement or entry, shall be subject to the penalties including fine or imprisonment or both as set forth under 18 U.S.C. 100 , and that violations of this paragraph may jeopardize the validity of the application or this document, or the validity or enforceability of any patent, trademark registration, or certificate resulting therefrom.

Full name of first joint inventor: Hongmei Zhang
Inventor's Signature: [signature] Date: 08/08/02
Residence: San Jose, California
Post Office Address: 1330 Rodney Drive
San Jose, California 95118
Citizenship: People of Republic China

Full name of second joint inventor: Mukundan Narasimhan
Inventor's Signature: [signature] Date: 08/08/02
Residence: San Jose, California
Post Office Address: 293 Bluefield Drive
San Jose, California 95136
Citizenship:

Full name of third joint inventor: Ravi B. Mullapudi
Inventor's Signature: [signature] Date: 08/08/02
Residence: San Jose, California
Post Office Address: 2117 Shiangzone Court
San Jose, California 95121
Citizenship: India

Full name of fourth joint inventor: Richard E. Demaray
Inventor's Signature: [signature] Date: 8/8/02
Residence: Portola Valley, California
Post Office Address: 190 Fawn Lane
Portola Valley, California 94028
Citizenship: USA

BEST AVAILABLE COPY

#4

BEST AVAILABLE COPY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Hongmei Zhang, Mukundan Narasimhan, Ravi B. Mullapudi and Richard E. Demaray

Assignee: Symmorphix, Inc.

Title: Biased Pulse DC Reactive Sputtering Of Oxide Films

Serial No.: 10/101,863 Filing Date: March 16, 2002

Examiner: Unknown Group Art Unit: Unknown

Docket No.: M-12245 US

San Jose, California
August 19, 2002

BOX Missing Parts
COMMISSIONER FOR PATENTS
Washington, D. C. 20231

PETITION FOR EXTENSION OF TIME

Dear Sir:

Applicants respectfully petition for a 1-month extension of time within which to respond to the May 17, 2002 outstanding Notice to File Missing Parts, such extension allowing the undersigned until August 19, 2002 (as August 17, 2002 is a Saturday) to respond.

Please charge the amount of $55.00 as set forth in the enclosed Response to Notice to File Missing Parts.

I hereby certify that this correspondence is being deposited with the United States Postal Service as First Class Mail in an envelope addressed to: Box Missing Parts, Commissioner for Patents, Washington, D.C. 20231, on August 19, 2002.

[signature] 8/19/02
Attorney for Applicants Date of Signature

Respectfully submitted,

[signature]

Gary J. Edwards
Attorney for Applicants
Reg. No. 41,008

LAW OFFICES OF
SKJERVEN MORRILL LLP
25 METRO DRIVE
SUITE 700
SAN JOSE, CA 95110
(408) 453-9200
FAX (408) 453-7979

08/28/2002 MAHMED1 00000073 132386 10101863
05 FC:215 55.00 CH

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

7590 10/02/2003

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

EXAMINER
ESTRADA, MICHELLE

ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 10/02/2003

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	**Application No.** 10/101,863	**Applicant(s)** ZHANG ET AL.	
	Examiner Michelle Estrada	**Art Unit** 2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE _1_ MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☐ Responsive to communication(s) filed on ____ .

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) _1-39_ is/are pending in the application.

4a) Of the above claim(s) ____ is/are withdrawn from consideration.

5)☐ Claim(s) ____ is/are allowed.

6)☐ Claim(s) ____ is/are rejected.

7)☐ Claim(s) ____ is/are objected to.

8)☒ Claim(s) _1-39_ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on ____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

11)☐ The proposed drawing correction filed on ____ is: a)☐ approved b)☐ disapproved by the Examiner.

If approved, corrected drawings are required in reply to this Office action.

12)☐ The oath or declaration is objected to by the Examiner.

Priority under 35 U.S.C. §§ 119 and 120

13)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. ____ .

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

14)☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. § 119(e) (to a provisional application).

a) ☐ The translation of the foreign language provisional application has been received.

15)☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. §§ 120 and/or 121.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO-1449) Paper No(s) ____ .
4) ☐ Interview Summary (PTO-413) Paper No(s). ____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: .

DETAILED ACTION

Election/Restrictions

I. Claims 1-14 and 20-24, drawn to a coating method, classified in class 427, subclass 1+.

II. Claims 15-19 and 38-39, drawn to a coating apparatus, classified in class 118, subclass 1+.

III. Claims 25-37, drawn to a process of making a semiconductor device, classified in class 438, subclass 761.

Inventions I and II are related as process and apparatus for its practice. The inventions are distinct if it can be shown that either: (1) the process as claimed can be practiced by another materially different apparatus or by hand, or (2) the apparatus as claimed can be used to practice another and materially different process. (MPEP § 806.05(e)). In this case the apparatus as claimed can be used to practice another and materially different process such as one that does not require providing a process gas between the target and the substrate.

Inventions I and III are related as combination and subcombination. Inventions in this relationship are distinct if it can be shown that (1) the combination as claimed does not require the particulars of the subcombination as claimed for patentability, and (2) that the subcombination has utility by itself or in other combinations (MPEP § 806.05(c)). In the instant case, the combination as claimed does not require the particulars of the subcombination as claimed because the combination does not require providing an undercladding layer, patterning the film to form a core and depositing an

for making

uppercladding layer over the core. The subcombination has separate utility such as a waveguide amplifier to use in semiconductor devices.

Inventions II and III are related as process and apparatus for its practice. The inventions are distinct if it can be shown that either: (1) the process as claimed can be practiced by another materially different apparatus or by hand, or (2) the apparatus as claimed can be used to practice another and materially different process. (MPEP § 806.05(e)). In this case the apparatus as claimed can be used to practice another and materially different process such as one that does not require providing an undercladding layer and an uppercladding layer.

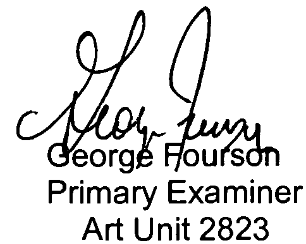
Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be amended in compliance with 37 CFR 1.48(b) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. Any amendment of inventorship must be accompanied by a request under 37 CFR 1.48(b) and by the fee required under 37 CFR 1.17(i).

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is (703) 308-0729. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri can be reached on 703-306-2794. The fax phone numbers

for the organization where this application or proceeding is assigned are 703-308-7722 for regular communications and 703-308-7724 for After Final communications.

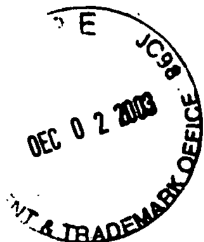
Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 703-308-0956.



George Fourson
Primary Examiner
Art Unit 2823

MEstrada
September 28, 2003

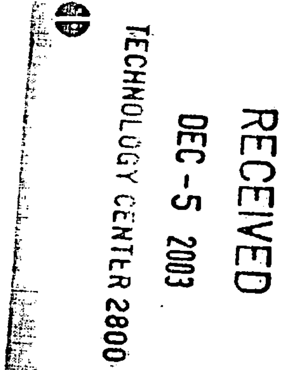
41



PATENT
Customer No. 22,852
Attorney Docket No. 09140.0016
(formerly M-12245 US)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
Zhang, et al.	) Group Art Unit: 2816
	)
Application No.: 10/101,863	) Examiner: Unassigned
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)
	)



Commissioner for Patents
Washington, DC 20231

Sir:

REVOCATION OF POWER OF ATTORNEY
AND GRANT OF NEW POWER OF ATTORNEY

The undersigned, a representative authorized to sign on behalf of the Assignee owning all of the interest in this patent, hereby revokes all previous powers of attorney or authorization of agent granted in this application before the date of execution hereof. The undersigned verifies that Symmorphix, Inc. is the Assignee of the entire right, title, and interest in the patent application identified above by virtue of the attached assignment document, which is being concurrently filed for recordation. The undersigned certifies that the evidentiary documents have been reviewed and to the best of the undersigned's knowledge and belief, title is in the Assignee Symmorphix, Inc.

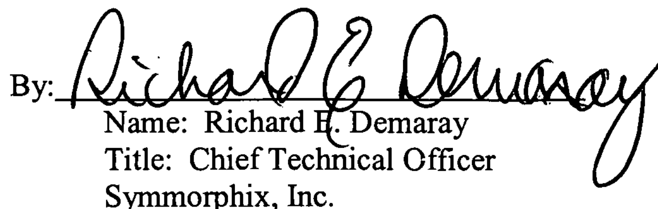
The undersigned hereby grants its power of attorney to **FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.,** Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsvold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Hefter, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zotter, Reg. No. 27,680; Dennis P. O'Reilley, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg. No. 25,387; Richard L. Stroup, Reg. No. 28,478; David W. Hill, Reg. No. 28,220; Thomas L. Irving, Reg. No. 28,619; Charles E. Lipsey, Reg. No. 28,165; Thomas W. Winland, Reg. No. 27,605; Basil J. Lewris, Reg. No. 28,818; Martin I. Fuchs, Reg. No. 28,508; E. Robert Yoches, Reg. No. 30,120; Barry W. Graham, Reg. No. 29,924; Susan Haberman Griffen, Reg. No. 30,907; Richard B. Racine, Reg. No. 30,415; Thomas H. Jenkins, Reg. No. 30,857; Robert E. Converse, Jr., Reg. No. 27,432; Clair X. Mullen, Jr., Reg. No. 20,348; Christopher P. Foley, Reg. No. 31,354; Roger D. Taylor, Reg. No. 28,992; John C. Paul, Reg. No. 30,413; David M. Kelly, Reg. No. 30,953; Kenneth J. Meyers, Reg. No. 25,146; Carol P. Einaudi, Reg. No. 32,220; Walter Y. Boyd, Jr., Reg. No. 31,738; Steven M. Anzalone, Reg. No. 32,095; Jean B. Fordis, Reg. No. 32,984; Barbara C. McCurdy, Reg. No. 32,120; James K. Hammond, Reg. No. 31,964; Richard V. Burgujian, Reg. No. 31,744; J. Michael Jakes, Reg. No. 32,824; Thomas W. Banks, Reg. No. 32,719; Christopher P. Isaac, Reg. No. 32,616; Bryan C. Diner, Reg. No. 32,409; M. Paul Barker, Reg. No. 32,013; Andrew Chanho Sonu, Reg. No. 33,457; David S. Forman, Reg. No. 33,694; Vincent P. Kovalick, Reg. No. 32,867; James W.

Edmondson, Reg. No. 33,871; Michael R. McGurk, Reg. No. 32,045; Joann M. Neth, Reg. No. 36,363; Gerson S. Panitch, Reg. No. 33,751; Cheri M. Taylor, Reg. No. 33,216; Charles E. Van Horn, Reg. No. 40,266; Linda A. Wadler, Reg. No. 33,218; Jeffrey A. Berkowitz, Reg. No. 36,743; Michael R. Kelly, Reg. No. 33, 921; James B. Monroe, Reg. No. 33,971; Doris Johnson Hines, Reg. No. 34,629; Lori Ann Johnson, Reg. No. 34,498; R. Bruce Bower, Reg. No. 37,099; John Rissman, Reg. No. 33,764; Therese A. Hendricks, Reg. No. 30,389; Leslie I. Bookoff, Reg. No. 38,084; Michele C. Bosch, Reg. No. 40,524; Michael J. Flibbert, Reg. No. 33,234; Scott A. Herbst, Reg. No. 35,189; Leslie A. McDonell, Reg. No. 34,872; Thalia V. Warnement, Reg. No. 39,064; Ronald A. Bleeker, Reg. No. 27,773; Kathleen A. Daley, Reg. No. 36,116; C. Gregory Gramenopoulos, Reg. No. 36,532; Anthony M. Gutowski, Reg. No. 38,742; Yitai Hu, Reg. No. 40,653; Lionel M. Lavenue; Reg. No. 46,859; Christine E. Lehman, Reg. No. 38,535; and Gary J. Edwards, Reg. No. 41,008; both jointly and separately as their attorneys with full power of substitution and revocation to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and to receive the Letters Patent.

Please send all future correspondence concerning this application to Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P. at the following address:

Finnegan, Henderson, Farabow,
Garrett & Dunner, L.L.P.
1300 I Street, N.W.
Washington, D.C. 20005-3315

Dated: Nov 18, 2003

By: 

Name: Richard E. Demaray
Title: Chief Technical Officer
Symmorphix, Inc.

Attorney Docket No. 09140.0016
(Former Attorney Docket No. M-12245 US)

JOINT INVENTION
(Worldwide Rights)

ASSIGNMENT

WHEREAS WE, the below named inventors, {hereinafter referred to as Assignor], have made an invention entitled:

BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

for which we executed an application for United States Letters Patent concurrently herewith or filed an application for United States Letters Patent March 16, 2002, (Application No. 10/101,863); and

WHEREAS, **SYMMORPHIX, INC.**, a corporation of Delaware, whose post office address is 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (hereinafter referred to as Assignee), is desirous of securing the entire right, title, and interest in and to this invention in all countries throughout the world, and in and to the application for United States Letters Patent on this invention and the Letters Patent to be issued upon this application;

NOW THEREFORE, be it known that for good and valuable consideration the receipt of which from Assignee is hereby acknowledged, we, as Assignors, have sold, assigned, transferred, and set over, and do hereby sell, assign, transfer, and set over unto the Assignee, its lawful successors and assigns, my entire right, title, and interest in and to this invention; and this application, Application No. 10/101,863, filed March 16, 2002; and all divisions, and continuations thereof, and all Letters Patent of the United States which may be granted thereon, and all reissues thereof, and all rights to claim priority on the basis of this application, Application No. 10/101,863, filed March 16, 2002, and all applications for Letters Patent which may hereafter be filed for this invention in any foreign country and all Letters Patent which may be granted on this invention in any foreign country, and all extensions, renewals, and reissues thereof; and we hereby authorize and request the Commissioner of Patents and Trademarks of the United States and any official of any foreign country whose duty it is to issue patents on applications as described above, to issue all Letters Patent for this invention to Assignee, its successors and assigns, in accordance with the terms of this Assignment;

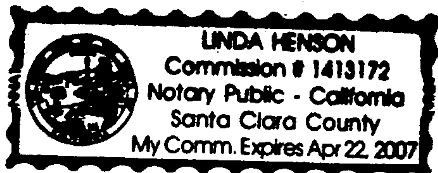
AND, WE HEREBY covenant that we have the full right to convey the interest assigned by this Assignment, and we have not executed and will not execute any agreement in conflict with this Assignment;

AND, WE HEREBY further covenant and agree that we will, without further consideration, communicate with Assignee, its successors and assigns, any facts known to us respecting this invention, and testify in any legal proceeding, sign all lawful papers when called upon to do so, execute and deliver any and all papers that may be necessary or desirable to perfect the title to this invention in said Assignee, its successors or assigns, execute all divisional, continuation, and reissue applications, make all rightful oaths and generally do everything possible to aid Assignee, its successors and assigns, to obtain and enforce proper patent protection for this invention in the United States and any foreign country, it being understood that any expense incident to the execution of such papers shall be borne by the Assignee, its successors and assigns.

IN TESTIMONY WHEREOF, we have hereunto set our hands.

State of CALIFORNIA)
) ss.
County of SANTA CLARA)

NAME: Hongmei Zhang
ADDRESS: 1330 Rodney Drive
San Jose, CA 95118



BY: [signature]
Hongmei Zhang

DATE: 6/18/2003

Subscribed and sworn to before me this 18th day of June, 2003.

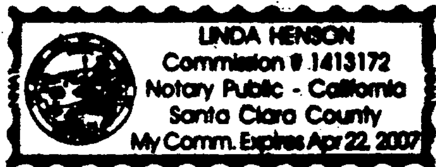
[signature] Notary Public

Attorney Docket No. 09140.0016
(Former Attorney Docket No. M-12245 US)

JOINT INVENTION
(Worldwide Rights)

State of CALIFORNIA)
) ss.
County of SANTA CLARA)

NAME: Mukundan Narasimhan
ADDRESS: 293 Bluefield Drive
San Jose, CA 95136


LINDA HENSON
Commission # 1413172
Notary Public - California
Santa Clara County
My Comm. Expires Apr 22, 2007

BY: N. M[signature]
Mukundan Narasimhan

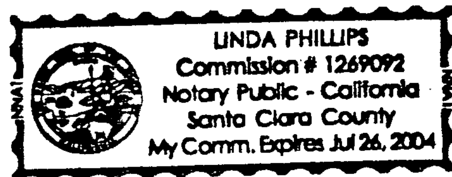
DATE: 06/18/03

Subscribed and sworn to before me this 18th day of June, 2003.

[signature], Notary Public

State of CALIFORNIA)
) ss.
County of SANTA CLARA)

NAME: Ravi B. Mullapudi
ADDRESS: 2117 Shiangzone Court
San Jose, CA 95121


LINDA PHILLIPS
Commission # 1269092
Notary Public - California
Santa Clara County
My Comm. Expires Jul 26, 2004

BY: [signature]
Ravi B. Mullapudi

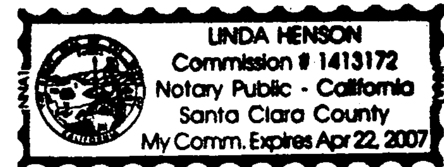
DATE: 10/27/03

Subscribed and sworn to before me this 27 day of October, 2003.

[signature], Notary Public

State of CALIFORNIA)
) ss.
County of SANTA CLARA)

NAME: Richard E. Demaray
ADDRESS: 190 Fawn Lane
Portola Valley, CA 94028

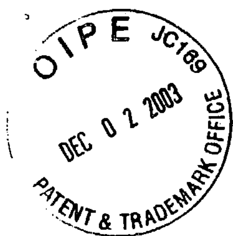

LINDA HENSON
Commission # 1413172
Notary Public - California
Santa Clara County
My Comm. Expires Apr 22, 2007

BY: [signature]
Richard E. Demaray

DATE: June 18 2003

Subscribed and sworn to before me this 18th day of June, 2003.

[signature], Notary Public



PATENT
Customer No. 22,852
Attorney Docket No. 09140.0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Hongmei Zhang

Serial No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: Michelle Estrada

RECEIVED
DEC 11 2003
TECHNOLOGY CENTER 2800

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

RESPONSE TO RESTRICTION REQUIREMENT

In a restriction requirement dated October 2, 2003, the Examiner required restriction under 35 U.S.C. § 121 between Group I (Claims 1-14 and 20-24, drawn to a coating method, classified in class 427, subclass 1+), Group II (Claims 15-19 and 38-39, drawn to a coating apparatus, classified in class 118, subclass 1+), and Group III (Claims 25-37, drawn to a process of making a semiconductor device, classified in class 438, subclass 761.) Applicants provisionally elect to prosecute **Group I**, claims 1-14 and 20-24 drawn to a coating method.

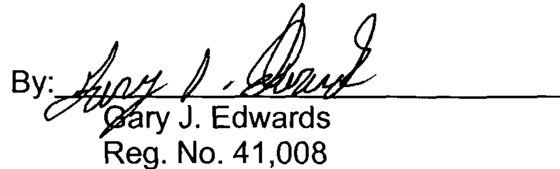
Please grant a one-month extension of time required to enter this response and charge the required small entity extension fee of $55.00 under 37 C.F.R. 1.17(a)(1) to the deposit account No. 06-0916. Petition for 1-month Extension of Time is being filed concurrently.

If there is any additional fee due in connection with the filing of this Response, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 2, 2003



By: ______________________
Gary J. Edwards
Reg. No. 41,008

CERTIFICATE UNDER 37 CFR § 1.10 OF
MAILING BY "EXPRESS MAIL"

EL 974556529 US	December 2, 2003
USPS Express Mail Label Number	Date of Deposit

I hereby certify that this correspondence is being deposited with the United States Postal Services "Express Mail Post Office to Addressee" service under 37 CFR § 1.10 on the date indicated above and is addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

By: ______________________
Veronica Weinstein

PATENT
Customer No. 22,852
Attorney Docket No. 09140.0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
Hongmei Zhang) Group Art Unit: 2823
Application No.: 10/101,863) Examiner: Michelle Estrada
Filed: March 16, 2002)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS)

RECEIVED
DEC 11 2003
TECHNOLOGY CENTER 2800

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

Applicants hereby petition for a one month extension of time to reply to the Office Action of October 2, 2003. This Petition is accompanied by a small entity extension fee of $55.00 as specified by Section 1.17(a)(1). Please charge $55.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter the accompanying response and charge any additional required fees to our deposit account 06-0916.

12/08/2003 HGUTEMA1 00000005 060916 10101863
01 FC:2251 55.00 DA

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: December 2, 2003

By: [signature]
Gary J. Edwards
Reg. No. 41,008

CERTIFICATE UNDER 37 CFR § 1.10 OF
MAILING BY "EXPRESS MAIL"

EL 974556529 US
USPS Express Mail Label Number

December 2, 2003
Date of Deposit

I hereby certify that this correspondence is being deposited with the United States Postal Services "Express Mail Post Office to Addressee" service under 37 CFR § 1.10 on the date indicated above and is addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

By:
Veronica Weinstein

L Number	Hits	Search Text	DB	Time stamp
1	1	(target with "metallic mode") and (target with "poisonous")	USPAT; US-PGPUB	2004/02/12 13:34
-	41231	"DC power"	USPAT; US-PGPUB	2004/02/11 10:13
-	16262	bias with substrate	USPAT; US-PGPUB	2004/02/11 10:13
-	995	"DC power" with target	USPAT; US-PGPUB	2004/02/11 10:14
-	322	((bias with substrate) and ("DC power" with target)) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 10:23
-	0	(((bias with substrate) and ("DC power" with target)) not (@ad>20020316 or @rlad>20020316)) and ("DC pwer" with filter)	USPAT; US-PGPUB	2004/02/11 10:23
-	20	(((bias with substrate) and ("DC power" with target)) not (@ad>20020316 or @rlad>20020316)) and ("DC power" with filter)	USPAT; US-PGPUB	2004/02/11 10:35
-	197	438/769.ccls.	USPAT; US-PGPUB	2004/02/11 10:35
-	0	((bias with substrate) and ("DC power" with target)) and 438/769.ccls.	USPAT; US-PGPUB	2004/02/11 10:35
-	611	438/787.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	2	((bias with substrate) and ("DC power" with target)) and 438/787.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	453	438/770.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	0	((bias with substrate) and ("DC power" with target)) and 438/770.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	89	438/771.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	0	((bias with substrate) and ("DC power" with target)) and 438/771.ccls.	USPAT; US-PGPUB	2004/02/11 10:36
-	443	438/788.ccls.	USPAT; US-PGPUB	2004/02/11 10:37
-	1	((bias with substrate) and ("DC power" with target)) and 438/788.ccls.	USPAT; US-PGPUB	2004/02/11 10:37
-	242	427/533.ccls.	USPAT; US-PGPUB	2004/02/11 10:37
-	1	((bias with substrate) and ("DC power" with target)) and 427/533.ccls.	USPAT; US-PGPUB	2004/02/11 10:37
-	89227	427/$.ccls.	USPAT; US-PGPUB	2004/02/11 10:38
-	33	((bias with substrate) and ("DC power" with target)) and 427/$.ccls.	USPAT; US-PGPUB	2004/02/11 10:38
-	30	(((bias with substrate) and ("DC power" with target)) and 427/$.ccls.) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 10:40
-	74451	438/$.ccls.	USPAT; US-PGPUB	2004/02/11 10:40
-	107	((bias with substrate) and ("DC power" with target)) and 438/$.ccls.	USPAT; US-PGPUB	2004/02/11 10:40
-	87	(((bias with substrate) and ("DC power" with target)) and 438/$.ccls.) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 10:40
-	1466	204/192.12.ccls.	USPAT; US-PGPUB	2004/02/11 11:40
-	98	((bias with substrate) and ("DC power" with target)) and 204/192.12.ccls.	USPAT; US-PGPUB	2004/02/11 11:38
-	89	(((bias with substrate) and ("DC power" with target)) and 204/192.12.ccls.) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 11:38
-	19	((((bias with substrate) and ("DC power" with target)) and 204/192.12.ccls.) not (@ad>20020316 or @rlad>20020316)) and filter	USPAT; US-PGPUB	2004/02/11 11:39

-	8	(((((bias with substrate) and ("DC power" with target)) and 204/192.12.ccls.) not (@ad>20020316 or @rlad>20020316)) and filter) and (oxide or oxynitride)	USPAT; US-PGPUB	2004/02/11 11:39
-	1572	204/192.15.ccls.	USPAT; US-PGPUB	2004/02/11 11:40
-	68	((bias with substrate) and ("DC power" with target)) and 204/192.15.ccls.	USPAT; US-PGPUB	2004/02/11 11:41
-	43	(((bias with substrate) and ("DC power" with target)) and 204/192.15.ccls.) and (oxide or oxynitride)	USPAT; US-PGPUB	2004/02/11 11:41
-	39	((((bias with substrate) and ("DC power" with target)) and 204/192.15.ccls.) and (oxide or oxynitride)) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 16:23
-	4	(((((bias with substrate) and ("DC power" with target)) and 204/192.15.ccls.) and (oxide or oxynitride)) not (@ad>20020316 or @rlad>20020316)) and filter	USPAT; US-PGPUB	2004/02/11 11:44
-	56595	filter with band	USPAT; US-PGPUB	2004/02/11 16:23
-	365	(bias with substrate) and ("DC power" with target)	USPAT; US-PGPUB	2004/02/11 16:31
-	7	(filter with band) and ((bias with substrate) and ("DC power" with target))	USPAT; US-PGPUB	2004/02/11 16:26
-	6	((bias with substrate) and ("DC power" with target)) and "cladding layer"	USPAT; US-PGPUB	2004/02/11 16:28
-	2007	(deposit$3 with "cladding layer")	USPAT; US-PGPUB	2004/02/11 16:29
-	0	((bias with substrate) and ("DC power" with target)) with (deposit$3 with "cladding layer")	USPAT; US-PGPUB	2004/02/11 16:30
-	0	((bias with substrate) and ("DC power" with target)) same (deposit$3 with "cladding layer")	USPAT; US-PGPUB	2004/02/11 16:30
-	5	((bias with substrate) and ("DC power" with target)) and (deposit$3 with "cladding layer")	USPAT; US-PGPUB	2004/02/11 16:30
-	197	((bias with substrate) and ("DC power" with target)) and nitrogen	USPAT; US-PGPUB	2004/02/11 16:32
-	559562	oxide or oxynitride	USPAT; US-PGPUB	2004/02/11 16:32
-	140	(((bias with substrate) and ("DC power" with target)) and nitrogen) and (oxide or oxynitride)	USPAT; US-PGPUB	2004/02/11 17:14
-	3362	target with "magnetic field"	USPAT; US-PGPUB	2004/02/11 16:38
-	107	((bias with substrate) and ("DC power" with target)) and (target with "magnetic field")	USPAT; US-PGPUB	2004/02/11 16:40
-	21	deposit$3 with (backside with target)	USPAT; US-PGPUB	2004/02/12 12:12
-	5	((bias with substrate) and ("DC power" with target)) and (deposit$3 with (backside with target))	USPAT; US-PGPUB	2004/02/12 12:12
-	262448	@ad>20020316 or @rlad>20020316	USPAT; US-PGPUB	2004/02/11 17:15
-	122	((((bias with substrate) and ("DC power" with target)) and nitrogen) and (oxide or oxynitride)) not (@ad>20020316 or @rlad>20020316)	USPAT; US-PGPUB	2004/02/11 17:15
-	16	(deposit$3 with (backside with target)) not (((bias with substrate) and ("DC power" with target)) and (deposit$3 with (backside with target)))	USPAT; US-PGPUB	2004/02/12 12:11
-	0	(deposit$3 with ("backside of the target")) not (((bias with substrate) and ("DC power" with target)) and (deposit$3 with (backside with target)))	USPAT; US-PGPUB	2004/02/12 12:11
-	0	((bias with substrate) and ("DC power" with target)) and (deposit$3 with ("backside of the target"))	USPAT; US-PGPUB	2004/02/12 12:12
-	0	deposit$3 with ("backside of the target")	USPAT; US-PGPUB	2004/02/12 12:13
-	0	("backside of the target")	USPAT; US-PGPUB	2004/02/12 12:13

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

7590 02/24/2004

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

DATE MAILED: 02/24/2004

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No. 10/101,863	Applicant(s) ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *02 December 2003*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-39* is/are pending in the application.

4a) Of the above claim(s) *15-39* is/are withdrawn from consideration.

5)☐ Claim(s) ____ is/are allowed.

6)☒ Claim(s) ~~1-13~~ 1-6+8-13 *and 20* is/are rejected.

7)☒ Claim(s) *7 and 21-24* is/are objected to.

8)☐ Claim(s) ____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on ____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. ____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date ____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. ____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: ____.

DETAILED ACTION

Election/Restrictions

Applicant's election of Group I (claims 1-14 and 20-24) in Paper filed 12/02/03 is acknowledged. Because applicant did not distinctly and specifically point out the supposed errors in the restriction requirement, the election has been treated as an election without traverse (MPEP § 818.03(a)).

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-13 and 20 are rejected under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938).

With respect to claim 1, Le et al. disclose providing pulsed DC power (22) to a target (14) (Page 4, Paragraph [0070]); providing bias power to a substrate (16) positioned opposite the target; providing process gas between the target and the substrate (Page 4, Paragraph [0067]).

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

With respect to claim 8, Le et al. disclose wherein the process gas includes a mixture of oxygen and argon (Page 4, Paragraph [0067]).

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

With respect to claim 10, Le et al. disclose wherein the process gas further includes nitrogen (Page 5, Paragraph [0074]).

With respect to claim 11, Le et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 3).

With respect to claim 12, Le et al. disclose further including uniformly sweeping the target with a magnetic field (Page 5, Paragraph [0073]).

With respect to claim 13, Le et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Page 5, Paragraph [0073]).

With respect to claim 20, Le et al. disclose conditioning a target (Page 4, Paragraph [0070]); preparing the substrate (Page 3, Paragraph [0065]); adjusting the bias power to the substrate (Page 4, Paragraph [0041]); setting the process gas flow (Page 4, Paragraph [0067]); and applying pulsed DC power to the target to deposit the film (Page 4, Paragraph [0071]).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine

experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed. Furthermore, Le et al. disclose that sets of process parameters depend on the specific process chamber (Page 6, Paragraph [0081]).

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power,

time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Le et al. do not disclose providing a DC power through a filter.

With respect to claims 1 and 5, Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form the DC power supply (Col. 6, lines 32-37).

Allowable Subject Matter

Claims 7 and 21-24 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri can be reached on 571-272-1855. The fax phone numbers

for the organization where this application or proceeding is assigned are 703-308-7722 for regular communications and 703-308-7724 for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

MEstrada
February 12, 2004

OLIK CHAUDHURI
SUPERVISORY PATENT EXAMINER
TECHNOLOGY CENTER 2800

Notice of References Cited	Application/Control No. 10/101,863	Applicant(s)/Patent Under Reexamination ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-2003/0077914	04-2003	Le et al.	438/763
	B	US-5,755,938	05-1998	Fukui et al.	204/298.23
	C	US-5,830,330	11-1998	Lantsman, Alexander D.	204/192.12
	D	US-5,607,560	03-1997	Hirabayashi et al.	204/192.15
	E	US-2003/0022487	01-2003	Yoon et al.	438/642
	F	US-5,942,089	08-1999	Sproul et al.	204/192.13
	G	US-2003/0042131	03-2003	Johnson, Wayne L.	204/192.12
	H	US-5,849,163	12-1998	Ichikawa et al.	204/192.23
	I	US-2003/0141186	07-2003	Wang et al.	204/298.07
	J	US-2003/0079838	05-2003	Brcka, Jozef	156/345.48
	K	US-6,488,822	12-2002	Moslehi, Mehrdad M.	204/192.12
	L	US-6,057,557	05-2000	Ichikawa, Takeshi	257/59
	M	US-			

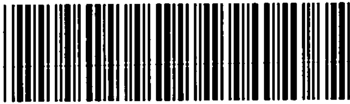
FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Search Notes	Application No.	Applicant(s)	
	10/101,863	ZHANG ET AL.	
	Examiner	**Art Unit**	
	Michelle Estrada	2823	

SEARCHED

Class	Subclass	Date	Examiner
438	769		
438	770		
438	771		
438	787		
438	788		
427	533		
204	192.12		
204	192.15	2/12/2004	ME

INTERFERENCE SEARCHED

Class	Subclass	Date	Examiner

SEARCH NOTES (INCLUDING SEARCH STRATEGY)

	DATE	EXMR
See East search attached	2/12/2004	ME

ISSUE SLIP STAPLE AREA (for additional cross-references)

ISSUING CLASSIFICATION

BEST AVAILABLE COPY

ORIGINAL		CROSS REFERENCE(S)						
CLASS	SUBCLASS	CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					
INTERNATIONAL CLASSIFICATION								
/								
/								
/								
/								
/								

^ Continued on Issue Slip Inside File Jacket

INDEX OF CLAIMS

✓ .... Rejected
= .... Allowed
– (Through numeral) ... Canceled
\+ .... Restricted
N .... Non-elected
I .... Interference
A .... Appeal
O .... Objected

Claim Final	Claim Original	Date 03/12/04	Claim Final	Claim Original	Date	Claim Final	Claim Original	Date
1	1	✓		51			101	
	2	|		52			102	
	3	|		53			103	
	4	|		54			104	
	5	|		55			105	
	6	✓		56			106	
	7	O		57			107	
	8	✓		58			108	
	9	|		59			109	
	10	|		60			110	
	11	|		61			111	
	12	|		62			112	
	13	✓		63			113	
	14	N		64			114	
	15	|		65			115	
	16	|		66			116	
	17	|		67			117	
	18	|		68			118	
	19	N		69			119	
	20	✓		70			120	
	21	O		71			121	
	22	O		72			122	
	23	O		73			123	
	24	O		74			124	
	25	N		75			125	
	26	|		76			126	
	27	|		77			127	
	28	|		78			128	
	29	|		79			129	
	30	|		80			130	
	31	|		81			131	
	32	|		82			132	
	33	|		83			133	
	34	|		84			134	
	35	|		85			135	
	36	|		86			136	
	37	|		87			137	
	38	|		88			138	
	39	N		89			139	
	40			90			140	
	41			91			141	
	42			92			142	
	43			93			143	
	44			94			144	
	45			95			145	
	46			96			146	
	47			97			147	
	48			98			148	
	49			99			149	
	50			100			150	

If more than 150 claims or 9 actions staple additional sheet here

BEST AVAILABLE COPY

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	
H. Zhang, et al.	Group Art Unit: 2823
Application No.: 10/101,863	Examiner: Michelle Estrada
Filed: March 16, 2002	
For: Biased Pulsed DC Reactive Sputtering of Oxide Films	Confirmation No.: 6938

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

REPLY TO OFFICE ACTION

In reply to the Office Action mailed February 24, 2004, please amend the above-identified application as follows:

Amendments to the Specification are included starting on page 2.

Amendments to the Claims are reflected in the listing of claims starting on page 6.

Remarks/Arguments are included in this paper starting on page 9.

AMENDMENTS TO THE SPECIFICATION:

Please amend the specification as follows:

Please amend paragraph **[0048]** as indicated below:

[0048] RF sputtering of oxide films is discussed in Application Serial No. 09/903,050 (the '050 application) (now U.S. Patent No. 6,506,289) by Demaray et al., entitled "Planar Optical Devices and Methods for Their Manufacture," assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, targets that can be utilized in a reactor according to the present invention are discussed in U.S. Application serial no. ~~{Attorney Docket No. M-12247 US} (the '247 application)~~ 10/101,341 (the '341 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. A gain-flattened amplifier formed of films deposited according to the present invention are described in U.S. Application serial no. ~~{Attorney Docket No. M-12652 US} (the '652 application)~~ 10/101,493 (the '493 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, a mode size converter formed with films deposited according to the present invention is described in U.S. Application serial no. ~~{Attorney Docket No. M-12138 US} (the '138 application)~~ 10/101,492 (the '492 application), filed concurrently with the present disclosure, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety.

Please amend paragraph **[0060]** as indicated below:

[0060] Target 12 can be formed of any materials, but is typically metallic materials such as, for example, combinations of Al and Si. Therefore, in some embodiments, target 12 includes a metallic target material formed from ~~intermetalic~~ intermetallic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form ~~intermetalics~~ intermetallics. ~~*See* the '247 application.~~ *See* the '341 application.

Please amend paragraph **[0062]** as indicated below:

[0062] Several useful examples of target 12 that can be utilized in apparatus 10 according to the present invention include the following targets compositions: (Si/Al/Er/Yb) being about (57.0/41.4/0.8/0.8), (48.9/49/1.6/0.5), (92/8/0/0), (60/40/0/0), (50/50/0/0), (65/35/0/0), (70/30/0,0), and (50,48.5/1.5/0) cat. %, to list only a few. These targets can be referred to as the 0.8/0.8 target, the 1.6/.5 target, the 92-8 target, the 60-40 target, the 50-50 target, the 65-35 target, the 70-30 target, and the 1.5/0 target, respectively. The 0.8/0.8, 1.6/0.5, and 1.5/0 targets can be made by pre-alloyed targets formed from an atomization and hot-isostatic pressing (HIPing) process as described in ~~the '247 application~~ the '341 application. The remaining targets can be formed, for example, by HIPing. Targets formed from Si, Al, Er and Yb can have any composition. In some embodiments, the rare earth content can be up to 10 cat. % of the total ion content in the target. Rare earth ions are added to form active layers for amplification. Targets utilized in apparatus 10 can have any composition and can include ions other than Si, Al, Er and Yb, including: Zn, Ga, Ge, P, As, Sn, Sb, Pb, Ag, Au, and rare earths: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy Ho, Er, Tm Yb and Lu.

Please amend paragraph **[0084]** as indicated below:

[0084] Figure 5 shows the voltage on target 12 of an embodiment of apparatus 10 according to the present invention as a function of process gas constitution. In the example illustrated in Figure 5, for example, a metallic target with composition .8 cat. % Er, .8 cat. % Yb, 57.4 cat. % Si and 41 cat. % Si, which can be formed as described in ~~the '247 application~~ the '341 application, was sputtered in an embodiment of apparatus 10 based on the AKT-1600 PVD system with 6 kW of pulsed DC power at a frequency of 120 kHz and a reverse time of 2.3 micro seconds. The Argon gas flow was set at 60 sccm and the Oxygen gas flow was varied from zero up to 40 sccm. For more details regarding this deposition, see Example 1 below.

Please amend paragraph **[0112]** as indicated below:

[0112] An AKT 1600 based reactor can be utilized to deposit a film. In this example, a wide area metallic target of dimension 550X 650 mm with composition (Si/Al/Er/Yb) being about 57.0 cat. % Si, 41.4 cat. % Al, 0.8 cat. % Er, and 0.8 cat. % Yb (a ".8/.8" target) was fabricated as described in ~~the '247 patent~~ the '341 application.

Please amend paragraph **[0119]** as indicated below:

[0119] A waveguide amplifier can be deposited according to the present invention. An embodiment of target 12 having composition 57.4 cat. % Si, 41.0 cat. % Al, 0.8 cat. % Er 0.8 cat. % Yb (the ".8/.8 target") can be formed as disclosed in ~~the '245 application~~ the '341 application. The Er-Yb (0.8/0.8) co-doped Alumino-Silicate film was deposited onto a 6 inch wafer of substrate 16 which includes a 10 μm thick thermal oxide substrate, which can be purchased from companies such as Silicon Quest International, Santa Clara, CA. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The power supplied to target 12 during conditioning was kept at about 6 kW.

Please amend paragraph **[0123]** as indicated below:

[0123] This example describes production of a dual core Erbium/Yttrbium co-doped amplifier according to the present invention. In one example, substrate 16 is a silicon substrate with an undercladding layer of thermally oxidized SiO_2 of about 15 μm thick. Substrate 16 with the thermal oxide layer can be purchased from companies such as Silicon Quest International, Santa Clara, CA. A layer of active core material is then deposited on substrate 16 with a Shadow Mask as described in ~~the '138 application~~ the '492 application. Use of a shadow mask results in a vertical taper on each side of a finished waveguide which greatly enhances the coupling of light into and out of the waveguide.

Please amend paragraph **[0128]** as indicated below:

[0128] A reverse taper mode size converter, *see* ~~the '138 application~~ the '492 application, is utilized for coupling light into waveguide amplifier 300. The insertion loss at 1310 nm is about

2 dB. Figure 26 shows the amplifier performance of this example. In Figure 26, amplifier 300 is pumped with 150 mW from one side pumping with 984 nm light. Gain flattening is achieved within about 1 dB in the range 1528 nm to 1562 nm for small input signals (-20 dBm). For large input signals (0 dBm), gain flattening is also achieved within about 1 dB.

Please amend paragraph **[0136]** as indicated below:

[0136] This example describes the fabrication of another Er-Yb codoped waveguide amplifier according to the present invention. The active core is deposited with an embodiment of target 12 with composition about **49 cat. % Si, 48 cat. % Al, 1.6 cat. % Er and 0.5 cat. % Yb**, which can be fabricated as described in ~~the '247 application~~ the '341 application. Target 12 was first cleaned by sputtering with Ar (80 sccm) only in the metallic mode. Target 12 was then conditioned in poison mode by flowing 60 sccm of Argon and 40 sccm of oxygen respectively. The pulsed DC power supplied to target 12 was kept at 5 kW. Table 4 shows photoluminescence and index of refraction of as-deposited films from this example at some typical process conditions. The units for photoluminescence are the number of counts per micron. Lifetime and photoluminescence measured after annealing at various different temperatures are shown in Table 5.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

Please cancel claims 15-19 and 25-39, without prejudice.

Claim 1 (Original): A method of depositing a film on a substrate, comprising:

providing pulsed DC power through a filter to a target;

providing bias power to a substrate positioned opposite the target;

providing process gas between the target and the substrate,

wherein the filter protects a pulsed DC power supply from the bias power.

Claim 2 (Original): The method of Claim 1, further including holding the temperature of the substrate substantially constant.

Claim 3 (Original): The method of Claim 1, wherein providing pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

Claim 4 (Original): The method of Claim 1, wherein providing bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

Claim 5 (Original): The method of Claim 4, wherein the filter is a band reject filter at the frequency of the bias power.

Claim 6 (Original): The method of claim 4, wherein the bias power is zero.

Claim 7 (Original): The method of Claim 1, wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

Claim 8 (Original): The method of Claim 1, wherein the process gas includes a mixture of Oxygen and Argon.

Claim 9 (Original): The method of Claim 9, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

Claim 10 (Original): The method of Claim 8, wherein the process gas further includes nitrogen.

Claim 11 (Original): The method of Claim 1, wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate.

Claim 12 (Original): The method of Claim 1, further including uniformly sweeping the target with a magnetic field.

Claim 13 (Original): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

Claim 14 (Original): The method of Claim 1, further including depositing a film on the backside of target 12.

Claims 15-19 (Canceled).

Claim 20 (Currently Amended): A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting [[the]] a bias power to the substrate;

setting [[the]] a process gas flow; and

applying pulsed DC power to the target through a filter to deposit the film.

Claim 21 (Original): The method of Claim 20, wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

Claim 22 (Original): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

Claim 23 (Original): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

Claim 24 (Original): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

Claims 25-39 (Canceled).

REMARKS

Claims 1-39 are pending in the above identified application. Claims 15-19 and 25-39 have been withdrawn from consideration in this application. Claims 1-14 and 20-24 are being considered in the present application. The Examiner has rejected claims 1-6, 8-13, and 20 and has objected to claims 7 and 21-24. Applicants herein traverse these rejections and request reconsideration by the Examiner. Applicants have amended the specification only to update references to pending applications that are referenced in the disclosure. Claim 20 has been amended. No new matter has been added by these amendments.

Election/Restrictions

The Examiner acknowledged Applicant's election of Group I claims for consideration in the present application. On the Office Action Summary form, the Examiner has incorrectly indicated that claims 15-39 have been withdrawn from this application. Instead, claims 15-19 and 25-39 have been withdrawing while claims 1-14 and 20-24 are to be considered in the present application.

Claim Rejections under 35 USC § 103

The Examiner has rejected claims 1-13 and 20 under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938). However, the combination of Le and Fukui does not teach all of the elements of the claims. Further, there is no motivation to combine the references Le and Fukui as suggested by the Examiner.

As is discussed in the MPEP,

> [t]o establish a prima facie case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on applicant's disclosure. In re Vaeck, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991). See MPEP § 2143 - § 2143.03 for decisions pertinent to each of these criteria.

MPEP § 2142. In particular, there is no motivation to combine Le and Fukui as is suggested by the Examiner. Further, even if Le and Fukui were combined as suggested by the Examiner, the combination does not teach or suggest all of the claim elements of claims 1-13 and 20.

1. Claims 1-13 and 20 are allowable over Le and Fukui because the combination of Le and Fukui does not teach all of the elements of these claims

Claim 1 recites "providing pulsed DC power through a filter to a target" and "providing bias power to a substrate . . . ." Claim 20 recites "adjusting a bias power to the substrate" and "applying pulsed DC power to the target through a filter to deposit the film." Le and Fukui do not teach the combination of providing pulsed DC power to the target and a bias power to the substrate or providing pulsed DC power through a filter.

Le teaches "processing of an anti-reflective coating on a substrate." (Le, par. 0001). In particular, Le teaches a process chamber, as shown in Figure 3 of Le, where

> [t]he substrate 16 is introduced into the chamber 36a through a substrate loading inlet (not shown) in a sidewall 45 of the chamber 36a and placed on the support 18. The support 18 can be lifted or lowered by support lift bellows (not shown) and a lift finger assembly (also not shown) can be used to lift and lower the

> substrate 16 onto the support 18 during transport of the substrate 16 into and out of the chamber 36a.

(Le, par. 0066). Process gas is introduced to the chamber through supply 23 of Figure 3. (*See,* Le, pars. 0067-0069). Additionally, Le teaches that

> [t]he PVD chamber 36a further comprises a sputtering target 14 comprising titanium, facing the substrate 16. A collimator (not shown) may be mounted between the target 14 and the substrate support 18 if desired. The PVD chamber 36a may also have a shield 20 to protect a wall 12 of the chamber 36a from sputtered material, and typically, to also serve as an anode grounding plane. The shield 20 is electrically floating or grounded. The target 14 is electrically isolated from the chamber 36a and is connected to a voltage source, such as a pulsed DC power source 22, but which may also be other types of voltage sources. In one version, the pulsed DC power source 22, target 14, and shield 20 operate as a gas energizer 90 that is capable of energizing the sputtering gas to sputter material from the plasma. The pulsed DC power source 22 applies a pulsed DC voltage to the target 14 relative to the shield 20. The electric field generated in the chamber 36a from the voltage applied to the sputtering target 14 energizes the sputtering gas to form a plasma that sputters off the target material.

(Le, par. 0070).

Therefore, as described in Le, a pulsed DC power supply is connected to the target. However, no bias is applied to the substrate as is suggested by the Examiner. (*See,* OA, pgs. 2). At best, Le teaches that "shield 20 is electrically floating or grounded," (Le, par. 0070), which is not a bias as claimed in claims 1 and 20 of the present application.

Furthermore, as opposed to the Examiner's suggestion, the teaching of Fukui et al. does not cure the defects in the teachings of Le. In particular, Fukui teaches "[a]n apparatus which allows a first film to be formed on a substrate by chemical vapor deposition (CVD) and a second film to be formed on the substrate by sputtering . . . ." (Fukui, abstract). In particular, Fukui teaches a process chamber as shown in Figure 1 of Fukui. As described by Fukui,

> [i]n the deposition chamber 10, as shown in FIG. 1, a first electrode 20 is disposed in a top portion thereof and a target 21 is detachably attached to a lower surface of the first electrode 20, while a second electrode 22 is disposed in a bottom portion of the deposition chamber 10 and a substrate 23 is detachably attached to an upper surface of the second electrode 22. The target 21 can be attached in place by using a known target mounting mechanism such an electrostatic chuck.

(Fukui, col. 6, lines 10-18). Further, Fukui teaches that

> [a]n RF power supply (first power supply) 25 for outputting RF power is connected to the first electrode 20 with a matching circuit 26 inserted between the first electrode 20 and the RF power supply 25. The matching circuit 26 serves to make zero reflected waves of the RF power.

(Fukui, col. 6, lines 26-30). Therefore, Fukui teaches that RF power is coupled to the target through a matching circuit. In addition, Fukui teaches that a DC power supply is coupled to bias the target. As Fukui states,

> [a]lso connected to the first electrode 20 is a dc power supply 28 through a band-pass filter 27 such as a low-pass filter for adjustment of impedance. The band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a dc power from the dc power supply 28.

(Fukui, col. 6, lines 26-36). Therefore, Fukui teaches utilizing a DC power supply coupled through a filter to the target. Additionally, Fukui teaches applying another RF power supply to the second electrode. As is stated in Fukui,

> [f]urther, an RF power supply (second power supply) 30 for outputting RF power is connected to the second electrode 22 with a matching circuit 31 inserted between the second electrode 22 and the RF power supply 30, the matching circuit 31 serving to act as with the matching circuit 26.

(Fukui, col. 6, lines 37-41).

Therefore, Fukui teaches applying RF power supplies to both target and substrate and applying a DC voltage to the target. Fukui does not teach a pulsed DC power supply or applying

power from a pulsed DC power supply through a filter to the target, as is suggested by the Examiner. (OA, page 5).

Therefore, the combination of Le and Fukui do not teach "providing pulsed DC power through a filter to a target" as is recited in claim 1 or "applying pulsed DC power to the target through a filter to deposit the film" as is recited in claim 20. Additionally, the combination of Le and Fukui does not suggest the combination of providing pulsed DC power to the target and a bias power to the substrate or providing pulsed DC power through a filter. Therefore, claims 1 and 20 are allowable over the combination of Le and Fukui because that combination does not teach all of the elements of the claims.

Claims 2-13 depend from claim 1 and are therefore allowable for at least the same reasons as is claim 1. The Examiner's comments with regard to claims 2-13 are rendered mute by this discussion and therefore Applicant's neither comments on nor agrees with those comments.

2. Claims 1-13 and 20 are allowable over Le and Fukui because there is no motivation to combine Le and Fukui as is suggested by the Examiner

The Examiner has not fulfilled the burden required to show obviousness of claims 1-13 and 20 over Le and Fukui. Instead, the Examiner has utilized impermissible hindsight to combine these two references. As discussed in the MPEP,

> [t]he initial burden is on the examiner to provide some suggestion of the desirability of doing what the inventor has done. "To support the conclusion that the claimed invention is directed to obvious subject matter, either the references must expressly or impliedly suggest the claimed invention or the examiner must present a convincing line of reasoning as to why the artisan would have found the claimed invention to have been obvious in light of the

> teachings of the references." Ex parte Clapp, 227 USPQ 972, 973 (Bd. Pat. App. & Inter. 1985). See MPEP § 2144 - § 2144.09 for examples of reasoning supporting obviousness rejections.

MPEP § 2142. The Examiner simply states that "[i]t would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form [sic] the DC power supply (Col. 6, lines 32-37)." (OA, page 5). However, Le utilizes a pulsed DC power supply and not a DC power supply. Therefore, utilizing a filter provided for a DC power supply is not obvious and may not be necessary in the system taught by Le because of the lack of a bias.

Fukui teaches an RF power supply coupled to the target but does not teach a pulsed DC power supply. Instead, Fukui utilizes a dual RF system where an RF power supply is coupled to the target and another RF power supply is coupled to the substrate. There is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply with a pulsed DC power supply. Further, there is no suggestion in Le to substitute a pulsed DC supply for an RF power supply.

Additionally, Fukui claims several advantages to utilizing separate RF power supplies on the two electrodes (i.e., coupled to the target and the substrate) during depositions, in effect teaching away from application of other power supplies. In particular, Fukui suggests that "[s]ince the first and second electrodes are provided in the deposition chamber and are supplied with the RF power separately, the ion bombardment energy and the ion flux can be controlled independently of each other." (Fukui, col. 9, lines 23-26). As a result, several benefits of the Fukui process are discussed in Fukui, including controlled cleaning of the deposition chamber,

See Fukui, col. 9, lines 26-29, film depositions can be performed in optimum conditions, *See* Fukui, col. 9, lines 35-36, and along with a small DC bias placed on the target, greater sputtering efficiency can be achieved, *See* Fukui, col. 9, lines 46-48.

As discussed above, therefore, there is no motivation for one skilled in the art to combine the references Le and Fukui in the fashion suggested by the Examiner. Therefore, claims 1 and 20 are not obvious from the references Le and Fukui. Claims 2-13 depend from claim 1 and are therefore allowable for at least the same reasons as is claim 1. The Examiner's comments with regard to claims 2-13 are rendered mute by this discussion and therefore Applicant's neither comments on nor agrees with those comments.

Allowable Subject Matter

The Examiner has objected to claims 7 and 21-24 "as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims." (OA, page 5). As discussed above, claim 1 is allowable over the cited art. Claim 7 depends from claim 1 and is therefore allowable for at least the same reasons as is claim 1. Applicants, therefore, decline to amend claim 7 to include the limitations of claim 1.

Similarly, claims 21-24 depend on the allowable claim 20 and are therefore allowable for at least the same reasons as is claim 20. Applicants, therefore, decline to amend claims 21-24 to include the limitations of claim 20 and any intervening claims.

Conclusion

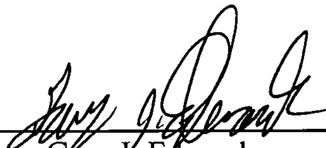
In view of the foregoing amendments and remarks, Applicant respectfully requests reconsideration and reexamination of this application and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: July 23, 2004

By: 
Gary J. Edwards
Reg. No. 41,008

2823

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
H. Zhang, et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: Michelle Estrada
	)	
Filed: March 16, 2002	)	Confirmation No.: 6938
	)	
For: BIASED PULSED DC REACTIVE SPUTTERING OF OXIDE FILMS	)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

TRANSMITTAL LETTER

Enclosed is a reply to the Office Action of February 24, 2004. The item(s) checked below are appropriate:

☒ Applicant(s) hereby petition(s) for a 2 month(s) extension of time to respond to the above Office Action. The Commissioner is hereby authorized to charge the fee of $210 for the Extension to our deposit account No. 06-0916.

The claims are calculated below:

	Claims Remaining After Amendment		Highest Number Previously Paid	Present Extra	Rate	Additional Fee
Total	24	-	39	0	x $ 18	$ 0
Indep.	2	-	5	0	x $ 86	$ 0
☐ First Presentation of Multiple Dep. Claim(s)					+$290	
					Subtotal	$
					Reduction by ½ if small entity	-
					TOTAL	$ 0

☐ A fee of $0 to cover the cost of the additional claims added by this reply is enclosed.

☒ Commissioner is hereby authorized to charge a fee of $180 to our deposit account No. 06-0916 to cover filing of Information Disclosure Statement under 37 C.F.R. §1.97(c).

☐ A check for $0 to cover the above fee(s) is enclosed.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 23, 2004

By:
Gary J. Edwards
Reg. No. 41,008

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
H. Zhang, et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: Michelle Estrada
	)	
Filed: March 16, 2002	)	Confirmation No.: 6938
	)	
For: Biased Pulsed DC Reactive Sputtering of Oxide Films	)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR 2 MONTH EXTENSION OF TIME

Applicants hereby petition for a two month extension of time to reply to the Office Action of February 24, 2004. Commissioner is hereby authorized to charge a fee of $210.00 to our deposit account No. 06-0916.

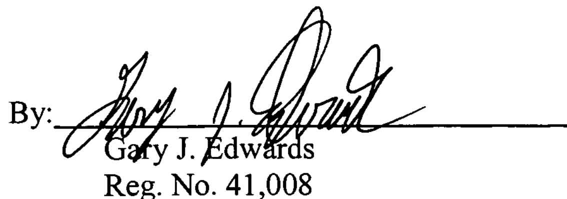
Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

07/26/2004 HDEMESS1 00000013 060916 10101863
02 FC:2252 210.00 DA

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: July 23, 2004

By: 
Gary J. Edwards
Reg. No. 41,008

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
H. Zhang, et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: Michelle Estrada
	)	
Filed: March 16, 2002	)	Confirmation No.: 6938
	)	
For: Biased Pulsed DC Reactive Sputtering of Oxide Films	)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants brings to the attention of the Examiner the documents listed on the attached PTO 1449. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge a fee of $180.00 as specified by Section 1.17(p) to our deposit account No. 06-0916.

Copies of the listed documents are attached.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are

07/26/2004 HDEMESS1 00000013 060916 10101863
01 FC:1806 180.00 DA

material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

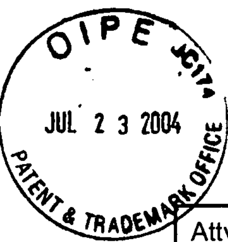
If there is any additional fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 23, 2004

By:
Gary J. Edwards
Reg. No. 41,008



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS							
Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
		2002/0106297		Ueno et al.	419	12	Aug. 08, 2002
		2003/0019326		Han et al.	45	245	Jan. 30, 2003
		2003/0063883		Demaray et al.	385	129	Apr. 3, 2003
		2003/0175142		Milonopoulou et al.	419	49	Sep. 18, 2003
		4,437,966	Mar. 7, 1961	Hope et al	204	298	
		4,915,810	Apr. 10, 1990	Kestigian et al.	204	298.04	
		4,978,437	Dec. 18, 1990	Wirz	204	192.	
		5,174,876	Dec. 29, 1992	Buchal et al.	427	526	
		5,200,029	Apr. 6, 1993	Bruce et al.	156	657	
		5,206,925	Apr. 27, 1993	Nakazawa et al.	385	142	
		5,225,288	Jul. 6, 1993	Beeson et al.	428	475.5	
		5,237,439	Aug. 17, 1993	Misono et al.	359	74	
		5,252,194	Oct. 12, 1993	Demaray et al.	204	298	
		5,303,319	Apr. 12, 1994	Ford et al.	385	131	
		5,381,262	Jan. 10, 1995	Arima et al.	359	341	
		5,427,669	Jun. 27, 1995	Drummond	204	298.2	
		5,475,528	Dec. 12, 1995	LaBorde	359	341	
		5,483,613	Jan. 9, 1996	Bruce et al.	385	129	
		5,555,127	Sep. 10, 1996	Abdelkader et al.	359	341	
		5,565,071	Oct. 15, 1996	Demaray et al.	204	192	
		5,603,816	Feb. 18, 1997	Demaray et al.	204	298	

Examiner	Date Considered
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OIPE JUL 23 2004 PATENT & TRADEMARK OFFICE

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
		5,613,995	Mar. 25, 1997	Bhandarkar et al.	65	384	
		5,654,054	Aug. 5, 1997	Tropsha et al.	428	36.6	
		5,693,956	Dec. 2, 1997	Shi et al.	257	40	
		5,718,813	Feb. 17, 1998	Drummond	204	192.2	
		5,719,976	Feb. 17, 1998	Henry et al.	385	50	
		5,792,550	Aug. 11, 1998	Phillips et al.	428	336	
		5,841,931	Nov. 24, 1998	Foresi et al.	385	131	
		5,847,865	Dec. 8, 1998	Gopinath et al.	359	343	
		5,855,744	Jan. 5, 1999	Halsey et al.	204	192	
		5,948,215	Sep. 7, 1999	Lantsman	204	192.12	
		5,961,682	Oct. 5, 1999	Lee et al.	65	384	
		5,977,582	Nov. 2, 1999	Fleming et al.	257	310	
		6,001,224	Dec. 14, 1999	Drummond	204	192.12	
		6,024,844	Feb. 15, 2000	Drummond et al.	204	192.12	
		6,051,114	Apr. 18, 2000	Yao et al.	204	192.3	
		6,093,944	Jul. 25, 2000	VanDover	257	310	
		6,162,709	Dec. 19, 2000	Raux et al.	438	513	
		6,176,986	Jan. 23, 2001	Watanabe et al.	204	298.13	
		6,248,291	Jun. 19, 2001	Nakagama et al.	419	46	
		6,280,585 B1	Aug. 28, 2001	Obinata et al.	204	298.19	
		6,287,986	Sep. 11, 2001	Mihara	438	763	

Examiner	Date Considered
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OIPE JUL 2 3 2004 PATENT & TRADEMARK OFFICE

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
		6,290,822	Sep. 18, 2001	Fleming et al.	204	192.22	
		6,344,419	Feb. 5, 2002	Forster et al.	438	758	
		6,350,353	Feb. 26, 2002	Gopalraja et al.	204	192.3	
		6,358,810	Mar. 19, 2002	Dornfest et al.	438	396	
		6,409,965	Jun. 25, 2002	Nagate et al.	419	26	
		6,413,382	Jul. 2, 2002	Wang et al.	204	192.12	
		6,537,428	Mar. 25, 2003	Xiong et al.	204	192.13	
		6,602,338	Aug. 5, 2003	Chen et al.	252	301.4	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No
		EP 0 820 088	01/21/98	Europe	H 01 J	37/34	
		EP 0 867 985 A1	09/01/98	Europe	H 01 S	3/06	
		JP 6-010127	01/18/94	Japan	C 23 C	14/35	Abstract
		JP 6-100333	12/04/94	Japan	C 03 C	21/00	Abstract
		WO 00/22742	04/01/00	PCT	H O4 B		
		WO 00/36665	06/22/00	PCT	H 01 L	51/20	
		WO 02/12932	02/14/02	PCT	H 01 S	3/16	
		WO 96/23085	08/01/96	PCT	C 23 C	14/34	
		WO 97/35044	09/25/97	PCT	C 23 C	14/40	

Examiner	Date Considered
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)	
	BARBIER, Denis, "Performances and potentioal applications of erbium doped planar waveguide amplifiers and lasers," GeeO, pp. 58-63.
	BELKIND et al., "Using pulsed direct current power for reactive sputtering of Al_2O_3," *J. Vac. Sci. Technol.* A 17(4), pp. 1934-40 (Jul. 1999).
	BYER et al., "Nonlinear Optics and Solid-state Lasers," *IEEE Journal on Selected Topics in Quantum Electronics*, Vol. 6, No. 6, pp. 921-929 (Nov. 2000).
	FUJII et al, "1.54 mm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals for Er^{3+}", *Appl. Phys. Lett.*, 71 (9), pp. 1198-1200 (September, 1997).
	KELLY et al., "Reactive pulsed magnetron sputtering process for alumina films," *J. Vac. Sci. Technol.* A 18(6), pp. 2890-96 (Nov. 2000).
	KELLY et al., "Control of the structure and properties of aluminum oxide coatings deposited by pulsed magnetron sputtering," *J. Vac. Sci. Technol.* A 17(3), pp. 945-953 (May 1999).
	PAN et al., "Planar Er3+-doped aluminosilicate waveguide amplifier with more than 10 dB gain across C-band," Optical Society of America, 3 pages (2000).
	ROBERTS et al., "The Photoluminescence of Erbium-doped Silicon Monoxide," Department of Electronics and Computer Science, 7 pages (June 1996).
	SCHILLER et al. "PVD Coating of Plastic Webs and Sheets with High Rates on Large Areas," European Materials Research Society 1999 Spring Meeting, Strasbourg, France (June 1-4, 1999).
	SHAW et al. "Use of Vapor Deposited Acrlate Coatings to Improve the Barrier Properties of MetallizedFilm," Society of Vacuum Coaters 505/856-7168, 37th Annual Technical Conference Proceedings, pp. 240-244 (1994).
	SHIN et al. "Dielectric and Electrical Properties of Sputter Grown (Ba,Sr)TiO_3 Thin Films," *J. Appl. Phys.*, Vol. 86, No. 1, pp. 506-513, (July 1, 1999).
	SHMULOVICH et al., "Recent progress in Erbium-doped waveguide amplifiers," Bell Laboratories, 3 pages (1999).
	TING et al., "Study of planarized sputter-deposited SiO2," *J. Vac. Sci. Technol.*, 15(3) pp. 1105-1112 (May/Jun. 1978).

Examiner	Date Considered
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
	VAN DOVER, R.B. "Amorphous Lanthanide-Doped TiO_x Dielectric Films," *Appl. Phys. Lett.*, Vol. 74, No. 20, pp. 3041-3 (May 17 1999).
	WESTLINDER et al. "Simulation and Dielectric Characterization of Reactive dc Magnetron Cosputtered $(Ta_2O_5)_{1-x}(TiO_2)_x$ Thin Films," *J. Vac. Sci. Technol.* B, Vol 20, No. 3, pp. 855-861 (May/Jun 2002).
	YOSHIKAWA, K. et al., "Spray formed aluminium alloys for sputtering targets," *Power Metallurgy*, Vol. 43, No. 3, pp. 198-99 (2000)
	ZHANG, Hongmei et al. "High Dielectric Strength, High k TiO_2 Films by Pulsed DC, Reactive Sputter Deposition," (2002).

Examiner	Date Considered
*Examiner:	Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

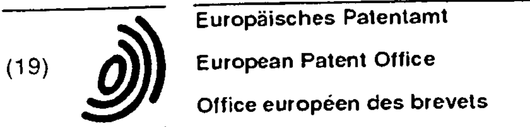
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

(19) 

(11) EP 0 820 088 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.01.1998 Bulletin 1998/04

(51) Int Cl.6: H01J 37/34

(21) Application number: 97305316.8

(22) Date of filing: 16.07.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: 19.07.1996 US 684446

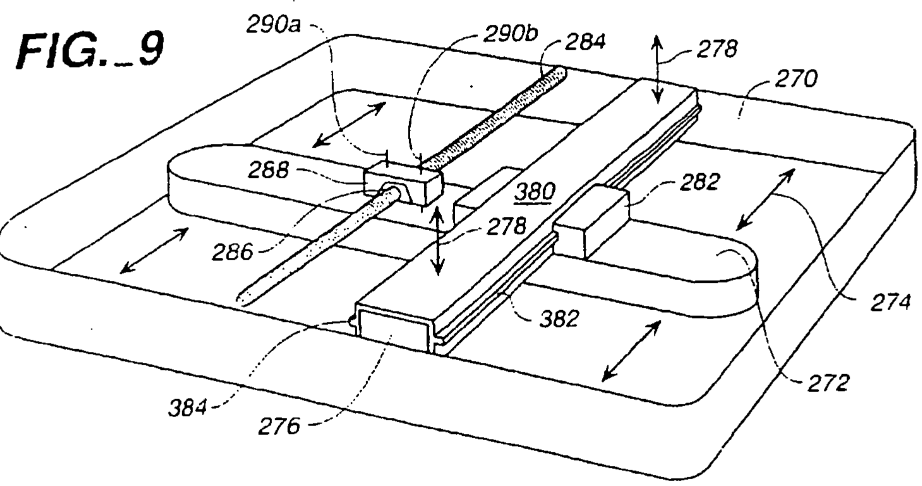
(71) Applicant: APPLIED KOMATSU TECHNOLOGY, INC.
Shinjuku, Tokyo (JP)

(72) Inventors:
- Halsey, Harlan L.
  Woodside, California 94062 (US)
- Demaray, Richard E.
  Portola Valley, California 94028 (US)
- Black, Russell
  Longmont, Colorado 80501 (US)
- Hosokawa, Akihiro
  Cupertino, California 95014 (US)
- de Salvo, Allan M.
  Los Gatos, California 95030 (US)
- Hall, Victoria L.
  Menlo Park, California 94025 (US)

(74) Representative: Bayliss, Geoffrey Cyril et al
BOULT WADE TENNANT,
27 Furnival Street
London EC4A 1PQ (GB)

(54) Non-planar magnet tracking device for magnetron sputtering apparatus

(57) The structure and method which improves the film thickness uniformity or thickness control when using magnetron sputtering by adjusting the distance between the magnetron (272) or a portion of the magnetron and the sputtering target to provide an improvement in the film thickness uniformity. Shimmed rails (382; 384) contoured rails, contoured surfaces (415, 418), cam plates (422), and cam plate control followers (442) are utilized to achieve an improvement in film thickness uniformity or thickness control due to anomalies in magnetic field as a magnetron assembly (272) moves back and forth when sputtering substrates (utilized primarily for rectangularly shaped substrates).



EP 0 820 088 A2

Printed by Jouve, 75001 PARIS (FR)

Description

This invention relates to the field of magnetrons and particular configurations for their use with sputtering chambers to control film thickness for sputter deposited film. In particular this invention relates to controlling the deposited film thickness on substrates by varying the distance between a portion of the permanent magnets comprising the magnet array in the magnetron and the sputtering target as the magnetron moves laterally across the back of the sputtering target during sputtering.

Sputtering describes a number of physical techniques commonly used in, for example, the semiconductor industry for the deposition of thin films of various metals such as aluminum, aluminum alloys, refractory metal silicides, gold, copper, titanium, titanium-tungsten, tungsten, molybdenum, tantalum and less commonly silicon dioxide and silicon on an item (a substrate), for example a substrate or glass plate being processed. In general, the techniques involve producing a gas plasma of ionized inert gas "particles" (atoms or molecules) by using an electrical field in an evacuated chamber. The ionized particles are then directed toward a "target" and collide with it. As a result of the collisions, free atoms or neutral or ionized groups of atoms of the target material are released from the surface of the target, essentially liberating target material are released from the surface of the target, essentially liberating atomic-level particles from the target material. Many of the free particles which escape the target surface condense and form (deposit) a thin film on the surface of the object (e.g. wafer, substrate) being processed, which is located a relatively short distance from the target.

One common sputtering technique is magnetron sputtering. When processing substrates using magnetron sputtering, sputtering action is concentrated in the region of the magnetic field on the target surface so that sputtering occurs at a higher rate and at a lower process pressure than possible without the use of magnets. The target itself is electrically biased with respect to the substrate and chamber, and functions as a cathode. Objectives in engineering the cathode and its associated magnetic field source include uniform erosion of the target and uniform deposition of pure target material on the substrate being processed.

If, during sputtering, magnets generating a magnetic field are stationary at a location, then continuous sputtering consumes a disproportionate fraction of the sputtering target thickness at that location quickly and generates hot spots at the locations of sputtering. Therefore magnets are continuously moved across the back side of the target in a path designed to cause uniform utilization of the target's surface and sputter deposit a correspondingly uniform film thickness on the substrate being processed. Sputtering a target creates a deposition pattern on the substrate which generally matches the utilization (erosion) pattern on the target surface.

To avoid contamination of the processing chamber and substrate processed therein, sputtering is stopped before the non-uniform sputtering wear pattern has consumed the full thickness of the target material at any point. If any point on the plate behind the target were to be reached, sputtering of the target backing plate material (often copper) would occur, contaminating the vacuum chamber and the substrate being processed with the target backing material. Because of the non-uniform pattern of target utilization, sputtering is usually stopped when a large percentage of the target remains.

As the target erodes, the distance between the target surface (which is eroding away) and the substrate being sputtered is slowly increasing. The change in the distance between the target surface and the substrate being sputtered creates a change in the qualities of the sputtered material deposited and its uniformity. When material is deposited on large areas such as glass plates, variations in the thickness of deposited sputtered material are measurable and, may be unacceptable.

In generating the gas plasma and creating ion streams impacting on the cathode, considerable energy is supplied. This energy must be dissipated to avoid melting or nearly melting the structures and components involved. A common technique used for cooling sputtering targets is to pass water or other cooling liquid through a fixed internal passage of the sputtering target. Another cooling technique which is commonly used is to expose a back side of a target to a cooling bath. Cooling liquid circulating through the bath container assists in controlling the temperature of the back of the target assembly. A magnet assembly (magnetron) located on the back side of the target with a backside cooling bath moves within the liquid of the cooling bath.

Figures 1, 2, and 3 show a prior art sputtering chamber 50 in which a rectangular substrate 64 (shown in dashed lines in Fig. 1) is supported on a pedestal 52. A target assembly 58, consisting of a target backing plate 56 and a target 54 having a front face facing the pedestal 52, covers the upper flange of the processing chamber sealing it. On the side of the target assembly opposite from the pedestal 52 a magnetron chamber 60 encloses a magnetron assembly 62. The magnetron chamber 60 can be made vacuum tight to reduce the differential pressure across the target assembly 58 (with cooling fluid being routed through the target assembly), or it can be filled with cooling liquid to provide a cooling bath in contact with the back side of the target assembly 58. To enhance sputtering of a rectangular shaped substrate 64 (generally matching the shape of the outside of the chamber 50) the magnetron assembly 62 is a linear bar with rounded ends. The magnetron assembly 62 moves in a horizontal, back and forth (reciprocal) pattern within the magnetron chamber 62 as shown in by the arrows 68. The magnetron assembly passes through the magnetron chamber 62 and to the dashed outline of the magnetron assembly 62a. The outline of the area covered

NSDOCID: <EP___0820088A2_I_>

by magnetron movement is shown by the dashed line 66.

The magnetron assembly 62 as shown in Figure 3 runs parallel to the target assembly 58 along one of a range of elevations between the low and high extremes (e.g., 96, 98), which are greatly exaggerated in this figure. The particular elevation (e.g., 96, 98) is dependent on the desired distance 92 from the front face of the target 54, which in turn determines the degree of sputtering enhancement desired for a particular process chamber pressure and sputtering process being used.

A conceptualized illustration of the magnetic field present around the strong Neodymium Boron Iron magnets used in the magnetron assembly is shown in the cross section of Figure 4. The positive poles 72, 74, 76, 78 of the magnets shown, e.g., 70, are on the top (away from the sputtering target) in the outside loop 84 (Fig. 1) of permanent magnets and on the bottom (close to the sputtering target) in the inside loop 82 (Fig. 1), although the polarities may be reversed. A magnet backing plate 80 bridges the magnetic field on the top side of the magnetron thus preventing the magnetic field from extending up from the top side of magnetron assembly. In contrast, the magnetic field on the bottom side between adjacent magnets is conceptualized by the loops 86 showing a diminishing magnetic field strength farther down from the magnetron assembly 62. The loops of the magnetic field lines 86, portray a comparatively strong magnetic field in the loop 88 adjacent to the magnets, and drop off in the magnetic field strength rapidly as a function of the distance to a comparatively weakened magnetic field strength at the loop 90 farthest from the magnets. (The loops show an approximation of the diminution of the magnet field strength with distance). Any vertical movement of the magnetron assembly 62 that increases the distance between the front face of the target and the magnetron assembly 62 from the distance 92 (Fig. 3) to the distance 94 (Fig. 5), reduces the magnetic field strength at the surface of the target facing the pedestal 52 by a factor of approximately 5, relative to the range of field strength loops shown in Figure 4.

Figure 6 shows a target erosion profile for a target of 6061 Al in 2000 kilowatt hour power range. The contours shown by the plot show a generally uniform utilization of the target with a slight increase in erosion near the ends of the profile (a dwell location). The pattern observable from at the dwell locations corresponds to the shape of the magnet field emanating from magnetron assembly. The target erosion profile as shown here is related to the rate of deposition and film thickness uniformity or thickness control on a substrate being sputtered located opposite such a target (areas showing greater erosion on the target result in areas having greater deposition on the substrate). In this particular instance, there are two areas of relatively high erosion, one at the upper right corner 242 and the other at lower left hand corner 244 of Figure 6, which produce corresponding deposition thickness anomalies on the substrate being sputtered.

The current specifications for target film thickness uniformity (even for large plates, such as the 50 by 60 centimeter plate shown in Figure 6) is 5% or better. The anomalies of high erosion at the corners of the target as shown by the regions 242, 244 cause great concern in meeting the specification as they distort the film thickness uniformity so that a film thickness uniformity of only approximately 7% can be achieved. To improve uniformity the excessive erosion in the two regions 242, 244 must be reduced or eliminated so that the specification for film thickness uniformity can be met.

The observation of the high erosion in the corners has initiated a great deal of scrutiny without an identification of its true source. The positioning of an array of permanent magnets in the magnetron assembly assures a uniform magnetic field throughout the magnetron assembly. The general uniformity of the magnet field emanating from the magnetron is confirmed by the generally uniform erosion profile across the center of face of the target. Speculation about the source of the reason for the anomaly in the corners included research to determine whether a source of electrical or magnetic field anomalies could be identified. None has been identified.

Figure 7 is a plot representing the film thickness on the surface of a substrate. It confirms the uniformity of the film thickness on the surface of a rectangular substrate. This plot shows an approximately mirror image correlation with the target erosion profile of Figure 6.

In the field of thin film deposition, a size of substrates is becoming larger and larger since there is increasing need for larger size LCD screen. For example, current substrate size for production is up to 400 mm X 500 mm, however, the size will be expanded up to 600 mm X 700 mm or larger in the future.

One of the most difficult tasks in thin film deposition is how to achieve uniform deposition over a substrate. This shortcoming becomes the dominant factor preventing the economical production of larger and larger LCD screens.

The shortcomings in film thickness uniformity or thickness control of the existing sputtering target systems as described above continue to inhibit the wide use of sputtering as an efficient and cost-effective means for applying surface coatings on large substrates.

A structure and method according to the invention reduces the film thickness anomalies as discussed above.

Where target erosion anomalies occur, a change in the strength of the magnetic field exposed to the target at those locations has been found to improve the uniformity or control the variation in thickness of the deposited film. One way to change the film thickness at any such location is to provide a localized change in the magnetic field strength while maintaining the uniformity of magnetic field strength over the rest of the target area.

A magnet member (the magnetron assembly) is lo-

BNSDOCID: <EP___0820088A2_I_>

cated in proximity to the sputtering target, and is provided with a magnetic member cycling system (drive system), which causes the magnet member to move in a set or-recurring pattern. The recurring pattern is defined by a set of points defining a pattern reference surface. The pattern reference surface is defined by a set of lateral coordinates and a set of vertical coordinates of the pattern. The lateral coordinates establish a grid defining the lateral locations at which the vertical coordinates define a set of elevations of the pattern reference surface, either on the reference surface or on an offset reference surface (which is parallel to but offset from the reference surface).

The pattern reference surface includes a divergent portion (a preset pattern of relative motion) having a subset of elevations which fall outside a range of tolerance for parallelism between the pattern surface and a reference surface of the sputtering target. Movement of the magnetron in the divergent portion reduces or increases the magnetron field strength at the surface of the target.

The reference surface of the sputtering target can be its front face. It could be a middle axis of the sputtering target. or it could be a back face. It should be obvious to persons of ordinary skill in the art that the intensity of the magnetic field should be approximately equal over the surface of the sputtering target facing the sputtering chamber. Therefore. the definition of the reference surface of a sputtering target can be any surface real or imagined that can be defined generally by geometric or mathematical means as being parallel to the surface of a sputtering target, whether that surface be straight or curved. It is assumed that such a straight or curved surface is a continuous one (without sudden steps) and is generally used as a reference for parallelism before sputtering occurs (an un-used pre-sputtering configuration). because after sputtering has begun the target erosion will deform the shape of the sputtering target and start to generate differences in the uniformity of film thickness due to small, but detectable, differences in the target erosion rate across its surface.

It may be desirable to have uniform film thickness over some portions of the substrate and have varying thicknesses in other regions. The structure and method according to the invention allows control of the film thickness deposited, by varying the strength of the magnetic field. An approximately uniform film thickness can be achieved, but so can a prescribed pattern of film thickness which is not necessarily uniform, for example one which is thicker at the edges to provide an easier connection to external wiring.

In one configuration, a change in the magnetic field strength can be accomplished when using a two bearing rail system merely by tilting opposite corners of opposing rails in opposite directions (the magnetron acting as a bearing truck between the rails). For example, by providing a high end and a low end on one bearing rail while the opposite bearing rail has its low end opposite the high end of the first bearing rail. Such a tilted configuration will cause a flight path or surface pattern (profile) for the magnetron assembly that includes regions of the surface pattern that fall outside a standard tolerance for parallelism between the magnetron path pattern reference surface and the reference surface of the target. In one configuration the magnetron is tilted in one direction at one end of the back and forth travel, and is tilted in the opposite direction at the opposite end of the back and forth travel. A change in rail elevation as small as 0.020" - 0.030" (500-750μm) in central regions of the travel has a noticeable effect because of the strength of the magnetic field decreases greatly over a small distance. The effect of a change in the elevation of a linear rail of 0.030" end to end of a 2-foot travel path provides an improvement in the variation in film thickness uniformity from approximately 8% to approximately 3-4% (providing a improvement which meets the 5% specification).

In another configuration, according to the invention, it is possible that when utilizing two bearing rails that they be curved or otherwise patterned to move the magnet member (magnetron assembly or one end of the assembly) close to and away from the target surface in a particularly described pattern to increase and decrease the magnetic field strength to promote an improvement in the control or uniformity of the deposited film thickness.

Utilizing a magnet member moving in the transverse (lateral) direction, it is possible to provide several tracks (more than two) to help guide the magnet member. The magnet member (magnetron) can be divided into two or more sub-sections to assist in maintaining a uniform target profile. For example, it is possible to provide three generally parallel bearing rails (a set of tracks) which support two magnet member sub-sections between them. The outside bearing rails can be relatively flat, while the inside bearing rail could dip down or rise up to change the magnetic field intensity. Similarly, the magnet member could be constructed of a series of magnet member sub-sections (connected in a housing or separate from one another) with each magnet subsection following the contour of its own rail or path as it moves from one end to the other end of the processing chamber.

In another configuration, a cam plate surface which includes a series of slots and surface followers which are connected to the subsections of the magnet member. Movement of the magnet member from one end to the other causes the elevation of each separate subsection of the magnet member to follow the pattern of the cam surface. Varying the elevation of various magnet subsections by the use of a mechanical cam surface - follower system can also be reproduced by utilizing vertical activation devices such as motors and vertical drives which cause each magnet member subsection to move vertically according to a pre-programmed contour depending on its lateral location. Such movement could

potentially change the sputtering intensity at the ostensible location of sputtering anomalies, which create an uneven erosion profile, to eliminate such anomalies and improve the film thickness uniformity.

It is known that the distance between the face of the sputtering target and the substrate being sputter deposited is one factor in determining the film thickness deposited on the substrate. However when sputtering large substrates, because the center of the target is farther away from the source of sputtering power, and there tends to be a drop in the sputtering intensity at the center of a large target. Therefore, to compensate for this drop, the magnet field at this location (region) could be gradually increased by moving the magnetron closer to the sputtering target at the center to improve the film thickness uniformity.

Another configuration for improving film thickness uniformity is to tilt (roll or pitch) only the end of the magnetron near the end of its travel. The bearing rails supporting the magnetron are kept straight and level and the end of the magnetron is tilted by utilizing a localized ramp (cam) and roller (cam follower). Either the ramp or the roller is located on the end of the magnetron and the ramp or follower is located on a stationary support fixed to the processing chamber. The lateral motion of the magnetron at a particular location causes the cam to engage the cam follower causing a tilting force to be generated. The tilting force pushes the end of the magnetron in a vertical direction to cause the magnet member reference surface to describe the divergent portion. The tilt can be a roll motion or a pitch motion as the terms roll and pitch are understood when referring to an aircraft's attitude - the magnet member (magnetron) relating to a fixed wing on an aircraft.

Electromagnets can be used in the magnetron and the magnetic field of the electromagnets can be varied to cause changes in the strength of the magnetic field to affect and control the film thickness desired.

A method according to the invention includes the steps of moving a magnet member laterally in the proximity of a sputtering target and moving portions of said magnet vertically, a distance greater than a tolerance for parallelism between a reference plane and the plane of motion at selected locations to vary the magnetic field strength causing a divergence from the plane to improve the film thickness control. Another method according to the invention includes the steps of moving a magnet member laterally along a track and moving portions of the magnet member in a vertical direction simultaneously with the lateral motion of the magnet member to change the magnetic field intensity utilized for sputtering at one or more locations along the track to improve film thickness uniformity for sputtering.

These structures and methods provide a degree of improvement in the control of film thickness not known or utilized in the prior art.

The following is a description of some specific embodiments of the invention, reference being made to the accompanying drawings, in which:

Figure 1 is a schematic top view of a prior art magnetron enclosure;
Figure 2 is a cross sectional end view of the sputtering chamber separated from the prior art magnetron chamber of Figure I by the target assembly;
Figure 3 is a side cross sectional view of the apparatus of Figure 2 showing the conceptualized magnetic field of the magnetron extending far beyond the sputtering target;
Figure 4 is a cross sectional view of the magnetron including permanent magnets and a conceptualization of the magnetic field emanating downwardly therefrom;
Figure 5 is a second side cross sectional view of the apparatus of Figure 2 showing the magnetron raised up to a higher elevation with the conceptualized magnetic field from the magnetron just barely extending beyond the sputtering target;
Figure 6 is a prior art target erosion profile showing the pattern of erosion (utilization) of the sputtering target during sputtering;
Figure 7 shows the film thickness profile on a substrate as determined from a sheet resistance analysis using a five point probe (which is inversely proportional to film thickness) for a sputtering target utilizing the prior art magnetron chamber;
Figure 8 is a plot of the film thickness contours of a sputtering target assembly from a sheet resistance analysis using a five point probe (which is inversely proportional to film thickness) when using a structure and method according to the invention;
Figure 9 is a schematic perspective view of a magnetron chamber utilizing a center bearing rail to support the magnetron;
Figure 10 is a schematic representation showing an exaggerated dimension of the center magnetron support beam of Figure 9 and its rotation as it travels along the center beam support;
Figure 11 is a cross sectional view of a magnetron support beam taken at 11-11 of Figure 14;
Figure 12 is a cross sectional view of a magnetron support beam taken at 12-12 of Figure 14;
Figure 13 is a cross sectional view of the magnetron support beam taken at 13-13 of Figure 14;
Figure 14 is a top view of a magnetron chamber according to the invention with a center magnetron support beam;
Figure 15 is a perspective view of a bearing channel beam with bearing tracks (rails) supported on the central beam as shown for example in Figure 9;
Figure 16 is a modified bearing support rail showing the channel being split and being raised one side of each end of the channel to provide the vertical travel of portions of the magnetron;
Figure 17 shows a top plan view of the end of the magnetron as shown in Figure 18 as it about to en-

BNSDOCID: <EP___0820088A2_I_>

gage the ramp (cam) to be lifted;
Figure 17A shows a top plan view of the end of the magnetron as shown in Figure 18A as it about to engage the ramp (cam) to be lifted;
Figure 18 is a partial cross sectional view of a magnetron chamber taken at 18-18 of Figures 20 and 24, showing the ramp which raises the end of the magnetron at opposite ends of the chamber;
Figure 18A is a partial cross sectional view of a magnetron chamber taken at 18A-18A of Figures 20A, showing the ramp which tips the edge of the magnetron at opposite ends of the chamber;
Figure 19 shows a cross sectional side view showing the position of the ramp in relation to the magnetron:
Figure 20 shows the top plan view of the magnetron chamber having a magnetron whose ends are subject to being raised by ramps at opposite corners;
Figure 20A shows the top plan view of the magnetron chamber having a magnetron whose ends are subject to being raised by ramps at its corners:
Figure 21 shows a schematic cross section of a deformable horizontal magnetron whose end is bent up in a curved shape, taken at 21-21 in Figure 24;
Figure 21A shows a schematic cross section of a rigid horizontal magnetron whose end is raised up, taken at 21-21 in Figure 24;
Figure 22 is a schematic cross sectional view of the deformable horizontal magnetron, taken at 22-22 in Figure 24;
Figure 22A is a schematic cross sectional view of the rigid horizontal magnetron, taken at 22-22 in Figure 24;
Figure 23 is a cross sectional view of the deformable horizontal magnetron whose end is bent up, taken at 23-23 in Figure 24;
Figure 23A is a cross sectional view of the rigid horizontal magnetron whose end is bent up, taken at 23-23 in Figure 24;
Figure 24 is a schematic top view of a magnetron chamber where the magnetron is supported near its center, including ramps at opposite corners to influence the vertical position of the end of the magnetron when the magnetron is moved near either end of its travel;
Figure 25 is a bottom plan view of a magnetron chamber utilizing a central beam support for the magnetron track;
Figure 26 is a cross sectional view of the magnetron chamber of Figure 25;
Figure 27 is a schematic perspective view of a magnetron chamber enclosing a traveling magnetron supported by two horizontal beams near its ends;
Figure 28 is a schematic representation of the elevation change (rotation) of the magnetron as it travels one end to the other along inclined tracks as shown in Figure 27;
Figure 29 is a schematic cross sectional view of a magnetron supported from two generally parallel rails (tracks) according to the invention;
Figure 30 is a cross sectional view showing the magnetron support rails and magnetron attitude, taken at 30-30 in Figure 33;
Figure 31 is a cross sectional view showing the magnetron support rails and magnetron attitude, taken at 31-31 in Figure 33;
Figure 32 is a cross sectional view showing the magnetron support rails and magnetron attitude, taken at 32-32 in Figure 33;
Figure 33 is a schematic top view of a magnetron chamber where the magnetron is supported near its ends by two horizontal support rails;
Figure 34 is a bottom plan view of a magnetron supported along two generally parallel beams at the edges of the magnetron chamber;
Figure 35 is a cross sectional end view of Figure 34;
Figure 36 shows a cross sectional view of a hinged magnetron in a magnetron chamber, for example as shown in Figure 37;
Figure 37 shows a schematic perspective view of a hinged magnetron with a bowed down center track according to the invention;
Figure 38 shows a moving magnetron assembly (device) having permanent magnet sub-sections whose vertical travel is influenced by a contour plate which changes the vertical spacing between each magnet sub-section and the target during sputtering as the magnetron moves laterally;
Figure 38A shows a moving magnetron assembly (device) having a deformable magnetron connected through several cam follower linkages to a contour plate, the vertical travel of portions of the magnetron connected to the cam follower linkages is influenced by a contour plate which changes the vertical distance between each portion of the magnetron and the target during sputtering as the magnetron moves laterally;
Figure 39 provides an alternate conceptualized magnetron reference surface pattern for a contour plate showing high points at the right and left corners and low points at the front and back corners of the conceptualized plate shown;
Figure 40 shows a conceptualized magnet reference surface pattern having a lateral central axis in a parabolic or circular concave down type shape with all paths perpendicular to the lateral axis being equal lengths;
Figure 41 shows a conceptualized magnet bowl-shaped type parabola pattern plate for use as a magnet section guide, the shape being similar to the shape pictured in Figure 38;
Figure 42 shows a conceptualized reference surface pattern convex surface to use as a magnet pattern contour plate;
Figure 43 shows a flat magnet contour plate assembly utilizing activators for raising and lowering the

BNSDOCID: <EP___0820088A2_I_>

magnet sections individually using electrical or other activators according to a pre-programmed pattern;

Figure 44 shows an magnetron whose magnets are electro-magnets, the strength of the magnetic field is controlled by varying the electrical energy supplied to each electro-magnet segment in the magnetron as the magnetron moves laterally during sputtering; and

Figure 45 shows a cross section of an electro-magnetic magnetron according to the invention as used in the configuration of Figure 44.

An understanding of the improvement the invention provides results from comparison of the film uniformity plots of Figures 7 and 8. In the plot 250 of Figure 7 the plots of the contour shows several heavy black contour lines showing the film thickness variation across areas of the substrate as the thickness is plotted from a center to an edge of the substrate. The non-symmetrical (skewed) plot shows that the upper left corner and the lower right corner depositions include severe variations at those locations. The variation in film thickness uniformity for the analysis of Figure 7 being approximately 8%. In comparison a similar plot 260 using a structure and method according to the invention results in the film uniformity plot as shown in Figure 8. The plot from the analysis is now generally symmetrical about the center and is rectangular without being skewed. The thickness variation from center to the edge being approximately equal on both sides of a vertical center axis. Figure 8 provides a smaller distance between the maximum and the minimum than the plot of Figure 7. The resulting variation in film thickness uniformity being approximately 4%.

Single Beam Bearing Support

Figure 9 shows a perspective schematized view of a device according to the invention wherein a magnetron assembly 272 is moved within a magnetron chamber 270 in the direction shown by the arrows 274. The magnetron assembly 272 is supported on a central bearing support beam 276 which can be moved vertically uniformly as shown by the arrows 278. A set of bearing rails, (e.g., 382, 384) supports the magnetron assembly 272 through a set of bearing truck receiving members (e.g., 282). The lateral motion of the magnetron assembly is produced by turning a threaded drive rod 284 which is engaged with a threaded drive nut 286 contained in a threaded drive nut housing 288. The threaded drive nut housing engages and can slide vertically on a pair of connecting pins 290a, 290b, which are fixed to and extend upwardly from the top of the magnetron assembly 272. The sliding connection between the connecting pins 290a, 290b and the threaded drive nut housing 288 accommodates differential vertical motion between the threaded drive rod 284 which is fixed to the walls of the magnetron chamber 270 and the magnetron 272 supported by the support beam 276. The sliding connection allows vertical motion of a portion of the magnetron as it cycles from end to end and tips as it cycles as shown in Figure 10.

Figure 10 shows an idealized exaggerated schematic perspective view of the motion of the magnetron assembly as shown in Figure 9. The magnetron assembly 300 moves laterally (horizontally in this case, but the lateral motion could be across a curved (e.g., spherical) substrate surface as well) supported on a central bearing support rail 302 showing a twist from end to end. Dashed lines 304, 306 show a change in the elevation of the ends of the magnetron assembly (roll - as that term is understood for aircraft motion) as the magnetron 300 moves laterally from one end of the chamber to the other. As the magnetron assembly 272, 300 moves from one end of the processing chamber to the other, its left and right ends rise and fall, respectively, thus becoming farther from and closer to the target assembly, respectively. The end (a portion) of the magnetron assembly that is farther from the target surface reduces the magnetic field influence enhancing sputtering, while an end of the magnetron that is closer to the target surface increases the magnetic field influence enhancing sputtering. This end to end tilting arrangement provides greater influence on sputtering at opposite corners of opposite ends of the magnetron chamber and magnetron respectively as the member moves from laterally from end to end.

Conventional thinking requires the magnet field strength to be held constant over the whole area of the target as the magnetron moves. Such thinking imposes a specification for flatness of the tracking or parallelism between the path of the magnetron and a reference surface (usually the front surface) of the target. The parallelism between members is intended to provide a constant magnetic field. Specification of the range of the usual tolerance for flatness or parallelism which is usually approximately 5 thousandths of an inch in l foot or less, is utilized to help define an aspect of the invention according to the claims. Such tolerances also exclude variations in alignment due to natural variation in manufacturing and practical limits in aligning of mechanically mating pieces. The actual difference in elevation of the ends of the magnetron according to the invention can be quite subtle. Variations in elevation slightly falling outside the natural range of the tolerance of the specification for flatness or parallelism as slight as 0.0075" per foot will have an effect on film thickness uniformity, because the magnetic field strength varies strongly with the distance. A localized variation in elevation will have a localized effect. The localized variation can be defined as a divergent portion (that portion of the reference surface of the magnetron motion that exceeds the tolerance for flatness or parallelism, both of which under normal circumstances are defined as plus or minus 0.005" elevation variation per lateral foot or less, less than 0.05%).

BNSDOCID: <EP__0820088A2_I_>

Therefore a configuration according to the invention can be defined in terms of the tolerance for flatness or parallelism. The imaginary surface formed by the lateral and vertical motion of the magnetron is evaluated for flatness or for parallelism against a reference surface. A configuration according to the invention provides that the imaginary surface include a divergent portion which has vertical components of the imaginary surface which fall outside the range of the conventional tolerance for flatness and/or parallelism and as a result of the motion of the magnetron in the divergent portion the motion produces an improvement in the uniformity of film thickness deposited on a substrate. Because the magnetic field strength varies strongly as a function of distance from the magnetron, progressively larger departures from flatness or parallelism create progressively larger changes in the film thickness achieved. A departure from flatness or parallelism of 0.030" at the end of the magnetron track, or as much as approximately 10 mm out of plane at the end of the magnetron, for the configuration of Figure 9, results in changes in film thickness uniformity at opposite corners of the substrate and target which provide an observable improvement when compared to the plot of Figures 7, (the setup in Figure 7 having the normal maximum range of 0.010" from rail end to rail end, when the tolerances for flatness or parallelism are met). The elevation change provides an improvement in film thickness uniformity to meet the specification requirements of a 5% variation, as shown in Figure 8.

While this example provides one configuration of the invention, this same technique can be used at other locations where the film thickness uniformity or thickness control needs to be improved. The motion of the magnetron is adjusted so that the imaginary surface pattern describing its motion includes divergent portions which exceed the normal tolerances for flatness or parallelism and create a change in the magnetic field at the surface of the target being sputtered, so that the film thickness uniformity or thickness control deposited on the substrate is improved.

The vertical motion of a portion exceeding the specification for flatness and for parallelism from end to end and side to side is measured against an imaginary reference surface superimposed on the imaginary reference surface pattern/profile created by the motion of the magnetron assembly 272. An elevation view showing the characteristics of the motion of the magnetron assembly 272 departing from flatness or parallelism is shown in Figures 11, 12, and 13 for tilting of a linear magnetron assembly 272, and in Figures 21, 22, and 30 for the bending of the magnetron assembly 272. In both configurations the ends of the magnetron assembly 272 near the end of its travel is raised to exceed the normal (or otherwise selected) tolerance (e.g., 0.005"/ft, 0.0075"/ft, 0.010"/ft, 0.015"/ft, 0.020"/ft, 0.025"/ft, 0.030"/ft, 0.0035"/ft, 0.040"/ft, or 0.0050"/ft (producing an approximately 10 mm change in elevation at the end of the magnetron)) to provide an improvement in the film thickness uniformity or thickness control across the surface of the substrate which is being sputter deposited.

Figure 11, 12, and 13 are progressive sectional cuts showing the attitude (tilt or bend - roll) of a magnetron assembly 272 as it moves from one end to the other end of the magnetron chamber 270 as shown in Figure 9. The center support rail 276 supports a one-piece bearing frame 380 as shown in Figures 9 and 15. Generally speaking, the bearing rails 382, 384 are constructed to be fixed parallel to one another. However, if a portion of the bearing rail as shown in Figure 16 is cut along a split separation 392 in the top of the channel, between the holes pictured therein, and shims typically multiples of 0.010" up to 0.060" depending upon the process, e.g., 0.050", for example 394, 396, are positioned and fixed in place between the center bearing support beam 276 and the one-piece bearing frame 380 on opposite sides at opposite ends. The shims cause a slight vertical bend in the bearing rails 382 and 384. The slight vertical offset 371 (Fig. 13) at the center bearing support is amplified as the magnetron projects further outward towards its end, where the vertical offset is a maximum (approximately 10 mm). The configuration of the bearing rails 382, 384 causes the magnetron assembly 272 to follow the path of the rails. Movement of the magnetron creates a series of points in an imaginary surface pattern (flight path) tracing the position of each point of the magnetron assembly 272 as it moves laterally. Some of the points in the imaginary surface pattem are vertically offset from an imaginary horizontal plane (in which the magnetron assembly would move if its bearing rails were not vertically offset from the neutral axis 368 (see Figure 12) of the lateral motion and intersecting with the pattern of the horizontal reference plane) a distance greater than a tolerance for flatness or parallelism with a reference surface. The vertical adjustment to the bearing rail position can also be done by using vertical slots through which bolts are tightened in the side of the one-piece bearing frame instead of or in addition to the shims 394, 396.

As shown in Figure 13, the offset in the vertical direction of the left side split bearing rail frame 360 in a vertical direction by a distance 370 causes the magnetron assembly to assume a roll attitude as shown by the dashed line 372. The offset of the bearing rail from a central axis 364 is set by a distance 366. Similarly in Figure 11 a right side split bearing rail 362 is shown such that the offset of the bearing rail on the right side from a central axis 368 by a distance 371 (approximately 10 mm) provides a magnetron roll attitude as shown by the dashed line 374. Thus, a small change in elevation near a central support will provide a much larger change in elevation at the extreme end of the magnetron assembly 272 extending out far beyond the central support rail 276.

Figures 17-20, 17A, 18A, 20A, and 21-24 show another configuration of a magnetron supported on a central support beam 276 according to the invention. In this

configuration instead of tilting the bearing rails, the bearing rails are maintained in their original flat horizontal attitude which without interference would provide a planar flat travel path for the magnetron parallel to a reference surface of the target assembly. In this configuration the magnetron assembly 272 is supported not just from the central bearing support beam 276, but as the magnetron assembly approaches the ends of the chamber a cam follower (roller) 442 engages a ramp (cam) 422 so that the end of the magnetron assembly is bent or tilted upwards away from the sputtering target assembly. Ramps 422, 428 are positioned at opposite corners of the chamber, corresponding to the locations on the sputtering target where the excessive erosion anomaly is observed (Fig. 6). In one configuration a rigid generally non-deformable magnetron housing can be used with a spring loaded joint to hold the magnetron to the bearing trucks of the center bearing rails. The springs are loaded to hold the magnetron straight and level with the bearing rails, and to allow hinging with a pivot axis at tne center bearing rail when the end of a magnetron comes in contact with a cam to raise it. In another configuration the magnetron housing is made of an easily deformable plastic. rubber or other similar material, with a rigid connection at the center rail to the center bearing truck(s), such that when the magnetron end comes in contact with a cam (i.e.. 422) it bends in a curve and to raise the end of the magnetron away from the target assembly. Compare the roll attitudes shown in Figures 21 versus 21A and 23 versus 23A.

Figures 17, 17A, 18, 18A, 19, 20, and 20A are a series of related cross sectional schematic views showing the motion of the end of the magnetron assembly 272 where a cam (ramp) and cam follower (roller) positioned a certain locations causes the whole magnetron or a portion of the magnetron to move toward or away from the target assembly. The magnetron assembly uses a cam follower (roller) 442 and cam surface (ramp) 422 to produces a vertical roll motion with a dimension 432 as shown in Figure 17. The end 440 of the magnetron assembly 272 includes a lift roller assembly frame 444 having a lift roller 442. The lift roller 442 and frame 444 travel with the magnetron assembly 272 at its ends (only one end 440, is shown), and when the lift roller 442 encounters the lift ramp 422 fixed to the chamber through a support fixture (e.g., support block 446), it rolls up the ramp 422 and as it is rolling up the ramp the end of the magnetron assembly is bent up a distance 432. In this configuration the translational force moving the magnetron assembly 272 from end to end also causes an end (e.g., 440) of the magnetron to be bent upwards when the ramps 422, 428 are encountered. The dashed lines, 424, 420, 430 in Figures 21, 22 and 23 represent the idealized bent, straight, and bent attitude (configurations), respectively, of the magnetron assembly 272 as it moves from end to end. In the idealized case, one side of the magnetron assembly 272 remains straight and parallel with the reference surface of the target assembly while the other side is bent up in a curve approximately as shown (the linear horizontal dashed lines are a reference against which the change in elevation at the end of the magnetron assembly can be evaluated), in practice there will be some impact on the free end of the assembly as there is some play between the linear bearings in the truck and the bearing rails and some vertical motion at the free end will occur.

In the top view of Figure 24, probable locations for an upper left corner ramp 422 and a lower right corner ramp 428 are shown (the locations providing elastic bending of the magnetron assembly without excessive material stress - for example when an easily deformable material such as rubber is used). When the magnetron assembly 270 moves from its centrally located horizontal attitude (configuration) 420 taken at 22-22 in Figure 24 to a first end of the chamber as shown by the attitude taken at 21-21, the resulting bending of the magnetron assembly is shown by the dashed line 424 and provides an offset dimension 426 from the center line (e.g., 420) at the end of the magnetron assembly. Similarly when the magnetron assembly 272 moves to the other end of the chamber as shown by the view taken at 23-23, the bent attitude of the magnetron assembly is shown by the dashed 430 provides a dimensional offset 432 from the center line (e.g., 420). In a symmetrical system the vertical offset dimensions 432, 426 due to the bend of the magnetron assembly at the two ends should be nearly identical, however it is possible to have a different vertical offset dimension at each end should empirical data show that such varying offsets are necessary. The control of sputtering to achieve non-uniform film thickness in a prescribed pattern can also be performed.

The illustrations of Figures 17A, 18A, and 20A show the use of four ramps (or cams) 415, 416, 417, 418, with a spring loaded center magnetron connection to the center bearing rails trucks (not shown here). The ends of he magnetron the top view of which is shown in Figure 17A includes two sets of rollers 434, 436 which are located above a side of the magnetron 272a. When the magnetron nears the end of its lateral travel two of its rollers on one side (only one of which is shown, e.g., 434) contacts two ramps (i.e.. 415. 418) and the magnetron undergoes an upward pitch to raise the edge of the magnetron nearest to the edge of the chamber by a distance 432a. This edge rise due a change in the pitch (again using an aircraft attitude reference) of the magnetron cause a reduction in the magnetic field at the edge of the target assembly and avoids excessive deposition due to edge effects which might otherwise be present. Thus the magnetron can undergo changes in its roll and pitch attitudes. A change in its yaw attitude would be possible if the bearing tracks were not generally linear or if the bearing trucks included a suspension allowing for some differential motion between adjacent bearing truck on a magnetron.

The conceptualized configurations of magnetron assemblies described above are carried out in practice

BNSDOCID: <EP__0820088A2_I_>

by mechanisms as shown in Figures 25 and 26.

Figures 25 and 26 show the bottom and cross sectional views of a magnetron assembly 118 supported by a central bearing support frame 136 consisting of a linear bearing support section 142 and a lateral extension section 144. The linear bearing support section 142 has fixed to each of its sides bearing rails 138, 140 (a set of tracks). The magnetron assembly 118 is supported from the bearing rails 138, 140 through a set of linear rail trucks 120, 121. The linear rail trucks are fixed to the magnetron assembly 118 and slide back and forth on the linear rails 138, 140. The motion of the magnetron assembly in a back and forth (lateral) direction is accomplished by rotation of a threaded drive rod (ball screw) 112, which is received by a ball screw receiving nut 122 that includes a set of nut housing pin receiving holes 126. 128. A set of drive pins extend vertically from the magnetron assembly 118 into the holes 126. 128 to slide vertically to avoid binding in the mechanism due to misalignment between the linear rails 138, 140 and the rotatable threaded drive rod 112. The threaded drive rod is turned by a ball screw drive motor 114 supported outside the chamber top while the second end of the ball screw is supported by a ball screw end bearing 116. In this configuration, the movement of the central bearing support frame 136 in a vertical direction is accomplished by rotating a set of vertically oriented lead screws 148, 150, 152, to which toothed drive belt pulleys have been attached. A drive pulley and motor 156, are linked to the toothed drive belt pulleys by a toothed drive belt 154. When the belt drive pulley and motor 156 are turned, the pulleys 148, 150, 152 turn simultaneously to turn equally pitched lead screws engaged with stationary nuts to move the central bearing support frame 136 up and down while maintaining parallelism between the linear bearing support section 142 and the target.

In a conventional configuration, the horizontal attitude of the magnetron assembly 118 is controlled through the sliding attachment to the very precisely aligned bearing rails 138, 140.

In this way, the movement of the magnetron assembly is uniform and parallel with the usually flat front face of an unsputtered target prior to its being eroded or utilized. This configuration is used for sputtering of relatively small rectangular substrates up to approximately 400 mm X 500 mm in size.

In the instance when the magnetron is to be tilted using a configuration according to the invention, the bearing rails 138, 140 are tilted (for example as shown by the configuration of Figure 22), while the central bearing support frame 136 continues to be moved up and down while being held in a parallel attitude with the target assembly.

A method according to the invention includes vertically moving the magnetron assembly as shown in Figures 25 and 26, as the magnetron assembly moves laterally across the target assembly. However, given the variations in the depth target erosion profile as shown in Figure 6, a parallel lifting of the magnetron assembly would not provide an improvement in the variation in film thickness uniformity or thickness control over the current vertically fixed arrangement. An alternate arrangement would be to drive each vertical support by separate motor/actuators, to control the vertical motion of the support beams and the magnetron assembly through electronic controls tied to the lateral position of the magnetron assembly.

Two Parallel Beam Bearing Supports

For large rectangular substrates approximately 600 mm X 700 mm in size, a second mechanism shown conceptualized in Figures 27, and 28 and in detail in Figures 34 and 35 is utilized.

Figure 27 shows the context of this second mechanism of the invention. A magnetron chamber 310 contains a magnetron assembly 312. The magnetron assembly 312 is supported by two bearing support beams 316, 317, which allow the magnetron assembly 312 fixed to a set of bearing trucks (e.g., 324) to move along a set of bearing rails (e.g., 322) in a lateral direction as shown by the arrows 314. The vertical movement of the bearing support beams 316, 318 is shown by the arrows 320. The lateral motion of the magnetron assembly 312 along the bearing rail 322 is produced by rotation of the threaded drive rod 326 which engages a threaded drive nut 328 contained within a threaded drive nut housing 330. The threaded drive nut housing 330 is fixed to a bowed section of a flexible spring-like connection 332, which is fixed to the magnetron assembly 312 such that misalignment or relative motion between the bearing support beams 316, 318 and threaded drive nut 326 provides a flexible connection in a vertical direction while providing rigidity in a transverse direction. The idealized tracking of the magnetron assembly 312 in the configuration of Figure 27 is shown in Figure 28. In Figure 28 a magnetron assembly 342 is supported on two bearing support rails 344, 346 supported by end frames 348, 350. The end frames 348, 350 in this configuration being level and parallel with each other. The positioning of the left side rail 344 showing a vertical progression of the left end of the magnetron 342 from a lower edge of the frame 348 to an upper edge of the frame 350 at the opposite end. The positioning of the right side bearing support 346 shows vertical progression from an upper edge of the end frame 348 to a lower edge of the end frame 350 at the opposite end.

A magnetron assembly supported by end rails is shown in Figures 29 through 33. Figure 29 shows the cross section of a processing chamber with the magnetron assembly 312 supported by two perimeter support rails 400, 402. This configuration is consistent with the conceptualized visualization of Figures 27 and 28. At one extreme end as can be seen in Figure 30 (taken at the location of 30-30 in Figure 33), the offset of the end of the rail 402 in a vertical direction an amount shown

BNSDOCID: <EP___0820088A2_I_>

by the distance 408a results in a magnetron assembly attitude (tilt) as shown approximated by the dashed line 412. At a central location as can be seen in Figure 31 (taken at the location of 31-31 in Figure 33) a horizontal attitude 404 configures the magnetron to be parallel with the target surface or target reference surface (usually a plane). At the second end of the processing chamber as shown in Figure 32 the cross section taken at 32-32 of Figure 33, the position of the bearing rail 400 above the reference plane (e.g. [illegible] parallel to 404 in Figure 31), of the target assembly causes the attitude (tilt) of the magnetron assembly 312 to be approximately as shown by the dashed line 414. The vertical offset distance is represented by 408b. In this instance the horizontal offset from a lateral center line [illegible] of the processing chamber is a distance 410 therefore the vertical offset dimensions at the beam [illegible] must be larger to achieve a similar change in attitude (tilt) when compared to the configuration of the magnetron assembly as is shown in Figures 11 through 16 [illegible] smaller vertical offset at the bearing rail [illegible] to the opposite support rail results in a [illegible] change (tilt) per unit length from one end [illegible] other end of the magnetron assembly 312.

The detailed [illegible] Figures 34 and 35 show a magnetron assembly [illegible] implemented in a magnetron chamber [illegible] sputtering chamber. A magnetron assembly [illegible] positions of which are shown in Figure [illegible] on a set of two bearing rails 206, 208 [illegible] on a set of pseudo parallel edge [illegible] 198, 200. A set of linear rail trucks 180, 182 [illegible] the bearing rails 206, 208, and move back [illegible] driven by a threaded drive rod (ball screw [illegible] by a dashed line in Figure 34). In this [illegible] back and forth motion of the magnetron [illegible] accomplished by the rotation of the [illegible] mounted between a ball screw drive motor [illegible] screw end bearing 176. The ball screw [illegible] ball screw receiving nut 184 captured [illegible] receiving housing 186. The ball screw [illegible] 186 is fixed to a flexible leaf spring-like [illegible] which is connected to the magnetron [illegible] its ends. The bearing rails 206, 208 [illegible] mentioned mechanism are precisely [illegible] with one another and with the face [illegible] sputtered so that uniform deposition [illegible] place.

The magnetron [illegible] Figures 34 and 35 is supported on [illegible] 198, 200 aligned to one another to [illegible] with a set of end support frame members [illegible]. To provide vertical adjustment, four [illegible] threaded support rods engaged with thread [illegible] nuts on the frame are fixed to toothed pulleys 210, 212, 214 and 216. A toothed drive belt 222 runs around the toothed pulleys 210, 212, 214, and 216 and around to idler pulleys 218, 220 to engage and be driven by a belt drive pulley and motor 224. When the belt drive pulley and motor 224 turn, each of the lead screws in the four corners are turned by the toothed pulleys fixed to the lead screws to cause parallel adjustment of the bearing support frame in a vertical direction. An alternate arrangement would be to drive each vertical support by separate motor/actuators, to control the vertical motion of the support beams and the magnetron assembly through electronic controls tied to the lateral position of the magnetron assembly.

Two-Piece Hinged Magnetron

Another configuration for a magnetron assembly 460 and its vertical manipulation is shown in Figures 36 and 37. These Figures show a cross section of a hinged magnetron assembly 460 utilizing a center support rail 462 which can be continuously bent as shown in Figure 37 or can be a series of linear segments. In these configurations a center intersection of the two hinged sections of the magnetron assembly 460 are supported from the center bearing rail 462 to provide variations in the distance from the sputtering target to the center of the magnetron assembly 460 as the magnetron assembly cycles from end to end. The variation in horizontal distances due to the different horizontal dimensions when comparing a hinged magnetron and a straight magnetron is accommodated by curving the perimeter bearing beams inward or by providing a fixed connection between the a bearing truck attached to the center support rail 462 while the bearing truck connections to the side support rails 464, 466, are free to move (slide) toward and away from the center bearing rail 462, details of such connections can be developed and executed by persons of ordinary skill in the art.

Segmented Magnetron Following Reference Contour

Another embodiment according to the invention is pictured in Figure 38. In this embodiment one or more cam surfaces and cam followers are utilized to change the distance between portions of a magnetron assembly having magnetron sub-sections which can move independently while maintaining a semblance of a continuous loop of adjacent permanent magnets in the magnet array in the magnetron. The magnet sub-sections (a series of magnet member subsections) can be pivotable and can be hinged together like a chain, to provide a continuous magnetic field, or can be encased in a flexible housing. As shown in Figure 38, several cam surfaces (a series of cam surfaces) can be combined to form a continuous cam surface plate 476 reflecting the profile/pattern to be followed by each sub-section of the magnetron and the magnetron assembly as a whole. The cam surface plate 476 includes several adjacent cam surface slots (e.g., 478) through which a cam follower rod (e.g., 474) connects a cam follower (e.g., 482) with a sub-section (e.g., 472) of the magnetron assembly. A magnetron contour tracking frame 486 maintains

BNSDOCID: <EP__0820088A2_I_>

the vertical alignment between the cam followers (e.g., 482) and magnetron sub-sections (e.g., 472) so that they track together (as driven by a lateral drive) to provide an improvement in the control of film thickness and/or its uniformity. Each track of the profile-surface pattern varies the distance between each particular sub-section (e.g., 472) of the magnetron assembly and the target below.

Another configuration according to the invention is shown in Figure 38A. In Figure 38A a magnetron 488 is constructed of a flexible material such that each vertical control member (of a series of vertical drives) controls the vertical elevation of a portion of the magnetron 488. The tracking frame 486 is cut away for clarity. In this configuration, the influence of the magnetron 488 on the target can be precisely controlled, by increasing the number of vertical control members (push/pull rods) and/or by providing such vertical control members on each side of the magnetron so that a desired pitch attitude can be achieved.

Figures 39-42 show conceptualized idealized approximations of three of a variety of surface patterns/profiles that might be utilized for the cam surface 476.

In Figure 39 a surface pattern/profile has a shape similar to the surface pattern/profile tracked by the magnetron assembly of the configuration as shown in Figures 9-15 (opposite corners being high, while adjacent opposite corners are low). In this profile a back corner 494 and a front corner 498 are low, while a right side corner 492 and a left side corner 496 are raised. Therefore, the elevation change between the rails which ostensibly connect the bottom corner 498 with the right corner 492 is from low to high, while the rail which connects from back corner 494 to left corner 496 is from high to low.

Figure 40 shows a surface following a two dimensional circular or parabolic shaped curve. A high point of the curve and the arc shaped surface is along the center lateral axis 503. In practice, a bearing rail elevation would follow a edge of the pictured surface, for example from the right corner 504 to the bottom corner 510 and from the top corner 506 to the left hand corner 508.

The surface profile/pattern contour of Figure 41 shows an upwardly parabolic or rounded type shape where all of the corners, right corner 516, back corner 518, left corner 520, and front corner 522 are approximately at equal high elevations, while a center 515 of the corners is at a low point. A magnetron assembly following this surface pattern will have magnet sub-sections in the magnet array of the a magnetron assembly which cause the center portion of the magnet array to approach the back of the target to increase the sputtering at that location. Alternately, the configuration may be used so that the magnetic field effect uniformly sputters a circularly or parabolically shaped target to sputter deposit a similarly shaped circularly or parabolically shaped substrate (e.g., a parabolic mirror) without having to form a specially shaped magnetron. In using this configuration the deposition film thickness can be kept relatively constant utilizing a magnetron sub-section surface pattern/profile as shown by Figure 41.

5 Figure 42 shows a concave down circular or parabolic surface shape with four corners 528, 530, 532 and 534 being the low point of the surface profile/pattern, while a high point of the surface profile/pattern is at a center 527.

10 A person of ordinary skill in the art will understand that the mechanical cam shape (e.g., of Figure 38) or any generally reasonably continuous cam surface profile/pattern can be utilized to change the distance between the magnetron sub-sections and the target as-15 sembly. The surface patterns/profiles shown are but several of the many varieties of surface patterns that might be utilized. Variations in the cam surface/profile can accommodate desired localized changes in the sputtering rate at those particular locations by forming 20 the cam surface accordingly.

Vertical Actuators

Another configuration of the device according to the 25 invention is to utilize a planar follower plate 546 which utilizes an approximately flat plate and a structure which correlates a lateral position and a vertical position of each sub-section (e.g., 542) of the magnetron as shown in Figure 43. Each sub-section (e.g., 542) is connected 30 through a vertical positioning rod (e.g., 544) to a contour plate follower activator (e.g., 552). These collectively makeup an activator assembly (e.g., 550). The activator assembly (e.g., 550) moves in a slot (e.g., 548) in the planar follower plate 546 according to the motion of a 35 magnetron contour tracking frame 558 (shown in dashed lines) which ties all of the activator assemblies together so that they move simultaneously in a lateral direction as the magnetron assembly (including all of the magnetron sub-sections) sweeps laterally across the 40 target assembly. The vertical position of each magnetron sub-section 542 is set according to a control system 554 which receives elevation control data which establishes an elevation for each magnetron sub-section location as the magnetron cycles from end to end. The 45 elevation control data causes the magnet sub-sections to moves in a programmed manner according to a programmed surface profile/pattern. The programmed pattern causes the magnet sub-section to move as if it were following a surface pattern of a mechanical cam surface 50 (i.e., as shown in Figure 38) utilizing electronic programming to cause the activators to move the magnetron sub-sections according to programming of a contour generator 556, which provides a reference contour to the control system 554. The programming of the contour 55 data is easily changed to adjust the magnetron tracking according to a desired surface pattern/profile.

INSDOCID: <EP___0820088A2_I_>

Electro-Magnet Magnetron Control of Sputtering

Figures 44 and 45 show a magnetron configuration using electro-magnets which can be used to control sputtering. A magnetron 560 held in a plane generally parallel to a target's surface is swept back and forth across the back of a target assembly. As the magnetron 560 is moved electromagnets in the magnetron are energized and the intensity of the magnetic field generated by each electro-magnet in the array is varied according to a contour plot 556a which sets out the desired film deposition profile based on empirically derived knowledge of variations in the physical configuration. Thus as the magnetron moves back and forth the magnetic field is electrically varied to achieve a result similar to that achieved by moving a magnetron with permanent magnets closer to and further away from the back of the target assembly. The magnet array in such a configuration may include a combination of permanent and electromagnets, and such electro magnets may be used in conjunction with a vertical motion or with motion in a plane. In the extreme, a static array of electromagnets could have an area covering the substrate surface and the movement of magnetic field would be electronically controlled by controlling the energization and deenergization of selected electromagnets.

Figure 45 shows a configuration of the magnetron 560 utilizing electro-magnets. The magnets are aligned in the same way as shown in Figure 4 except that each permanent magnet segment is replaced by a electromagnetic core (preferably iron) possibly in the shape of a spool 564 as shown, with each spool 564 being surrounded by a wire coil 568. The strength of the magnetic field is individually controlled by a circuit wires 576 connected to the contour controller 554a. As the magnetron travels back and forth the magnetic field strength is varied by changing the electrical power supplied to the electromagnetic coils and sputtering is enhanced accordingly.

A method according to the invention for selectively controlling the film thickness deposited on a substrate during sputtering includes the steps of moving a magnet member laterally in the proximity of a sputtering target and varying the strength of the magnetic field enhancing sputtering at the target surface as the magnet member moves laterally to deposit a particular film thickness pattern on the substrate during processing during sputtering. It may be desirable to have a different than uniform film thickness. for example it may be desirable to increase the film thickness at the edge of the substrate so that wiring connections between the conductive layers deposited on the substrate have an increased durability and are less subject to fracture. In general it is expected that the tolerances for film thickness uniformity over a substantial portion of the substrate will have to be maintained. whether localized anomalies in film thickness are desired or not The structure and method according to the invention provides uniformity where uniformity in film thickness is desired and provides non-uniformity where non-uniformity is desired

A method according to the invention utilizes moving magnet sections or magnetron assemblies laterally while utilizing a vertical support which changes the elevation of particular portions of the magnetron assembly according to its lateral position to improve film thickness uniformity.

A method according to the invention includes the steps of moving a magnet member laterally in the proximity of a sputtering target and moving portions of said magnet vertically, a distance greater than a tolerance for parallelism between a reference plane and the plane of motion at selected locations to vary the magnetic field strength causing a divergence from the plane to improve the film thickness uniformity. Another method according to the invention includes the steps of moving a magnet member laterally along a track and moving portions of the magnet member in a vertical direction simultaneously with the lateral motion of the magnet member to change the magnetic field intensity utilized for sputtering at one or more locations along the track to improve film thickness uniformity or thickness control for sputtering. The magnet member can be moved laterally along a track and while portions of the magnet member are moved in a vertical direction simultaneously with the lateral motion of the magnet member to change the magnetic field intensity utilized for sputtering at one or more locations along the track to improve the control of the film thickness deposited during sputtering.

In a method according to the invention the step of varying the strength of the magnetic field includes changing the strength of electro-magnets in the magnetic member according to a pattern depending on the lateral location of the magnet member.

While the invention has been described with regards to specific embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention.

Claims

1. A magnetron sputtering apparatus, comprising:

    a magnet member having a magnetic field emanating therefrom disposed in the proximity of a sputtering target,
    a magnet member cycling system which during sputtering of said sputtering target causes said magnet member to move in a set pattern,
    wherein said set pattern of motion is defined by a set of points defining a pattern reference surface, wherein the pattern reference surface is defined by a set of lateral coordinates and a set of vertical coordinates of the pattern,
    wherein said set of lateral coordinates establish

BNSDOCID: <EP 0820088A2 I >

a defined set of locations on an offset reference surface which is approximately parallel to a reference surface of said sputtering target and offset from it,
wherein said set of vertical coordinates establish a defined set of elevations for said set pattern at each respective lateral coordinate of said set of lateral coordinates,
wherein said pattern reference surface includes a divergent portion having a subset of said defined set of elevations establishing the elevation of the pattern reference surface within said divergent portion at a distance from said offset reference surface at each respective lateral coordinate of said set of lateral coordinates, wherein the elevation of the pattern reference surface within said divergent portion falls outside a range of tolerance for parallelism between said offset reference surface and said reference surface of said sputtering target.

2. The magnetron sputtering apparatus as in Claim 1,
wherein motion of said magnet member following said divergent portion of said pattern reference surface. rather than following a non-divergent portion of said pattern in which said distance would fall within the range of tolerance for parallelism between offset reference surface and said reference surface of said sputtering target, provides an improvement in the uniformity or thickness control of film thickness deposited on the surface of a substrate, located opposite said sputtering target, being sputter deposited.

3. The magnetron sputtering apparatus as in Claim 1,
wherein said reference surface of said sputtering target is defined by unused pre-sputtering configuration surface of said sputtering target facing said processing chamber.

4. The magnetron sputtering apparatus as in Claim 2,
wherein said reference surface of said sputtering target is defined by an unused pre-sputtering configuration of a front surface of said sputtering target facing said processing chamber.

5. The magnetron sputtering apparatus as in Claim 1, 2, 3, or 4,
wherein said tolerance for parallelism is 0.0075 inches per foot of motion along said offset reference surface.

6. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.010 inches per foot of motion along said offset reference surface.

7. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.015 inches per foot of motion along said offset reference surface.

8. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.020 inches per foot of motion along said offset reference surface.

9. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.025 inches per foot of motion along said offset reference surface.

10. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.030 inches per foot of motion along said offset reference surface.

11. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.035 inches per foot of motion along said offset reference surface.

12. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.040 inches per foot of motion along said offset reference surface.

13. The magnetron sputtering apparatus as in Claim 1, 2, or 3,
wherein said tolerance for parallelism is 0.050 inches per foot of motion along said offset reference surface.

14. The magnetron sputtering apparatus as in Claim 1,

wherein said set pattern of said cycling system results from a motion along a set of tracks supporting and guiding the magnet member,
wherein the configuration of said set of tracks establishes said set of lateral coordinates and said set of vertical coordinates of said set pattern, including said divergent portion.

15. The magnetron sputtering apparatus as in Claim 14,
wherein said motion along said set of tracks is a back and forth motion.

16. The magnetron sputtering apparatus as in Claim 1,

further comprising:

a set of tracks supporting and guiding the magnet member
a cam surface fixed to a first of either said magnet member or a fixed support adjacent said tracks and a cam follower fixed to a second of either said magnet member or said fixed support,
wherein a divergent portion of said motion. corresponding to said divergent portion of said pattern reference surface, results from a motion along said set of tracks,
wherein said set pattern of said cycling system results at least partially from a motion along said set of tracks where during said set motion said cam follower comes into contact with said cam surface and urges said magnet member in a vertical direction to follow a motion corresponding to the divergent portion of said pattern reference surface.

17. The magnetron sputtering apparatus as in Claim 1,

wherein said magnet member includes a series of magnet member subsections,
wherein said magnetron apparatus further comprises:

a set of tracks, wherein each one of said set of tracks supports and guides a corresponding subset of said series of magnet member subsections,
a series of cam surfaces, each one of said series of cam surfaces being fixed to a first of either a subsection of said series of magnet member subsections or a fixed support adjacent said tracks and a cam follower fixed to a second of either a subsection of said series of magnet member subsections or said fixed support,

wherein a divergent portion of said motion. corresponding to said divergent portion of said pattern reference surface,
wherein said set pattern of said cycling system results at least partially from a motion along said set of tracks where during said set motion said cam follower comes into contact with said cam surface and causes at least one of said series of magnet member sections to move in a vertical direction to follow a motion corresponding to the divergent portion of said pattern reference surface.

18. The magnetron sputtering apparatus as in Claim 17,

wherein said series of cam surfaces form a continuous cam plate surface.

19. The magnetron sputtering apparatus as in Claim 18,

wherein travel of said magnet member following said divergent portion, rather than following said plane. provides an improvement in the uniformity of film thickness deposited on the surface of a substrate, located opposite said sputtering target, being sputter deposited.

20. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.0075 inches per foot of motion along said track.

21. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.010 inches per foot of motion along said track.

22. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.015 inches per foot of motion along said track.

23. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.020 inches per foot of motion along said track.

24. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.025 inches per foot of motion along said track.

25. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.030 inches per foot of motion along said track.

26. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.035 inches per foot of motion along said track.

27. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.040 inches per foot of motion along said track.

28. The magnetron sputtering apparatus as in Claim 18 or 19,

wherein said tolerance for parallelism is 0.050 inches per foot of motion along said track.

29. An magnet scanning mechanism comprising:

BNSDOCID: <EP___0820088A2_I_>

a magnet member supported on series of rails, where the magnet member acts as a truck that rides said series of rails,
wherein said rails run adjacent to one another to accommodate an approximately constant track width of said truck as it moves from a first end of said series of rails to a second end of said series of rails,
wherein said movement of said magnet member as it moves from said first end of said series of rails to said second end of said series of rails describes a reference surface, wherein said reference surface diverges from flatness by dimensional tolerances greater than a range of tolerance for flatness.

30. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.0075 inches per foot of motion along said rails.

31. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.010 inches per foot of motion along said rails.

32. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.015 inches per foot of motion along said rails.

33. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.020 inches per foot of motion along said rails.

34. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.025 inches per foot of motion along said rails.

35. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.030 inches per foot of motion along said rails.

36. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.035 inches per foot of motion along said rails.

37. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.040 inches per foot of motion along said rails.

38. The magnetron sputtering apparatus as in Claim 29,
wherein said tolerance for flatness is 0.050 inches per foot of motion along said rails.

39. A magnetron scanning apparatus comprising:
a magnet member running as a truck on a set of separated linear bearing rails which are approximately parallel, where during sputtering to improve the uniformity of film thickness sputter deposited on a substrate opposite a target disposed between said target assembly and said magnet member a first end of a first rail of said set of bearing rails is raised to be further from the target than a second end of said first rail of said set of bearing rails.

40. A magnetron scanning apparatus as in Claim 39,
where during sputtering to further improve the uniformity of film thickness sputter deposited, a second end of a second rail of said set of bearing rails is raised to be further from the target than a first end of said second rail of said set of bearing rails, wherein said second end of said second rail of said set of bearing rails corresponds to said second end of said first rail of said set of bearing rails.

41. A magnetron sputtering apparatus as in Claim 40,
wherein a set of vertical positions of said first and said second ends of said rails is set by a vertical travel mechanism which can raise and lower said first and said second ends of said first and second rails to set the tracking of the magnet member.

42. A magnetron sputtering apparatus as in Claim 41,
wherein said vertical travel mechanism operates during sputtering and tracking of said magnet member.

43. The magnetron sputtering apparatus as in Claim 18,
wherein said magnet member includes a series of magnet member subsections,
wherein movement along said track results from a programming of a motor to raise and lower each subsection of said set of subsections according a programmed pattern depending on the lateral position of said magnet member as it moves laterally.

44. The magnetron sputtering apparatus as in Claim 18,
wherein the magnet member includes at least two section with a center track of said set of tracks supporting an end of each section of said at least two sections, said magnet member appearing to be hinged at said center track.

45. A magnetron apparatus comprising:
a magnet member supported on two rails set

BNSDOCID: <EP 0820088A2 I >

at a selected amount of non-parallelism.

46. A magnetron member comprising:
a magnet member supported on two rails, selectively controllable in an amount of non-parallelism during a scanning of the magnet member.

47. A method for selectively controlling the film thickness deposited on a substrate during sputtering comprising the steps of:

moving a magnet member laterally in the proximity of a sputtering target and
varying the strength of the magnetic field enhancing sputtering at the target surface as the magnet member moves laterally to deposit a particular film thickness pattern on the substrate during processing during sputtering.

48. The method for selectively controlling the film thickness deposited on a substrate during sputtering as in Claim 47,
wherein the step of varying the strength of the magnetic field includes moving portions of said magnet member vertically.

49. The method for selectively controlling the film thickness deposited on a substrate as in Claim 48,
wherein the step of moving portions of the magnet member vertically provides that the vertical distance is a distance greater than a tolerance for parallelism between a reference plane and the plane of motion at selected locations to vary the magnetic field strength causing a divergence from the plane to control the film thickness uniformity.

50. The method for selectively controlling the film thickness deposited on a substrate during sputtering as in Claim 47,
wherein the step of varying the strength of the magnetic field includes changing the strength of electro-magnets in said magnetic member according to a pattern depending on the lateral location of the magnet member.

51. A method for selectively controlling the film thickness deposited on a substrate during sputtering comprising the steps of:

moving a magnet member laterally along a track and
moving portions of the magnet member in a vertical direction simultaneously with the lateral motion of the magnet member to change the magnetic field intensity utilized for sputtering at one or more locations along the track to improve the control of the film thickness deposited during sputtering.

52. A method for selectively controlling the film thickness deposited on a substrate during sputtering comprising the steps of:

locating a magnetic field opposite a sputtering target;
moving the magnetic field laterally across the target;
varying the strength of the magnetic field at locations where a localized change in the deposited film thickness is desired.

53. The magnetron sputtering apparatus as in Claim 1,

wherein said magnet member includes a series of magnet member subsections,
wherein said magnetron apparatus further comprises:

a set of tracks, wherein each one of said set of tracks supports and guides a corresponding subset of said series of magnet member subsections as a lateral drive moves each one of said series of magnet member subsections in a lateral direction,
a series of vertical drives, each one of said series of vertical drives being fixed to provide relative motion between each respective subsection of said series of magnet member subsections and said lateral drive,

wherein a divergent portion of said motion, corresponding to said divergent portion of said pattern reference surface,
wherein said recurring pattern of said cycling system results at least partially from a vertical motion provided by said vertical drive as a result of programming the control of said vertical drive to provide a preset pattern of relative motion corresponding to the divergent portion of said pattern reference surface.

54. A magnetron sputtering apparatus comprising:

a sputtering target assembly having a first side opposite a second side wherein a target surface on said first side is exposed to a sputtering chamber;
a traveling magnet member disposed to travel along a track on a second side of said target assembly, said magnet member including components which produce a magnetic field extending beyond the surface of said magnet member toward said target surface.
wherein a portion of said magnet member travels in a plane approximately parallel to an unused pre-sputtering configuration of said surface of said first side of said target, except in a

BNSDOCID: <EP 0820088A2 I >

divergent portion, where the distance of a portion of the magnetic member and said unused configuration of said surface of said first side of said target assembly exceed a range of tolerance for parallelism between said plane and said unused pre-sputtering configuration of said surface of said first side of said target.

5

10

15

20

25

30

35

40

45

50

55

BNSDOCID: <EP___0820088A2_I_>

FIG._1
(PRIOR ART)

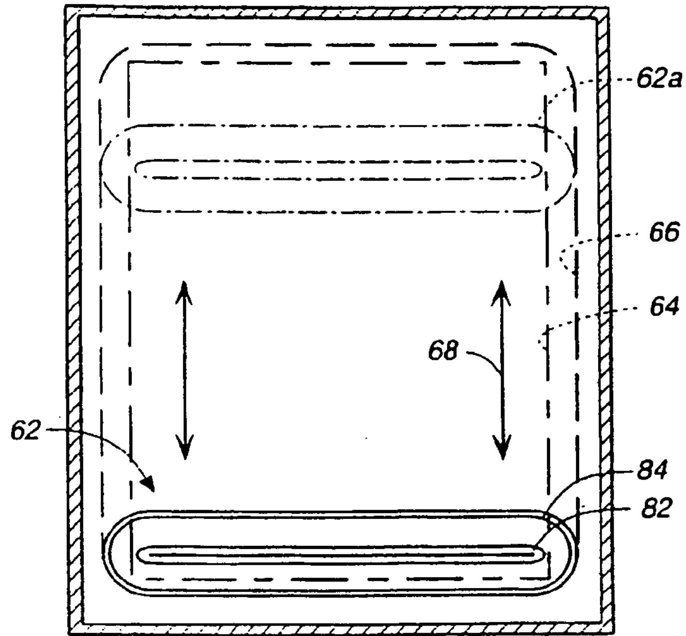


FIG._2
(PRIOR ART)

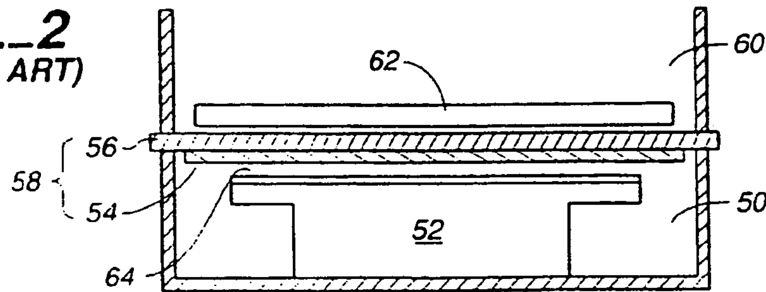
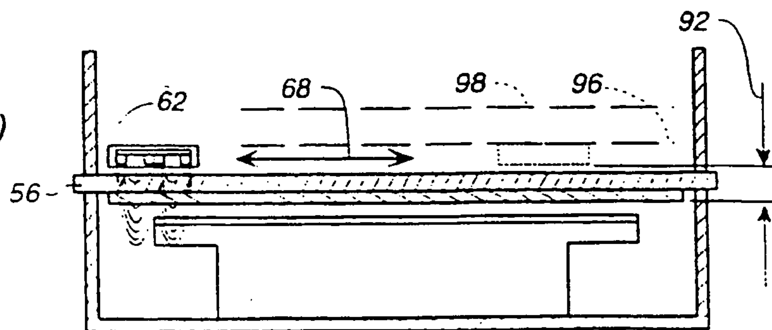


FIG._3
(PRIOR ART)



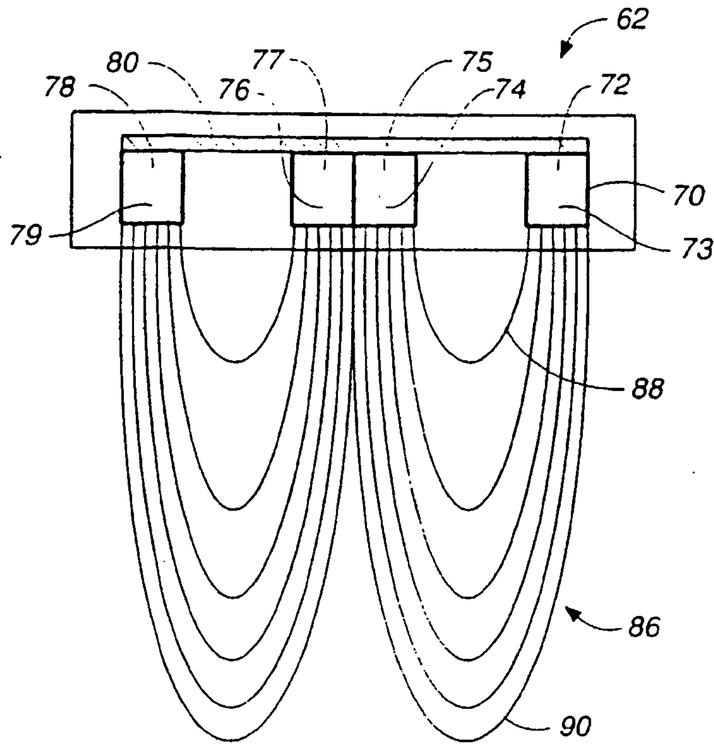


FIG._4
(PRIOR ART)

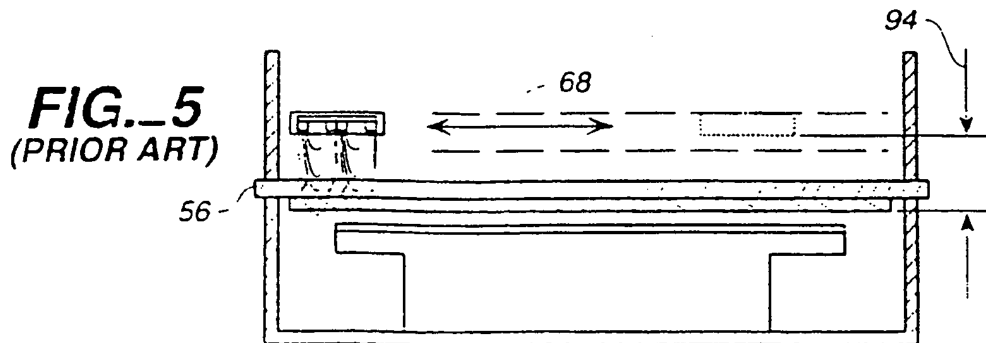


FIG._5
(PRIOR ART)

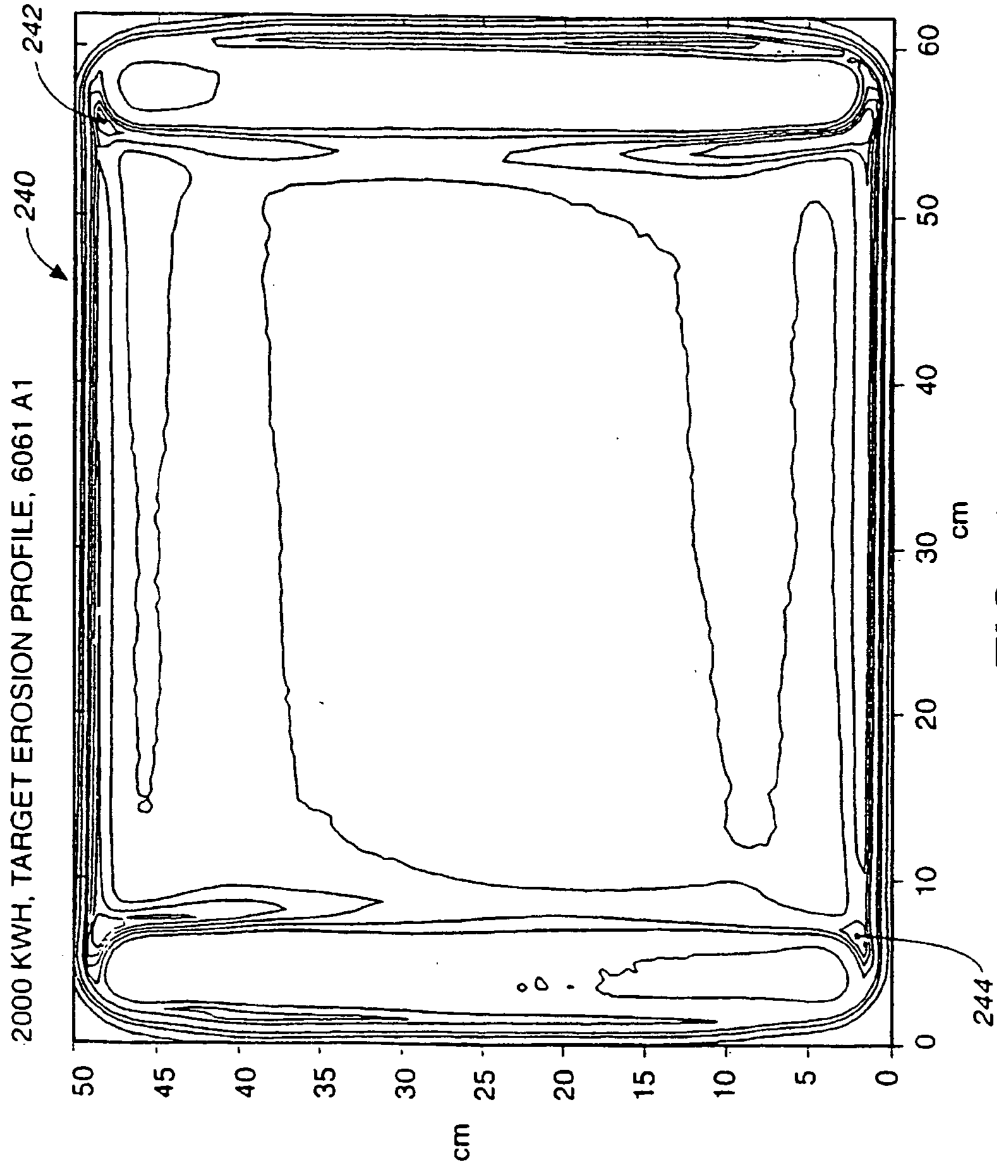


FIG._6 (PRIOR ART)

BNSDOCID: <EP___0820088A2_I_>

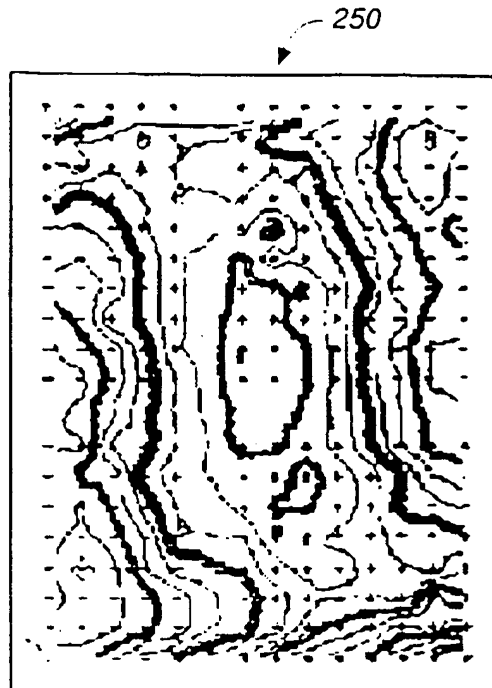


FIG._7
(PRIOR ART)

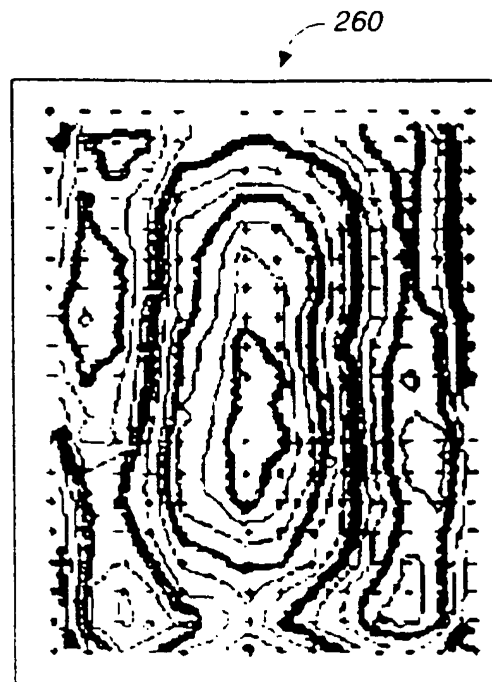
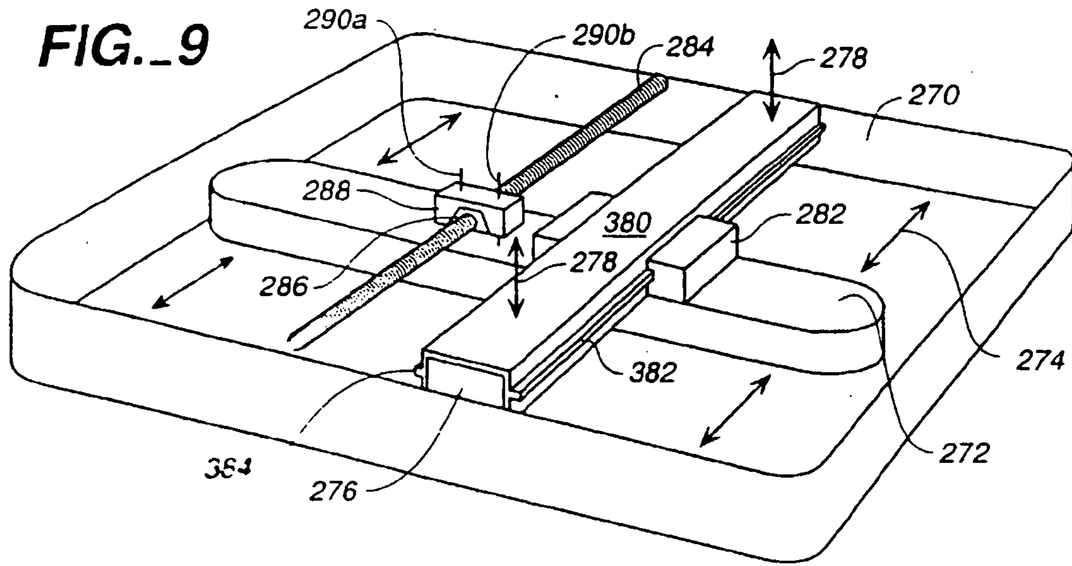
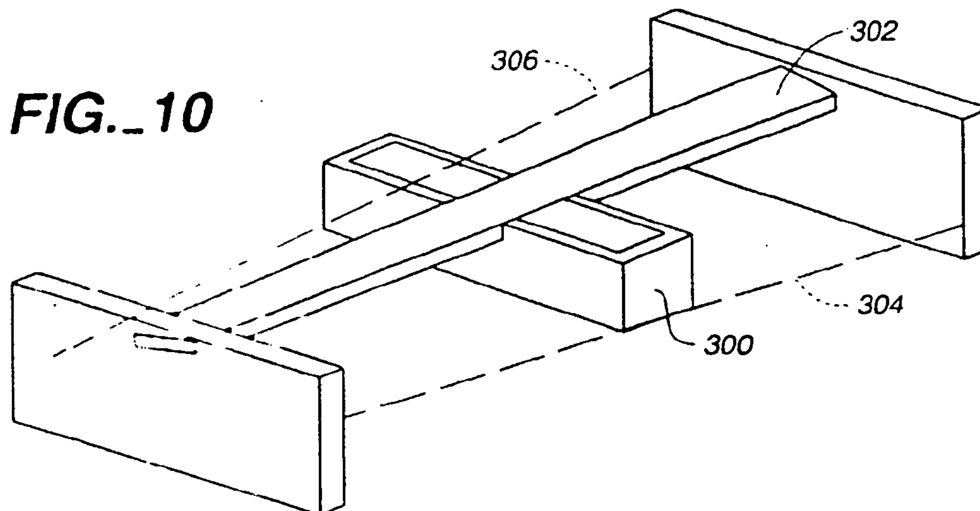


FIG._8

BNSDOCID: <EP___0820088A2_I_>





BNSDOCID: <EP___0820088A2_I_>

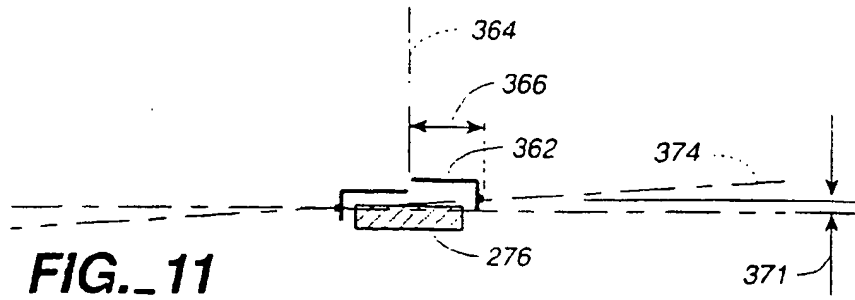


FIG._11

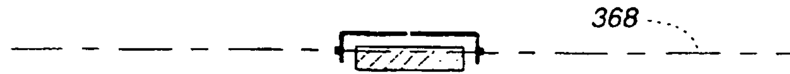


FIG._12

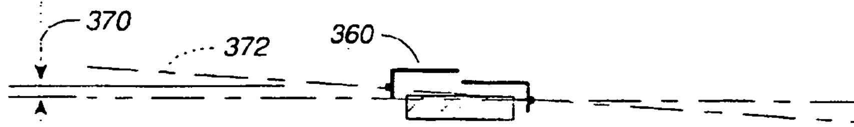
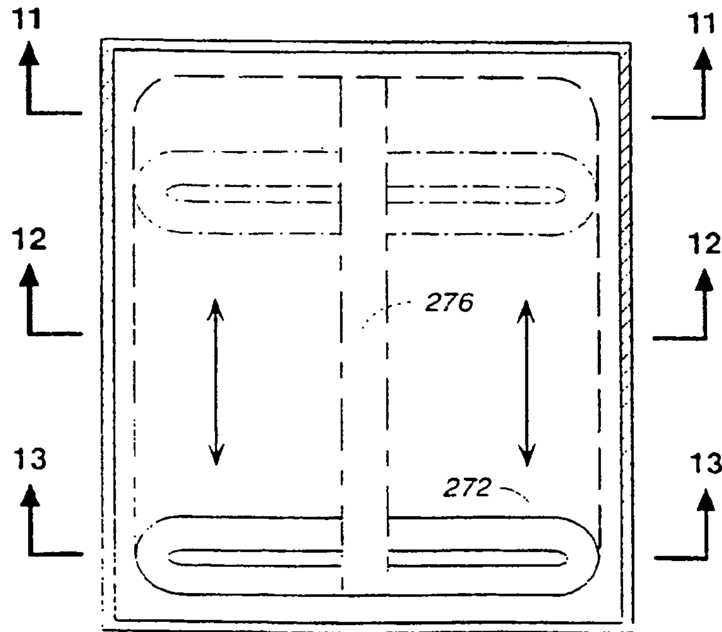


FIG._13

FIG._14



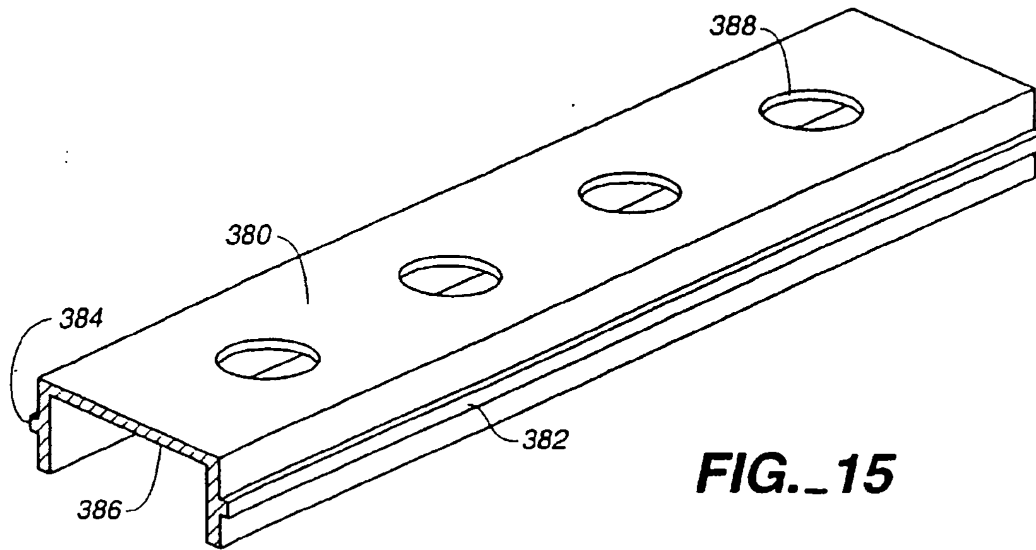


FIG._15

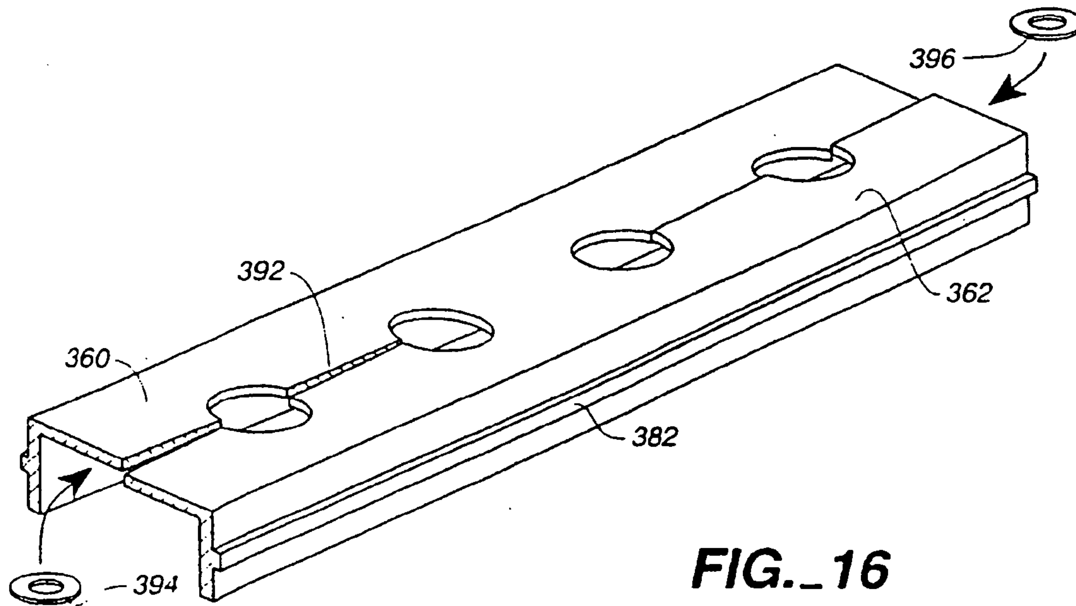


FIG._16

FIG._17

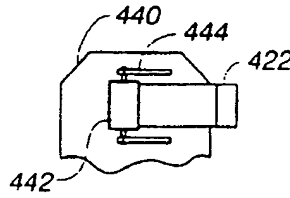


FIG._18

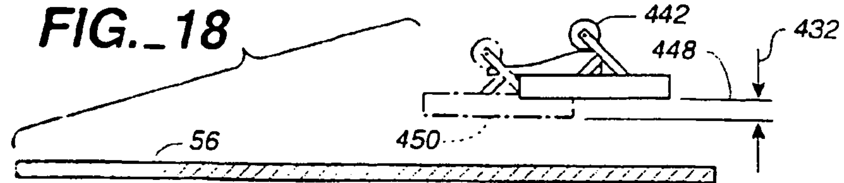


FIG._19

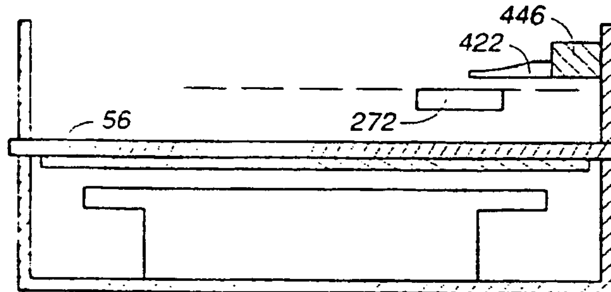
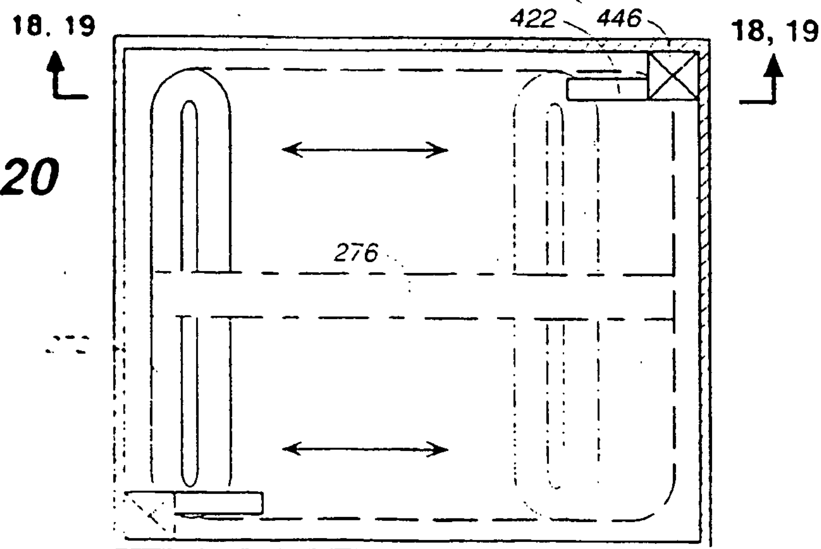
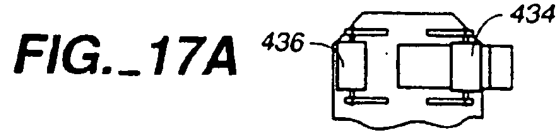
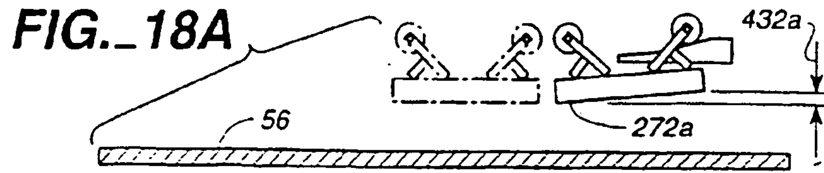
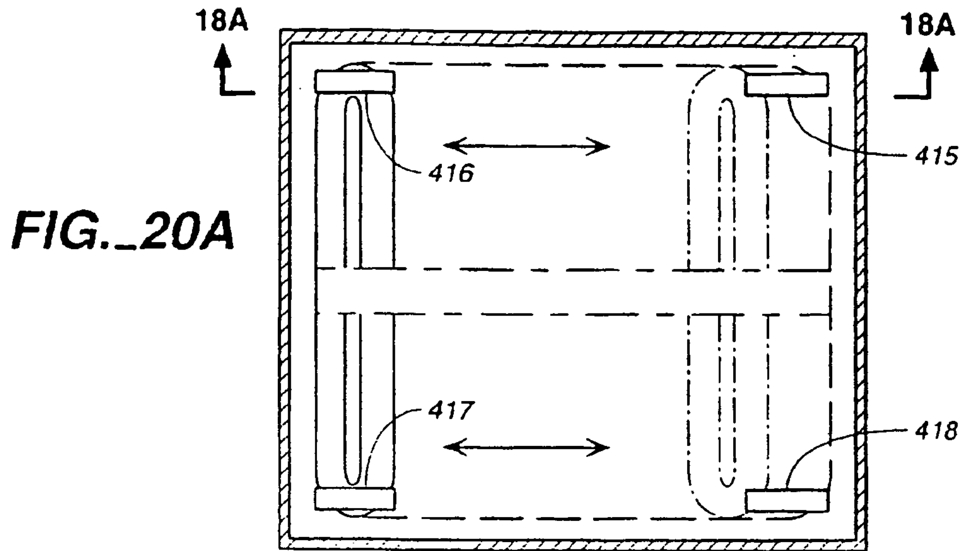


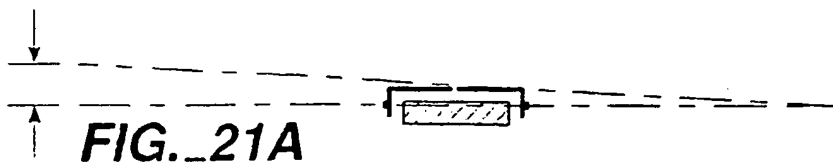
FIG._20

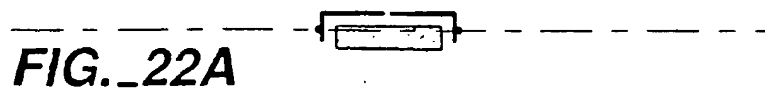


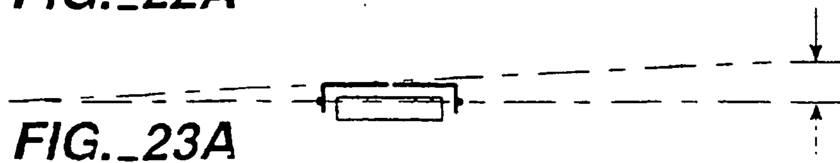












BNSDOCID: <EP 0820088A2 I >

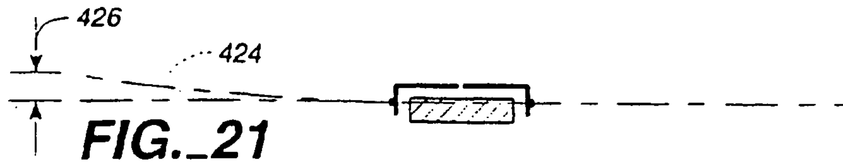


FIG._21

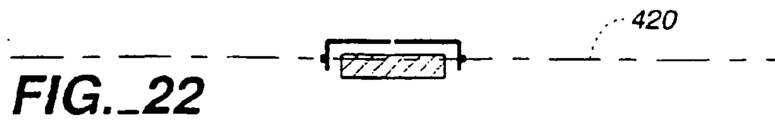


FIG._22

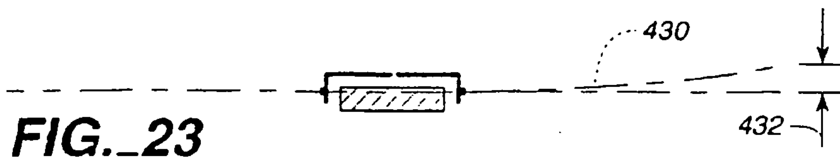
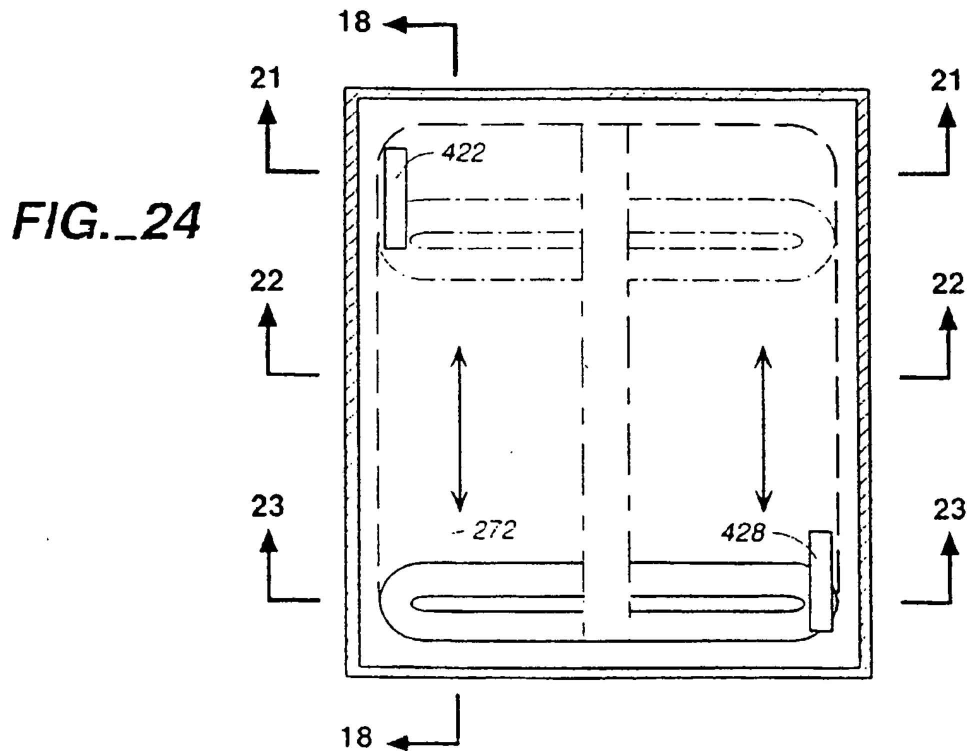


FIG._23

FIG._24



BNSDOCID: <EP___0820088A2_I_>

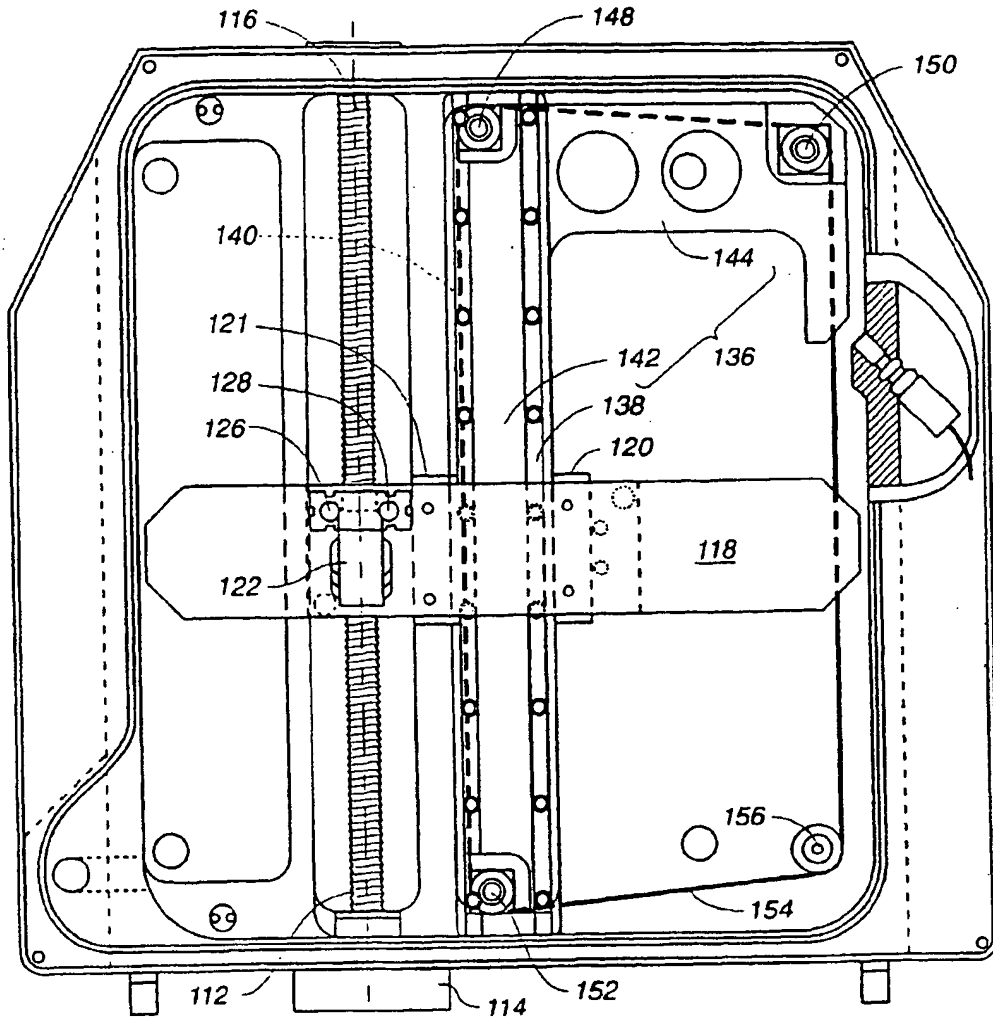


FIG._25

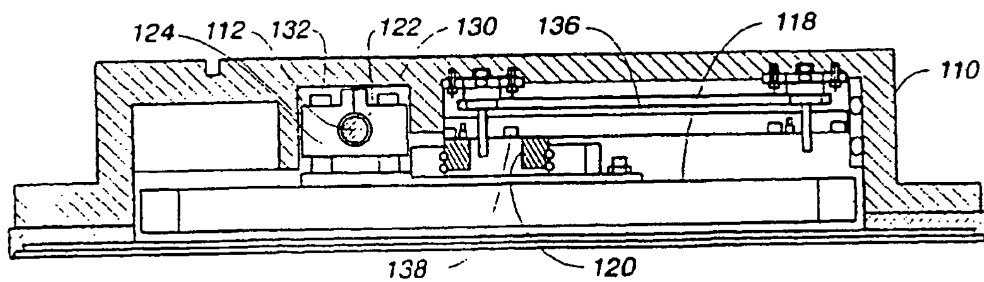


FIG._26

BNSDOCID: <EP___0820088A2_I_>

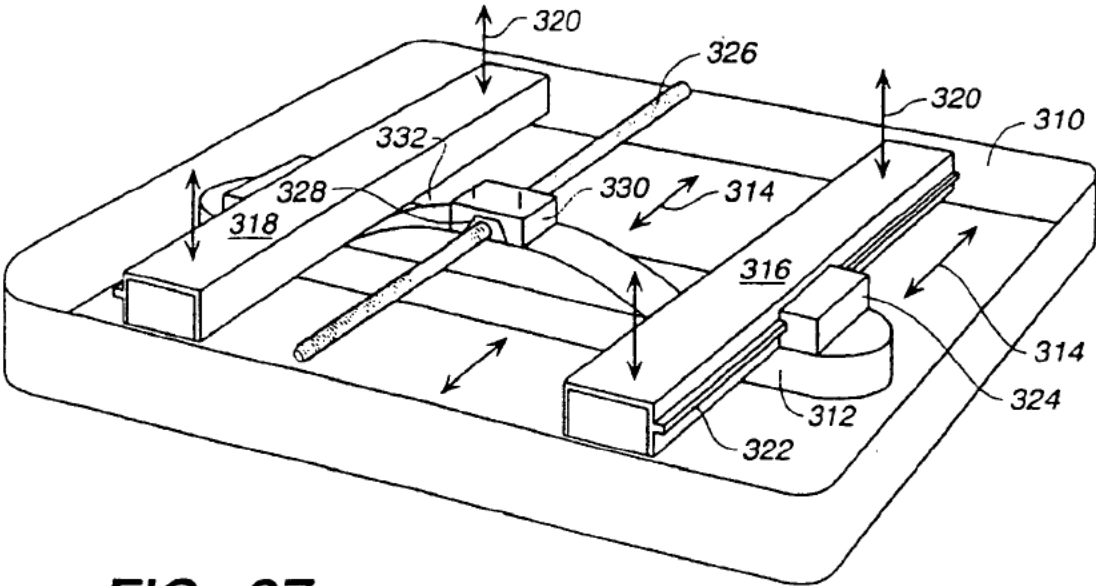


FIG._27

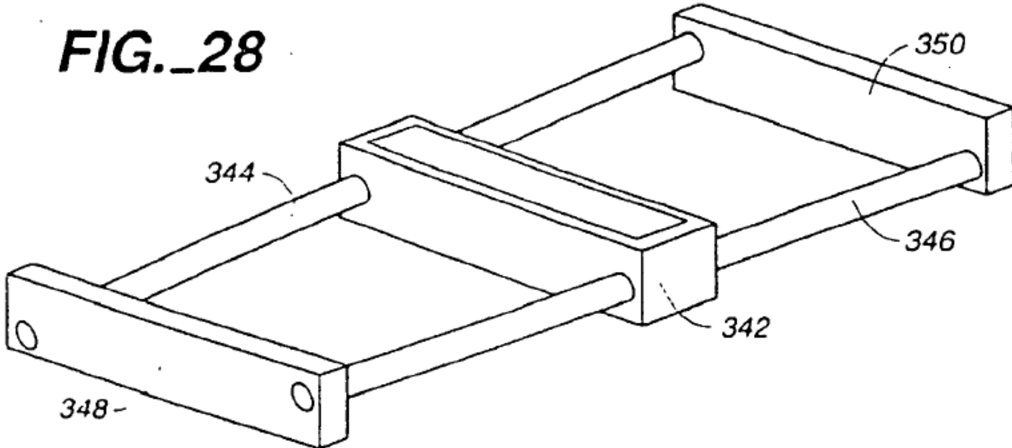


FIG._28

FIG._29

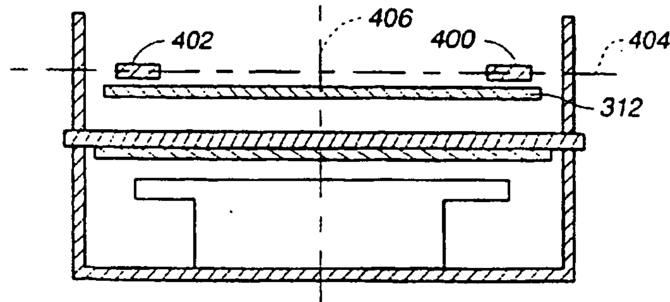


FIG._30

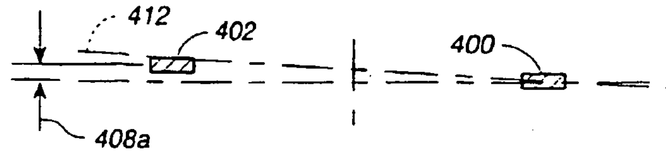


FIG._31

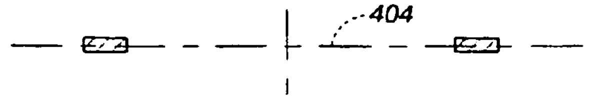


FIG._32

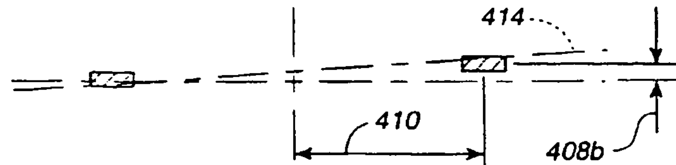
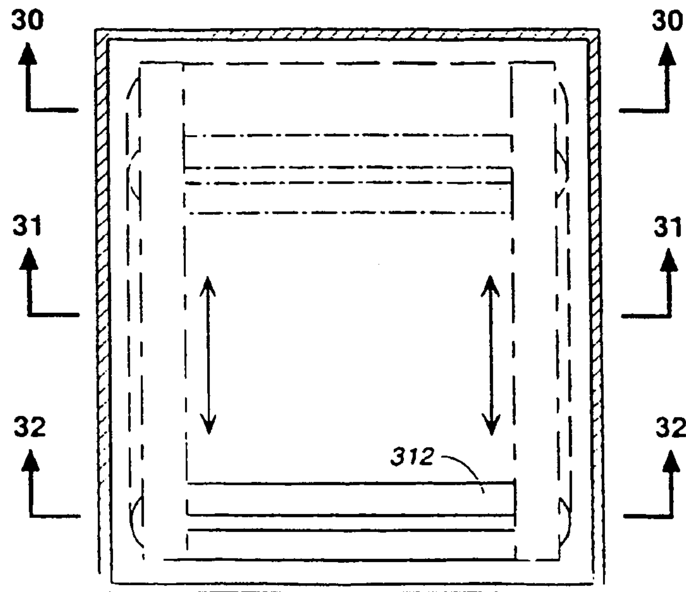


FIG._33



BNSDOCID: <EP___0820088A2_I_>

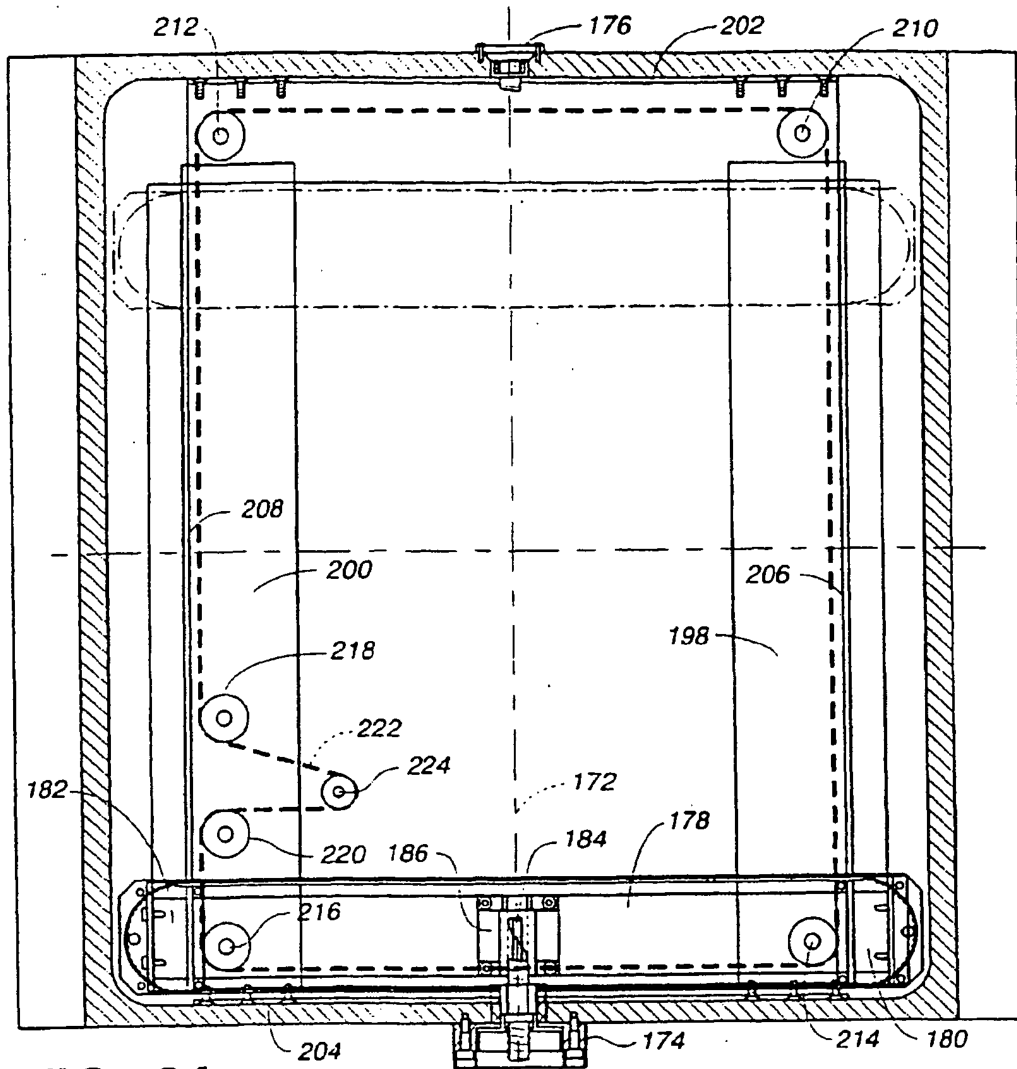


FIG._34

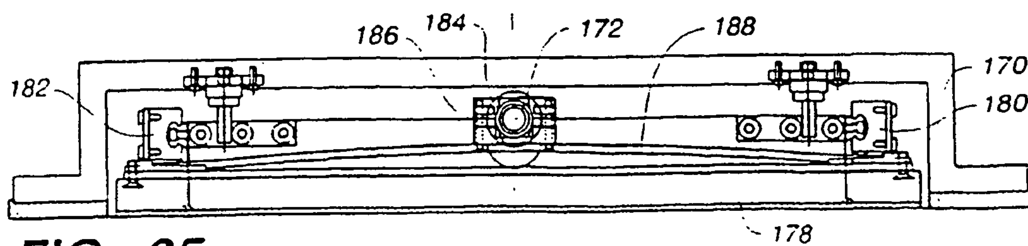


FIG._35

BNSDOCID: <EP___0820088A2_I_>

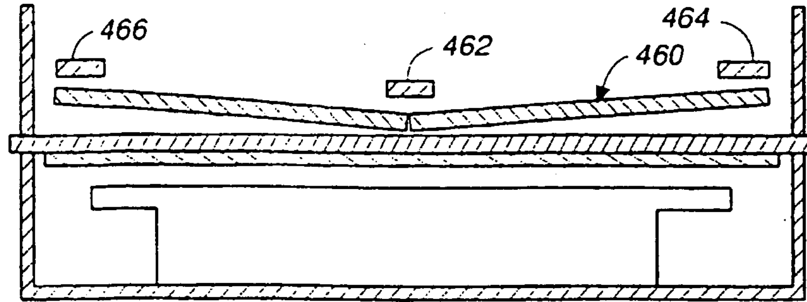


FIG._36

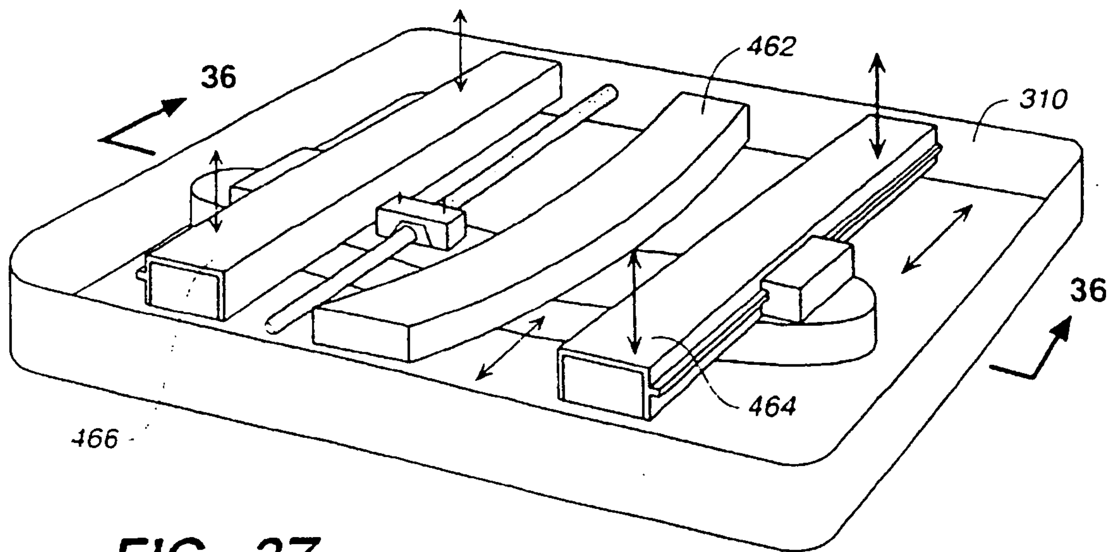


FIG._37

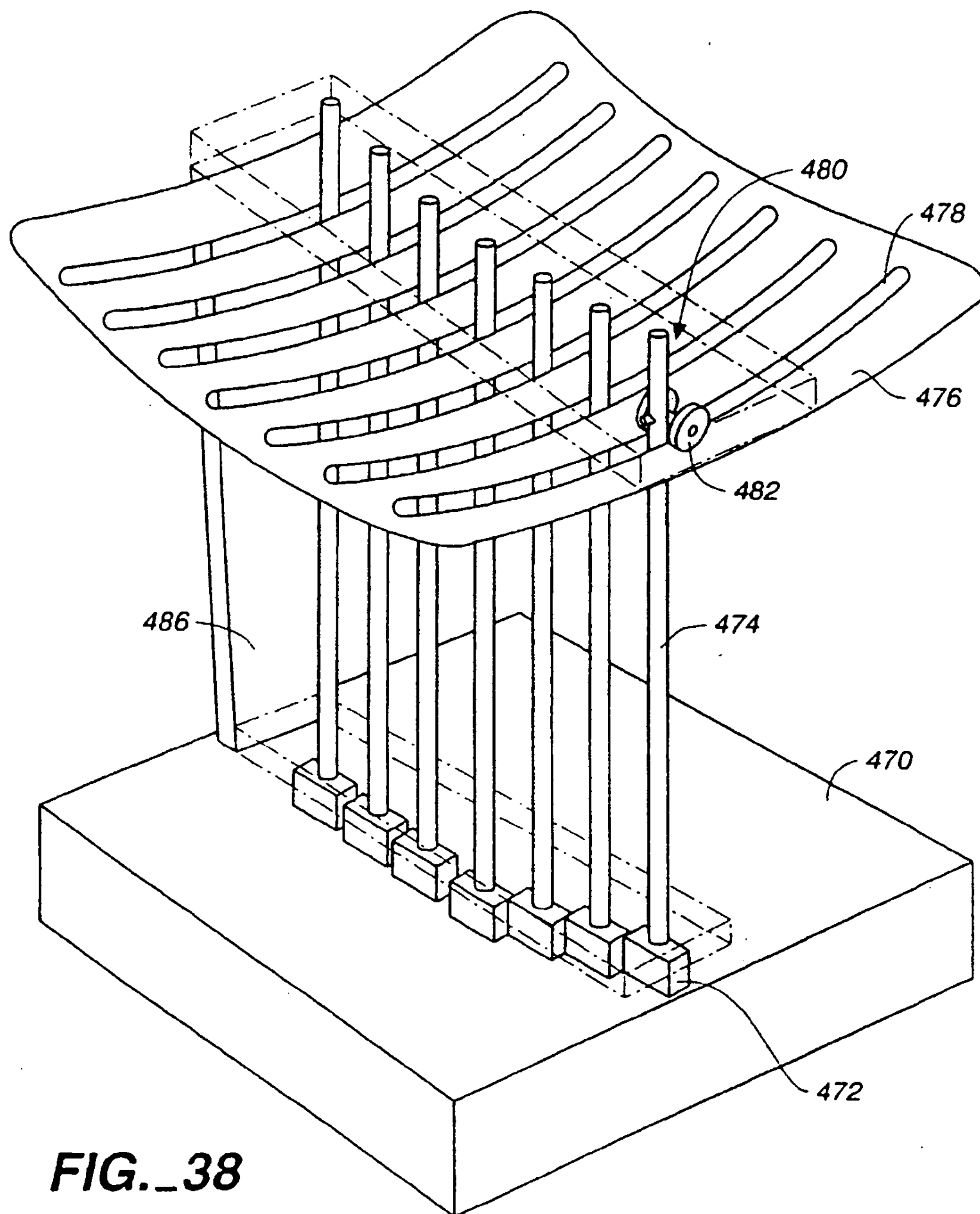


FIG._38

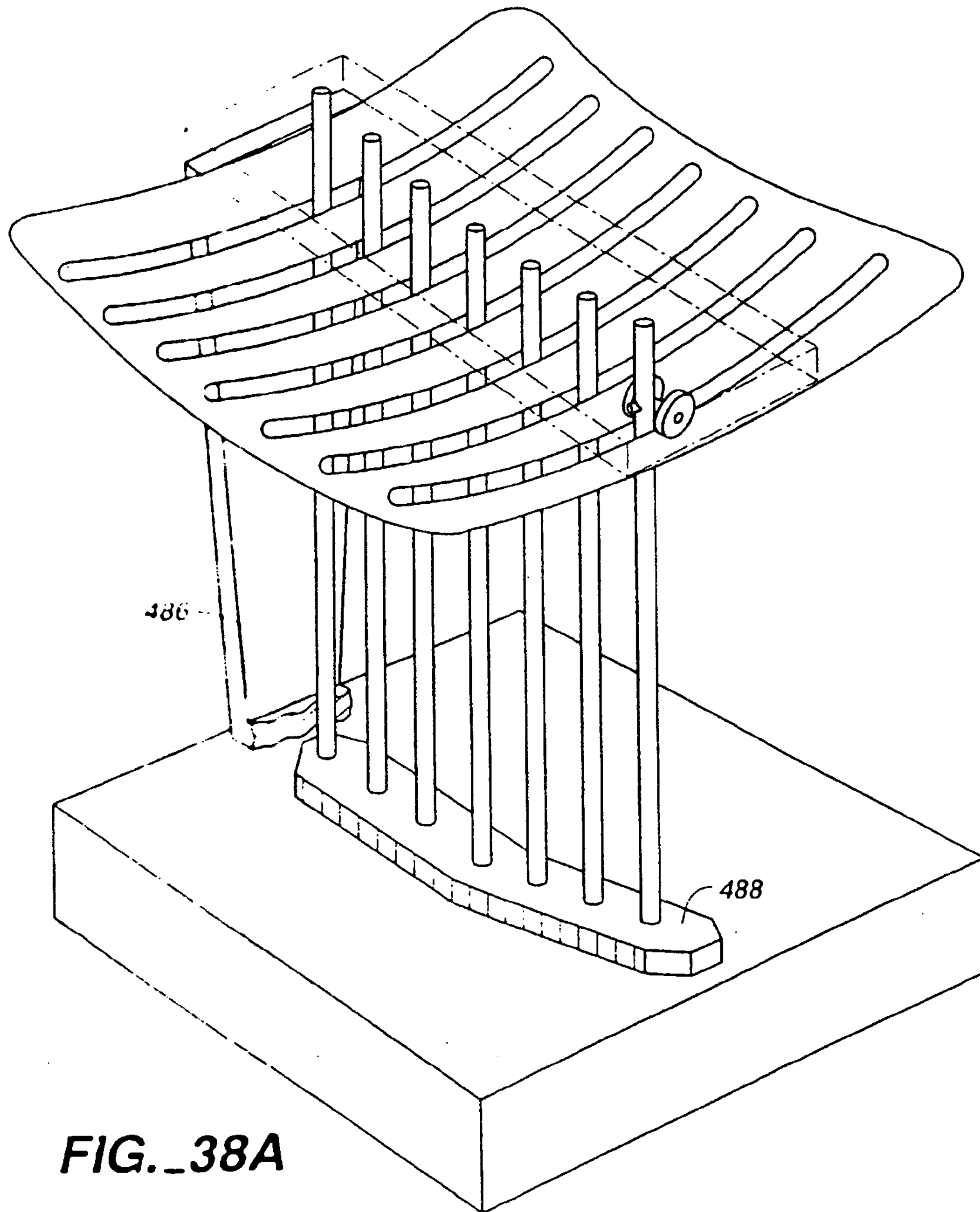


FIG._38A

BNSDOCID: <EP___0820088A2_I_>

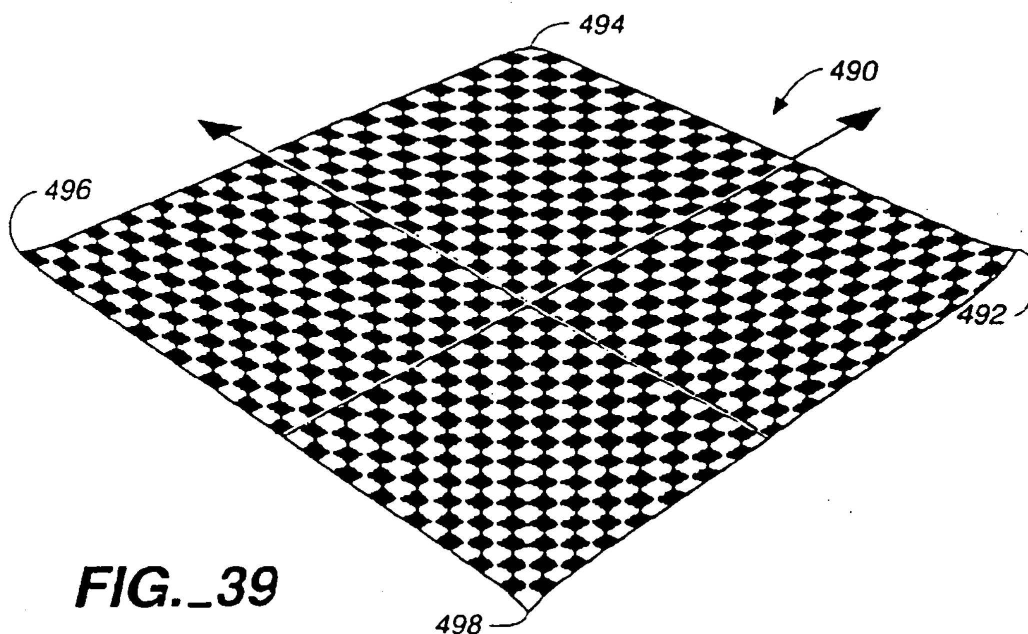


FIG._39

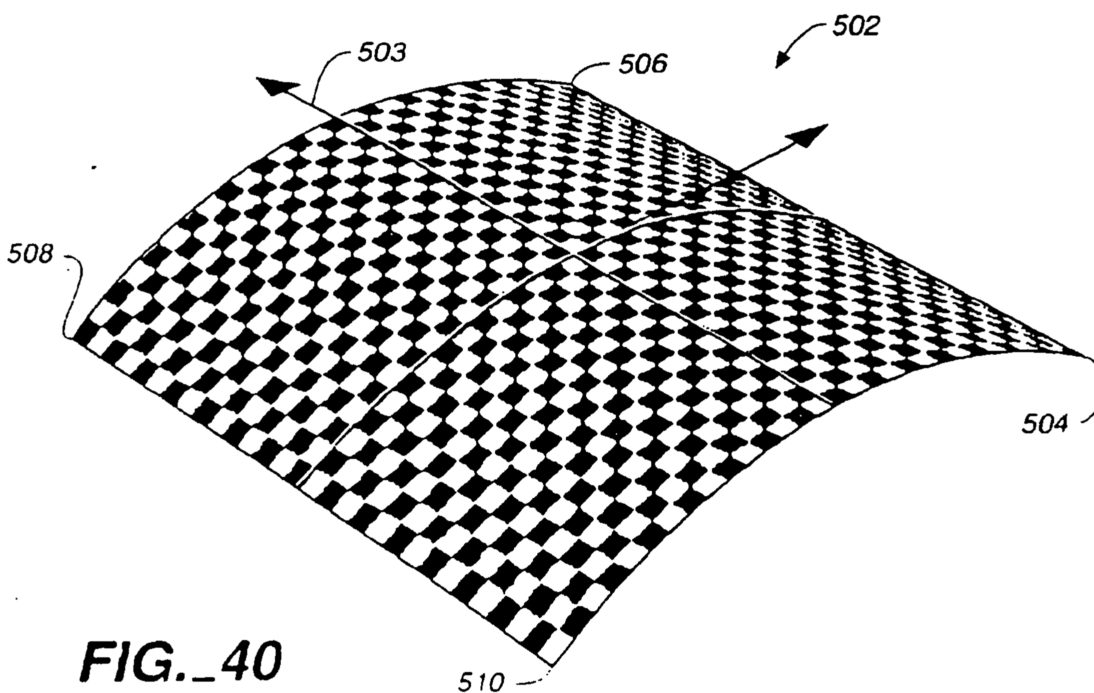


FIG._40

BNSDOCID: <EP___0820088A2_I_>

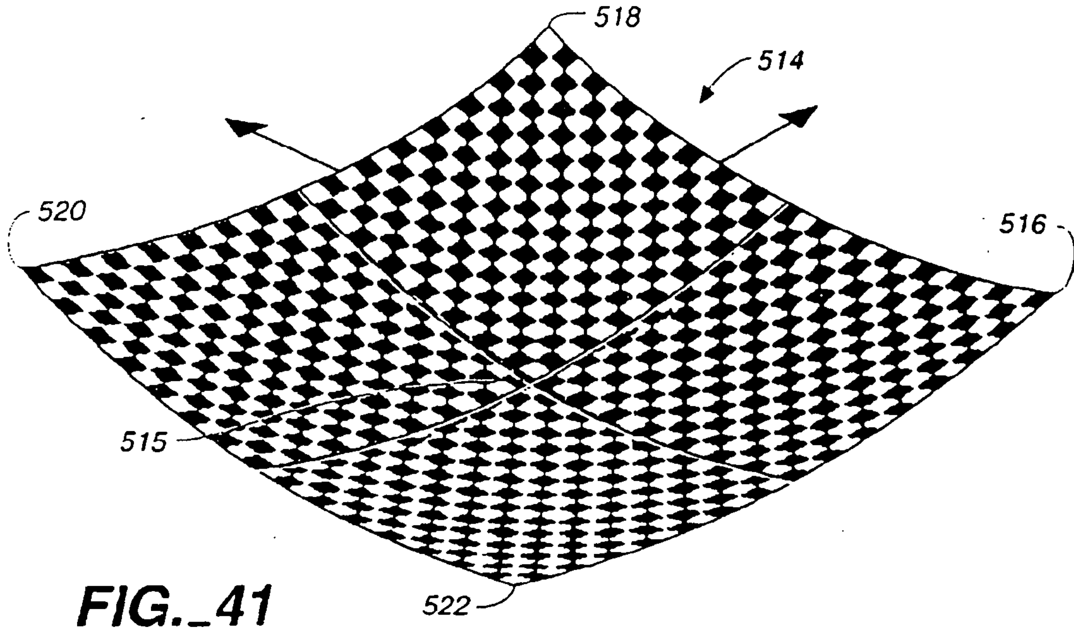


FIG._41

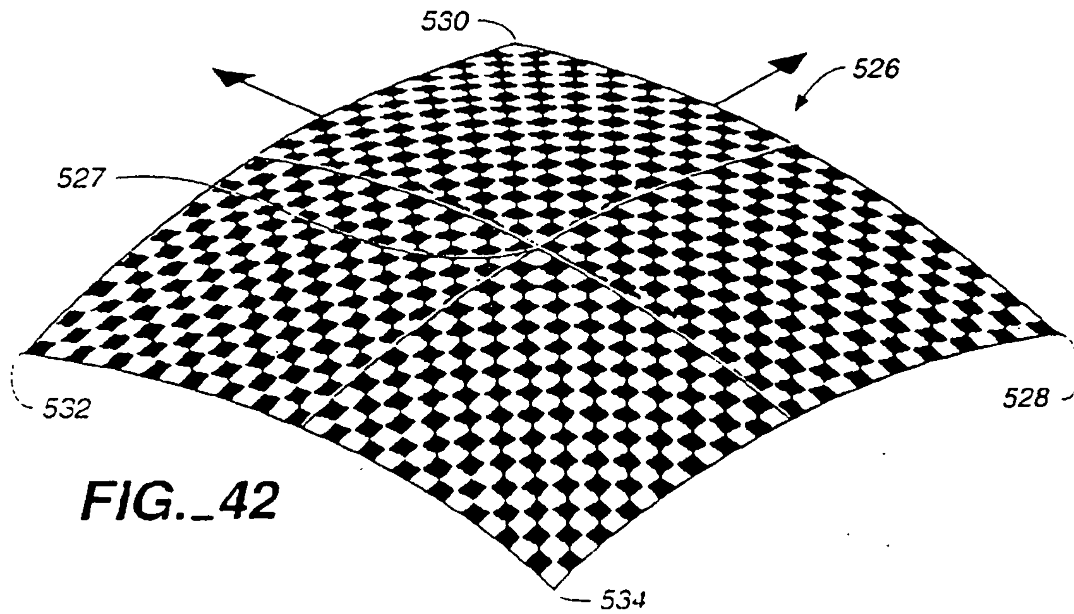


FIG._42

BNSDOCID: <EP___0820088A2_I_>

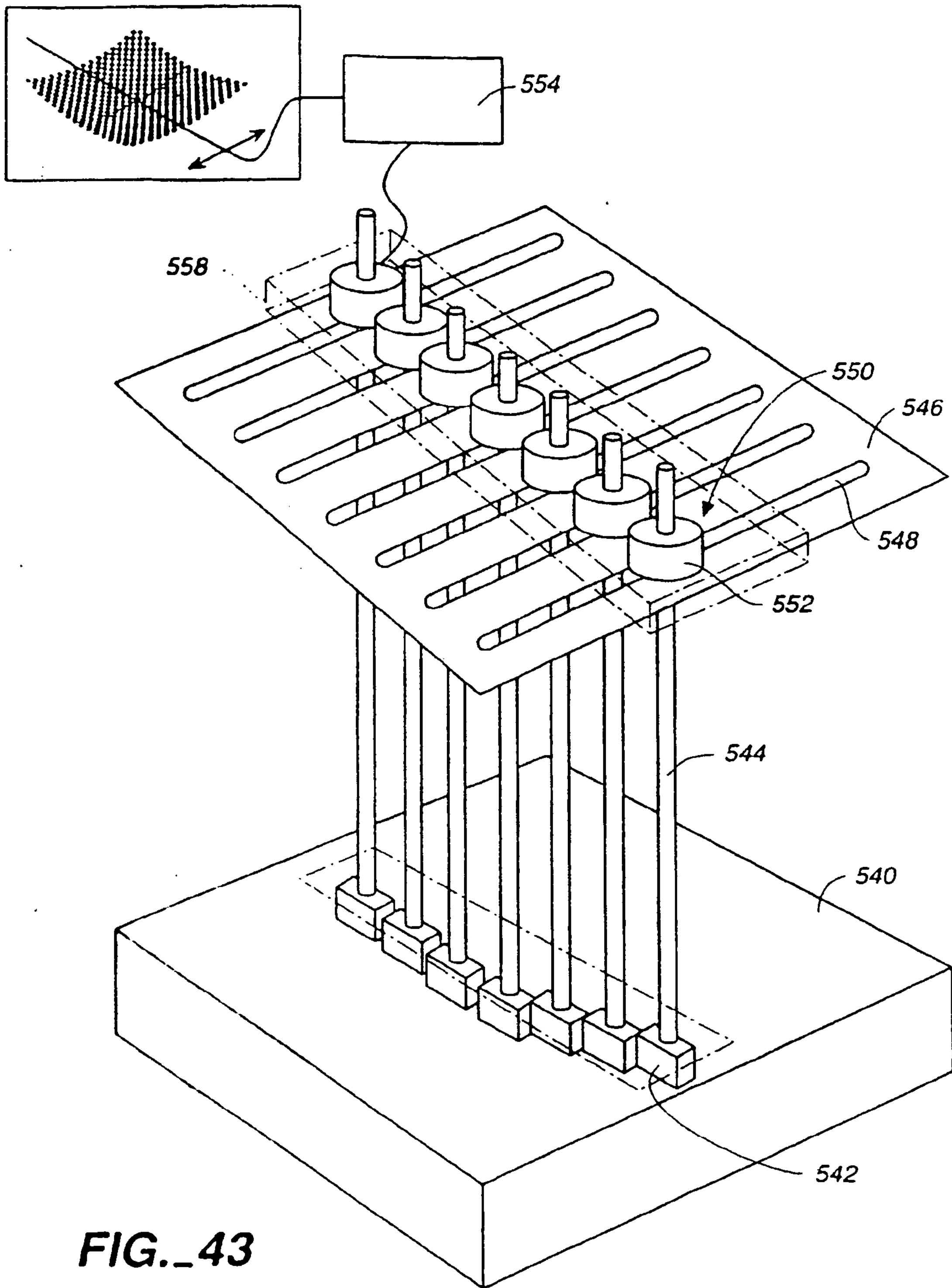


FIG._43

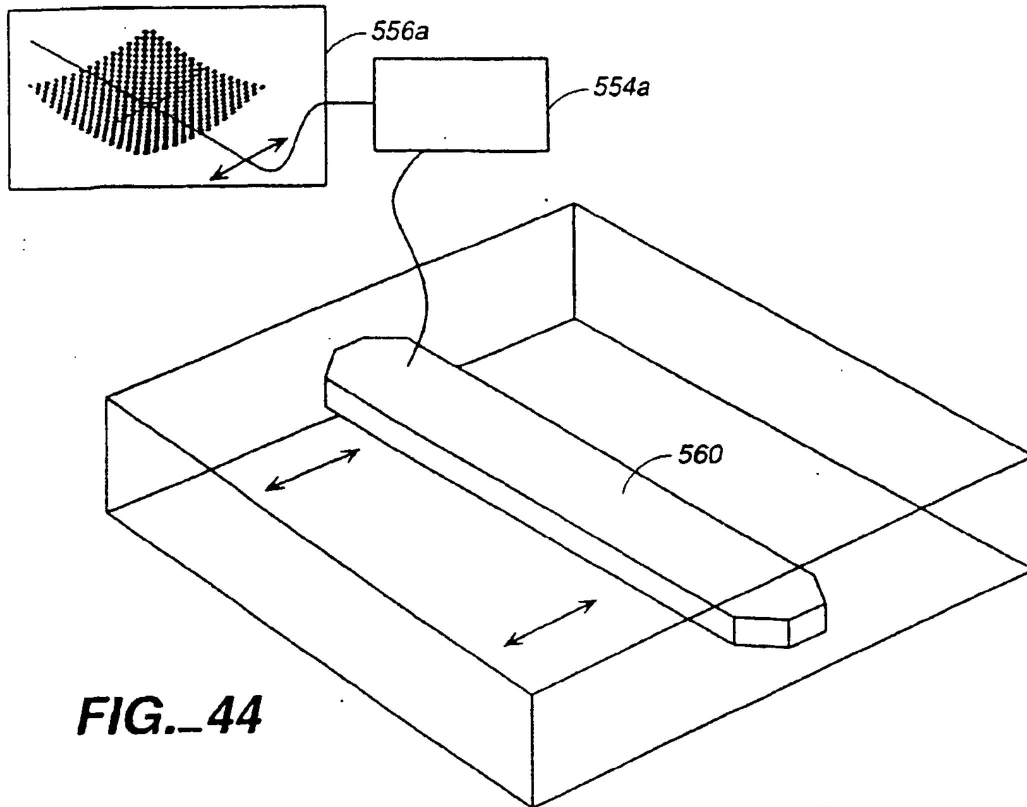


FIG._44

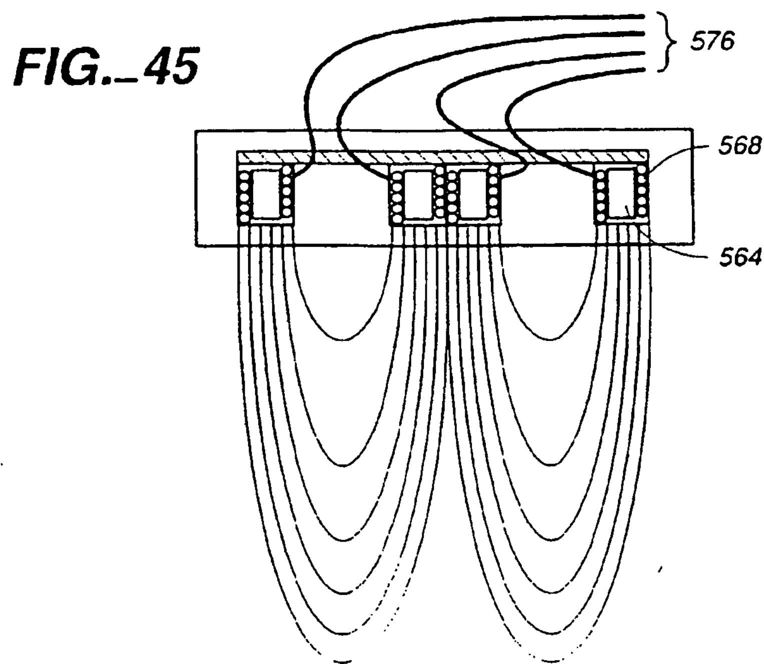
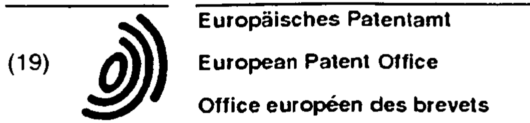


FIG._45

(19) 
Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 820 088 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
25.10.2000 Bulletin 2000/43

(51) Int Cl.7: **H01J 37/34**

(43) Date of publication A2:
21.01.1998 Bulletin 1998/04

(21) Application number: **97305316.8**

(22) Date of filing: **16.07.1997**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **19.07.1996 US 684446**

(71) Applicant: **APPLIED KOMATSU TECHNOLOGY, INC.**
Shinjuku, Tokyo (JP)

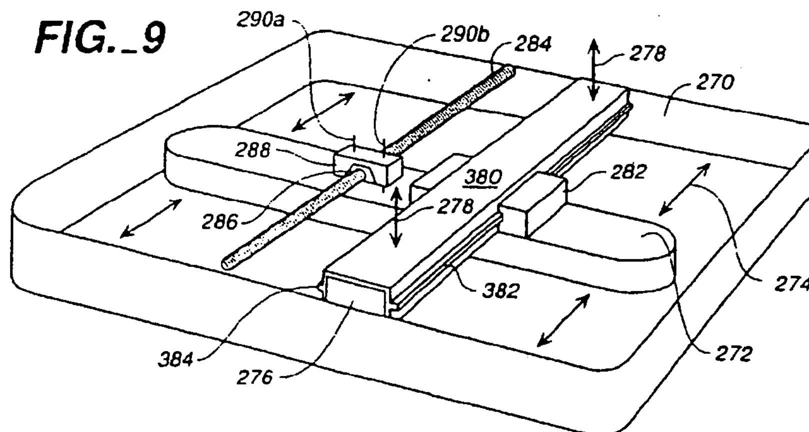
(72) Inventors:
- **Halsey, Harlan L.**
  Woodside, California 94062 (US)
- **Demaray, Richard E.**
  Portola Valley, California 94028 (US)
- **Black, Russell**
  Longmont, Colorado 80501 (US)
- **Hosokawa, Akihiro**
  Cupertino, California 95014 (US)
- **de Salvo, Allan M.**
  Los Gatos, California 95030 (US)
- **Hall, Victoria L.**
  Menlo Park, California 94025 (US)

(74) Representative: **Bayliss, Geoffrey Cyril et al**
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(54) **Non-planar magnet tracking device for magnetron sputtering apparatus**

(57) The structure and method which improves the film thickness uniformity or thickness control when using magnetron sputtering by adjusting the distance between the magnetron (272) or a portion of the magnetron and the sputtering target to provide an improvement in the film thickness uniformity. Shimmed rails (382, 384) contoured rails, contoured surfaces (415, 418), cam plates (422), and cam plate control followers (442) are utilized to achieve an improvement in film thickness uniformity or thickness control due to anomalies in magnetic field as a magnetron assembly (272) moves back and forth when sputtering substrates (utilized primarily for rectangularly shaped substrates).

FIG._9



EP 0 820 088 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 5316

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	US 5 262 030 A (POTTER ROBERT J) 16 November 1993 (1993-11-16) * column 3, line 3 - line 52 * * column 7, line 28 - line 43 *	52 1,2,47	H01J37/34
Y A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 644 (C-1134), 30 November 1993 (1993-11-30) & JP 05 202471 A (FUJITSU LTD;OTHERS: 01), 10 August 1993 (1993-08-10) * abstract; figures 1,2 *	47,51 1,2,29, 39,45	
Y	US 4 600 492 A (OOSHIO HIROSUKE ET AL) 15 July 1986 (1986-07-15) * column 1, line 52 - column 2, line 25 * * figure 1 *	47,51	
A	US 5 079 481 A (MOSLEHI MEHRDAD M) 7 January 1992 (1992-01-07) * column 4, line 23 - line 37 * * column 8, line 33 - line 52 * * column 9, line 61 - column 10, line 9 * * column 19, line 6 - line 13 * * figures 4,5 *	1,2,29, 47,52	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01J
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 09, 31 October 1995 (1995-10-31) & JP 07 166346 A (ULVAC JAPAN LTD), 27 June 1995 (1995-06-27) * abstract; figures 5,7 *	1,2,29, 39,47, 51,52	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 August 2000	Aguilar, M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

BNSDOCID: <EP_ 0820088A3 I >

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 97 30 5316

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

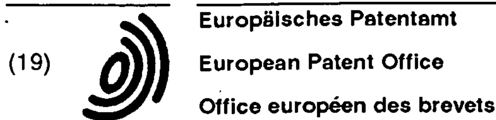
30-08-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5262030 A	16-11-1993	NONE	
JP 05202471 A	10-08-1993	NONE	
US 4600492 A	15-07-1986	JP 61034177 A DE 3580412 D EP 0169532 A	18-02-1986 13-12-1990 29-01-1986
US 5079481 A	07-01-1992	NONE	
JP 07166346 A	27-06-1995	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

BNSDOCID: <EP___0820088A3_I_>

(19) 
Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 867 985 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
14.02.2001 Bulletin 2001/07

(51) Int Cl.7: **H01S 3/06**, C03C 3/17, C03C 4/00

(21) Application number: **97200930.2**

(22) Date of filing: **27.03.1997**

(54) **Erbium-doped planar waveguide**

Erbiumdotierter planarer Wellenleiter

Guide d'onde planaire dopée à l'erbium

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB IT LI NL SE

(43) Date of publication of application:
30.09.1998 Bulletin 1998/40

(73) Proprietor: **NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO**
2628 VK Delft (NL)

(72) Inventors:
- **Yan, Yingchao**
  5600 AN Eindhoven (NL)
- **Faber, Anne Jans**
  5600 AN Eindhoven (NL)

(74) Representative:
Smulders, Theodorus A.H.J., Ir. et al
Vereenigde
Postbus 87930
2508 DH Den Haag (NL)

(56) References cited:
US-A- 5 491 708

- **YINGCHAO YAN ET AL: "Er/sup 3+/ phosphate glass optical waveguide amplifiers at 1.5 mu m on silicon" FUNCTIONAL PHOTONIC AND FIBER DEVICES, SAN JOSE, CA, USA, 30 JAN.-1 FEB. 1996, vol. 2695, ISSN 0277-786X, PROCEEDINGS OF THE SPIE - THE INTERNATIONAL SOCIETY FOR OPTICAL ENGINEERING, 1996, SPIE-INT. SOC. OPT. ENG, USA, pages 144-148, XP002037998**
- **YINGCHAO YAN ET AL: "Luminescence quenching by OH groups in highly Er-doped phosphate glasses" JOURNAL OF NON-CRYSTALLINE SOLIDS, FEB. 1995, NETHERLANDS, vol. 181, no. 3, ISSN 0022-3093, pages 283-290, XP002037999**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 867 985 B1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a planar optical waveguide.

[0002] An optical waveguide is an important component in the field of telecommunication. A special type of optical waveguide is a planar optical waveguide, which can be manufactured as a part of an integrated circuit.

[0003] Nowadays, optical signals are very important for transmitting information. However, when an optical signal is transmitted through an optical fiber, attenuation will always occur to a certain extent, such that it is necessary to amplify the signal after a certain distance (typically in the order of about 50-100 km). Conventionally, for that purpose an electronic amplifier is used. At the amplifier station, the optical signal must then be converted into an electrical signal, which is amplified in an electronic amplifer, after which the amplified electrical signal is converted back into an optical signal. This involves not only the disadvantage that an amplifier station has a rather complicated structure with rather a large number of parts, among which optical/electrical converters and electrical/optical converters, but this also implies that the bandwith and bit-rate of the overall system is limited by the electronical components.

[0004] Therefore, optical fibre amplifiers have recently been developed, i.e. amplifiers which amplify the optical signal directly and do not need a conversion into an electrical signal.

[0005] Similarly, integrated planar waveguide amplifiers are of necessity in order to realize all-optical telecommunication. For example, a planar waveguide amplifier can be integrated with a passive splitter as loss-compensating components. Due to their small sizes, planar optical waveguide amplifiers are expected to be of low cost, and more importantly, they offer the promise of integrating passive and active functions on the same substrate.

[0006] Materials for planar optical waveguides can be divided into different categories, among which:

(1) crystalline materials ($LiNbO_3$, Al_2O_3, Y_2O_3, etc.)
(2) glassy materials, such as silicate-glass (based on SiO_2), phosphate-glass (based on P_2O_5), etc.

[0007] The present invention relates to an optical waveguide material of this last-mentioned category, more specifically, phosphate-glass.

[0008] An optical waveguide material of this category is described in US patent 5.491.708. This publication describes a substrate having the following composition:

P_2O_5	50 - 70 mol%
Al_2O_3	4 - 13 mol%
Na_2O	10 - 35 mol%
La_2O_3	0 - 6 mol%
R_2O_3	>0 - 6 mol%

wherein R is a lanthanide.

[0009] The lanthanide used in such composition can be considered as "active" component, as will be explained later. Generally speaking, in view of the fact that a planar waveguide device has a rather short length in the order of a few centimeters, the concentration of the lanthanide needs to be relatively high, and the pump power density needs to be relatively high for obtaining a sufficient optical amplifcation gain. Although it is technically possible to manufacture a waveguide material with a relatively high concentration of the lanthanide, the luminescence will be quenched by energy transfer processes due to ion-ion interactions. Furthermore, another cooperative upconversion quenching process dominates the amplification process of the devices when a high pump power is applied. These two luminescence quenching processes strongly influence the amplifier efficiency of planar waveguides amplifiers.

[0010] In the publication "Fabrication of Er Doped Glass Films as used in Planar Optical Waveguides" by Gates cs in Mat. Res. Soc. Symp. Proc. Vol. 392, 1995, an Er-doped soda-lime silicate glass film on silicon is described. In a specific experiment, represented in figure 10 of said publication, a 4.5 cm long waveguide containing 5.5 wt% Er_2O_3 was found to achieve about 4.2 dB/cm gain. However, in order to achieve result, this prior art waveguide needs a pump power in excess of 350 mW.

[0011] It is a particular purpose of the invention to provide an improved planar optical waveguide which can function as an optical amplifier.

[0012] It is a more particular purpose of the invention to provide an improved planar optical waveguide which can function as an optical amplifier for optical signals having wavelengths in the range of about 1.53 μm.

[0013] Especially, the present invention seeks to provide a material for an optical waveguide which has a good efficiency and which shows a relatively high amplification with relatively low pump power.

[0014] The invention is defined by claim 1. Various embodiments are defined by the dependent claims.

[0015] Hereinafter, the invention will be explained in more detail with reference to the drawing, in which:

Figure 1 schematically shows a cross-section of a planar optical waveguide device;
Figure 2 schematically shows an energy diagram for Er;
Figure 3 shows a schematic illustration of an amplification process;
and figure 4 schematically illustrates a co-operative upconversion process.

5

[0016] Figure 1 schematically shows a cross-section of a planar optical waveguide device, generally indicated at 10. The planar optical waveguide device 10 comprises a substrate 11, a buffer layer 12 arranged on a surface 9 of the substrate 11, an active guiding layer 13 arranged on the buffer layer 12, and a top cladding layer 14 arranged on the active guiding layer 13. The active guiding layer 13, which can for instance have a thickness of about 1 μm, functions
10
as the actual guide for light beams in a direction parallel to said surface 9.

[0017] The light beam can not escape from the active guiding layer 13 in the direction perpendicular to said surface 9, also indicated as the transverse direction, because the refractive indices of the buffer layer 12 and the top cladding layer 14 are lower than the refractive index of the active guiding layer 13. In an effective embodiment, the buffer layer 12 consists of SiO_2, which can be arranged on the substrate 11 by thermally oxidising the substrate 11, as is known
15
per se; the buffer layer 12 can for instance have a thickness of about 6.5 μm. Similarly, the top cladding layer 14 can consist of SiO_2, which can be arranged on the active guiding layer 13 by sputtering, as is known per se; the top cladding layer 14 can for instance have a thickness of about 0.5 μm.

[0018] Further, within the active guiding layer 13 the light beam can only be transported in one direction parallel to said surface 9, indicated here as the guiding direction. The direction parallel to said surface 9 but perpendicular to said
20
guiding direction will be indicated here as lateral direction. The light is confined in the lateral direction by a suitable shaping of either the active guiding layer 13 or the top cladding layer 14 such that a suitable refractive index profile is obtained in the lateral direction, as is known per se and not shown in figure 1.

[0019] The active guiding layer 13 has to satisfy several requirements in order for the guiding layer to be suitable in an optical waveguide, in an optical amplifier, or in a laser. The active guiding layer 13 should have a relatively high
25
refractive index and a low optical attenuation, preferably <1dB/cm at the applied wavelengths. Further, the active guiding layer 13 should have efficient optical amplification properties, for instance characterised by the luminescence efficiency of the active ions, like Er-ions. A very important feature of the active guiding layer 13 is the optical gain at a specific wavelength (region), expressed in dB/cm: it is a specific objective of the invention to obtain a relatively high gain with a relative low pump power. More specifically, it is an objective of the invention to provide an active guiding
30
layer 13 which offers a gain of >4 dB/cm at a relatively low pump power (preferably less than 50 mW) for the wavelength of about 1.53 μm.

[0020] According to an important feature of the invention, the active guiding layer 13 is manufactured as a phosphate glass having the following composition:

35

Al_2O_3	8 - 20 mol%	
Na_20	5 - 18 mol%	
La_2O_3	6 - 35 mol%,	preferably 10 - 30 mol%
R_2O_3	>0 - 6 mol%,	preferably 0.5 - 1.5 mol%
P_2O_5	balance	

40

[0021] Herein, R represents Erbium (Er), Neodymium (Nd), or Ytterbium (Yb), or a combination of Er + Yb, depending on the wavelength of the optical waves which are to be guided and amplified. For applications where the optical wavelength is about 1.53 μm, R represents Er.
45
[0022] For applying the active guiding layer 13 onto the buffer layer 12, several techniques can be used. A method which is particularly suitable, and which is used in the present invention, is RF sputtering. This technique is known per se, for which reason it will be discussed here only briefly. In a vacuum chamber, a target having a suitable composition with regard to the desired composition of the active guiding layer to be deposited, is arranged opposite a substrate. In the vacuum chamber, argon and oxygen are introduced, such that the pressure in the vacuum chamber is in the range
50
of about 0.3 to 5 Pa. RF power is applied to the target. The target is hit by argon atoms, such that atoms and/or molecules of the target are emitted from the target and deposited on the substrate. This process is continued until the deposited layer has sufficient thickness.

[0023] It will be clear to a person skilled in the art, that other techniques can be used for applying the active guiding layer 13 onto the substrate, and that the invention is not restricted to the technique described above.
55
[0024] The present invention relates particularly to an optical waveguide device having an active guiding layer which comprises Erbium as active component. Therefore, in the following a description will be given of an optical amplification mechanism based on Erbium.

[0025] Erbium is a well-known rare-earth metal. The electronic structure of Er^{3+} is $[Xe]4f^{11}$, of which the partially

filled 4f shell is electronically shielded by the outlying filled $5s^25p^6$ shells from the Xe configuration. Figure 2 shows schematically the energy diagram for the 4f electrons of a free Er^{3+} ion (left hand side) and of an Er^{3+} ion is a solid (right hand side). The various levels arise from spin-spin interactions and spin-orbit interactions. The energy levels are labeled as $^{2S+1}L_J$, wherein S represents the spin, L represents the orbit, and J represents the total angular momentum.

5 **[0026]** In the free Er^{3+} ion, the 4f transitions are parity forbidden. In a solid such as a glass, however, the presence of surrounding atoms weakly perturbs the 4f states. The electric dipole transitions become allowed due to admixing of states of opposite parity from higher configuration into the 4f configuration. Due to the Stark-effect, the degenerate levels split into manifolds (see the right hand side of figure 2). In addition to this host-dependent forced electric dipole contribution, the $^4I_{13/2}$ - $^4I_{15/2}$ transition of Erbium at 1.53 μm has considerable magnetic dipole strength which is rel-
10 atively insensitive to the host material. The spontaneous emission lifetime of the $^4I_{13/2}$ - $^4I_{15/2}$ transition of Erbium at 1.53 μm in a solid can be as long as about 10 ms.

[0027] Figure 3 shows a schematic illustration of the amplification process for the three-level system of Er^{3+}, involving the states $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$.

[0028] By absorbing pump energy, Er^{3+} ions can be excited to a state lying above the $4I_{13/2}$ state, such as the $4I_{11/2}$
15 state exemplified in figure 3. From this excited state, Er^{3+} ions quickly decay to the metastable $4I_{13/2}$ manifold via non-radiative relaxation. Stimulated emission from the $4I_{13/2}$ state to the ground $4I_{15/2}$ state can cause amplification of light at 1.53 μm. The light amplification due to electronic transitions of Er^{3+} works in a three-level lasing scheme. Light amplification in a three-level system can occur only when more than half of the population is excited to the upper lasing level (i.e. the $4I_{13/2}$ level for Er^{3+}).

20 **[0029]** The principles of Er-doped optical amplifiers are the same for fiber waveguides and planar waveguides. However, in view of the required high Er doping levels in planar waveguide devices, planar waveguide devices are less efficient than fiber waveguide devices. The efficiency of the Er-doped waveguide amplifiers is influenced by two quenching processes, which are both related to the high Er doping levels, as will be discussed hereunder.

[0030] The first quenching process is concentration quenching. With increasing concentration of Er in the waveguide,
25 the probability increases that an excited Er^{3+} ion transfers its energy to a neighboring Er^{3+} ion in the ground state via ion-ion interaction. Such process may be repeated until the energy is transferred to an Er^{3+} ion correlated with a defect or an impurity ion, and the energy may be lost via non-radiative decay.

[0031] The second quenching process, which is believed to be the dominant process causing the inefficiency of prior Er-doped waveguide devices, is a co-operative upconversion process, which is also due to ion-ion interactions. This
30 process, which plays a role especially when the population inversion is high, is illustrated in figure 4. With increasing concentration of Er in the waveguide, the probability increases that an excited Er^{3+} ion transfers its energy to a neighboring excited Er^{3+} ion. Then, the first Er^{3+} ion may decay non-radiatively to the ground $^4I_{15/2}$ state, while the second Er^{3+} ion is excited to a higher lying state $^4I_{9/2}$. This second Er^{3+} ion then has a high probability to decay to the $^4I_{13/2}$ state via non-radiative relaxation. The net result of this upconversion process is that the population in the upper lasing
35 state of $^4I_{13/2}$ is strongly reduced and the efficiency of light amplification at 1.53 μm by stimulated emission is strongly decreased.

[0032] The upconversion quenching process is a property which is related to the host material, i.e. the waveguide material into which the Er ions are embedded, since it is caused by the ion-ion interactions of Er^{3+} ions in the host.

[0033] Therefore, an important feature of the present invention is the composition of the host material.

40

EXAMPLE

[0034] An optical waveguide device was manufactured in accordance with figure 1. As basis material, a standard silicon substrate was used, in the shape of a circular disk having a diameter of about 7,5 cm. By way of a standard
45 thermal oxidisation process, a buffer layer 12 having a thickness of about 6.5 μm was applied on the substrate.

[0035] A suitable glass target was prepared by mixing and melting Al_2O_3, Na_20, La_2O_3, P_2O_5, and Er_2O_3, in a suitable proportion. This target was positioned opposite said oxidised substrate in a standard sputtering chamber, and by way of a standard low-pressure magnetron RF sputtering process as briefly discussed above, an active guiding layer 13 having a composition (determined by X-ray photoelectron spectroscopy) as specified hereunder in Table 1 was applied
50 on the buffer layer 12.

TABLE 1

P_2O_5	42-45 mol%
Al_2O_3	16-18 mol%
Na_2O	8.5-11 mol%
La_2O_3	27-28 mol%
Er_2O_3	0.9-1.2 mol%

55

[0036] The process was continued for about 4 hours. The thickness of the active guiding layer 13 was measured, and appeared to be about 1 μm.

[0037] By way of a standard sputtering process, a top cladding layer 14 of SiO_2 was applied over said structure, the top cladding layer 14 having a thickness of about 0.5 μm.

5 **[0038]** Then, by way of standard photolithography and etching processes, most part of the layer 14 was removed to form stratified line strips of 4 μm wide, providing lateral confinement of the guided light in the active layer 13.

[0039] Finally, the active guiding layer 13 was made into a structure having a length of 10 mm by cleaving the silicon substrate.

[0040] This planar waveguide device was tested for its optical properties. It appeared that the active guiding layer 10 13 had a refractive index of about 1.56 at 633 nm; with such a high refractive index, a high light confinement can be obtained in the waveguide, which leads to a high density of the pump power. For a wavelength of 1.53 μm, an optical confinement of about 70 % was obtained.

[0041] The optical amplification for light having a wavelength of 1.53 μm was measured, wherein pump light having a wavelength of 980 nm was applied to the planar waveguide device. For this experimental planar waveguide device 15 having a length of 10 mm, a net optical gain of 4.1 dB was measured with a pump power of about 65 mW. This pump power is already very low. It is noted, however, that in this experiment the coupling efficiency of the pump light into the active guiding layer 13 appeared to be about 30%, so that the amount of pump light which actually entered the active guiding layer 13 was about 20 mW. In this experiment, no effort was taken to improve the coupling efficiency, but it will be evident for a skilled person that improvement of the coupling efficiency to about 80% or more is possible. Therefore, 20 it is reasonable to expect that an optical waveguide device with a length of 4 cm, having the structure as described, wherein the active guiding layer 13 has the composition as described, will yield an optical gain of 15 dB or more with a launched pump power of 40 mW or less.

[0042] From the experimental data, it was calculated that the upconversion coefficient (as defined and used in the publication "Cooperative upconversion in Erbium implanted sodalime silicate glass optical waveguides" by E. Snoeks 25 et al in J.Opt.Soc.Am.B., 12, 1468 (1995)) of the active guiding layer 13 had a value of about $2.6 \cdot 10^{-18}$ cm^3/s. This value is one of the lowest values reported to date.

[0043] Further, it was found that in the active guiding layer, the luminescence lifetime of Er was about 7.2 ms.

[0044] It will be clear to a person skilled in the art that the invention is not limited to the above-described examples but that variations and modifications will be possible without going beyond the scope of the invention as described in 30 the claims. For instance, although in the examples the active guiding layer 13 is manufactured by way of an RF sputtering process, as an alternative other processes may be used for manufacturing the active guiding layer.

[0045] Further, in practice, it may happen that the material of the active guiding layer 13 comprises impurities such as for instance Mg, Ca, Cr, Ba, Zn, Pb, Li, K. Although small amounts of such impurities can be permitted, according to the invention it is preferred that the amounts of such impurities are as low as possible, preferably zero, such that 35 the active guiding layer 13 is composed substantially only of P_2O_5, Al_2O_3, Na_2O, La_2O_3 and Er_2O_3.

[0046] Further, according to an important feature of the invention, the optical device may be provided with at least one element for achieving optical feedback, for instance a mirror or other reflective element, such that the device can function as a laser.

40

Claims

1. A planar optical waveguide device, comprising:

45
 a substrate (11);
 an active guiding layer (13) arranged on the substrate (11);
 a bottom layer (12) arranged between the active guiding layer (13) and the substrate (11);
 a top cladding layer (14) arranged over the active guiding layer (13);

50 wherein the active guiding layer (13) has the following composition:

Al_2O_3	8 - 20 mol%	
Na_20	5 - 18 mol%	
La_2O_3	6 - 35 mol%,	preferably 10 - 30 mol%
R_2O_3	>0 - 6 mol%,	preferably 0.5 - 1.5 mol%
P_2O_5	balance	

55

wherein, R represents Erbium (Er), Neodymium (Nd), or Ytterbium (Yb), or a combination of Er + Yb.

2. A planar optical waveguide device according to claim 1, wherein the active guiding layer (13) has the following composition:

5

P_2O_5	42-45 mol%
Al_2O_3	16-18 mol%
Na_20	8.5-11 mol%
La_2O,	27-28 mol%
Er_2O_3	0.9-1.2 mol%

10

3. A planar optical waveguide device according to any of claims 1-2, wherein the optical waveguide device is an optical amplifier.

15

4. A planar optical waveguide device according to any of claims 1-3, wherein the substrate (11) is made of Si, wherein the bottom layer (12) is made of SiO_2, and wherein the top cladding layer (14) is made of SiO_2.

5. A planar optical waveguide device according to any of the claims 1-4, wherein the amplification gain for wavelengths of light which results by transition of Er^{3+} ions from the $^4I_{13/2}$ state to the $^4I_{15/2}$ state is at least 4.1 dB/cm with a pump power of no more than 65 mW, and wherein the active guiding layer (13) has a refractive index of 1.54 - 1.65 at 632.8 nm.

20

6. An optical device according to any of claims 1, 2, 4, further comprising at least one optical feedback element, e. q. a coating mirror, such that the device can function as a laser.

25

Patentansprüche

30

1. Planares Lichtwellenleiterbauteil, umfassend:

ein Substrat (11);
eine aktive Leitschicht (13), die auf dem Substrat (11) angeordnet ist;
eine untere Schicht (12), die zwischen der aktiven Leitschicht (13) und dem Substrat (11) angeordnet ist;
eine obere Mantelschicht (14), die über der aktiven Leitschicht (13) angeordnet ist;

35

wobei die aktive Leitschicht (13) die folgende Zusammensetzung hat:

Al_2O_3	8 - 20 Mol-%
Na_2O	5 - 18 Mol-%
La_2O_3	6 - 35 Mol-%, vorzugsweise 10 - 30 Mol-%
R_2O_3	>0- 6 Mol-%, vorzugsweise 0,5 - 1,5 Mol-%
P_2O_5	Rest,

40

45

wobei R Erbium (Er), Neodym (Nd) oder Ytterbium (Yb) oder eine Kombination von Er + Yb bedeutet.

2. Planares Lichtwellenleiterbauteil gemäß Anspruch 1, wobei die aktive Leitschicht (13) die folgende Zusammensetzung hat:

50

P_2O_5	42 - 45 Mol-%
Al_2O_3	16 - 18 Mol-%
Na_2O	8,5 - 11 Mol-%
La_2O_3	27 - 28 Mol-%
Er_2O_3	0,9 - 1,2 Mol-%.

55

3. Planares Lichtwellenleiterbauteil gemäß einem der Ansprüche 1-2, wobei das Lichtwellenleiterbauteil ein optischer

Verstärker ist.

4. Planares Lichtwellenleiterbauteil gemäß einem der Ansprüche 1-3, wobei das Substrat (11) aus Si besteht, wobei die untere Schicht (12) aus SiO_2 besteht und wobei die obere Mantelschicht (14) aus SiO_2 besteht.

5. Planares Lichtwellenleiterbauteil gemäß einem der Ansprüche 1-4, wobei die Verstärkung für Lichtwellenlängen, die sich durch Übergang von Er^{3+}-Ionen vom $^4I_{13/2}$-Zustand zum $^4I_{15/2}$-Zustand ergibt, wenigstens 4,1 dB/cm mit einer Pumpleistung von nicht mehr als 65 mW beträgt und wobei die aktive Leitschicht (13) einen Brechungsindex von 1,54-1,65 bei 632,8 nm hat.

6. Optisches Bauteil gemäß einem der Ansprüche 1, 2, 4, das weiterhin wenigstens ein optisches Rückkopplungselement, z.B. einen Beschichtungsspiegel, umfasst, so dass das Bauteil als Laser fungieren kann.

Revendications

1. Dispositif à guide d'onde optique plan, comprenant : un substrat (11),

   une couche active de guidage (13) disposée sur le substrat (11),
   une couche inférieure (12) placée entre la couche active de guidage (13) et le substrat (11), et
   une couche supérieure de revêtement (14) disposée sur la couche active de guidage (13),

   dans lequel la couche active de guidage (13) a la composition suivante :

Al_2O_3	8 à 20 mol %
Na_2O	5 à 18 mol %
La_2O_3	6 à 35 mol %, de préférence 10 à 30 mol %
R_2O_3	> 0 à 6 mol %, de préférence 0,5 à 1,5 mol %
P_2O_5	le reste

   dans laquelle R représente l'erbium (Er), le néodyme (Nd) ou le l'ytterbium (Yb) ou une combinaison Er + Yb.

2. Dispositif à guide d'onde optique plan selon la revendication 1, dans lequel la couche active de guidage (13) a la composition suivante :

P_2O_5	42 à 45 mol %
Al_2O_3	16 à 18 mol %
Na_2O	8,5 à 11 mol %
La_2O_3	27 à 28 mol %
Er_2O_3	0,9 à 1,2 mol %

3. Dispositif à guide d'onde optique plan selon l'une des revendications 1 et 2, dans lequel le dispositif à guide d'onde d'onde optique est un amplificateur optique.

4. Dispositif à guide d'onde optique plan selon les revendications 1 à 3, dans lequel le substrat (11) est formé de Si, la couche inférieure (12) est formée de SiO_2, et la couche supérieure de revêtement (14) est formée de SiO_2.

5. Dispositif à guide d'onde optique plan selon l'une quelconque des revendications 1 à 4, dans lequel le gain d'amplification pour les longueurs d'onde de la lumière qui proviennent de la transition des ions Er^{3+} de l'état $^4I_{13/2}$ à l'état $^4I_{15/2}$ est d'au moins 4,1 dB/cm avec une puissance de pompage ne dépassant pas 65 mW, et la couche active de guidage (13) a un indice de réfraction compris entre 1,54 et 1,65 à 632,8 nm.

6. Dispositif optique selon l'une quelconque des revendications 1, 2 et 4, comprenant en outre au moins un élément optique de réaction, tel qu'un miroir possédant un revêtement, si bien que le dispositif peut jouer le rôle d'un laser.

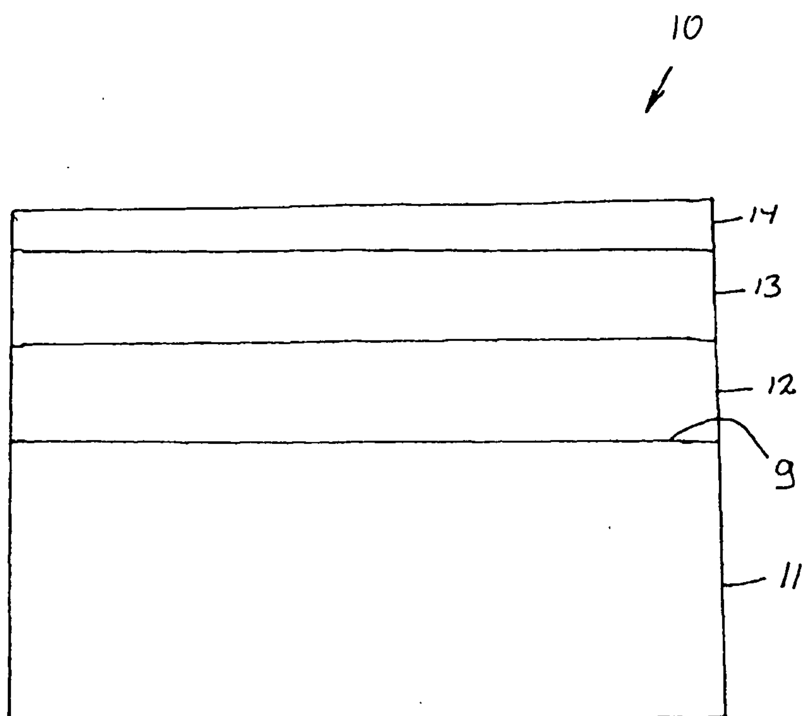


FIG. 1

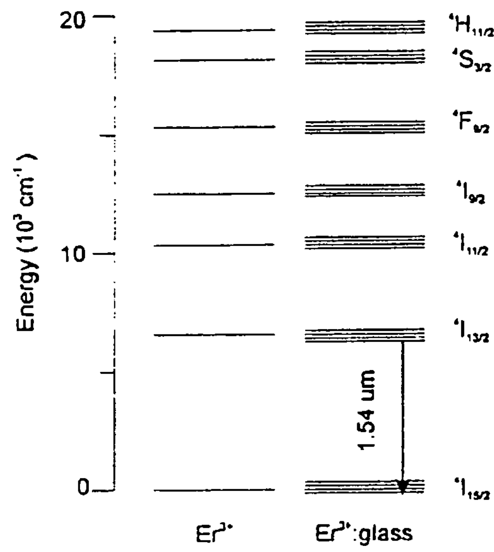


FIG. 2

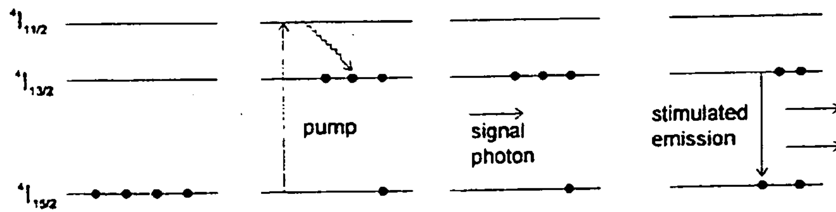


FIG.3

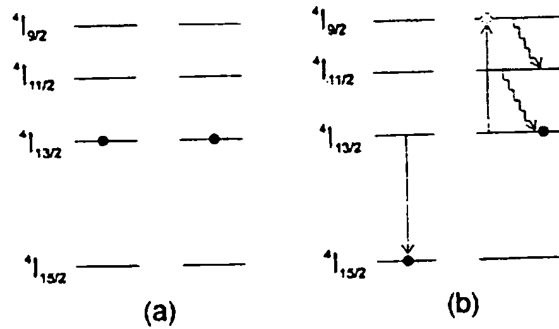


FIG.4

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 06010127
PUBLICATION DATE : 18-01-94

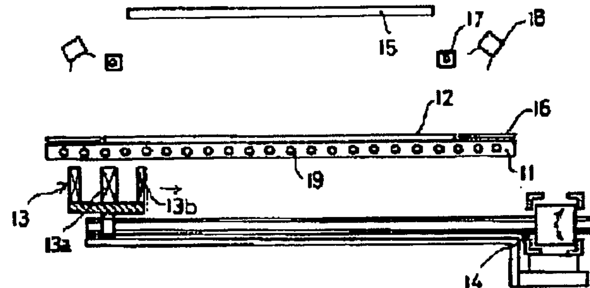
APPLICATION DATE : 28-06-92
APPLICATION NUMBER : 04193348

APPLICANT : ULVAC JAPAN LTD;

INVENTOR : TSUKAGOSHI OSAMU;

INT.CL. : C23C 14/35

TITLE : MAGNETRON SPUTTERING DEVICE



ABSTRACT : PURPOSE: To provide the magnetron sputtering device which improves the efficiency of using a target and can prevent the generation of impurities by sputtering, etc.

CONSTITUTION: A moving means 14 is mounted to a magnet device 13 installed on the rear surface side of a backing plate 11 mounted with the target 12 on its front surface and this magnet device 13 is moved along the rear surface of the backing plate 11. In addition, the magnet device 13 is so moved that high-density plasma is protruded at both ends between one end and the other end of the target 12 by this movement.

COPYRIGHT: (C)1994,JPO&Japio

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号

特開平6－10127

(43)公開日　平成6年(1994)1月18日

(51)Int.Cl.5	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｃ２３Ｃ　14/35		9046－4Ｋ		

審査請求　未請求　請求項の数8（全　9　頁）

(21)出願番号　特願平4－193348

(22)出願日　平成4年(1992)6月28日

(71)出願人　000231464
日本真空技術株式会社
神奈川県茅ヶ崎市萩園2500番地

(72)発明者　内田　岱二郎
神奈川県茅ヶ崎市萩園2500番地日本真空技術株式会社内

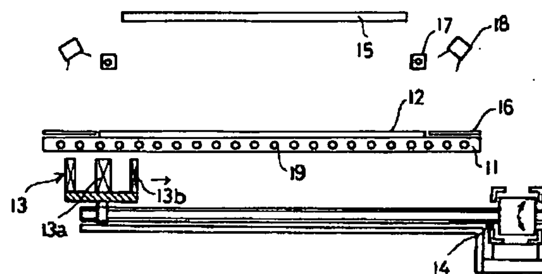
(72)発明者　塚越　修
神奈川県茅ヶ崎市萩園2500番地日本真空技術株式会社内

(54)【発明の名称】　マグネトロンスパッタ装置

(57)【要約】　（修正有）

【目的】この発明の目的は、ターゲットの使用効率を向上させると共に、スパッタによる不純物の発生等を防止することの可能なマグネトロンスパッタ装置を提供することにある。

【構成】この発明のマグネトロンスパッタ装置は、ターゲット１２を表面に取り付けたバッキングプレート１１の裏面側に配設した磁石装置１３に移動手段１４を取り付け、その磁石装置１３をバッキングプレート１１の裏面に沿って移動させ、かつ、その移動により、高密度のプラズマがターゲット１２の一端部と他端部との間で各端部においてはみ出すようになるまで、磁石装置１３を動かすことを特徴とするものである。



【特許請求の範囲】
【請求項１】バッキングプレートの表面にターゲットを取り付け、バッキングプレートの裏面側に磁石装置を配設し、この磁石装置によってターゲット表面近傍の空間に湾曲した磁場を形成し、この湾曲した磁場によりターゲット表面近傍の空間に高密度のプラズマを発生し、この高密度のプラズマ中のイオンをターゲットに加速衝突させてターゲットをスパッタして、ターゲットに対向して配置された基板に薄膜を形成するマグネトロンスパッタ装置において、上記磁石装置に移動手段を取り付け、この移動手段によって上記磁石装置を上記バッキングプレートの裏面に沿って移動させ、かつ、その移動により上記高密度のプラズマが上記ターゲットの一端部と他端部との間で各端部においてはみ出すようになるまで、上記磁石装置を動かすことを特徴とするマグネトロンスパッタ装置。
【請求項２】上記ターゲットの端部の廻りを取り囲むように、この端部と隙間をもってアースシールドを配置し、上記隙間にプラズマを流入させないことを特徴とする請求項１記載のマグネトロンスパッタ装置。
【請求項３】上記磁石装置は、中央部磁石と、この中央部磁石の廻りにこれと間隔をおいて配置された周縁部磁石とを備えることを特徴とする請求項１又は２記載のマグネトロンスパッタ装置。
【請求項４】上記磁石装置は少なくとも２つの棒状磁石を間隔をおいて平行に配置したものであって、各棒状磁石は上記ターゲットの端部と同方向に伸びていることを特徴とする請求項１又は２記載のマグネトロンスパッタ装置。
【請求項５】上記ターゲットの端部に近紫外又は紫外線を照射して光電子を発生させ、その光電子をプラズマに供給する電子供給手段を備えていることを特徴とする請求項３又は４記載のマグネトロンスパッタ装置。
【請求項６】上記ターゲットの端部に熱電子を供給する電子供給手段を備えていることを特徴とする請求項３又は４記載のマグネトロンスパッタ装置。
【請求項７】上記ターゲットに高周波電力供給手段を備えたことを特徴とする請求項３又は４記載のマグネトロンスパッタ装置。
【請求項８】上記ターゲットの端部にマイクロ波電力供給手段を備え、その部分に局部的に電子サイクトロン共鳴（ＥＣＲ）放電を起こさせる特徴とする請求項３又は４記載のマグネトロンスパッタ装置。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】この発明は、ターゲットを表面に取り付けたバッキングプレートの裏面側に配設した磁石装置を移動させるマグネトロンスパッタ装置に関するものである。
【０００２】
【従来の技術】従来、ターゲットを表面に取り付けたバッキングプレートの裏面側に磁石装置を配設し、この磁石装置によりターゲットの表面近傍の空間にマグネトロン放電を起こさせて、高密度のプラズマを発生させ、ターゲット材料のＩＴＯ（インジュウム・スズ・酸化物）等をスパッタして、基板にＩＴＯ等の薄膜を形成するマグネトロンスパッタ装置が広く工業的に用いられてきた。
【０００３】従来のマグネトロンスパッタ装置の一例が図１８、図１９、図２０に示されている。これらの図において、バッキングプレート１の表面にはターゲット２が取り付けられ、また、バッキングプレート１の裏面側には磁石装置３が移動できないように配設されている。磁石装置３は中央部磁石３ａの廻りにこれと間隔をおいて配置された周縁部磁石３ｂとが備えられている。ターゲット２の上方にはこれと対向するように基板４が配置され、また、ターゲット２の端部の廻りには接地されたアースシールド５がターゲット２を取り囲むように端部と隙間をもって配置され、隙間にプラズマが流入しないようにしている。ターゲット２と基板４との間の空間にはリング状のアノード電極６が配置され、このアノード電極６は接地電位となっている。一方、バッキングプレート１には負電圧が印加されている。
【０００４】なお、図中、７は磁石ケース、８は冷却パイプである。
【０００５】従来のマグネトロンスパッタ装置では、図２１に示されるようにターゲット２の表面近傍の空間において磁石装置３による湾曲したポロイダル磁場が形成されると共に、ターゲット２とアノード電極６との間の電位差による電場が形成され、これらの磁場と電場とによって直交電磁場が生じるようになる。ターゲット２の表面から宇宙線、自然放射能による二次電子またはエキソ電子が放射されたとすると、これらの電子はターゲット２の表面近傍の空間の直交電磁場により、これに垂直な方向で電場ベクトル（Ｅ）と磁場ベクトル（Ｂ）とのベクトル積（Ｅ×Ｂ）の向きに数回のサイクロイドを描きながら運動する。この間にキャリヤー・ガス（普通アルゴンが用いられる）分子と衝突してエネルギーの一部を失った電子は、電子に対するポテンシャルの高いターゲット２には戻れず直交電磁場中をトロコイド軌道を描きながら、レース・トラック状のポロイダル磁場の中をドリフトしてゆく。１ｃｍドリフトして行く間のトロコイド軌道の延べ軌道長は数十ｃｍから数百ｃｍに達する。此の間にキャリア・ガスと衝突してイオン化し、電子とイオンを発生させる（α作用）機会を生じ、生じた電子はやはりトロコイド軌道を描きながらドリフトし、生じたイオンはターゲット２へと加速されてこれと衝突し、ターゲット２の材料のスパッタと二次電子の放出を行い（γ（ガンマー）作用）、放出された二次電子は一次電子と同様のことをおこなう。この様にして、プラズ

マが成長し、ターゲット２の表面近傍の空間にレース・トラック状のプラズマが発生する。ターゲット２、プラズマ間のシース電圧によってキャリア・ガスのイオンがターゲット２へと加速され、ターゲット２の材料をスパッタして基板４に薄膜を形成させる。上記のトロコイド軌道を描きながらベクトル積（Ｅ×Ｂ）の方向にドリフトをしてゆく電子は図２１に示されるように磁力線が上方に凸に湾曲しているため、シースまたはシースの遷移領域における電場と直交しない場合には、電子が電場ベクトル（Ｅ）からうける力　－ｅ×ベクトル（Ｅ）の磁力線方向の力の成分により湾曲している磁力線の頂点の方向へと曲がってゆき、この部分がもっとも電子の濃度が高くなる。従ってイオンも此処に集まりプラズマはこの部分が最も粒子密度が高くなり、従ってこの部分に対応するターゲット２の部分が最もスパッタされ、部分的にエロードされる。

【０００６】

【発明が解決しようとする課題】従来のマグネトロンスパッタ装置は、上記のようにターゲット２を表面に取り付けたバッキングプレート１の裏面側に移動できない磁石装置３を配設しているので、ターゲット２の表面近傍の空間において形成される湾曲したポロイダル磁場により高密度のプラズマが形成されるようになる。そのため、ターゲット２の上では、形成された高密度のプラズマ直下の部分が最もスパッタされ、部分的にエロードされるようになる。逆にいえば、ターゲット２の周縁部ではスパッタされる機会に恵まれず、ターゲット２の使用効率が低下する原因となっていた。

【０００７】従来のマグネトロンスパッタ装置の他の一例が図２２、図２３に示されている。これらの図において、バッキングプレート１の表面にはターゲット２が取り付けられ、また、バッキングプレート１の裏面にはターゲット２の表面にレーストラック状のポロイダル磁場を発生させる磁石装置３と、この磁石装置３をバッキングプレート１の裏面に沿って移動させる移動装置９が取り付けられている。但し、磁石装置３はターゲット２の表面に発生したプラズマがターゲット２外にはみ出さない範囲で移動し、また、ターゲット２の端部に特別に電子を発生させるような外部電子発生装置は設けていない。

【０００８】この従来のマグネトロンスパッタ装置の他の一例では、プラズマは磁石装置３の移動と共に、ターゲット２の表面に沿って移動し、磁石装置の固定型で見られるような部分的にエロードされる領域がターゲット２にそって動いてゆくので、磁石装置の固定型より広い範囲のターゲット２がエロードされる。しかし、ターゲット２の端に特別に電子を発生させるような外部電子発生装置は設けていないので、プラズマがターゲット２の外にはみ出すような位置まで移動させると、レーストラック状のポロイダル磁場の中をトロコイド軌跡を描きながら運動して、α作用によって、イオン・電子対を発生させていた電子の道筋が、プラズマの一部がターゲット２の外にはみ出した途端に中断されて、プラズマが消えてしまうので、磁石装置３を、ターゲット２をはみ出さない所までしか移動させることができない。したがって、ターゲット２の周辺部がエロードされずに残り、又、磁石装置３の移動にも制限がつけられるので、ターゲット２の使用効率は十分にあがらない。又、エロードされずに残った部分にスパッタされたターゲット材料が付着して、はがれ、好ましくないゴミ（パーティキュレイト）を発生し、又、異常放電を発生させる原因となる。

【０００９】この発明の目的は、従来の上記問題等を解決して、ターゲットの使用効率を向上させると共に、スパッタによる不純物の発生等を防止することの可能なマグネトロンスパッタ装置を提供することにある。

【００１０】

【課題を解決するための手段】上記目的を達成するために、この発明は、バッキングプレートの表面にターゲットを取り付け、バッキングプレートの裏面側に磁石装置を配設し、この磁石装置によってターゲット表面近傍の空間に湾曲した磁場を形成し、この湾曲した磁場によりターゲット表面近傍の空間に高密度のプラズマを発生し、この高密度のプラズマ中のイオンをターゲットに加速衝突させてターゲットをスパッタして、ターゲットに対向して配置された基板に薄膜を形成するマグネトロンスパッタ装置において、上記磁石装置に移動手段を取り付け、この移動手段によって上記磁石装置を上記バッキングプレートの裏面に沿って移動させ、かつ、その移動により上記高密度のプラズマが上記ターゲットの一端部と他端部との間で各端部においてはみ出すようになるまで、上記磁石装置を動かすことを特徴とするものである。

【００１１】なお、この発明においては、上記ターゲットの端部の廻りを取り囲むように、この端部と隙間をおいてアースシールドを配置する。そして、上記隙間にプラズマを流入させないようにすることが必要である。また、上記磁石装置は、中央部磁石と、この中央部磁石の廻りにこれと間隔をおいて配置された周縁部磁石とを備えたものを使用することが必要である。更に、上記磁石装置は少なくとも２つの棒状磁石を間隔をおいて平行に配置したものであって、各棒状磁石は上記ターゲットの端部と同方向に伸びているものを使用することも必要である。更にその上、上記ターゲットの端部に光電子又は熱電子を供給する電子供給手段、もしくは、上記ターゲットに接続する高周波電力供給手段、又は、ターゲットの端部に局所的にマイクロ波電力を供給する手段を備え、この部分に電子サイクロトロン共鳴（ＥＣＲ）放電を起こさせることも必要である。

【００１２】

【作用】この発明においては、磁石装置に移動手段を取り付け、この移動手段によって磁石装置をバッキングプレートの裏面に沿って移動させ、その移動により高密度のプラズマをターゲットの一端部と他端部との間で各端部においてはみ出すようになるまで動かしているので、ターゲットの周縁部においてもスパッタされ、ターゲットが全体にわたって均等にスパッタされるようになる。

【0013】なお、ターゲットの端部の廻りを取り囲むように、端部と隙間をもってアースシールドを配置し、隙間にプラズマを流入させないようにしたときには、ターゲット以外の物質をスパッタすることがなくなるので、スパッタによる不純物の発生を防止させることができるようになる。また、ターゲットの端部に光電子又は熱電子を供給する電子供給手段、もしくは、ターゲットに接続する高周波電力供給手段、又は、マイクロ波電力供給手段を備えているときには、プラズマの出発点で光電子、熱電子の補給、ＲＦ電圧による強勢、又はマイクロ波によるＥＣＲ放電が起こり、上記の手段を設けない従来の他の一例では、レーストラック状のプラズマの一部分がターゲットの外側にはみ出すような位置まで磁石装置が移動してきたとき、ターゲットの外側にはみ出した部分のプラズマが消えるばかりでなく、磁石装置の他の一部がターゲットの下にあるような部分までプラズマが非常に弱くなるが、本発明のように上記の手段を設けることにより、このような位置まで磁石装置が動いてきたときもターゲットの外側にはみ出したプラズマの部分は消えるが、磁石装置の他の一部がターゲットの下にあるような部分では、磁石装置がターゲットの下にある部分のはじまりの場所からプラズマが強く立ち上がり、プラズマを出発点から強くし、ターゲットの外にはみ出した一部は消えても、残りの部分では磁石装置がターゲットの外にはみ出さない場合と全く同一の強度となり、スパッタの不均一性を生じさせなくなる。

【0014】更に、２本の棒状磁石の場合（棒状磁石といってもこの言葉から連想されるように長手方向の両端にＮ極とＳ極とがあるものとは全くことなり、上方にＳ極、下方にＮ極をもつ立方体磁石辺を横一列に図９、図１０のように並べたものと、上方にＮ極、下方にＳ極をもつ立方体磁石辺を横一列に並べたものとを、図９、図１０のように向い合せたものであるが、以後、棒状磁石（直線コース状磁石）と称するが、直線コース状磁石ではターゲット上に上方に凸の磁場トンネルができるが、これはレーストラック状磁石のように環状に閉じているものではないので、レーストラック状磁石の場合、環状ポロイダル磁場中をレースライン磁場の一端から発生し、長手方向に成長して行かねばならぬ。このとき、特別の電子発生装置がない場合にはこの部分に発生する電子が少なく長手方向にトロコイド運動をしながら進んでいって数を増してゆくのであるが、普通の条件ではプラズマが成長するまでに進まねばならぬ距離が１０ｃｍにもなり、この間はプラズマは非常に弱いものである。しかし、上記の特別に電子を発生させる手段の一つを備えていれば、始めから十分な数の電子が存在し、プラズマは１～２ｃｍで十分強くなり、プラズマの弱い部分は無視できるほど短くなる。

【００１５】

【実施例】以下、この発明の実施例を図面に基づいて説明する。この発明の第１実施例は図１および図２に示されており、これらの図において、バッキングプレート１１の表面にはターゲット１２が取り付けられ、また、バッキングプレート１の裏面側には磁石装置１３が配設されている。磁石装置１３にはネジ棒をもった移動手段１４が取り付けられ、この移動手段１４によって磁石装置１３がバッキングプレート１１の裏面に沿って直線移動するようになっている。磁石装置１３は中央部磁石１３ａの廻りにこれと間隔をおいて配置された周縁部磁石１３ｂとが備えられている。ターゲット１２の上方にはこれと対向するように基板１５が配置され、また、ターゲット１２の端部の廻りには接地されたアースシールド１６がターゲット１２を取り囲むように端部と隙間をもって配置され、隙間にプラズマが流入しないようにしている。ターゲット１２と基板１５との間の空間にはリング状のアノード電極１７が配置され、このアノード電極１７は接地電位となっている。一方、バッキングプレート１１には負電圧が印加されている。ターゲット１２の左右端部上方の空間には紫外線または近紫外線光源１８が配置され、この光源１８からの紫外線または近紫外線を当てて光電子をターゲット１２の左端部の符号１２ａの場所および右端部の符号１２ｂの場所に補給している。バッキングプレート１１内には冷却パイプ１９が配設されている。

【００１６】第１実施例においては、ターゲット１２の表面近傍の空間において磁石装置１３による湾曲したポロイダル磁場が形成されると共に、ターゲット１２とアノード電極１７との間の電位差による電場が形成され、これらの磁場と電場とによって直交電磁場が生じるようになる。しかしながら、移動手段１４によって磁石装置１３をバッキングプレート１１の裏面に沿って直線移動させるようにしているので、直交電磁場もそれに伴って移動し、高密度のプラズマがターゲット１２の左端部と右端部との間で各端部においてはみ出すようになるまで動くようになる。その際、ターゲット１２の左端部の符号１２ａの場所および右端部の符号１２ｂの場所に光源１８からの紫外線または近紫外線を当てて光電子を補給すると、磁石装置１３がターゲット１２よりはみ出していても、プラズマ３０は図１７に示されるようにターゲット１２の左端部又は右端部においても発生するようになる。電子はターゲット２の表面近傍の空間の直交電磁場により、これに垂直な方向で電場ベクトル（Ｅ）と磁場ベクトル（Ｂ）とのベクトル積（Ｅ×Ｂ）の向きに数

回のサイクロイドを描きながら運動する。この間にキャリヤー・ガス（普通アルゴンが用いられる）分子と衝突してエネルギーの一部を失った電子は、電子に対するポテンシャルの高いターゲット１２には戻れず直交電磁場中をトロコイド軌道を描きながら、レース・トラック状のポロイダル磁場の中をドリフトしてゆく。１ｃｍドリフトして行く間のトロコイド軌道の延べ軌道長は数十ｃｍから数百ｃｍに達する。此の間にキャーリヤー・ガスと衝突してイオン化し、電子とイオンを発生させる（α作用）機会を生じ、生じた電子はやはりトロコイド軌道を描きながらドリフトし、生じたイオンはターゲット１２へと加速されてこれと衝突し、ターゲット１２の材料のスパッタと二次電子の放出を行い（γ（ガンマー）作用）、放出された二次電子は一次電子と同様のことをおこなう。この様にして、ターゲット１２の表面近傍の空間にレース・トラック状のプラズマが成長する。しかし、ターゲット１２の端部の廻りを取り囲むように、端部と隙間をもってアースシールド１６を配置し、隙間にプラズマを流入させないようにしていると、プラズマはターゲット１２の手前で切れ、アースシールド１６までも広がらず、しかも、ターゲット１２以外の物質をスパッタすることがなく、スパッタによる不純物の発生を防止させることができるようになる。

【００１７】次に、第２実施例は図３および図４に示されている。第２実施例は第１実施例の紫外線または近紫外線光源１８の代わりに、熱陰極２０を用いて、熱電子を補給するものである。

【００１８】第３実施例は図５および図６に示されている。第３実施例は第１実施例の紫外線または近紫外線光源１８の代わりに、ターゲット１２に高周波電力供給手段２１を接続したものである。

【００１９】第４実施例は図７および図８に示されている。第４実施例は第１実施例の紫外線または近紫外線光源１８の代わりに、マイクロ波電力供給手段２２を備えたものである。

【００２０】第５実施例は図９および図１０に示されている。第５実施例は第１実施例の磁石装置１３の代わりに、少なくとも２つの棒状磁石（レースライン磁石）１３ｃ、１３ｄを間隔をおいて平行に配置し、各棒状磁石１３ｃ、１３ｄをターゲット１２の端部と同方向に伸ばした磁石装置１３を用いたものである。レースライン磁石は、上方にＮ極、下方にＳ極をもつ立方体磁石片を横一列に並べたもの、及び、上方にＳ極、下方にＮ極をもつ立方体磁石片を横一列に並べたものがあり、図９、図１０のように配置されている。

【００２１】第６実施例は図１１および図１２に示されている。第６実施例は第５実施例の紫外線または近紫外線光源１８の代わりに、熱陰極２０を用いて、熱電子を補給するものである。

【００２２】第７実施例は図１３および図１４に示されている。第７実施例は第５実施例の紫外線または近紫外線光源１８の代わりに、ターゲット１２に高周波電力供給手段２１を接続したものである。

【００２３】第８実施例は図１５および図１６に示されている。第８実施例は第５実施例の紫外線または近紫外線光源１８の代わりに、マイクロ波電力供給手段２２を備えたものである。

【００２４】

【発明の効果】この発明においては、磁石装置に移動手段を取り付け、この移動手段によって磁石装置をバッキングプレートの裏面に沿って移動させ、その移動により高密度のプラズマをターゲットの一端部と他端部との間で各端部においてはみ出すようになるまで動かしているので、ターゲットの周縁部においてもスパッタされ、ターゲットが全体にわたって均等にスパッタされるようになる。また、ターゲットの端部の廻りを取り囲むように、端部と隙間をもってアースシールドを配置し、隙間にプラズマを流入させないようにしたときには、ターゲット以外の物質をスパッタすることがなくなるので、スパッタによる不純物の発生を防止させることができるようになる。更に、ターゲットの端部に電子を供給する電子供給手段、もしくは、ターゲットに接続する高周波電力供給手段、又は、マイクロ波電力供給手段を備えているときには、プラズマの出発点で光電子、熱電子の補給、ＲＦ電圧による強勢、又はマイクロ波によるＥＣＲ放電が起こり、プラズマを出発点から強くし、スパッタの不均一性を生じさせなくなる。更に、図１７ａ、１７ｂにプラズマの成長が示されている。レーストラック状磁石の一部が図１７ａのようにターゲットの外にまではみ出すような位置まで動いてくると、プラズマははみ出し部分はとぎれ、磁石がターゲットにかかっている部分から徐々に１０ｃｍ位の暗部をへ発生するが、非常に弱い。しかし、光電子、熱電子、ｒｆ放電、マイクロ波による電子サイクトロン放電（ＥＣＲ）放電が端部にあって、十分な電子を補給すると、図１７ｂのように端部１～２ｃｍから太く強いプラズマが立ち、スパッタリングの端部における効率低下が全然起こらなくなり、ターゲットは全面的に一様にスパッタエロードされる。

【図面の簡単な説明】

【図１】この発明の第１実施例の正面図

【図２】この発明の第１実施例の平面図

【図３】この発明の第２実施例の正面図

【図４】この発明の第２実施例の平面図

【図５】この発明の第３実施例の正面図

【図６】この発明の第３実施例の平面図

【図７】この発明の第４実施例の正面図

【図８】この発明の第４実施例の平面図

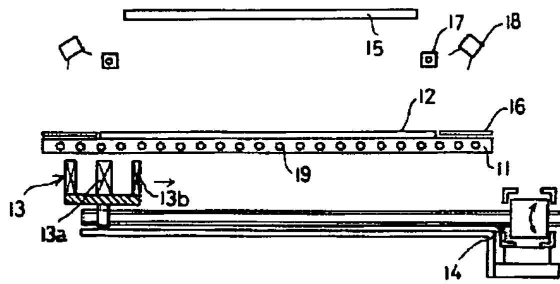
【図９】この発明の第５実施例の正面図

【図１０】この発明の第５実施例の平面図

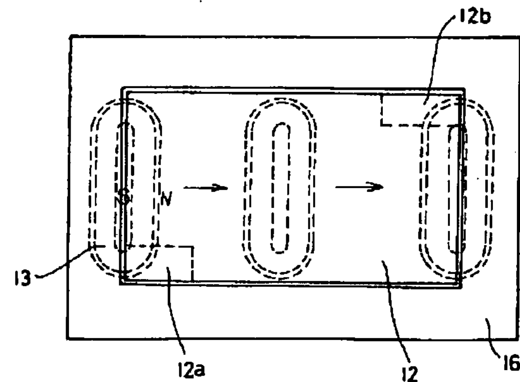
【図１１】この発明の第６実施例の正面図

【図１２】この発明の第６実施例の平面図
【図１３】この発明の第７実施例の正面図
【図１４】この発明の第７実施例の平面図
【図１５】この発明の第８実施例の正面図
【図１６】この発明の第８実施例の平面図
【図１７ａ】この発明の第１実施例においてプラズマの成長を示す説明図
【図１７ｂ】この発明の第１実施例においてプラズマの成長を示す説明図
【図１８】従来のマグネトロンスパッタ装置の正面図
【図１９】従来のマグネトロンスパッタ装置の平面図
【図２０】従来のマグネトロンスパッタ装置の斜視図
【図２１】従来のマグネトロンスパッタ装置の磁場等を示す説明図
【図２２】従来のマグネトロンスパッタ装置の正面図
【図２３】従来のマグネトロンスパッタ装置における磁石装置の移動を示す説明図
【符号の説明】
１１・・・・・・バッキングプレート
１２・・・・・・ターゲット
１３・・・・・・磁石装置
１４・・・・・・移動手段
１５・・・・・・基板
１６・・・・・・アースシールド
１７・・・・・・アノード電極
１８・・・・・・光源
２０・・・・・・熱陰極
２１・・・・・・高周波電力供給手段
２２・・・・・・マイクロ波電力供給手段

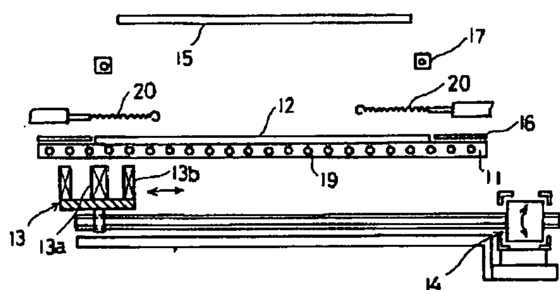
【図１】



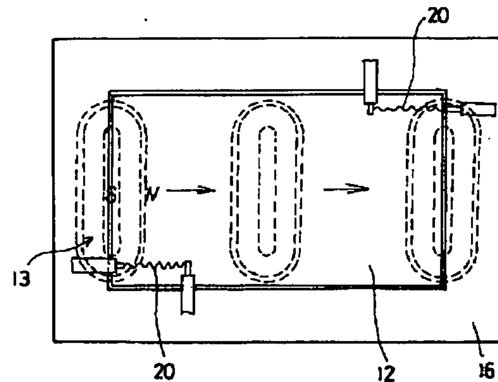
【図２】



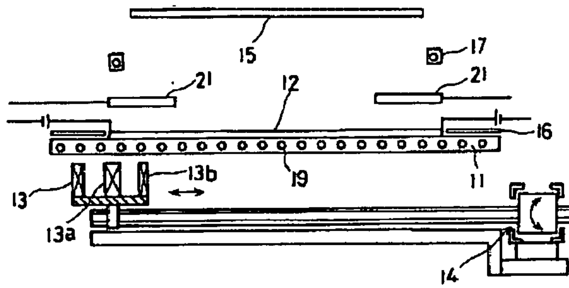
【図３】



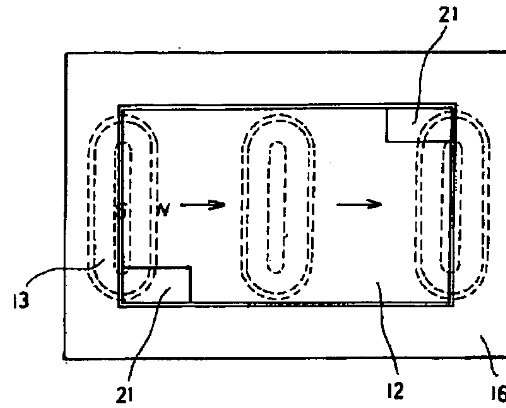
【図４】



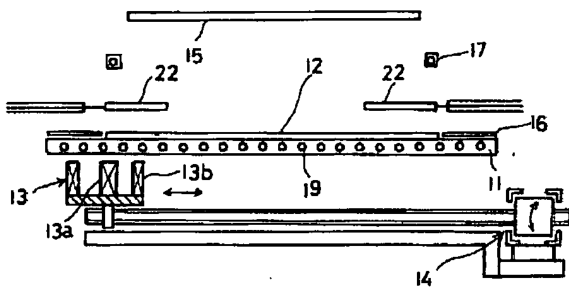
【図５】



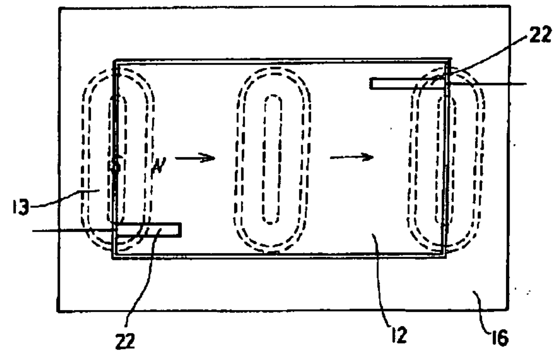
【図６】



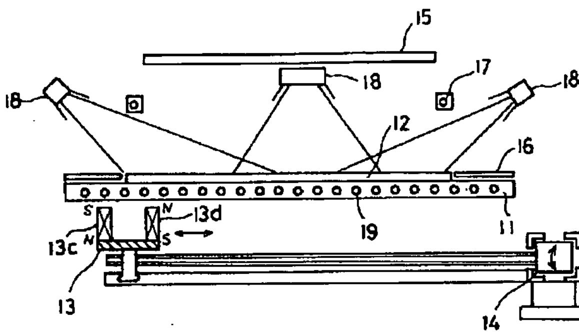
【図７】



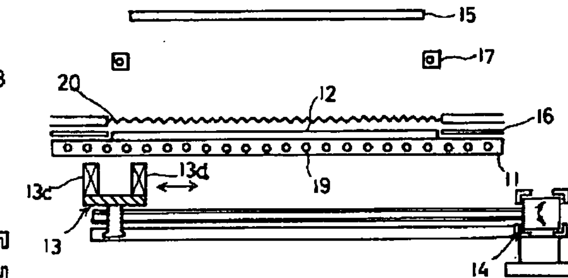
【図８】



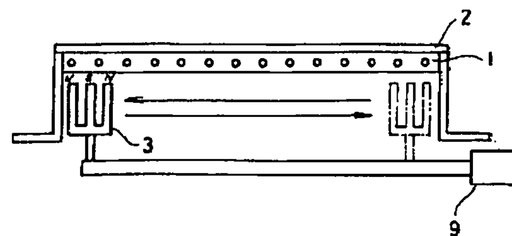
【図９】



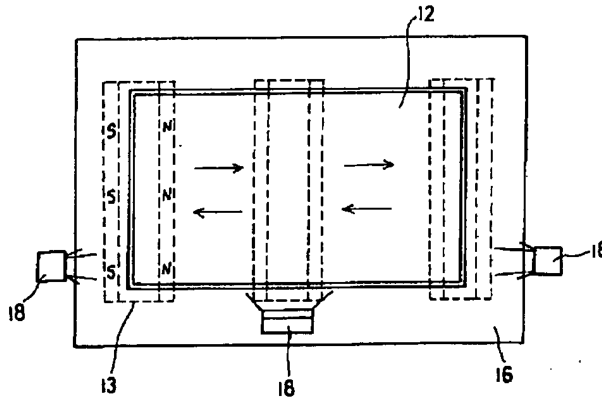
【図１１】



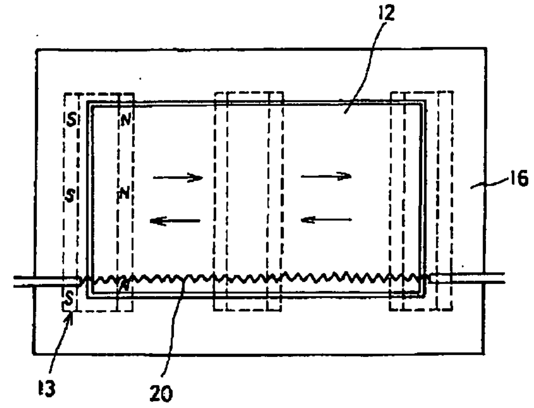
【図２２】



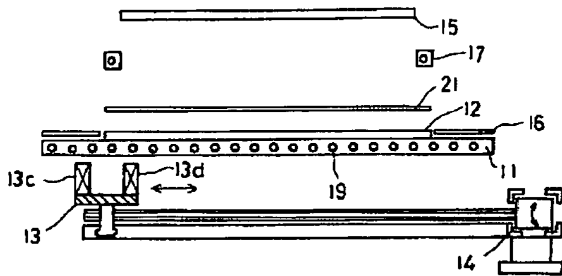
【図１０】



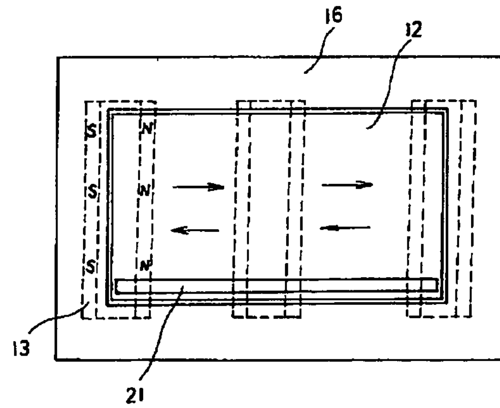
【図１２】



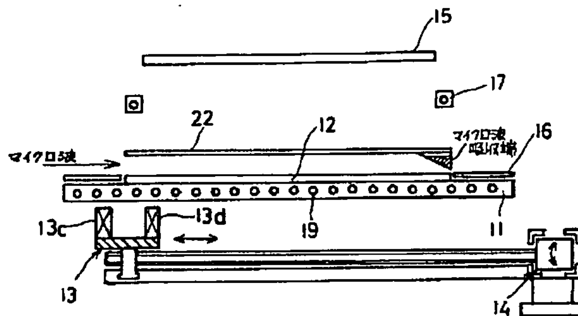
【図１３】



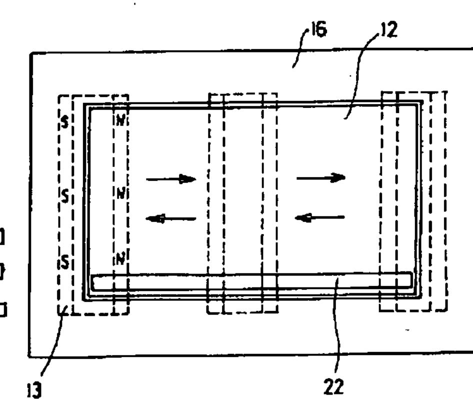
【図１４】



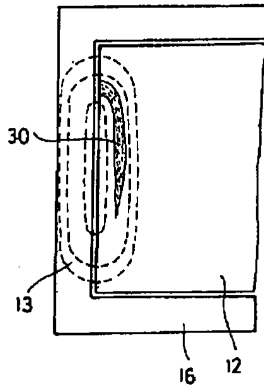
【図１５】



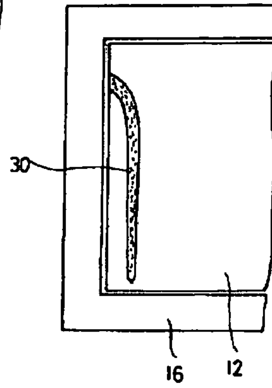
【図１６】



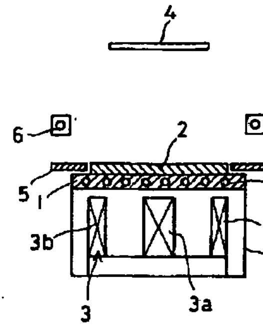
【図１７ａ】



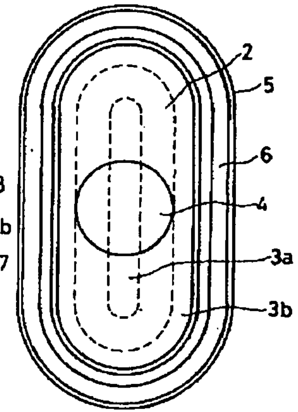
【図１７ｂ】



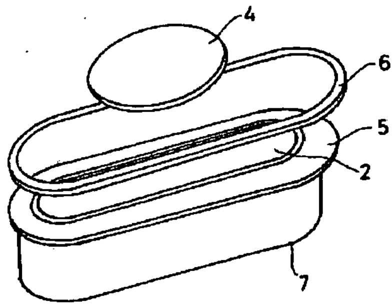
【図１８】



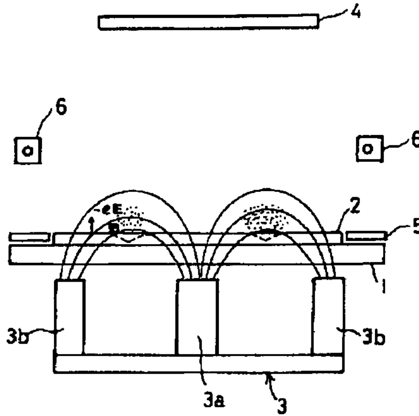
【図１９】



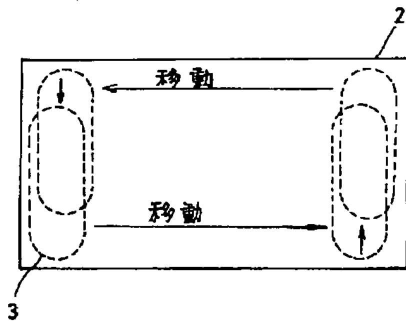
【図２０】



【図２１】



【図２３】



This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

WEST

Generate Collection

L33: Entry 2 of 3 File: DWPI Apr 12, 1994

DERWENT-ACC-NO: 1994-156455
DERWENT-WEEK: 199419
COPYRIGHT 2003 DERWENT INFORMATION LTD

TITLE: Metal ion implanted surface modified glass - by ion implanting metal ions e.g. copper and/or silver, into a glass substrate surface to form a modified layer

PATENT-ASSIGNEE:

ASSIGNEE	CODE
KOBE STEEL LTD	KOBM

PRIORITY-DATA: 1992JP-0246692 (September 16, 1992)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 06100333 A	April 12, 1994		005	C03C021/00

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
JP 06100333A	September 16, 1992	1992JP-0246692	

INT-CL (IPC): C03C 21/00

ABSTRACTED-PUB-NO: JP 06100333A
BASIC-ABSTRACT:

The glass is obtd. by ion implanting metal ions e.g. Cu and/or Ag ions into a glass substrate surface to form a modified layer for absorbing and reflecting a particular wavelength light ray selectively onto the surface layer part of the glass substrate.

USE - Used for giving unique optical characteristics to a glass substrate.

CHOSEN-DRAWING: Dwg.0/4

TITLE-TERMS: METAL ION IMPLANT SURFACE MODIFIED GLASS ION IMPLANT METAL ION COPPER SILVER GLASS SUBSTRATE SURFACE FORM MODIFIED LAYER

DERWENT-CLASS: L01

CPI-CODES: L01-G05A;

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1994-071675

(19)日本国特許庁（JP）　(12) 公開特許公報(A)　(11)特許出願公開番号

特開平6−100333

(43)公開日 平成6年(1994)4月12日

(51)Int.Cl.⁵	識別記号	庁内整理番号	FI	技術表示箇所
C03C 21/00	Z	7003−4G		
	102	7003−4G		

審査請求 未請求 請求項の数1(全 5 頁)

(21)出願番号 特願平4−246692

(22)出願日 平成4年(1992)9月16日

(71)出願人 000001199
株式会社神戸製鋼所
兵庫県神戸市中央区脇浜町1丁目3番18号

(72)発明者 犬石 典之
兵庫県神戸市中央区脇浜町1丁目3番18号
株式会社神戸製鋼所神戸本社内

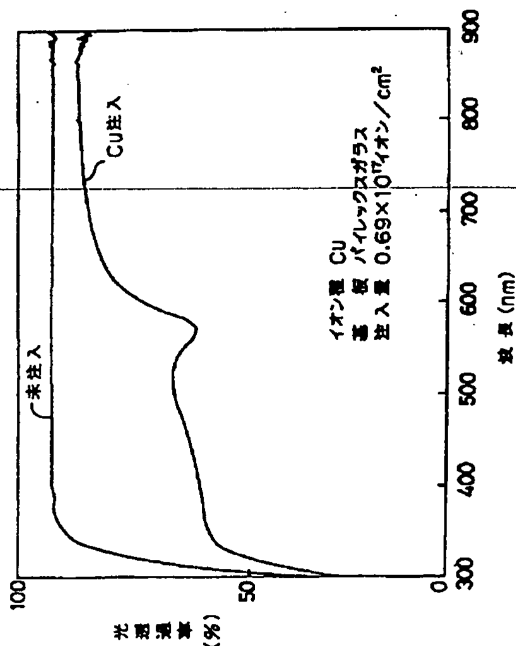
(72)発明者 宗政 淳
兵庫県神戸市中央区脇浜町1丁目3番18号
株式会社神戸製鋼所神戸本社内

(72)発明者 熊切 正
兵庫県神戸市中央区脇浜町1丁目3番18号
株式会社神戸製鋼所神戸本社内

(74)代理人 弁理士 植木 久一

(54)【発明の名称】 金属イオン注入表面改質ガラス

(57)【要約】
【目的】 イオン注入法を適用して特定の金属イオンをガラス基板に注入することによって、これまでにない新しい光学特性を付与した金属イオン注入表面改質ガラスを提供する。
【構成】 ガラス基板表面に、Cuおよび／またはAgの金属元素をイオン注入し、ガラス基板の表層部に、特定波長の光を選択的に吸収・反射する改質層を形成したものである。



WEST

1

【特許請求の範囲】
【請求項１】 ガラス基板表面に、Ｃｕおよび／またはＡｇの金属元素をイオン注入し、ガラス基板の表層部に、光の選択的透過層を形成したものであることを特徴とする金属イオン注入表面改質ガラス。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は、特定波長の光を選択的に吸収および／または反射して透過させないマイナスフィルターと呼ばれる光学素子の素材として、或は建築物や自動車用の紫外線カットガラスとして有用な、金属イオン注入表面改質ガラスに関するものである。
【０００２】
【従来の技術】ガラス製品は、例えば画像や文字を表示するディスプレイ、太陽光を利用するソーラーセルや太陽電池、建築物や自動車の窓等、様々な分野で利用されている。そしてディスプレイにおける表示を正確で美しいものとする為、またソーラーセルや太陽電池における効率を良くする為、更には快適な居住空間を形成する為には、これらに使用されるガラス製品の光吸収や光反射を適切に調節して光を有効に利用することが重要である。
【０００３】近年、ガラス製品に上記の様な機能を付与する為の方法が、様々な角度から検討されている。その代表的な方法としては、ガラス基板表面にコーティング膜を形成する方法が挙げられる。例えば太陽光の熱線を遮蔽して、夏期における室内の冷房負荷が大きくなるのを防止する目的で、TiO_2，ＣｏＯ等の金属酸化物膜を熱分解法によってガラス基板表面にコーティングしたガラスが開発されている。また真空蒸着法やスパッタ法によって、ＴｉやＣｒの様な金属膜を、ガラス基板表面にコーティングしたガラスも知られている。一方、特定の波長の光を選択的に吸収または透過させる光学フィルターにおいても、ガラス基板に屈折率の異なる薄膜をコーティングしたガラスが知られている。
【０００４】しかしながらガラス基板にコーティング膜を形成したものでは、ガラス基板とコーティング膜の密着性が十分でなく、外部からの衝撃によって疵が付き易いという欠点がある。また腐食性環境下では、コーティング膜が変質してしまい、光学特性が変化してしまうという欠点もある。こうした不都合を回避する技術として、例えば特開平3-257042号公報の様な技術も提案されている。この技術は、Ｓｉ，Ａｌ，Ｔｉ，Ｃｒ，Ｃｏ，Ｎｉ等の元素を、イオン注入法によってガラス基板に打ち込み、該ガラス基板の内部の表面近傍に光の選択的透過層を形成して、光透過率を調整するものであり、上記の様な不都合を基本的に含まない新しい技術として注目されている。
【０００５】
【発明が解決しようとする課題】本発明はこうした状況

2

の基になされたものであって、その目的は、イオン注入法を適用して特定の金属イオンをガラス基板に注入することによって、これまでにない新しい光学特性を付与した金属イオン注入表面改質ガラスを提供することにある。
【０００６】
【課題を解決するための手段】上記目的を達成し得た本発明とは、ガラス基板表面に、Ｃｕおよび／またはＡｇの金属元素をイオン注入し、ガラス基板の表層部に、光の選択的透過層を形成したものである点に要旨を有する金属イオン注入表面改質ガラスである。
【０００７】
【作用】本発明で利用されるイオン注入の手法は、加速された高エネルギーの金属イオンを目的深さまで打ち込んでガラス基板の表層部を改質するものであり、半導体分野における不純物ドーピング手段として利用されている他、鋼を中心とする金属材料の表面改質にもその適用が進められているが、半導体分野を除けばこれまでのところ実用化はあまり進んでいなかった。
【０００８】本発明者らは、かねてよりイオン注入法について研究を進めてきており、種々の材料に対するイオン注入による表面改質について検討してきた。そして近年の状況に鑑み、且つ研究の一環として、種々の金属イオンについてのイオン注入実験を重ね、ガラス基板の光学特性に及ぼす金属イオンの影響について検討した。その結果、ガラス基板にＣｕやＡｇ等の金属元素をイオン注入すれば、ガラス基板の表層部に、特定波長の光を選択的に吸収・反射する改質層が形成され、これによってガラス基板に特異な光学特性を付与できることを見出し、本発明を完成した。即ち本発明者らが、ＣｕやＡｇをイオン注入した表面改質ガラスについて、その光透過率を調査したところ、後記実施例に示す様に、Ｃｕをイオン注入した場合は波長580nm 近傍に、Ａｇをイオン注入した場合は波長420nm 近傍に透過率減少ピークが夫々形成されることがわかった。
【０００９】この様に、特定波長の光を選択的に透過する表面改質ガラスは、その光学特性を利用してマイナスフィルターの素材としての適用が期待できる。即ち、Ｃｕをイオン注入した場合は、波長が５９０～４３０nm程度の範囲の光（黄，緑，青，紫色光）を吸収・反射して、これらの光を透過させないマイナスフィルターの素材としての適用が期待できる。またＡｇをイオン注入した場合は、波長が４９０～３８０nm程度の範囲の光（青，紫色光）を吸収・反射して、これらの光を透過させないマイナスフィルターの素材としての適用が期待できる。
【００１０】またＣｕまたはＡｇのいずれをイオン注入した場合であっても、未処理のガラス基板に比べ、紫外線領域（波長３８０nm以下）における光透過率が低下するので、本発明のガラスは紫外線カットガラスとしての

WEST

適用も考えられる。更に、イオン注入することによって、ガラス基板はピンク色（Cuをイオン注入した場合）や黄色（Agをイオン注入した場合）等に着色されるので本発明の表面改質ガラスは、装飾用ガラスとしての応用も考えられる。尚これまでの説明では、CuまたはAgのいずれかを単独でイオン注入する場合について説明したが、もとより両者を複合的にイオン注入することも可能であり、この場合は複合的な透過率減少ピークが認められる。

【0011】本発明の表面改質ガラスは上記作用効果を奏するものであるが、これらの作用効果を得るには、金属イオンを夫々または合計で1×10^{15}イオン／cm^2 以上注入するのが良い。またガラス表面の耐摩耗性や耐薬品性を考慮すると、金属イオンの注入位置はできるだけ深い方が好ましく、こうした観点からして、注入エネルギーは30KeV以上とするのが良い。一方、過剰にイオン注入すると、注入エネルギーに応じてスパッタ現象による表面切削現象が顕著になるので、注入エネルギーおよび注入量は慎重に決定する必要がある。こうした観点か＊

＊らすれば、注入エネルギーは250 KeV以下とし、且つ注入量は5×10^{18}イオン／cm^2 以下に抑えることが望ましい。

【0012】本発明においては、CuやAgの高エネルギーイオンをガラス基板の表層部に強制的に注入するが、表面にコーティング膜を形成する場合と異なり、イオン注入表面層とガラス基板との一体性は極めて良好であり、剥離の問題は生じない。また表面はガラス基板本来の耐食性を維持したままである。

10

【0013】以下本発明を実施例によって更に詳細に説明するが、下記実施例は本発明を限定する性質のものではなく、前・後記の趣旨に徴して設計変更することはいずれも本発明の技術的範囲に含まれるものである。

【0014】

【実施例】表1に示す各種イオン注入ガラスについて、光透過率の測定を、可視・紫外領域（波長300 ～900nm）について行なった。

【0015】

【表1】

No.	注入イオン種	ガラス基板	注入エネルギー（KeV）	注入量（イオン／cm^2）
1	Cu	パイレックスガラス	119	0.69×10^{17}
2	Cu	スライドガラス	119	0.82×10^{17}
3	Ag	パイレックスガラス	124	0.69×10^{17}
4	Ag	スライドガラス	124	0.64×10^{17}

【0016】その結果を図1～4に示すが、いずれも特定波長領域に特異的な透過率減少ピークが認められ、マイナスフィルターとして有用なガラスができていることがわかる。また未注入のガラス基板の透過率と比較して明らかな様に（図1および図3）、紫外線（波長380nm以下）の透過率も低下していることから、本発明の表面改質ガラスは紫外線カットガラスとしての適用も可能である。

【0017】

【発明の効果】本発明は以上の様に構成されており、CuやAg等の金属元素をイオン注入することによって、特定波長の光を選択的に吸収・反射して透過させないマ※

40

※イナスフィルターの素材として、或は紫外線カットガラスとして有用な表面改質ガラスが得られた。

【図面の簡単な説明】

【図1】パイレックスガラス基板にCuをイオン注入したガラスの分光曲線である。

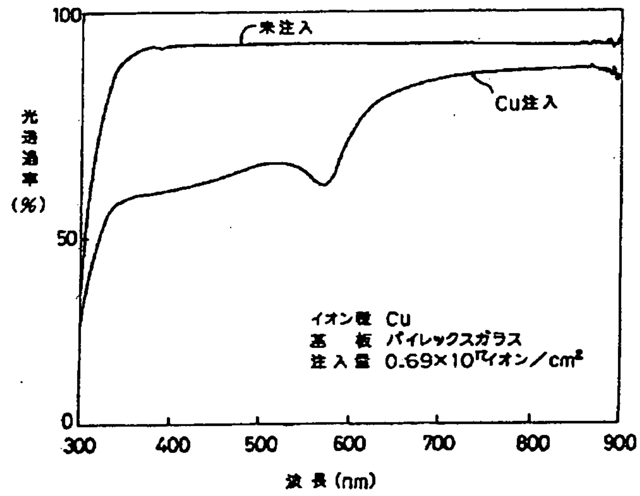
【図2】スライドガラス基板にCuをイオン注入したガラスの分光曲線である。

【図3】パイレックスガラス基板にAgをイオン注入したガラスの分光曲線である。

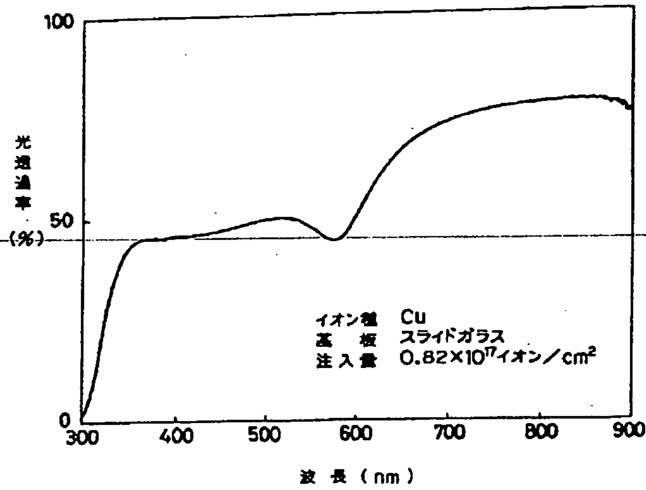
【図4】スライドガラス基板にAgをイオン注入したガラスの分光曲線である。

JEST

【図1】

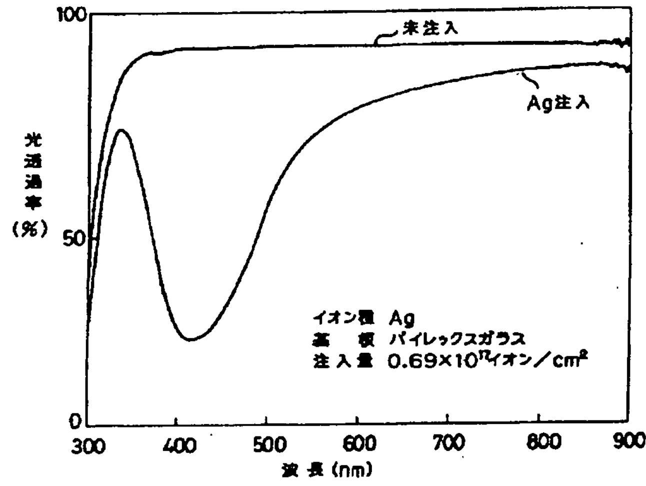


【図2】

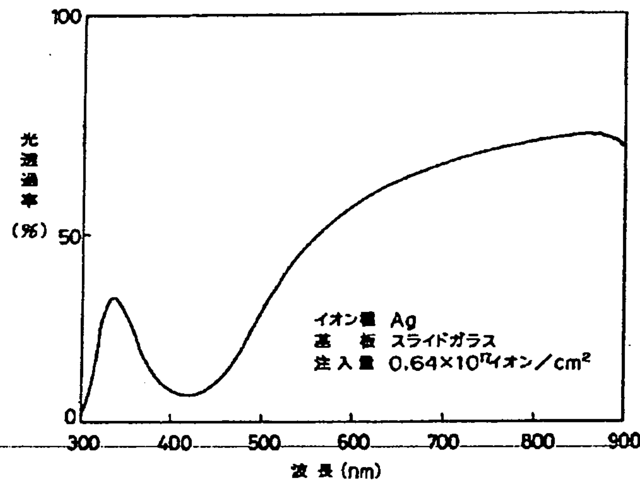


WEST

【図3】



【図4】



PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H04B | A2

(11) International Publication Number: WO 00/22742

(43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/US99/22102

(22) International Filing Date: 23 September 1999 (23.09.99)

(30) Priority Data:

60/101,853	25 September 1998 (25.09.98)	US
09/246,985	9 February 1999 (09.02.99)	US

(71) Applicant: FIVER LABORATORIES [US/US]; Suite 316, 48521 Warm Springs Blvd., Fremont, CA 94539 (US).

(72) Inventors: WU, Weiti; 328 Sandhurst Drive, Milpitas, CA 95035 (US). KO, Yu-Li; 45654 Cheyenne Place, Fremont, CA 94539 (US). CHUNG, Gary; 41366 Charlita Court, Fremont, CA 94539 (US).

(74) Agents: HAVERSTOCK, Thomas, B. et al.; Haverstock & Owens LLP, Suite 420, 260 Sheridan Avenue, Palo Alto, CA 94306 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: ALL FIBER GAIN FLATTENING OPTICAL FILTER

(57) Abstract

An all fiber optical filter is formed by streching an optical fiber. The all fiber filter includes a core, an inner cladding, and an outer cladding. A core index of refraction is greater than an outer cladding index of refraction. The outer cladding index of refraction is greater than an inner cladding index of refraction. The all fiber optical filter attenuates a portion of an optical signal by transferring optical energy from the core to the outer cladding by evanescent coupling. The all fiber optical filter has a compact structure, which prevents bending and provides stable temperature performance. The all fiber optical filter is preferably used in Wavelength Division Multiplexing (WDM) systems for gain flattening of gain responses from Erbium Doped Fiber Amplifiers (EDFAs). Alternatively, the all fiber optical filter is used in other applications where optical filtering or attenuation is needed. The all fiber optical filter is manufactured by holding a length of an appropriate optical fiber between two clamps, heating the optical fiber, stretching the optical fiber until a predetermined charachteristic of the all fiber optical filter is achieved.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

ALL FIBER GAIN FLATTENING OPTICAL FILTER

RELATED APPLICATIONS

This application claims priority under 35 U.S.C. § 119(e) of the co-pending U.S. provisional application Serial Number 60/101,853 filed on September 25, 1998 and entitled "ALL-FIBER EDFA GAIN FLATTENING FILTER." The provisional application Serial Number 60/101,853 filed on September 25, 1998 and entitled "ALL-FIBER EDFA GAIN FLATTENING FILTER" is also hereby incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the field of fiber optic communications. More particularly, the present invention relates to the field of filtering of amplified signals used in fiber optic communications systems.

BACKGROUND OF THE INVENTION

Fiber optic communication systems use optical fibers to carry a modulated lightwave signal between a transmitter and a receiver. A cross-section of a typical optical fiber is illustrated in FIG. 1. The optical fiber 2 includes a core 4 and a cladding 6. Optionally, the optical fiber 2 includes a jacket 8. In a typical optical fiber, the core 4 has an index of refraction greater than the cladding 6, thereby forming an optical waveguide. By maintaining the core diameter within an allowed range, light traveling within the core 4 is limited to a single mode. If included, the jacket 8 protects the outer surface of the cladding 6 and absorbs stray light traveling within the cladding 6. A typical single mode optical fiber intended for use in communication systems operating at a 1300 nm wavelength band or a 1550 nm wavelength band has a core diameter of about 8 μm and a cladding outside diameter of 125 μm. If the jacket 8 is included, the jacket 8 typically has an outside diameter of 250 μm.

In Wavelength Division Multiplexing (WDM) systems, multiple signals are carried by various wavelengths of light through a single optical fiber. A typical WDM system is shown in FIG. 2. The WDM system 10 includes a transmission system 11, which includes a series of transmitters 12, 14, and 16, each coupled to a multiplexer 18. The multiplexer 18 provides an output, which is coupled to an optical fiber 20. Over long distances amplifiers 22 are included along the optical fiber 20. The optical fiber 20 is then also

coupled to a receiving system 23, which includes a demultiplexer 24 and a series of receivers 26, 28, and 30. The optical fiber 20 is coupled to an input of the demultiplexer 24 of the receiving system 23. Outputs of the demultiplexer 24 are coupled to the series of receivers 26, 28, and 30.

5 In the WDM system 10, a first transmitter 12 transmits a light signal at a first wavelength (λ_1), a second transmitter 14 transmits a light signal at a second wavelength (λ_2), and so forth until an nth transmitter 16 transmits a light signal at an nth wavelength (λ_n). The shortest wavelength signal and the longest wavelength signal form a wavelength band. The signals are combined by the multiplexer 18, which then transmits the light 10 signals along the optical fiber 20. Over distance the power of the light signals decrease due to attenuation. The light signals are typically amplified about every 50 - 100 km. For the 1550 nm wavelength band, this amplification is generally performed by an Erbium Doped Fiber Amplifier (EDFA) 22. When the light signals reach their destination they are separated by the demultiplexer 24. The light signals are then received by the receivers 26, 15 28, and 30. Light signal intensity versus wavelength for a typical wavelength band of WDM light signals is illustrated in FIG. 3.

Flat gain response for EDFAs is crucial to the performance of the WDM system 10, since small variations in gain for various wavelengths will grow exponentially over a series of in-line EDFAs 22. Agrawal in "Fiber Optic Communication Systems," (Wiley, 2nd ed., 20 1997, pp 414 - 415) teaches that numerous methods can be used to flatten the gain response of these amplifiers. One method of flattening this gain response is to use channel filters to equalize the gain for various wavelengths. Another method is to adjust the input powers of different wavelengths so that amplification results in uniform intensity for various wavelengths. A third method is to use inhomogeneous broadening of the EDFA 25 gain spectrum to equalize wavelength intensity. A fourth method is to use multiple EDFAs tuned to different wavelength ranges and configured with feedback loops. A final method is to use a filter or series of filters to selectively attenuate the gain response of an EDFA.

A typical gain versus wavelength response for an EDFA is shown in FIG. 4A. When utilizing a filter or series of filters to flatten gain response, an optical filter, with an 30 attenuation curve as shown in FIG. 4B, can be used to selectively attenuate the gain response. The resulting attenuated EDFA gain is shown in FIG. 4C. As shown in FIG.

4C, this attenuated EDFA gain is substantially flat over a range of wavelengths including 1530 nm to 1560 nm. Without a substantially flat gain, the quality of the signal received by the receivers 26, 28, and 30 will be poor.

There are many different known methods for selectively attenuating the gain
5 response of an EDFA in order to improve the signal quality of the signals received by the receivers 26, 28, and 30. U.S. Pat. No. 5,260,823 to Payne et al. entitled, "Erbium-Doped Fibre Amplifier with Shaped Spectral Gain," teaches that a wavelength-selective resonant coupling between a propagating core mode to a cladding leaky mode can be used for filtering a wavelength band for EDFA gain flattening. A periodic perturbation of the core
10 forms a grating and the selected wavelength is attenuated by the resonant coupling between the core and the cladding. By varying the perturbation length, various selected wavelengths can be attenuated. Payne et al. also teach that multilayered dielectric coatings can be used for making an optical filter for EDFA gain flattening. A multilayered filtering apparatus includes two coupling lenses and a multilayered dielectric filter. The two
15 coupling lenses connect to an optical fiber and sandwich the multilayered dielectric filter. The multilayered dielectric filter is designed to cancel out the larger gain around the peak wavelength and to be transparent elsewhere.

U.S. Pat. No. 5,473,714 to Vengsarkar entitled, "Optical Fiber System Using Tapered Fiber Devices," teaches that tapered fiber devices can be used for filtering in an
20 optical telecommunications system. Vengsarkar teaches that by tapering an optical fiber, light can be attenuated by wavelength cutoff and direct coupling from a core to a cladding. The tapered fiber device is formed from the optical fiber by heating the optical fiber and stretching it. The taper reduces the diameter of the core to a value close to the cutoff wavelength. Light with wavelengths near and above the cutoff wavelength are coupled
25 directly to the cladding.

U.S. Pat. No. 5,583,689 to Cassidy et al. entitled "Filter With Preselected Attenuation/Wavelength Characteristic," teaches that a fiber grating, with spatially separated parts having different attenuation characteristics, can perform filtering for EDFA gain flattening. The fiber grating is preferably a side-tap Bragg fiber grating. By varying the
30 pitch along the fiber grating an appropriate attenuation profile can be provided for flattening the EDFA gain response.

U.S. Pat. No. 5,067,789 to Hall et al. entitled, "Fiber Optical Coupling Filter and Amplifier," teaches that a light-attenuating light path adjacent to a first core within a cladding can be used to filter wavelengths about a specific wavelength for EDFA gain flattening. The light attenuating light path is preferably one or more lossy cores that are evanescently coupled to the first core. The evanescent coupling between the first core and the light attenuating light path is greatest where the effective index of refraction of the first core equals the effective index of refraction of the light attenuating light path. By choosing a single mode or a higher multimode optical waveguide structure for the light attenuating light path, the effective index of refraction for the light attenuating light path can be varied. Hall et al. teach that the index of refraction for the material for the light attenuating light path should be greater than the index of refraction for the material for the first core. Hall et al. further teach that as an alternative embodiment the lossy core could be a lossy annular region located concentrically about the first core and within the cladding. A necessary feature of this filter is that the lossy core or the lossy annular region has specific light absorption characteristics. Since the lossy core or the lossy annular region is contained completely within the cladding, the specific light absorption characteristics dissipates light energy that has been filtered from the first core to the lossy core or the lossy annular region. The absorption characteristics of the lossy core or the lossy annular region determine an amount of attenuation of the filtered wavelengths.

Each of these known methods for filtering an amplified signal from an EDFA can be inefficient, unreliable, and expensive. There is currently a lack of efficient filters for gain flattening in fiber optic systems, which are easy to manufacture and use within a WDM system.

SUMMARY OF THE INVENTION

An all fiber optical filter is formed by stretching an optical fiber. The all fiber filter includes a core, an inner cladding, and an outer cladding. A core index of refraction is greater than an outer cladding index of refraction. The outer cladding index of refraction is greater than an inner cladding index of refraction. The all fiber optical filter attenuates a portion of an optical signal by transferring optical energy from the core to the

outer cladding by evanescent coupling. The all fiber optical filter has a compact structure, which prevents bending and provides stable temperature performance.

The all fiber optical filter is preferably used in Wavelength Division Multiplexing (WDM) systems for gain flattening of gain responses from Erbium Doped Fiber Amplifiers
5 (EDFAs). Alternatively, the all fiber optical filter is used in other applications where optical filtering or attenuation is needed.

The all fiber optical filter is manufactured by holding a length of an appropriate optical fiber between two clamps, heating the optical fiber, and stretching the optical fiber until a predetermined characteristic of the optical fiber is achieved.

10

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a cross section of an optical fiber of the prior art.

FIG. 2 illustrates a block diagram of a WDM system of the prior art.

FIG. 3 illustrates a graph of intensity versus wavelength for a wavelength band of
15 WDM light signals of the prior art.

FIG. 4A illustrates an EDFA gain curve over a range of wavelengths of the prior art.

FIG. 4B illustrates a filter attenuation curve over a range of wavelengths for gain band flattening of the prior art.

20 FIG. 4C illustrates an attenuated EDFA gain curve over a range of wavelengths using a filter of the prior art.

FIG. 5 illustrates a linear cross section of an all fiber optical filter of the present invention.

FIG. 6 illustrates a cross-section of the all fiber optical filter of the present
25 invention.

FIG. 7 illustrates the all fiber optical filter and additional structure of the present invention.

FIGS. 8A, 8B, and 8C illustrate configurations including an EDFA, a first all fiber optical filter, and a second all fiber optical filter of the present invention.

30 FIGS. 9A and 9B illustrate intensity versus wavelength for an EDFA gain response and a filtered EDFA gain response of the present invention.

FIG. 10 illustrates an EDFA and an all fiber optical filter of the present invention.

FIG. 11 illustrates a WDM system including the all fiber optical filter of the present invention.

FIG. 12 illustrates a first apparatus for making the all fiber optical filter of the present invention.

FIG. 13 illustrates a second apparatus for making the all fiber optical filter of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A linear cross section of an all fiber optical filter of the present invention is illustrated in FIG. 5. The all fiber optical filter 32 has a core 34, an inner cladding 36, an outer cladding 38, and a filter length 40. A cross-section of the all fiber optical filter 32 showing the core 34, the inner cladding 36, and the outer cladding 38 is illustrated in FIG. 6. The core 34 has a core diameter. The inner cladding 36 has an inner cladding thickness. The outer cladding 38 has an outside diameter. Indexes of refraction for the core 34, the inner cladding 36, and the outer cladding 38 are referred to as a core index of refraction, an inner index of refraction, and an outer index of refraction, respectively. The core index of refraction is preferably greater than the outer index of refraction. The outer index of refraction is preferably greater than the inner index of refraction. By an appropriate selection of the core index of refraction, the inner index of refraction, and the outer index of refraction as well as selecting the core diameter and the inner cladding thickness, optical energy from an optical signal within a wavelength range is transferred from the core 34 to the outer cladding 38 by evanescent coupling.

The core 34 of the all fiber optical filter 32 is a single mode waveguide. A convention used when discussing optical waveguides is to refer to an effective index of refraction, which is defined as a waveguide propagation constant β divided by a free space wave number k_o. The effective index of refraction is both wavelength dependent and mode dependent. A core effective index of refraction for the core 34 has a value between the inner index of refraction and the core index of refraction. Reducing the core diameter reduces the core effective index of refraction provided that the single mode continues to propagate. The outer cladding 38 is a multimode waveguide. The outer cladding is

sufficiently large that an outer effective index of refraction for a first mode is equal to the outer index of refraction. The inner cladding 36 forms a barrier between the core 34 and the outer cladding 38. Optical energy will transfer from the core 34 to the cladding 38 by evanescent coupling if the core effective index of refraction is near to the outer index of
5 refraction and the barrier is sufficiently narrow. Since the core effective index of refraction depends upon the core diameter, the core diameter determines a wavelength range that could couple from the core 34 to the outer cladding 38.

The core diameter, the core effective index of refraction, and the outer index of refraction determine a peak attenuation wavelength and a wavelength band about the peak
10 attenuation wavelength that couples from the core 34 to the outer cladding 38. Optical energy that couples from the core 34 to the outer cladding 38 and is propagating in the first mode can couple back to the core 34. Accordingly, the outer diameter of the outer cladding and the filter length 40 adjust the peak attenuation wavelength and the wavelength band about the peak wavelength. Depending upon a variation of the core effective index
15 of refraction with wavelength, other peak attenuation wavelengths and wavelength bands could couple from the core 34 to the outer cladding 38.

The all fiber optical filter 32 and additional structure is illustrated in FIG. 7. The additional structure includes an input length 42, an output length 44, a first transition 46, and a second transition 48. The input length 42 connects to the first transition 46, which
20 connects to the all fiber optical filter 32. The all fiber optical filter 32 connects to the second transition 48, which connects to the output length 44. The core 34, the inner cladding 36, and the outer cladding 38 of the all fiber optical filter 32 extend through the input length 42, the first transition 46, the second transition 48, and the output length 44. The thickness of the inner cladding 36, within the input length 42 and the output length 44,
25 is greater than an evanescent coupling thickness that allows evanescent coupling between the core 34 and the outer cladding 38 within the input length 42 and the output length 44. The input length 42 and the output length 44 are coupled to an optical fiber system by appropriate means available for coupling optical fiber components.

An exemplary configuration including an EDFA and a cascaded series of all fiber
30 optical filters used to flatten the EDFA gain over wavelength ranges of 1529 nm to 1562 nm and 1580 nm to 1620 mn is illustrated in FIG. 8A. The EDFA 52 is coupled to a first

all fiber optical filter 54. The first all fiber optical filter 54 is coupled to a second all fiber optical filter 56. An input optical signal 58 is provided to the EDFA 52, which amplifies the input optical signal 58 and provides an amplified optical signal. The amplified optical signal is then provided to the first all fiber optical filter 54, which filters the amplified
5 optical signal and provides a first filtered optical signal. The first filtered optical signal is then provided to the second all fiber optical filter 56, which filters the first filtered optical signal and provides an output optical signal 60.

Other configurations for the EDFA 52, first all fiber optical filter 54, and the second all fiber optical filter 56 are illustrated in FIGS. 8B and 8C. In FIG. 8B, the first
10 all fiber optical filter 54 is coupled to the EDFA 52, which is coupled to the second all fiber optical filter 56. In FIG. 8C, the first all fiber optical filter 54 is coupled to the second all fiber optical filter, which is coupled to the EDFA 52.

In the preferred embodiment of the present invention, intended to operate in the wavelength ranges of 1529 nm to 1562 mn and 1580 nm to 1620 nm, the core 34, the
15 inner cladding 36, and the outer cladding 38 are silica glasses. The indexes of refraction are preferably 1.467 for the core index of refraction, 1.411 for the inner index of refraction, and 1.424 for the outer index of refraction. The core diameter is preferably within the range and including 3 μm and 6 μm. An outer diameter for the inner cladding 36 is preferably within the range and including 12 μm and 30 μm. The outside diameter
20 of the outer cladding 38 is preferably within the range and including 50 μm and 85 μm. The filter length 40 is preferably within the range and including 10 mm and 20 mm. Specific dimensions for the preferred embodiment are a result of a forming process, which preferably uses an optical spectrum response for the all fiber optical filter 32 as a critical parameter.

25 The preferred embodiment for the all fiber optical filter 32 is formed by identifying a preferred peak EDFA gain response and a preferred wavelength band about the preferred peak gain response that is to be flattened. An inverse of the gain response for the preferred wavelength band becomes a preferred target response for the all fiber optical filter 32 such that the all fiber optical filter 32 provides a preferred attenuation response
30 that is near to the preferred target response after the forming process.

Referring to FIG. 8A, the EDFA 52 provides the amplified optical signal, which is used to determine the first peak EDFA gain response and the first wavelength band. For a test EDFA used in testing an all fiber optical filter of the present invention, the preferred peak EDFA gain response was found to be at 1533 nm with a preferred relative gain response of 6.0 dB. The relative gain response is defined as the difference between a specific gain response for a specific wavelength and a minimum gain response for the wavelength range. The preferred target response about 1533 nm was used in the forming process so that after the forming process, the all fiber optical filter 32 provided the preferred attenuation curve.

An alternative embodiment is formed by identifying an alternate target response for an alternate peak EDFA gain response and an alternate wavelength band about the alternate peak EDFA gain response. For the test EDFA, the alternate peak wavelength was found to be at 1552 nm with an alternate relative gain response of 3.83 dB.

Referring to FIG. 8A, tests were performed in which the EDFA 52 was the test EDFA, the first all fiber optical filter 54 was the preferred embodiment of the all fiber optical filter described above and having the preferred attenuation response, and the second all fiber optical filter 56 was the alternative embodiment of the all fiber optical filter described above and having an alternate attenuation response. Test results using this configuration for the wavelength range from 1529 nm to 1562 nm are illustrated in FIG. 9A. The EDFA gain response is shown as the curve A. The first target response is the inverse of the EDFA gain response from 1529 nm to 1540 nm. The second target response is the inverse of the EDFA gain response from 1540 nm to 1562 nm. The output optical signal 60 is shown as the curve B, which shows a substantially flat attenuated EDFA gain curve over the wavelength range from 1529 nm to 1562 nm.

Test results using this configuration for the wavelength range from 1580 nm to 1620 are illustrated in FIG. 9B. The EDFA gain response is shown as the curve C. The output optical signal 60 is shown as the curve D, which shows a substantially flat attenuated gain curve over the wavelength range from 1580 nm to 1620 nm.

An alternative embodiment comprising the EDFA 52 and a single all fiber optical filter is illustrated in FIG. 10. Depending upon the gain response of the EDFA 52, the single all fiber optical filter 62 will suffice to flatten the gain response of the EDFA 52.

The EDFA 52 is coupled to the single all fiber optical filter 62. The input optical signal 58 is provided to the EDFA 52, which amplifies the input optical signal 58 and provides an amplified optical signal. The amplified optical signal is then provided to the single all fiber optical filter 62, which filters the amplified optical signal and provides the output
5 optical signal 60.

A WDM system with EDFA gain flattening including one or more all fiber optical filters according to the present invention is illustrated in FIG. 11. The WDM system 66 includes a transmission system 11, which includes a series of transmitters 12, 14, and 16 each coupled to a multiplexer 18. The multiplexer 18 provides an output, which is coupled
10 to an optical fiber 20. Over long distances EDFAs 22 and the one or more all fiber optical filters 68 are included along the optical fiber 20. The optical fiber 20 is then also coupled to a receiving system 23, which includes a demultiplexer 24 and a series of receivers 26, 28, and 30. The optical fiber 20 is coupled to an input of the demultiplexer 24 of the receiving system 23. Outputs of the demultiplexer 24 are coupled to the series of receivers
15 26, 28, and 30.

In the WDM system 66, a first transmitter 12 transmits a light signal at a first wavelength (λ_1), a second transmitter 14 transmits a light signal at a second wavelength (λ_2), and so forth until an nth transmitter 16 transmits a light signal at an nth wavelength (λ_n). The light signals are combined by the multiplexer 18, which then transmits the light
20 signals along the optical fiber 20. Over distance the power of the light signals decrease due to attenuation. The light signals are amplified approximately every 50 - 100 km by the EDFAs 22. The one or more all fiber optical filters 68 flatten the EDFA gain for the light signals, as discussed above. When the light signals reach their destination they are separated by the demultiplexer 24. The light signals are then received by the receivers 26,
25 28, and 30.

A first apparatus for manufacturing the all fiber optical filter of the present invention is illustrated in FIG. 12. The first apparatus 70 includes a heating source 72, a first clamp 74, a second clamp 76, a first stepper motor 78, a second stepper motor 79, a first drive means 80, and a second drive means 81. The first clamp 74 is placed to one
30 side of the heating source 72. The second clamp 76 is placed adjacent to the heating source 72 on the side opposite to the first clamp 74. The first clamp 74 is connected to the

first stepper motor 78 by the first drive means 80. The second clamp 76 is connected to the second stepper motor 79 by the second drive means 81.

A first method of manufacture uses the first apparatus 70. An initial length of optical fiber 82 is held between the first clamp 74 and the second clamp 76. The heating source 72 heats the optical fiber 82 to within an allowed temperature range. The first stepper motor 78 actuates the first drive means 80. The second stepper motor 79 actuates the second drive means 81. Consequently, the first clamp 74 and the second clamp 76 are further separated. This further separation stretches the optical fiber 82. When a predetermined stretch distance has been reached the first and second stepper motor 78 and 79 are stopped, which stops the first and second clamp 74 and 76. Finally, the heating source 72 is removed, the heating source 72 is turned off, or the optical fiber 82 is removed from the heating source 72. This results in an all fiber optical filter, according to the present invention, having a predetermined filter length.

A second and preferred apparatus for manufacturing the all fiber optical filter of the present invention is illustrated in FIG. 13. The second apparatus 84 includes the first apparatus 70, a process control unit 86, a light source 88, and an optical spectrum analyzer 90. The light source 88 is located at one end of the optical fiber 82. The optical spectrum analyzer 90 is located at the end of the optical fiber 82 opposite to the light source 88. The process control unit 86 controls and monitors the heating source 72 through a first control link 92. The process control unit 86 controls the first stepper motor 78 through a second control link 94. The process control unit 86 controls the second stepper motor 79 through a third control link 95. The process control unit 86 controls the light source 88 through a fourth control link 96. The process control unit 86 controls and monitors the optical spectrum analyzer 90 through a fifth control link 98.

A second and preferred method of manufacture uses the second apparatus 84. The initial length of optical fiber 82 is held between the first clamp 74 and the second clamp 76. The process control unit 86 signals and monitors the heating source 72. The heating source 72 heats the optical fiber to within the allowed temperature range. The process control unit 86 turns on the light source 88. The light source 88 couples light to the optical fiber 82. Preferably, the light source 88 is a white light source. The optical fiber 82 transmits the light to the end of the optical fiber 82 opposite the light source 88. The

light exits the optical fiber 82. The process control unit turns on the optical spectrum analyzer 90. The optical spectrum analyzer 90 detects the light that exits from the optical fiber 82. The process control unit 86 signals the first and second stepper motors 78 and 79. The first and second stepper motors 78 and 79 further separate the first and second
5 clamps 74 and 76. This further separation stretches the optical fiber 82. As the optical fiber 82 is stretched, the light signal at the end of the optical fiber adjacent to the optical spectrum is monitored for a predetermined optical spectrum response that is based on the target response, as described above. When the optical spectrum analyzer 90 detects the predetermined optical spectrum response, the process control unit 86 stops the first and
10 second stepper motors 78 and 79, thereby stopping the first and second clamp 74 and 76. Finally, the process control unit signals the heating source 72 to stop heating. This results in an all fiber optical filter, according to the present invention, having a desired attenuation response.

Preferably, the optical fiber 82 used to form the all fiber optical filter 32 of the
15 present invention has a core with an initial diameter of 8.3 μm, an inner cladding with an initial outside diameter of 45 μm, and an outer cladding with an initial outside diameter of 125 μm. Preferably, a length of 6 mm is heated by the heating source 72 to a temperature within the range between 900 °C and 1100 °C. The optical fiber 82 is stretched to a length of about 15 mm. Preferably, the specific stretch length and other dimensions of the all
20 fiber optical filter are determined by the predetermined optical spectrum response.

It will be readily apparent to one skilled in the art that other various modifications may be made to the preferred embodiment without departing from the spirit and scope of the invention as defined by the appended claims. Specifically, the all fiber optical filter of the present invention could be used to flatten the gain of other rare earth doped fiber
25 amplifiers or the all fiber optical filter of the present invention could be used to filter or attenuate any optical signal.

CLAIMS

We claim:

1 1. An all fiber optical filter formed from stretching an optical fiber and
2 comprising a fiber optic core, an inner cladding formed concentrically about the fiber optic
3 core, and an outer cladding formed concentrically about the inner cladding, wherein an
4 outer index of refraction of the outer cladding is less than a core index of refraction of the
5 fiber optic core and further wherein the outer index of refraction is greater than an inner
6 index of refraction of the inner cladding.

1 2. The all fiber optical filter as claimed in claim 1 wherein the optical fiber is
2 stretched until evanescent coupling is achieved between the fiber optic core and the outer
3 cladding.

1 3. The all fiber optical filter as claimed in claim 2 wherein the all fiber optical
2 filter is configured to receive an optical signal, including a gain, from a fiber amplifier.

1 4. The all fiber optical filter as claimed in claim 3 wherein the optical signal is
2 filtered by the evanescent coupling between the fiber optic core and the outer cladding to
3 flatten the gain.

1 5. The all fiber optical filter as claimed in claim 1 wherein the optical fiber is
2 stretched until a filter optical response is approximately equal to a target optical spectrum
3 response.

1 6. The all fiber optical filter as claimed in claim 5 wherein the target optical
2 spectrum response is an inverse of a portion of an amplifier gain spectrum.

1 7. An all fiber optical filter formed by stretching an optical fiber and
2 comprising:

3 a. a single mode fiber optic core having a core index of refraction;
4 b. an inner cladding formed concentrically about the single mode fiber
5 optic core, the inner cladding having an inner index of refraction, the inner
6 index of refraction being less than the core index of refraction; and
7 c. an outer cladding formed concentrically about the inner cladding, the
8 outer cladding having an outer index of refraction, the outer index of
9 refraction being less than the core index of refraction, the outer index being
10 greater than the inner index of refraction;
11 wherein the optical fiber is stretched until a filter optical response is approximately equal to
12 a target optical spectrum response.

1 8. The all fiber optical filter as claimed in claim 7 wherein the target optical
2 spectrum response is an inverse of a portion of an amplifier gain spectrum.

1 9. An optical filter comprising:
2 a. a fiber optic core having a first diameter, a filter length, and a first
3 index of refraction;
4 b. an inner cladding formed concentrically about the fiber optic core,
5 the inner cladding having a second index of refraction and a first thickness,
6 wherein the second index of refraction is less than the first index of
7 refraction; and
8 c. an outer cladding formed concentrically about the inner cladding, the
9 outer cladding having a third index of refraction, wherein the third index of
10 refraction is greater than the second index of refraction and less than the first
11 index of refraction, and further wherein the first diameter and the first
12 thickness are of dimensions to promote evanescent coupling between the
13 fiber optic core and the outer cladding.

1 10. The optical filter as claimed in claim 9 wherein the optical filter is
2 configured to receive an optical signal, including a gain, from a fiber amplifier.

1 11. The optical filter as claimed in claim 10 wherein the optical signal is filtered
2 by the evanescent coupling between the fiber optic core and the outer cladding to flatten
3 the gain.

1 12. The optical filter as claimed in claim 11 wherein the fiber optic core further
2 includes an input length with a second diameter and an output length with a third diameter,
3 wherein the input length is coupled to the filter length by a first transition length and the
4 output length is coupled to the filter length by a second transition length, and further
5 wherein the second diameter and the third diameter each are greater the first diameter.

1 13. The optical filter as claimed in claim 12 wherein the inner cladding includes
2 a second thickness formed about the input length of the fiber optic core and a third
3 thickness formed about the output length of the fiber optic core, the inner cladding having
4 a first smooth variation thickness form the first thickness to the second thickness and a
5 second smooth variation thickness from the first thickness to the third thickness, wherein
6 the second thickness and the third thickness are each greater than the first thickness.

1 14. The optical filter as claimed in claim 13 wherein the outer cladding includes
2 an input outer cladding formed about the second thickness and the first smooth variation
3 thickness.

1 15. The optical filter as claimed in claim 14 wherein the outer cladding includes
2 an output outer cladding formed about the third thickness and the second smooth variation
3 thickness.

1 16. An all fiber optical filter for flattening gain of an amplified optical signal
2 provided from a fiber amplifier comprising:
3 a. a fiber optic core having an input length, a filter length, an output
4 length and a first index of refraction, wherein the input length is separated
5 from the filter length by a first transition length and the filter length is
6 separated from the output length by a second transition length and further

7 wherein the first transition length has a decreasing diameter from the input
8 length to the filter length and the second transition length has an increasing
9 diameter form the filter length to the output length;
10 b. an inner cladding formed concentrically about the fiber optic core,
11 the inner cladding having a second index of refraction and an input thickness
12 formed about the input length of the fiber optic core and a filter thickness
13 formed about the filter length of the fiber optic core and a first smooth
14 variation thickness from the input thickness to the filter thickness, the inner
15 cladding having an output thickness formed about the output length of the
16 fiber optic core, the inner cladding having a second smooth variation
17 thickness form the filter thickness to the output thickness; and
18 c. an outer cladding formed concentrically about the inner cladding, the
19 outer cladding having a third index of refraction which is less than the first
20 index of refraction and greater than the second index of refraction.

1 17. The all fiber optical filter as claimed in claim 16 wherein a core diameter of
2 the fiber optic core and the filter thickness are of dimensions to promote evanescent
3 coupling between the fiber optic core and the outer cladding.

1 18. The all fiber optical filter as claimed in claim 17 wherein the optical filter is
2 configured to receive an optical signal, including a gain, from a fiber amplifier.

1 19. The all fiber optical filter as claimed in claim 18 wherein the optical filter is
2 filtered by the evanescent coupling between the fiber optic core and the outer cladding to
3 flatten the gain.

1 20. A fiber optic communication system for transmitting an optical signal
2 comprising:
3 a. a transmission system configured to receive and transmit the optical
4 signal;

5 b. a first length of optical fiber coupled to the transmission system for
6 carrying the optical signal;
7 c. an amplifier coupled to the first length of optical fiber for amplifying
8 the optical signal thereby forming an amplified signal having a gain;
9 d. an optical filter coupled to the amplifier for filtering the amplified
10 signal and flattening the gain, thereby forming a filtered signal, the optical
11 filter including:
12 i. a fiber optic core having a first diameter, a filter length, a first index
13 of refraction, a first end for receiving the amplified signal, and a
14 second end for transmitting the filtered signal;
15 ii. an inner cladding formed concentrically about the fiber optic core,
16 the inner cladding having a second index of refraction and a first
17 thickness, wherein the second index of refraction is less than the first
18 index of refraction; and
19 iii. an outer cladding formed concentrically about the inner cladding, the
20 outer cladding having a third index of refraction, wherein the third
21 index of refraction is greater than the second index of refraction and
22 the third index of refraction is less than the first index of refraction,
23 wherein the first diameter and the first thickness are of dimensions to
24 promote evanescent coupling between the fiber optic core and the
25 outer cladding to flatten the gain of the optical signal;
26 e. a second length of optical fiber coupled to the optical filter for
27 carrying the filtered signal; and
28 f. a receiving system coupled to the second length of optical fiber to
29 receive the filtered signal.

1 21. The fiber optic communication system as claimed in claim 20 wherein the
2 transmission system includes a multiplexer and a plurality of transmitters coupled to the
3 multiplexer for transmitting the optical signal.

1 22. The fiber optic communication system as claimed in claim 21 wherein the
2 receiving system includes a demultiplexer and a plurality of receivers coupled to the
3 demultiplexer for receiving the filtered signal.

1 23. A fiber optic communication system for transmitting an optical signal
2 comprising:
3 a. a transmission system configured to receive and transmit the optical
4 signal;
5 b. a first length of optical fiber coupled to the transmission system for
6 carrying the optical signal;
7 c. an optical filter coupled to the first length of optical fiber for filtering
8 the optical signal, thereby forming a filtered signal, the optical filter
9 including:
10 i. a fiber optic core having a first diameter, a filter length, a first index
11 of refraction, a first end for receiving the amplified signal, and a
12 second end for transmitting the filtered signal;
13 ii. an inner cladding formed concentrically about the fiber optic core,
14 the inner cladding having a second index of refraction and a first
15 thickness, wherein the second index of rcfraction is less than the first
16 index of refraction; and
17 iii. an outer cladding formed concentrically about the inner cladding, the
18 outer cladding having a third index of refraction, wherein the third
19 index of refraction is greater than the second index of refraction and
20 the third index of refraction is less than the first index of refraction,
21 wherein the first diameter and the first thickness are of dimensions to
22 promote evanescent coupling between the fiber optic core and the
23 outer cladding to filter the optical signal;
24 d. an amplifier coupled to the optical filter for amplifying the filtered
25 signal thereby forming an amplified signal having a flattened gain;
26 e. a second length of optical fiber coupled to the amplifier for carrying
27 the amplified signal having the flattened gain; and

28 f. a receiving system coupled to the second length of optical fiber to
29 receive the amplified signal having the flattened gain.

1 24. The fiber optic communication system as claimed in claim 23 wherein the
2 transmission system includes a multiplexer and a plurality of transmitters coupled to the
3 multiplexer for transmitting the optical signal.

1 25. The fiber optic communication system as claimed in claim 24 wherein the
2 receiving system includes a demultiplexer and a plurality of receivers coupled to the
3 demultiplexer for receiving the filtered signal.

1 26. A method of manufacturing an all fiber optical filter, which begins with an
2 optical fiber having a core, inner cladding, and outer cladding, comprising:
3 a. holding the optical fiber between a first clamp and a second clamp;
4 b. heating a length of the optical fiber between the first clamp and the
5 second clamp; and
6 c. stretching the optical fiber by further separating the first clamp and
7 the second clamp until a predetermined characteristic is achieved.

1 27. The method as claimed in claim 26 wherein the predetermined characteristic
2 is a stretch length of the optical fiber.

1 28. The method as claimed in claim 27 wherein the step of heating includes
2 heating the length of optical fiber to a temperature within the range of 900 °C to 1100 °C.

1 29. The method as claimed in claim 28 wherein the step of stretching is
2 completed by using a first stepper motor that controls the movement of the first clamp and
3 a second stepper motor that controls the movement of the second clamp.

1 30. The method of claim 26 wherein the predetermined characteristic is an
2 optical spectrum response of the optical fiber.

1 31. The method as claimed in claim 30 wherein the optical spectrum response is
2 measured using a white light source and an optical spectrum analyzer.

1 32. The method as claimed in claim 31 wherein the predetermined optical
2 spectrum response is based upon an inverse of a portion of an amplifier gain spectrum such
3 that upon cooling of the all fiber optical filter, the optical spectrum response will be nearly
4 equal to the inverse of the portion of the amplifier gain spectrum.

1 33. The method as claimed in claim 32 wherein the temperature is within the
2 range between and including 900 °C to 1100 °C.

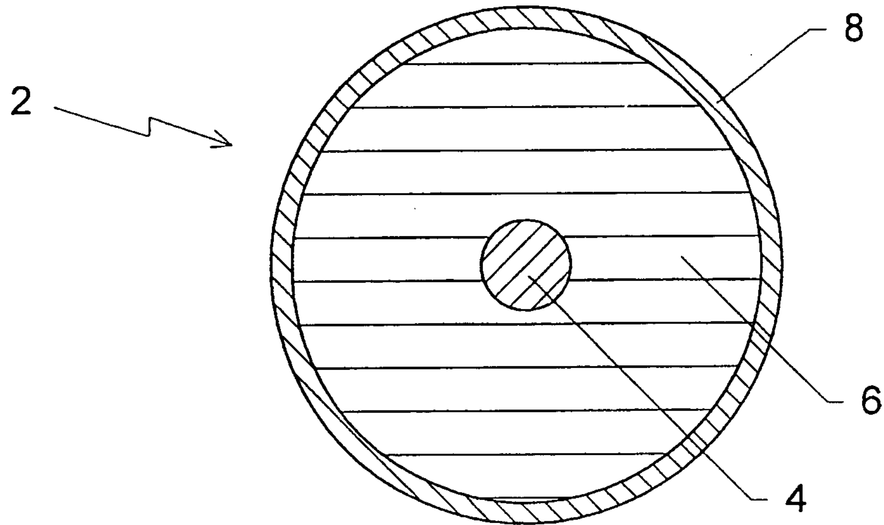


FIG. 1
(PRIOR ART)

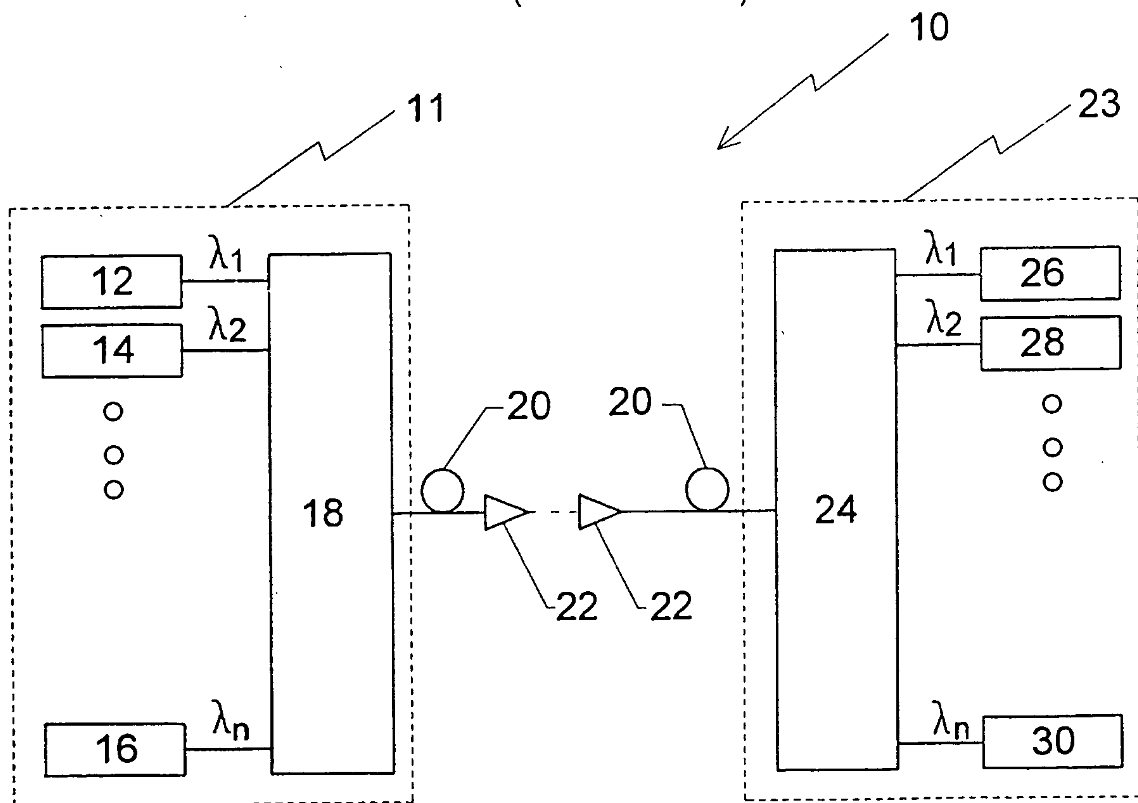


FIG. 2
(PRIOR ART)

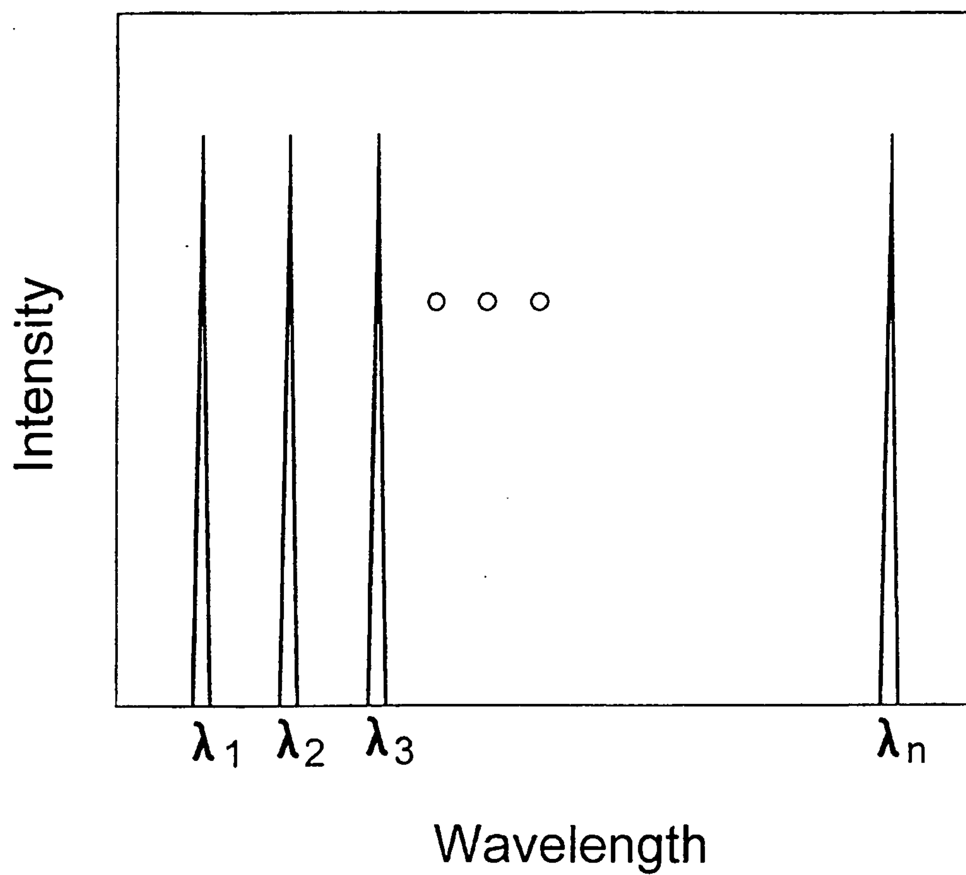


FIG. 3
(PRIOR ART)

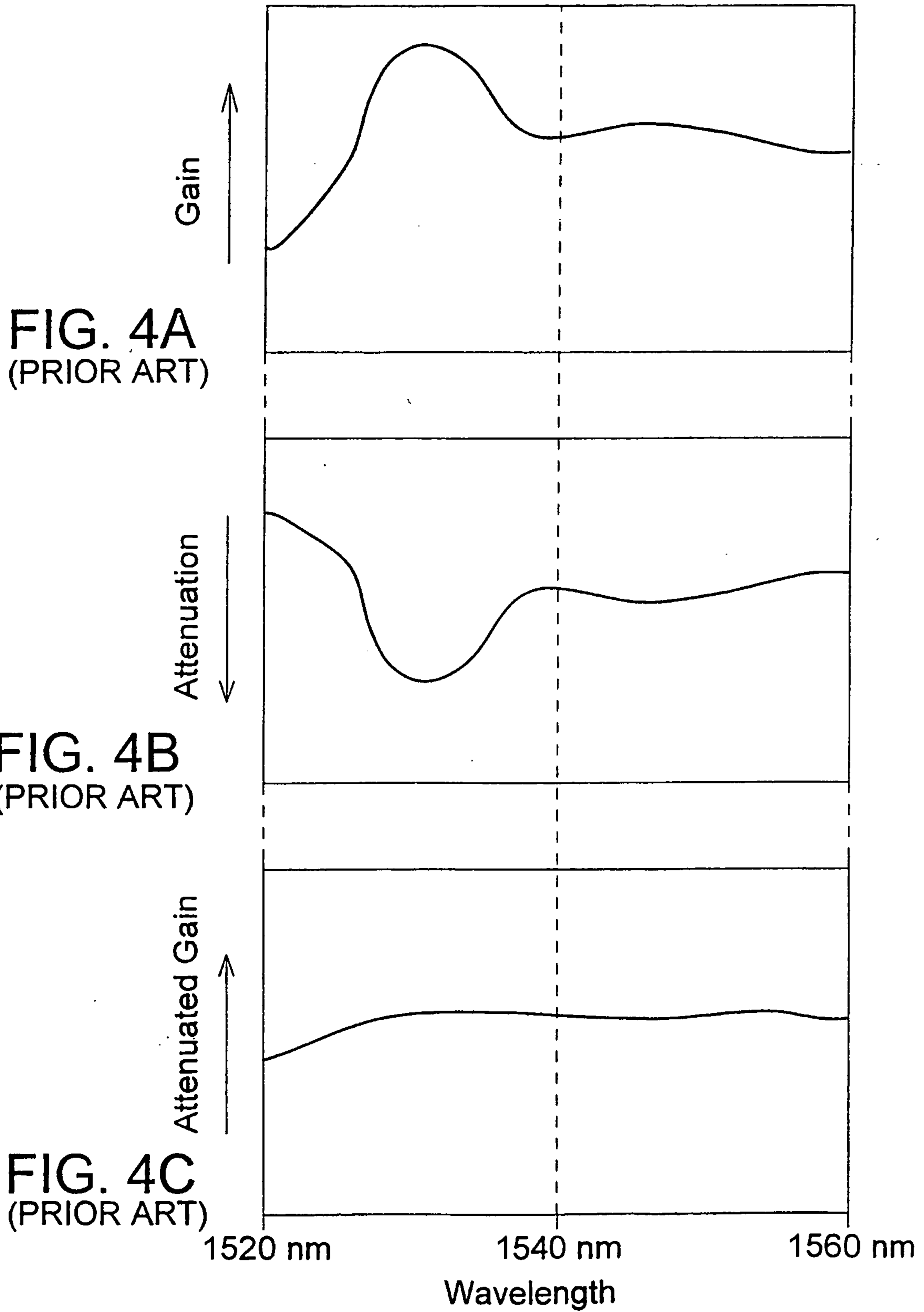


FIG. 4A (PRIOR ART)

FIG. 4B (PRIOR ART)

FIG. 4C (PRIOR ART)

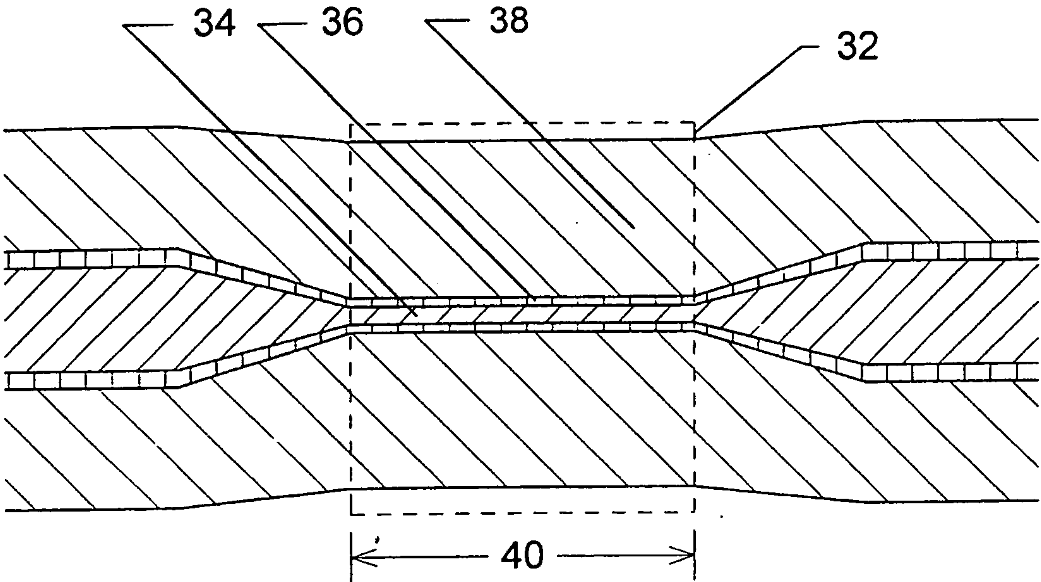


FIG. 5

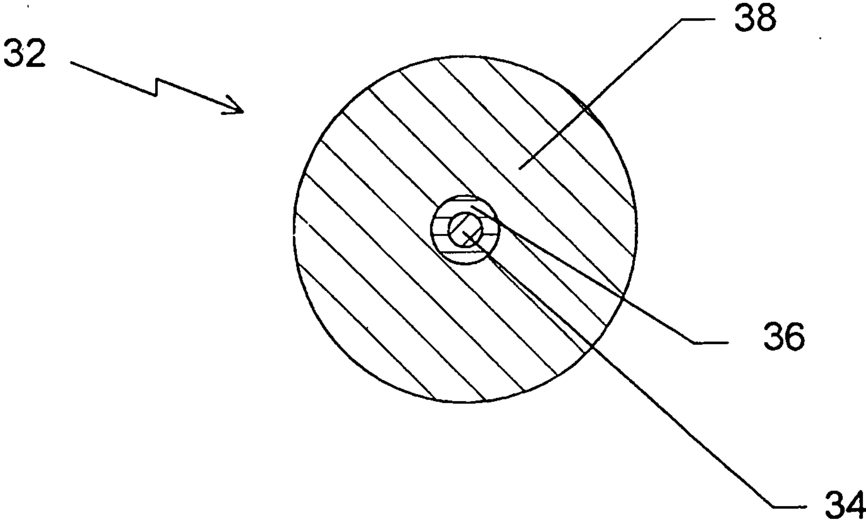


FIG. 6

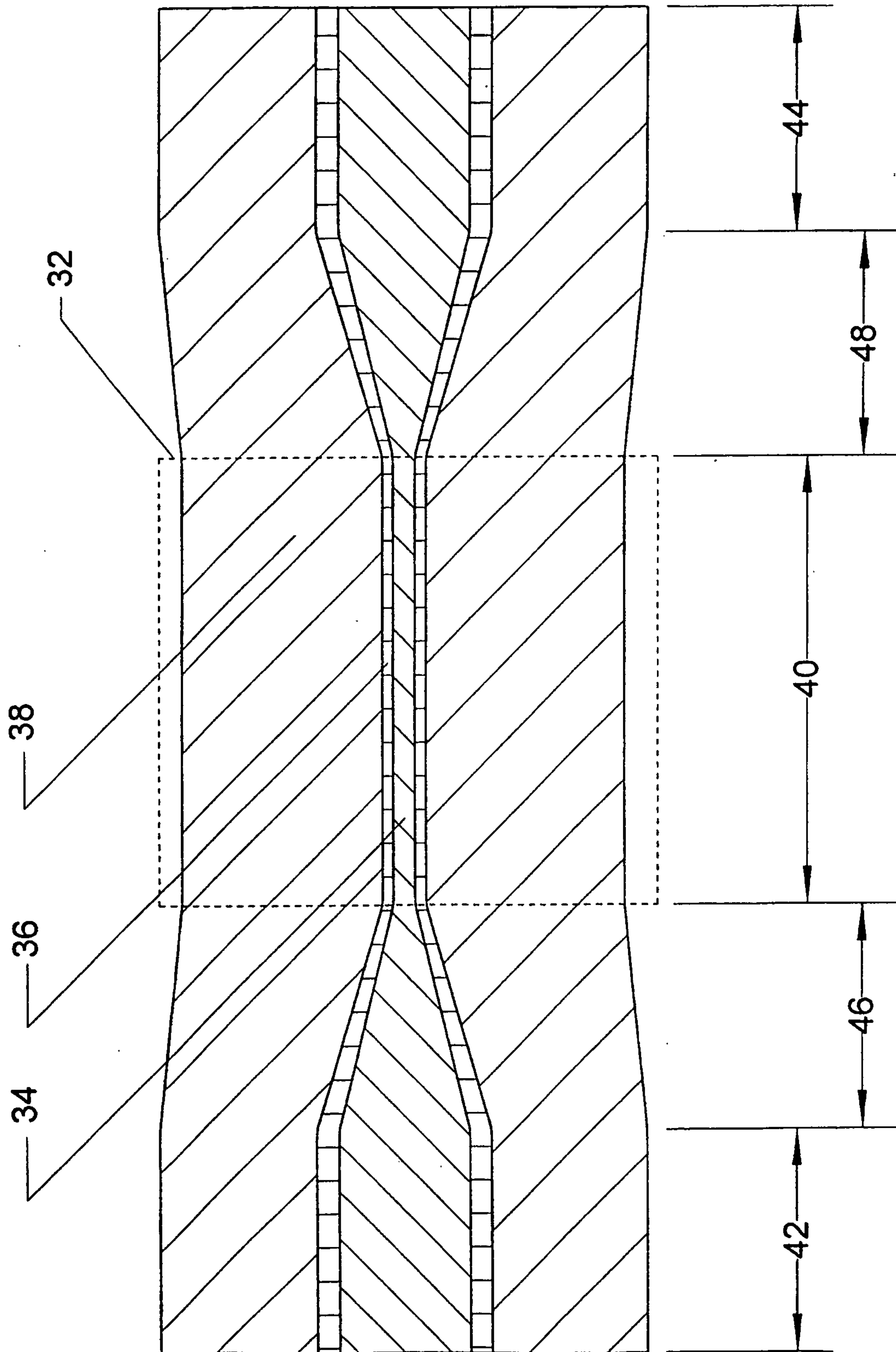


FIG. 7

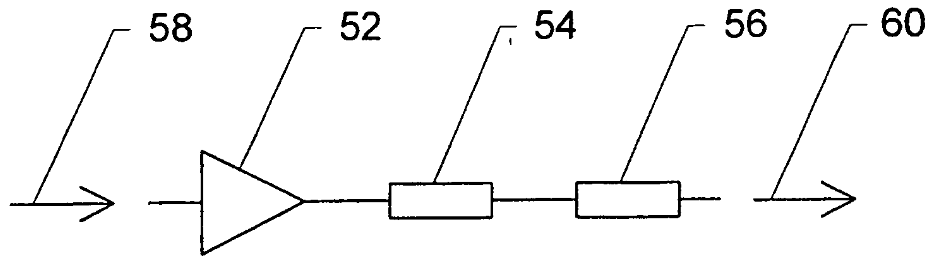


FIG. 8A

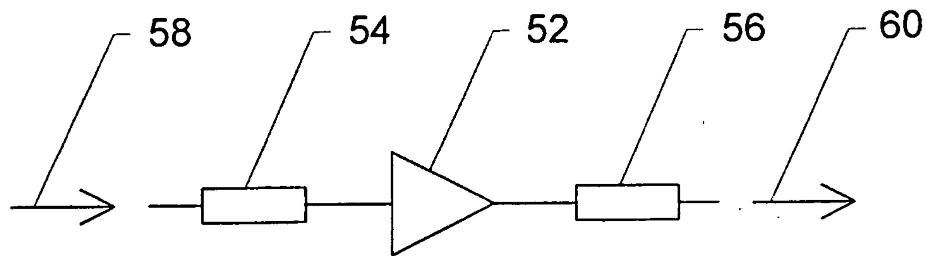


FIG. 8B

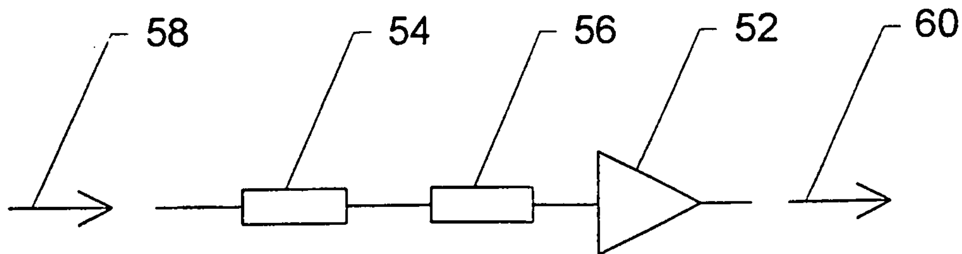


FIG. 8C

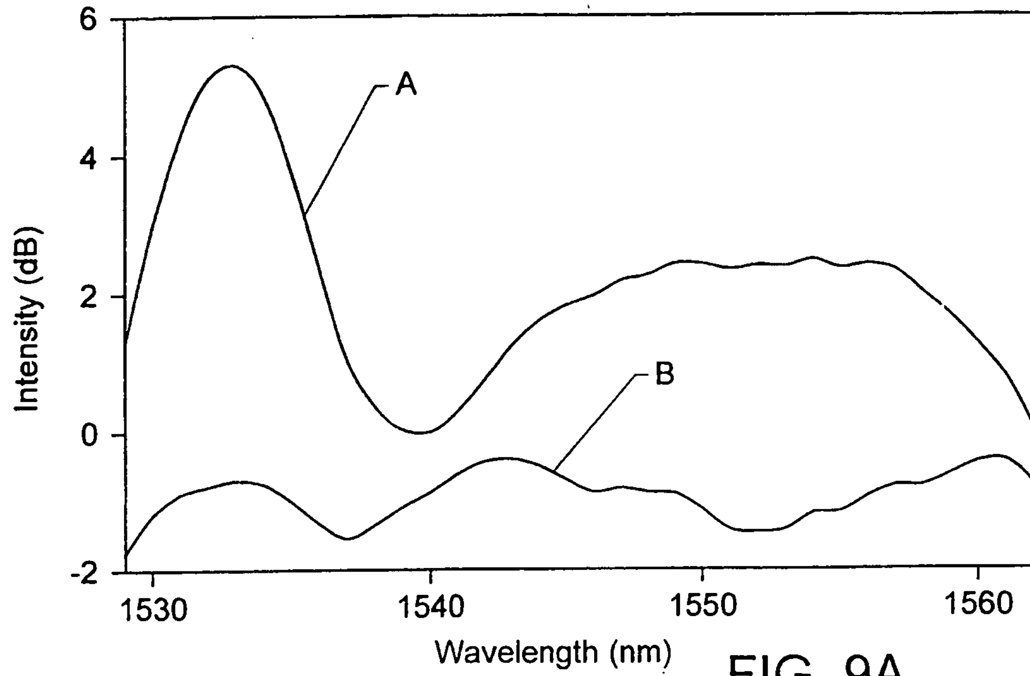


FIG. 9A

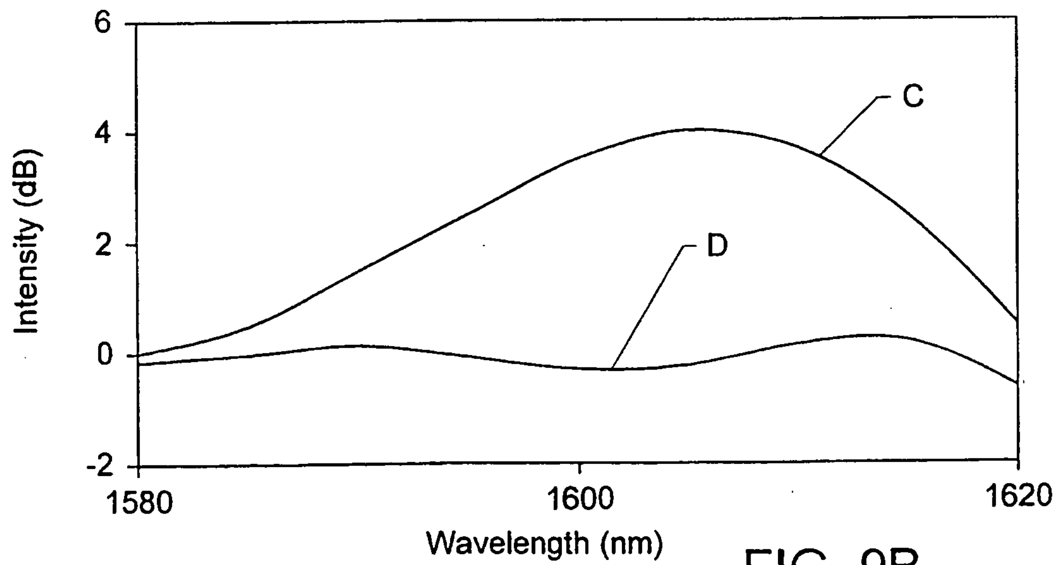


FIG. 9B

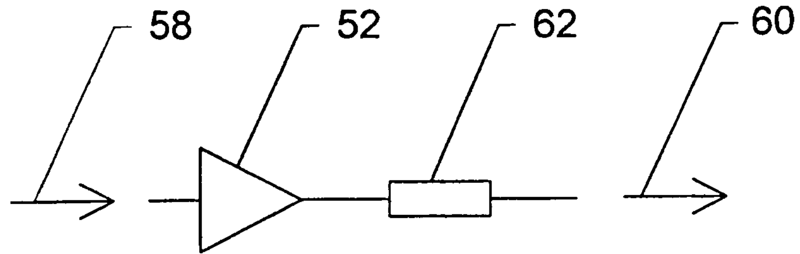


FIG. 10

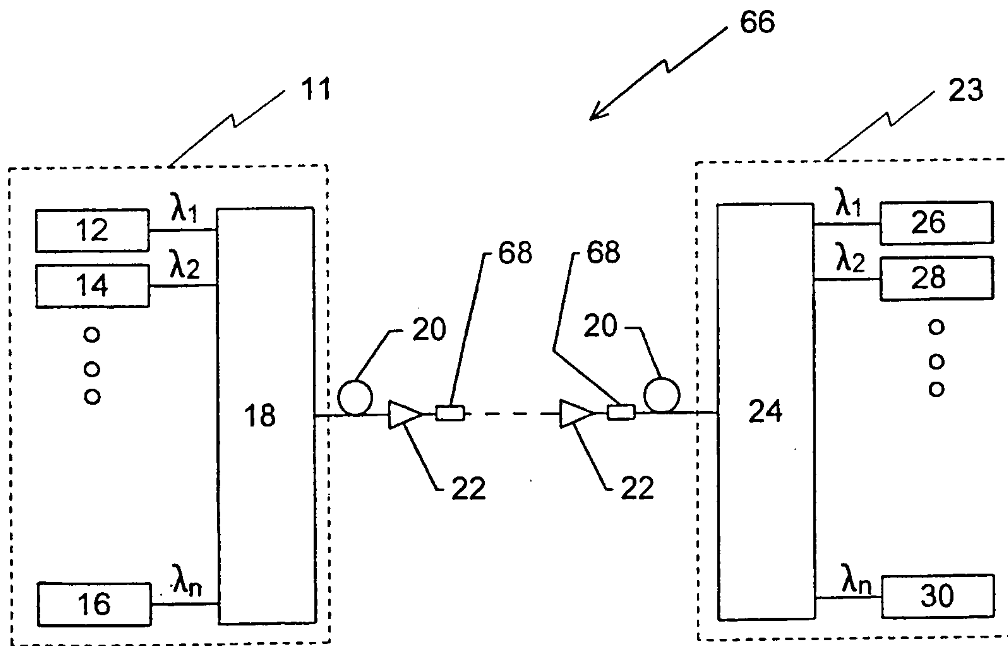


FIG. 11

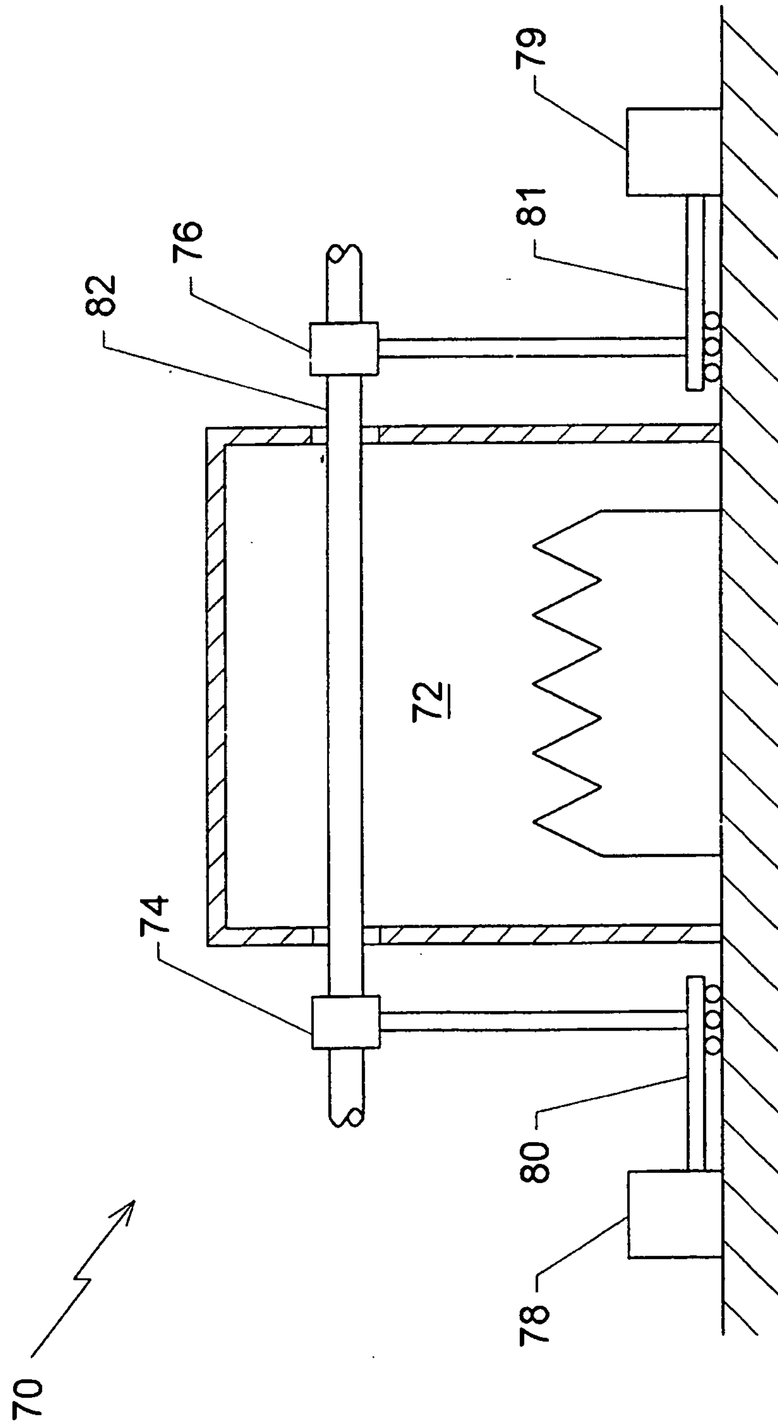


FIG. 12

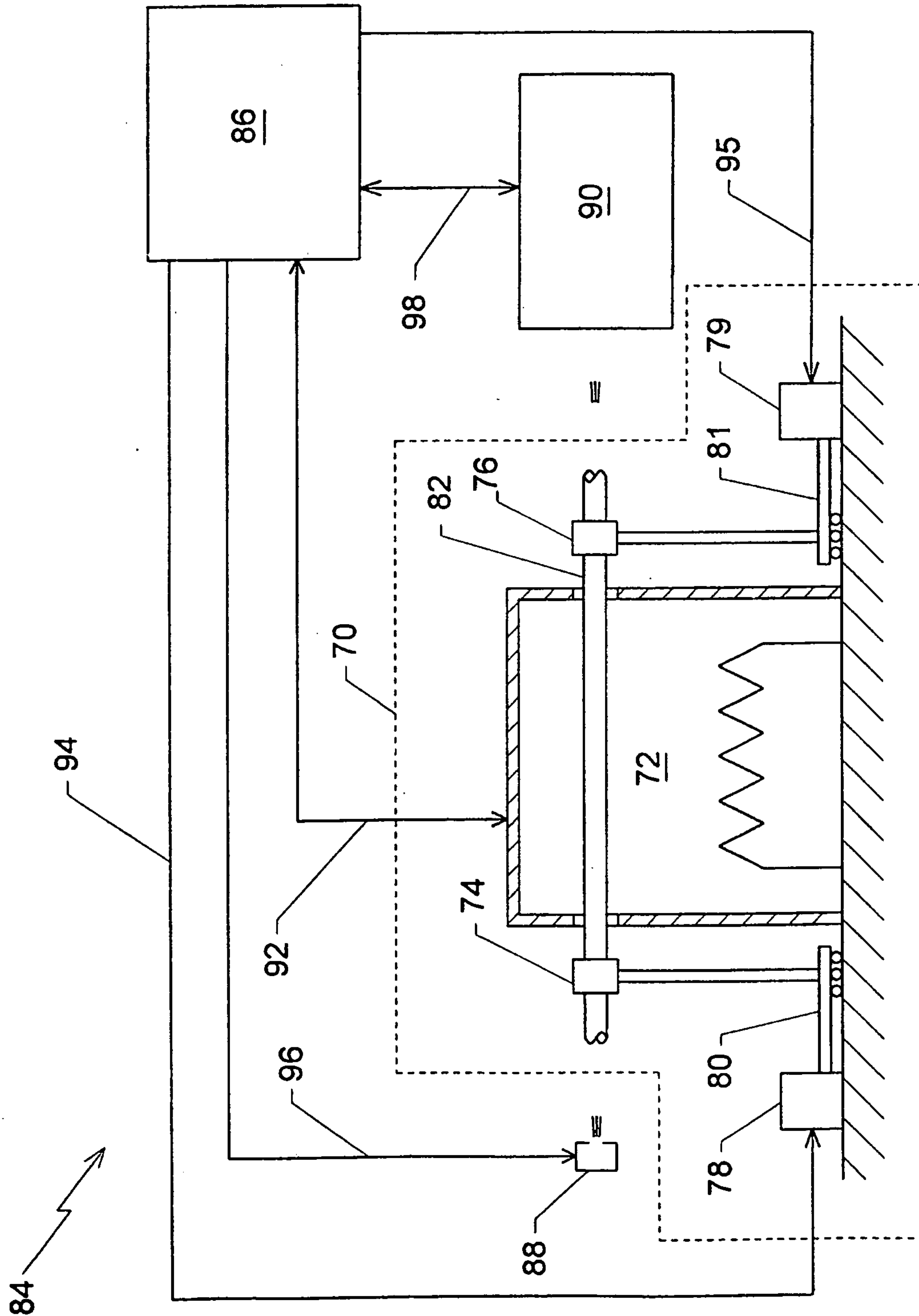


FIG. 13

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :		
G02B 6/26, 6/02, H01S 3/30	A3	(11) International Publication Number: **WO 00/22742** (43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/US99/22102

(22) International Filing Date: 23 September 1999 (23.09.99)

(30) Priority Data:

60/101,853	25 September 1998 (25.09.98)	US
09/246,985	9 February 1999 (09.02.99)	US

(71) Applicant: FIVER LABORATORIES [US/US]; Suite 316, 48521 Warm Springs Blvd., Fremont, CA 94539 (US).

(72) Inventors: WU, Weiti; 328 Sandhurst Drive, Milpitas, CA 95035 (US). KO, Yu-Li; 45654 Cheyenne Place, Fremont, CA 94539 (US). CHUNG, Gary; 41366 Charlita Court, Fremont, CA 94539 (US).

(74) Agents: HAVERSTOCK, Thomas, B. et al.; Haverstock & Owens LLP, Suite 420, 260 Sheridan Avenue, Palo Alto, CA 94306 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(88) Date of publication of the international search report: 13 July 2000 (13.07.00)

(54) Title: ALL FIBER GAIN FLATTENING OPTICAL FILTER

(57) Abstract

An all fiber optical filter (32) is formed by streching an optical fiber. The all fiber filter includes a core (34), an inner cladding (36), and an outer cladding (38). A core (34) index of refraction is greater than an outer cladding (38) indcx of refraction, and the outer cladding (38) index of refraction is greater than the inner cladding (36) index of refraction. The filter attenuates optical signals by transferring energy from the core (34) to the outer cladding (38) by evanescent coupling. The filter can be used for gain flattening in a WDM communication system (66) with EDFAs. The filter is manufactured by holding a length of an appropriate optical fiber (82) between two clamps (74, 76), heating the fiber (82) and stretching the fiber (82) until the desired filtering characteristics are achieved.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	State	Code	State	Code	State	Code	State
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/22102

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) :G02B 6/26, 6/02; H01S 3/30
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 359/337, 341, 566, 569, 572, 885; 385/30, 37, 127, 128, 131; 257/98; 248/290; 348/342

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

INSPEC, COMP, JAPIO, DERWENT, EPO, USPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,892,615 A (GRUBB ET AL) 06 April 1999, FIGURE 1, and COLUMNS 3-5	1-33
Y, P	US 5,857,053 A (KANE) 05 January 1999, FIGURES 2, 4 and COLUMN 2, LINES 15-21	1-33
Y	JP 61,279,805 A (YOKOHAMA ET AL) 10 December 1986, ABSTRACT	1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 MARCH 2000	26 APR 2000

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	NELSON MOSKOWITZ
Facsimile No. (703) 305-0285	Telephone No. (703) 306-4165

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/22102

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/22102

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

359/337, 341, 566, 569, 572, 885; 385/30, 37, 127, 128, 131; 257/98; 248/290; 348/342

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)1-19, drawn to an optical fiber filter.
Group II, claim(s) 20-25, drawn to an optical fiber communication system.
Group III, claim(s) 26-33, drawn to a method of manufacturing a fiber optic filter.

The inventions listed as Groups I, II, and III
do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Group II requires an optical communication system with a transmitter and a receiver not required by the claims of either Groups I and III. The claims of Group III are directed to a method of making an optical filter, an invention not present in the claims of Groups I and II.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01L 51/20	A1	(11) International Publication Number: WO 00/36665 (43) International Publication Date: 22 June 2000 (22.06.00)

(21) International Application Number: PCT/US99/29853

(22) International Filing Date: 15 December 1999 (15.12.99)

(30) Priority Data:
09/212,779 16 December 1998 (16.12.98) US
09/427,138 25 October 1999 (25.10.99) US

(71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).

(72) Inventors: GRAFF, Gordon, L.; 3750 Westlake Drive, West Richland, WA 99353 (US). GROSS, Mark, E.; 50 Deseret Drive, Pasco, WA 99301 (US). AFFINITO, John, D.; 2718 Kyle Road, Kennewick, WA 99338 (US). SHI, Ming-Kun; 2500 George Washington Way, Richland, WA 99352 (US). HALL, Michael, G.; 4125 Ironton Drive, West Richland, WA 99353 (US). MAST, Eric, S.; 634 Chesnut Avenue, Richland, WA 99352 (US).

(74) Agent: MAY, Stephen, R.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).

(81) Designated States: JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) **Title:** ENVIRONMENTAL BARRIER MATERIAL FOR ORGANIC LIGHT EMITTING DEVICE AND METHOD OF MAKING

190
170
180
220
210 235
230
200
160
140
150
130
120
110
105
100

(57) Abstract

An encapsulated organic light emitting device. The device includes a first barrier stack (110) comprising at least one first barrier layer (140) and at least one first polymer layer (150, 160). There is an organic light emitting layer stack (120) adjacent to the first barrier stack. A second barrier stack (130) is adjacent to the organic light emitting layer stack. The second barrier stack has at least one second barrier layer (170) and at least one second polymer layer (180, 190). A method of making the encapsulated organic light emitting device is also provided.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

ENVIRONMENTAL BARRIER MATERIAL FOR ORGANIC LIGHT EMITTING DEVICE AND METHOD OF MAKING

5

BACKGROUND OF THE INVENTION

The present invention relates to organic light emitting devices (OLEDs), and more particularly to OLEDs encapsulated in barrier stacks.

10 There is a need for versatile visual displays for electronic products of many different types. Light emitting diodes (LEDs) and liquid crystal displays (LCDs) have found many useful applications, but they are not adequate for all situations. OLEDs are a relatively new type of visual display which has shown great promise. An OLED basically includes an organic electroluminescent 15 substance placed between two electrodes. When an electric potential is applied across the electrodes, the electroluminescent substance emits visible light. Typically, one of the electrodes is transparent, allowing the light to shine through. U.S. Patent Nos. 5,629,389 (Roitman et al.), 5,747,182 (Friend et al.), 5,844,363 (Gu et al.), 5,872,355 (Hueschen), 5,902,688 (Antoniadis et al.), and 5,948,552 20 (Antoniadis et al.), which are incorporated herein by reference, disclose various OLED structures.

The use of OLEDs in flat panel displays and other information display formats is limited by the poor environmental stability of the devices. G.Gustafson, Y.Cao, G.M.Treacy, F.Klavetter, N.Colaneri, and A.J.Heeger, 25 Nature, Vol. 35, 11 June 1992, pages 477-479. Humidity and oxygen significantly reduce the useful life of most OLEDs. As a result, these devices are typically fabricated on glass substrates with glass covers laminated on top of the OLED and with the edges sealed to exclude water and oxygen from the active layers. U.S. Patent No. 5,872,355 discloses the use of a polymer such as saran 30 to seal the device. The water vapor permeation rates (WVTR) required to provide sufficient lifetime for OLEDs is calculated to be approximately 10^{-6} $g/m^2/day$. The best polymer films (such as saran) have WVTR values that are 5 orders of magnitude too high to be considered for OLED encapsulation.

Furthermore, saran cannot be deposited using flash evaporation, condensation, and in situ polymerization within a vacuum chamber.

Thus, there is a need for an improved lightweight, barrier construction which can be used to encapsulate the OLED and prevent the deterioration
5 caused by permeation of oxygen and water vapor and for a method of making such an encapsulated OLED.

SUMMARY OF THE INVENTION

10 These needs are met by the present invention, which is an encapsulated organic light emitting device (OLED). The device includes a first barrier stack comprising at least one first barrier layer and at least one first polymer layer. There is an organic light emitting layer stack adjacent to the first barrier stack. A second barrier stack is adjacent to the organic light emitting layer stack. The
15 second barrier stack has at least one second barrier layer and at least one second polymer layer. The device optionally includes at least one first intermediate barrier stack located between the substrate and the first barrier stack, and/or at least one second intermediate barrier stack located between the organic light emitting layer stack and either the first or second barrier stacks.
20 The first and second intermediate barrier stacks include at least one polymer layer and at least one barrier layer.

Preferably, either one or both of the first and second barrier layers of the first and second barrier stacks is substantially transparent. At least one of the first and second barrier layers preferably comprises a material selected from
25 metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof. The metal oxides are preferably selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof, the metal nitrides are preferably selected from aluminum nitride, silicon nitride, and combinations thereof, the metal carbide is preferably silicon carbide, and the
30 metal oxynitride is preferably silicon oxynitride.

The encapsulated OLED can also include a substrate adjacent to the first barrier stack on a side opposite to the organic light emitting layer stack. The

substrate can be either a flexible substrate or a rigid substrate. It is preferably a flexible substrate material, which can be polymers, metals, paper, fabric, and combinations thereof. The rigid substrate is preferably glass, metal, or silicon. If a rigid substrate is used, it can be removed prior to use if desired.

5 The polymer layers of the first and second barrier stacks and the polymer layers in the first and second intermediate barrier stacks are preferably acrylate-containing polymers (as used herein, the term acrylate-containing polymer includes acrylate-containing polymers, methacrylate-containing polymers, and combinations thereof). The polymer layers in the first and/or the second barrier 10 stacks can be the same or different.

The organic light emitting layer stack preferably comprises a first electrode, an electroluminescent layer, and a second electrode. The electroluminescent layer preferably includes a hole transporting layer, and an electron transporting layer, as is known in the art and shown in the patents 15 whose disclosures have been specifically incorporated herein.

The invention also involves a method of making the encapsulated organic light emitting device. The method includes forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer, forming an organic light emitting layer stack, forming a second barrier stack 20 comprising at least one second barrier layer and at least one second polymer layer, and combining the first barrier stack, the organic light emitting layer stack, and the second barrier stack to form the encapsulated organic light emitting device. Intermediate barrier stacks can optionally be formed. The layers are preferably formed by vacuum deposition.

25 The organic light emitting layer stack can be combined with the first barrier stack and/or the second barrier stack by laminating them together. Alternatively, they can be combined simultaneously with forming by depositing one layer on the other.

In an alternative embodiment, the invention involves an encapsulated 30 organic light emitting device having a substrate, an organic light emitting layer stack adjacent to the substrate, and a barrier stack comprising at least one barrier layer and at least one polymer layer, the barrier stack adjacent to the

organic light emitting layer stack. The invention also involves methods of making the encapsulated organic light emitting device. One method includes providing a substrate having an organic light emitting layer stack thereon, and laminating a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting barrier layer stack. The barrier stack is preferably laminated (edge sealed) using an adhesive, but other methods can be used including heat.

Another method involves vacuum depositing the barrier stack on a substrate having an organic light emitting layer stack thereon. Still another method involves providing a substrate with an organic light emitting layer stack thereon, vacuum depositing at least one barrier layer on the organic light emitting layer stack, and depositing at least one first polymer layer on the at least one barrier layer. At least one second polymer layer can be deposited on the organic light emitting layer stack before the barrier layer is deposited.

Accordingly, it is an object of the present invention to provide an encapsulated OLED, and to provide a method of making such a device.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-section of one embodiment of the encapsulated OLED of the present invention.

Fig. 2 is a cross-section of an alternate embodiment of the encapsulated OLED of the present invention.

Fig. 3 is a cross-section of an embodiment of an encapsulated OLED of the present invention.

DESCRIPTION OF THE INVENTION

One embodiment of the present invention is an encapsulated OLED 100 as shown in Fig. 1. The encapsulated OLED 100 includes substrate 105, a first barrier stack 110, an organic light emitting layer stack 120, and a second barrier stack 130. The first barrier stack 110 has a first barrier layer 140 and two

polymer layers 150, 160. The second encapsulation layer 130 includes a second barrier layer 170 and two polymer layers 180, 190.

Although the Figures show barrier stacks with a single polymer layer on both sides of a single barrier layer, the barrier stacks can have one or more
5 polymer layers and one or more barrier layers. There could be one polymer layer and one barrier layer, there could be multiple polymer layers on one side of one or more barrier layers, or there could be one or more polymer layers on both sides of one or more barrier layers. The important feature is that the barrier stack have at least one polymer layer and at least one barrier layer.

10 The organic light emitting layer stack 120 includes a first electrode layer 200, an electroluminescent layer 210, and a second electrode 220. The electroluminscent layer 210 can include a hole transport layer 230, and an electron transport layer 235. The exact form and composition of the organic light emitting layer stack is not critical. The organic light emitting layer stack includes
15 first and second electrode layers on opposite sides of one or more active layers. The electrode layers are connected to a power source. At least one of the electrodes is transparent. The electroluminescent layer may be multiple layers as shown, or a single layer. The electroluminescent layer typically includes a hole injection layer, a hole transport layer, an electron transport layer, and an
20 emissive layer, and combinations thereof. Additional layers may also be present, including dielectric layers. The organic light emitting layer stack can be made using known techniques, such as those described in U.S. Patent Nos. 5,629,389 (Roitman et al.), 5,844,363 (Gu et al.), 5,872,355 (Hueschen), 5,902,688 (Antoniadis et al.), and 5,948,552 (Antoniadis et al.), which have been
25 incorporated herein by reference.

The present invention is compatible with organic light emitting layer stacks made with light emitting polymers and small molecules.

In the alternate embodiment shown in Fig. 2, the encapsulated OLED 300 also includes a first intermediate barrier stack 240 and a second intermediate
30 barrier stack 270. The first intermediate barrier stack is located between the substrate 105 and the first barrier stack 110, and it includes a polymer layer 250 and a barrier layer 260. The second intermediate barrier stack 270 includes a

polymer layer 280 and a barrier layer 290. The second intermediate barrier stack 270 is located between the organic light emitting layer stack 120 and the second barrier stack 130. Alternatively, the second intermediate layer could be located between the first barrier layer and the organic light emitting layer stack.
5 In addition, there could be multiple first intermediate barrier stacks on top of one another to provide enhanced barrier protection. Similarly, there could be multiple second intermediate barrier stacks on top of one another. The order of the barrier and polymer layers in the intermediate barrier stacks is not critical. It depends on where the intermediate barrier stack is located and what layers are
10 next to them.

The encapsulated OLED can be made by forming the first barrier stack 110, the organic light emitting layer stack 120, and the second barrier stack 130. The stacks are combined to form the encapsulated OLED.

Preferably, the stacks are combined by forming them using vacuum
15 deposition. In this method, one layer is vacuum deposited on the previous layer, thereby combining the layers simultaneously with forming them. Alternatively, the organic light emitting layer stack can be combined with the first and second barrier stacks by laminating it between the first and second barrier stacks and sealing it along the edges with adhesive, glue, or the like, or by heating. The first
20 and second barrier stacks include at least one barrier layer and at least one polymer layer. If a polymer/barrier/polymer structure is desired, it can be preferably formed as follows. These barrier stacks can be formed by depositing a layer of polymer, for example an acrylate-containing polymer, onto a substrate or previous layer. Preferably, an acrylate-containing monomer, oligomer or resin
25 (as used herein, the term acrylate-containing monomer, oligomer, or resin includes acrylate-containing monomers, oligomers, and resins, methacrylate-containing monomers, oligomers, and resins, and combinations thereof) is deposited and then polymerized *in situ* to form the polymer layer. The acrylate-containing polymer layer is then coated with a barrier layer. Another polymer
30 layer is deposited onto the barrier layer. U.S. Patent Nos. 5,440,446 and 5,725,909, which are incorporated herein by reference, describe methods of depositing thin film, barrier stacks.

The barrier stacks are preferably vacuum deposited. Vacuum deposition includes flash evaporation of acrylate-containing monomer, oligomer, or resin with *in situ* polymerization under vacuum, plasma deposition and polymerization of acrylate-containing monomers, oligomer, or resin, as well as vacuum
5 deposition of the barrier layers by sputtering, chemical vapor deposition, plasma enhanced chemical vapor deposition, evaporation, sublimation, electron cyclotron resonance-plasma enhanced vapor deposition (ECR-PECVD), and combinations thereof.

It is critical to protect the integrity of the barrier layer to avoid the formation
10 of defects and/or microcracks in the deposited layer. The encapsulated OLED is preferably manufactured so that the barrier layers are not directly contacted by any equipment, such as rollers in a web coating system, to avoid defects that may be caused by abrasion over a roll or roller. This can be accomplished by designing the deposition system such that a set of layers of
15 polymer/barrier/polymer are deposited prior to contacting or touching any handling equipment.

The substrate can be flexible or rigid. The flexible substrate may be any flexible material, including, but not limited to, polymers, for example polyethlyene terephthalate (PET), polyethylene naphthalate (PEN), or high temperature
20 polymers such as polyether sulfone (PES), polyimides, or Transphan™ (a high Tg cyclic olefin polymer available from Lofo High Tech Film, GMBH of Weil am Rhein, Germany), metal, paper, fabric, and combinations thereof. The rigid substrate is preferably glass, metal, or silicon. If a flexible, encapsulated OLED is desired and a rigid substrate was used during manufacture, the rigid substrate
25 is preferably removed prior to use.

The polymer layers of the first and second barrier stacks and the polymer layers of the first and second intermediate barrier stacks are preferably acrylate-containing monomer, oligomer or resin, and combinations thereof. The polymer layers of the first and second barrier stacks and first and second intermediate
30 stacks can be the same or they can be different. In addition, the polymer layers within the each barrier stack can be the same or different.

The barrier layers in the barrier stacks and the intermediate barrier stacks may be any barrier material. The barrier materials in the first and second barrier stacks and first and second intermediate barrier stacks can be the same or different. In addition, multiple layers of the same or different barrier layers can
5 be used in a stack. Preferred transparent barrier materials include, but are not limited to, metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof. The metal oxides are preferably selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof, the metal nitrides are preferably selected from aluminum nitride, silicon
10 nitride, and combinations thereof, the metal carbide is preferably silicon carbide, and the metal oxynitride is preferably silicon oxynitride.

Since only one side of the device must be transparent, only one of the barrier layers must be transparent. In this situation, the barrier layer on the opposite side could be an opaque barrier material, including, but not limited to,
15 metal, ceramic or polymer.

An alternate encapsulated OLED is shown in Fig. 3. The encapsulated OLED 400 has a substrate 105 on which is fabricated an organic light emitting layer stack 120. A barrier stack 130 is deposited conformally over the organic light emitting layer stack 120, encapsulating it. The polymer layers in the barrier
20 stack can be deposited in vacuum or by using atmospheric processes such as spin coating and/or spraying. A preferred method of forming the barrier stack is flash evaporating acrylate-containing monomers, oligomers or resins, condensing on the OLED layer stack, and polymerizing in-situ in a vacuum chamber. The barrier layer is then deposited on the polymer layer using
25 conventional vacuum processes such as evaporation, sputtering, CVD, PECVD or ECR-PECVD. A second polymer layer is then deposited on the barrier layer using the process described above.

Alternatively, the OLED device could also be encapsulated by laminating a lid structure, containing the barrier stack, to the substrate over the organic light
30 emitting layer structure. The lamination can be performed using either adhesive, or glue, or the like, or by heating. The encapsulated OLED could also include an

intermediate barrier stack 270 as shown. If the substrate is transparent, then the barrier material could be opaque, or vice versa, as discussed above.

A single pass, roll-to-roll, vacuum deposition of a three layer combination on a PET substrate, i.e., PET substrate/polymer layer/barrier layer/polymer layer,
5 can be more than five orders of magnitude less permeable to oxygen and water vapor than a single oxide layer on PET alone. See J.D.Affinito, M.E.Gross, C.A.Coronado, G.L.Graff, E.N.Greenwell, and P.M.Martin, Polymer-Oxide Transparent Barrier Layers Produced Using PML Process, 39th Annual Technical Conference Proceedings of the Society of Vacuum Coaters, Vacuum Web
10 Coating Session, 1996, pages 392-397; J.D.Affinito, S.Eufinger, M.E.Gross, G.L.Graff, and P.M.Martin, PML/Oxide/PML Barrier Layer Performance Differences Arising From Use of UV or Electron Beam Polymerization of the PML Layers, Thin Solid Films, Vol.308, 1997, pages 19-25. This is in spite of the fact that the effect on the permeation rate of the polymer multilayers (PML) layers
15 alone, without the barrier layer (oxide, metal, nitride, oxynitride) layer, is barely measurable. It is believed that the improvement in barrier properties is due to two factors. First, permeation rates in the roll-to-roll coated oxide-only layers were found to be conductance limited by defects in the oxide layer that arose during deposition and when the coated substrate was wound up over system
20 idlers/rollers. Asperities (high points) in the underlying substrate are replicated in the deposited inorganic barrier layer. These features are subject to mechanical damage during web handling/take-up, and can lead to the formation of defects in the deposited film. These defects seriously limit the ultimate barrier performance of the films. In the single pass, polymer/barrier/polymer process, the first acrylic
25 layer planarizes the substrate and provides an ideal surface for subsequent deposition of the inorganic barrier thin film. The second polymer layer provides a robust "protective" film that minimizes damage to the barrier layer and also planarizes the structure for subsequent barrier layer (or organic light emitting layer stack) deposition. The intermediate polymer layers also decouple defects
30 that exist in adjacent inorganic barrier layers, thus creating a tortuous path for gas diffusion. The permeability of the barrier stacks used in the present invention is shown below.

Table 1

Sample	Oxygen Permeation Rate ($cc/m^2/day$)		Water vapor Permeation ($g/m^2/day$)+
	23°C*	38°C+	38°C+
1-barrier stack	<0.005	<0.005	0.46
2- barier stacks	<0.005	<0.005	<0.005
5-barrier stacks	<0.005	<0.005	<0.005

* 38°C, 90% RH, 100% O_2
\+ 38°C, 100% RH

NOTE: Permeation rates of <0.005 are below the detection limits of current instrumentation (Mocon OxTran 2/20L).

As can be seen from the data in Table 1, the barrier stacks used in the present invention provide exceptional environmental protection, which was previously unavailable with polymers.

We have also compared the performance of OLED devices (fabricated on glass and silicon) before and after encapsulation using the barrier stacks of the present invention. After encapsulation, the current density-versus-voltage and brightness-versus-current density characteristics were identical (within experimental error) to the measured behavior of the pristine (unencapsulated) devices. This shows that the barrier stacks and deposition methods are compatible with OLED device manufacturing.

Thus, the present invention provides a barrier stack with the exceptional barrier properties necessary for hermetic sealing of an OLED. It permits the production of an encapsulated OLED.

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is:

1. An encapsulated organic light emitting device comprising:

5 a first barrier stack comprising at least one first barrier layer and at least one first polymer layer;

an organic light emitting layer stack adjacent to the first barrier stack; and

a second barrier stack comprising at least one second barrier layer and at least one second polymer layer, the second barrier stack adjacent to the organic

10 light emitting layer stack.

2. The encapsulated organic light emitting device of claim 1 further comprising a substrate adjacent to the first barrier stack on a side opposite to the organic light emitting layer stack.

15

3. The encapsulated organic light emitting device of claim 2 further comprising at least one first intermediate barrier stack located between the substrate and the first barrier stack, the first intermediate barrier stack comprising at least one third polymer layer and at least one third barrier layer.

20

4. The encapsulated organic light emitting device of claim 1 further comprising at least one second intermediate barrier stack located between the organic light emitting layer stack and either the first or second barrier stacks, the second intermediate barrier stack comprising at least one fourth polymer layer

25 and at least one fourth barrier layer.

5. The encapsulated organic light emitting device of claim 1 wherein the at least one first barrier layer is substantially transparent.

30 6. The encapsulated organic light emitting device of claim 1 wherein the at least one second barrier layer is substantially transparent.

7. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first and second barrier layers comprise a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

5

8. The encapsulated organic light emitting device of claim 7 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

10 9. The encapsulated organic light emitting device of claim 7 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

10. The encapsulated organic light emitting device of claim 1 wherein
15 the at least one first barrier layer is substantially opaque.

11. The encapsulated organic light emitting device of claim 1 wherein the at least one second barrier layer is substantially opaque.

20 12. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first and second barrier layers is selected from opaque metals, opaque polymers, and opaque ceramics.

13. The encapsulated organic light emitting device of claim 2 wherein
25 the substrate comprises a flexible substrate material.

14. The encapsulated organic light emitting device of claim 13 wherein the flexible substrate material is selected from polymers, metals, paper, fabric, and combinations thereof.

30

15. The encapsulated organic light emitting device of claim 2 wherein the substrate comprises a rigid substrate material.

16. The encapsulated organic light emitting device of claim 15 wherein the rigid substrate material is selected from glass, metal, and silicon.

17. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first polymer layers comprises an acrylate-containing polymer.

18. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one second polymer layers comprises an acrylate-containing polymer.

19. The encapsulated organic light emitting device of claim 3 wherein at least one of the at least one third polymer layers comprises an acrylate-containing polymer.

20. The encapsulated organic light emitting device of claim 4 wherein at least one of the at least one fourth polymer layers comprises an acrylate-containing polymer.

21. The encapsulated organic light emitting device of claim 1 wherein the organic light emitting layer stack comprises a first electrode, an electroluminescent layer, and a second electrode.

22. The encapsulated organic light emitting device of claim 21 wherein the electroluminescent layer comprises a hole transporting layer, and an electron transporting layer.

23. A method of making an encapsulated organic light emitting device comprising:

forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer;

forming an organic light emitting layer stack;

forming a second barrier stack comprising at least one second barrier layer and at least one second polymer layer; and

combining the first barrier stack, the organic light emitting layer stack adjacent to the first barrier stack, and the second barrier stack adjacent to the
5 organic light emitting layer stack to form the encapsulated organic light emitting device.

24. The method of claim 23 further comprising providing a substrate and forming the first barrier stack on the substrate.

10

25. The method of claim 24 further comprising placing at least one first intermediate barrier stack comprising at least one third polymer layer and at least one third barrier layer between the substrate and the first barrier stack.

15 26. The method of claim 23 further comprising placing at least one second intermediate barrier stack comprising at least one fourth polymer layer and at least one fourth barrier layer between the organic light emitting layer stack and either the first or second barrier stacks.

20 27. The method of claim 23 wherein the organic light emitting layer stack is combined with the first barrier stack by laminating the organic light emitting layer stack to the first barrier stack.

28. The method of claim 23 wherein the organic light emitting layer
25 stack is combined with the first barrier stack simultaneously with forming by depositing the organic light emitting layer stack on the first barrier stack.

29. The method of claim 23 wherein the second barrier stack is combined with the organic light emitting layer stack by laminating the second
30 barrier stack over the organic light emitting layer stack.

30. The method of claim 23 wherein the second barrier stack is combined with the organic light emitting layer stack simultaneously with forming by depositing the second barrier stack on the organic light emitting layer stack.

5 31. The method of claim 24 wherein the substrate comprises a flexible material.

32. The method of claim 24 wherein the substrate comprises a rigid material.

10

33. The method of claim 24 wherein the substrate is removed from the encapsulated organic light emitting device.

34. The method of claim 23 wherein the first barrier stack is formed by
15 vacuum deposition.

35. The method of claim 23 wherein the organic light emitting layer stack is formed by vacuum deposition.

20 36. The method of claim 23 wherein the second barrier stack is formed by vacuum deposition.

37. The method of claim 23 wherein at least one of the at least one first and second barrier layers is substantially transparent.

25

38. The method of claim 23 wherein at least one of the first and second barrier layers comprises a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

30 39. The method of claim 38 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

40. The method of claim 38 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

41. The method of claim 23 wherein at least one of the at least one first
5 and second barrier layers is substantially opaque.

42. The method of claim 23 wherein at least one of the at least one first and second barrier layers is selected from opaque metals, opaque polymers, and opaque ceramics.

10

43. The method of claim 31 wherein the flexible substrate material is selected from polymers, metals, paper, fabric, and combinations thereof.

44. The method of claim 32 wherein the rigid substrate material is
15 selected from glass, metal, and silicon.

45. The method of claim 23 wherein at least one of the at least one first and second pairs of polymer layers comprises an acrylate-containing polymer.

20 46. The method of claim 25 wherein the third polymer layer comprises an acrylate-containing polymer.

47. The method of claim 26 wherein the fourth polymer layer comprises an acrylate-containing polymer.

25

48. An encapsulated organic light emitting device comprising:

a first intermediate barrier stack comprising at least one polymer layer and at least one barrier layer ;

a first barrier stack comprising at least one first barrier layer and at least
30 one first polymer layer adjacent to the first intermediate barrier stack;

an organic light emitting layer stack adjacent to the first barrier stack;

a second intermediate barrier stack comprising at least one polymer layer and at least one barrier layer, the second intermediate barrier stack adjacent to the organic light emitting layer stack; and

a second barrier stack comprising at least one second barrier layer and at 5 least one second polymer layer, the second barrier stack adjacent to the second intermediate barrier stack.

49. The encapsulated organic light emitting device of claim 48 further comprising a substrate adjacent to the first intermediate barrier stack on a side 10 opposite to the first barrier stack.

50. A method of making an encapsulated organic light emitting device comprising:

forming a first intermediate barrier stack comprising at least one polymer 15 layer and at least one barrier layer;

forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer adjacent to the first intermediate barrier stack;

forming an organic light emitting layer stack adjacent to the first barrier stack;

20 forming a second intermediate barrier stack comprising at least one polymer layer and at least one barrier layer adjacent to the organic light emitting layer stack; and

forming a second barrier stack comprising at least one second barrier layer and at least one second polymer layer adjacent to the second intermediate 25 barrier stack; and

combining the first intermediate barrier stack, the first barrier stack, the organic light emitting layer stack, the second intermediate barrier stack, and the second barrier stack to form the encapsulated organic light emitting device.

30 51. The method of claim 50 wherein the first intermediate barrier stack is formed by vacuum deposition.

52. The method of claim 50 wherein the first barrier stack is formed by vacuum deposition.

53. The method of claim 50 wherein the organic light emitting layer
5 stack is formed by vacuum deposition.

54. The method of claim 50 wherein the second intermediate barrier stack is formed by vacuum deposition.

10 55. The method of claim 50 wherein the second barrier stack is formed by vacuum deposition.

56. An encapsulated organic light emitting device comprising:
a substrate;
15 an organic light emitting layer stack adjacent to the substrate;
a barrier stack comprising at least one barrier layer and at least one polymer layer, the barrier stack adjacent to the organic light emitting layer stack.

57. The encapsulated organic light emitting device of claim 56 further
20 comprising an intermediate barrier stack located between the organic light emitting layer stack and the barrier stack, the intermediate barrier stack comprising at least one polymer layer and at least one barrier layer..

58. The encapsulated organic light emitting device of claim 56 wherein
25 the at least one barrier stack is substantially transparent.

59. The encapsulated organic light emitting device of claim 56 wherein the at least one barrier layer comprises a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

30

60. The encapsulated organic light emitting device of claim 59 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

5 61. The encapsulated organic light emitting device of claim 59 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

62. The encapsulated organic light emitting device of claim 56 wherein
10 the at least one barrier layer is substantially opaque.

63. The encapsulated organic light emitting device of claim 56 wherein the at least one barrier layer is selected from opaque metals, opaque polymers, and opaque ceramics.

15

64. The encapsulated organic light emitting device of claim 56 wherein at least one of the at least one polymer layers comprises an acrylate-containing polymer.

20 65. The encapsulated organic light emitting device of claim 56 wherein the substrate comprises a rigid substrate material.

66. The encapsulated organic light emitting device of claim 65 wherein the rigid substrate material is selected from glass, metal, and silicon.

25

67. The encapsulated organic light emitting device of claim 56 wherein the substrate comprises a flexible substrate material.

68. The encapsulated organic light emitting device of claim 67 wherein
30 the flexible substrate material is selected from polymers, metals, paper, fabric, and combinations thereof.

69. A method of making an encapsulated organic light emitting device comprising:

providing a substrate having an organic light emitting layer stack thereon; and

5 vacuum depositing a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting layer stack.

70. The method of claim 69 further comprising depositing an
10 intermediate barrier layer stack comprising at least one polymer layer and at least one barrier layer on the organic light emitting layer stack prior to vacuum depositing the barrier stack.

71. A method of making an encapsulated organic light emitting device
15 comprising:

providing a substrate having an organic light emitting layer stack thereon;

vacuum depositing at least one barrier layer over theorganic light emitting layer stack;

20 depositing at least one first polymer layer over the at least one barrier layer.

72. The method of claim 71 further comprising depositing at least one second polymer layer over the organic light emitting layer stack prior to vacuum
25 depositing the at least one barrier layer.

73. The method of claim 71 further comprising depositing an intermediate barrier layer stack comprising at least one polymer layer and at least one barrier layer on the organic light emitting layer stack prior to depositing
30 the at least one barrier layer.

74. The method of claim 71 wherein at least one of the at least one first polymer layers is deposited using a process at atmospheric pressure.

75. The method of claim 74 wherein the process at atmospheric
5 pressure is selected from spin coating and spraying.

76. The process of 71 wherein at least one of the at least one first polymer layers is deposited using a vacuum process.

10 77. The method of claim 72 wherein at least one of the at least one second polymer layers is deposited using a process at atmospheric pressure.

78. A method of making an encapsulated organic light emitting device comprising:
15 providing a substrate having an organic light emitting layer stack thereon; and
laminating a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting layer stack.

20

79. The method of claim 78 wherein the barrier stack is laminated using an adhesive.

80. The method of claim 78 wherein the barrier stack is laminated
25 using heat.

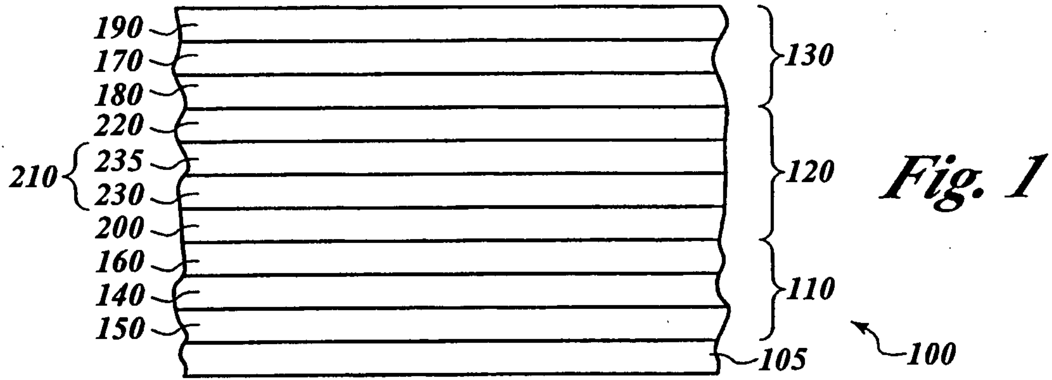


Fig. 1

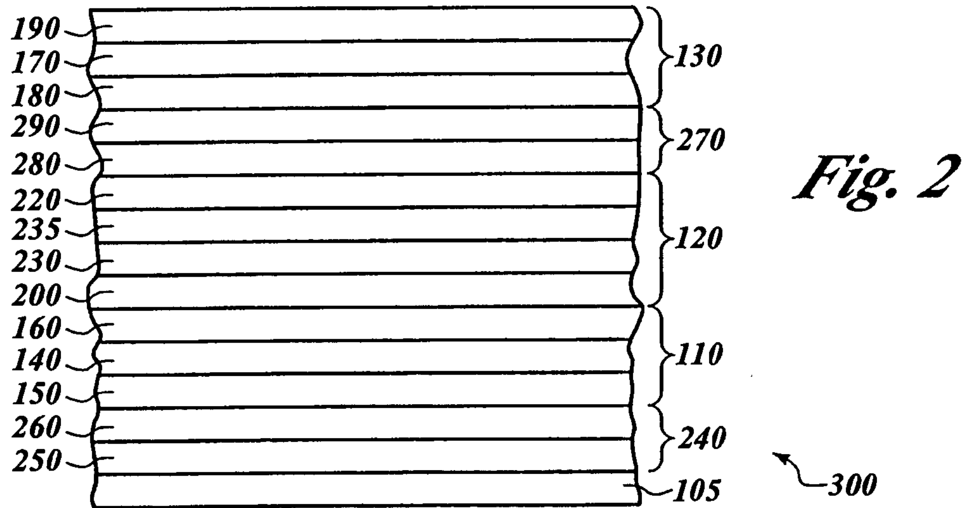


Fig. 2

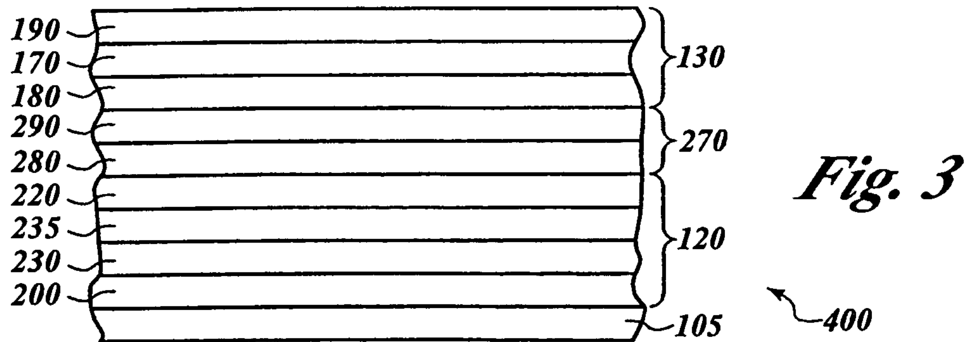


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29853

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 757 126 A (HARVEY III THOMAS B ET AL) 26 May 1998 (1998-05-26)	1-5,7-9, 11-14, 21-26, 28,30, 31,34, 35, 37-43, 48-53, 56,57, 62,63, 67,68
Y	the whole document	1-9, 11-14, 21-31, 34,35, 37-43, 48-53, 56-63,

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 February 2000	03/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Laere, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29853

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
		67,68, 78-80
A		10, 17-20, 36, 45-47, 54,55, 64,69-77

X	DE 196 03 746 A (BOSCH GMBH ROBERT) 24 April 1997 (1997-04-24)	56, 58-63, 67,68, 78-80
	the whole document	
Y		1-9, 11-14, 21-31, 34,35, 37-43, 48-53, 56-63, 67,68, 78-80
A		10,36, 55,69, 71,72, 74-77

A	AFFINITO J D ET AL: "PML/oxide/PML barrier layer performance differences arising from use of UV or electron beam polymerization of the PML layers" THIN SOLID FILMS,CH,ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 308-309, no. 1-4, 31 October 1997 (1997-10-31), pages 19-25, XP004110238 ISSN: 0040-6090 cited in the application	1,5,7,8, 13,14, 17,23, 24,31, 34, 37-39, 43, 48-50, 52,56, 58-60, 64, 67-69, 71,72, 76,78
	the whole document	

	-/--	

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29853

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 547 508 A (AFFINITO JOHN D) 20 August 1996 (1996-08-20) abstract column 3, line 65 -column 4, line 11 ---	1,5,7,8, 10, 12-14, 23,24, 31,33, 34, 37-39, 41-43, 48-50, 52,56, 58-60, 62,63, 67-69, 71,72, 76,78
E	EP 0 977 469 A (HEWLETT PACKARD CO) 2 February 2000 (2000-02-02) the whole document -----	1,2,5-9, 13,14, 17,18, 21-24, 28,30, 31, 34-40, 43,45, 56, 58-61, 64, 67-69, 71,72,76

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/29853

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5757126 A	26-05-1998	US 5686360 A	11-11-1997
		EP 0777280 A	04-06-1997
		JP 9161967 A	20-06-1997
DE 19603746 A	24-04-1997	WO 9716053 A	01-05-1997
US 5547508 A	20-08-1996	US 5395644 A	07-03-1995
		US 5260095 A	09-11-1993
		AT 170779 T	15-09-1998
		CA 2142895 A	03-03-1994
		DE 69320971 D	15-10-1998
		DE 69320971 T	27-05-1999
		EP 0655954 A	07-06-1995
		JP 8503099 T	02-04-1996
		WO 9404285 A	03-03-1995
EP 0977469 A	02-02-2000	NONE	

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12932 A2

(51) International Patent Classification[7]: G02B 6/00

(21) International Application Number: PCT/US01/22750

(22) International Filing Date: 18 July 2001 (18.07.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/633,307 7 August 2000 (07.08.2000) US
09/903,050 10 July 2001 (10.07.2001) US

(71) Applicant: **SYMMORPHIX, INC.** [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventors: **DEMARAY, Richard, E.**; 190 Fawn Lane, Portola Valley, CA 94028 (US). **WANG, Kai-An**; 1082 West Hill Court, Cupertino, CA 95014 (US). **MULLAPUDI, Ravi, B.**; 2117 Shiangzone Court, San Jose, CA 95121 (US). **STADTLER, Douglas, P.**; 18509 Murphy Court, Morgan Hill, CA 95037 (US). **ZHANG, Hongmei**; 1330 Rodney Drive, San Jose, CA 95118 (US). **PETHE, Rajiv**; 3680 Springbrook Avenue, San Jose, CA 95148 (US).

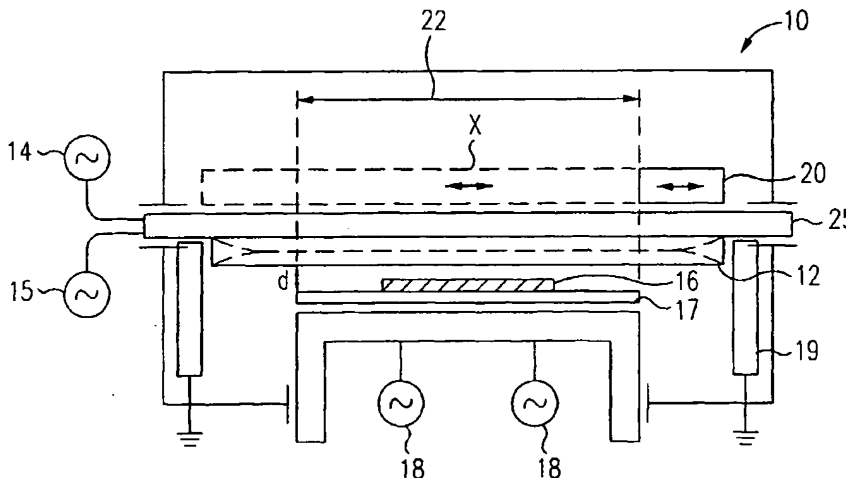
(74) Agents: **SAXON, Roberta, P.** et al.; Skjerven Morrill MacPherson LLP, 25 Metro Drive, Suite 700, San Jose, CA 95110 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PLANAR OPTICAL DEVICES AND METHODS FOR THEIR MANUFACTURE



(57) Abstract: Physical vapor deposition processes provide optical materials with controlled and uniform refractive index that meet the requirements for active and passive planar optical devices. All processes use radio frequency (RF) sputtering with a wide area target, larger in area than the substrate on which material is deposited, and uniform plasma conditions which provide uniform target erosion. In addition, a second RF frequency can be applied to the sputtering target and RF power can be applied to the substrate producing substrate bias. Multiple approaches for controlling refractive index are provided. The present RF sputtering methods for material deposition and refractive index control are combined with processes commonly used in semiconductor fabrication to produce planar optical devices such surface ridge devices, buried ridge devices and buried trench devices. A method for forming composite wide area targets from multiple tiles is also provided.

WO 02/12932 A2

WO 02/12932 A2

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

PLANAR OPTICAL DEVICES AND METHODS FOR THEIR MANUFACTURE

5 RELATED APPLICATIONS

This application claims benefit of Atty. Dkt. No. M-7637-1P US (USSN NOT YET KNOWN), filed 10 July 2001, which is a continuation-in-part of U.S. Serial No.: 09/633,307, filed 7 August 2000, both of which are incorporated herein by reference.

10 FIELD OF THE INVENTION

This invention relates generally to planar optical devices and materials and methods used in their manufacture, and, in particular, to optical components such as waveguides and amplifiers, and physical vapor deposition methods for their manufacture.

15 BACKGROUND

The increasing prevalence of fiber optic communications systems has created an unprecedented demand for devices for processing optical signals. Planar devices such as optical waveguides, couplers, splitters, and amplifiers, fabricated on planar substrates, like those commonly used for integrated circuits, and configured to receive and process signals 20 from optical fibers are highly desirable. Such devices hold promise for integrated optical and electronic signal processing on a single semiconductor-like substrate.

The basic design of planar optical waveguides and amplifiers is well known, as described, for example in U. S. Patent Nos. 5,119,460 to Bruce et al. 5,613,995 to Bhandarkar et al., (hereafter '995), 5,900,057 to Buchal et al., and 5,107,538 to Benton et 25 al, to cite only a few. The devices consist, very generally, of a core region, typically bar shaped, of a certain refractive index surrounded by a cladding region of a lower refractive index. In the case of an optical amplifier, the core region contains a certain concentration of a dopant, typically a rare earth ion such as an erbium or praseodymium ion which, when pumped by a laser, fluoresces, for example, in the 1550 nm and 1300 nm wavelength 30 range, respectively, used for optical communication, amplifying the optical signal passing through the core.

The performance of these planar optical devices depends sensitively on the value and uniformity of the refractive index of the core region and of the cladding region, and particularly on the difference in refractive index, Δn, between the regions. Particularly for

passive devices such as waveguides, couplers, and splitters, Δn needs to be sensitively controlled at values less than 1 % and the refractive index of both core and cladding need to be highly uniform, for some applications at the fewer than parts per thousand level. In the case of doped materials forming the core region of planar optical amplifiers, it is important that thc dopant be uniformly distributed so as to avoid non-radiative quenching or radiative quenching, for example by upconversion. The refractive index and other desirable properties of the core and cladding regions, such as physical and chemical uniformity, low stress, and high density, depend, of course, on the choice of materials for the devices and on the processes by which they are fabricated.

Because of their optical properties, silica and refractory oxides such as Al_2O_3, are good candidate materials for planar optical devices. Further, these oxides serve as suitable hosts for rare earth dopants used in optical amplifiers. A common material choice is so-called low temperature glasses, doped with alkali metals , boron, or phosphorous have the advantage of requiring lower processing temperatures. In addition, dopants are used to modify refractive index. Methods such as flame hydrolysis, ion exchange for introducing alkali ions in glasses, sputtering, and various chemical vapor deposition processes (CVD) have been used to form films of doped glasses. However, dopants, such as phosphorous and boron are hygroscopic, and alkalis are undesirable for integration with electronic devices. Control of uniformity of doping in CVD processes can be difficult and CVD deposited films can have structural defects leading to scattering losses when used to guide light. In addition, doped low temperature glasses may require further processing after deposition. A method for eliminating bubbles in thin films of sodium-boro-silicate glass by high temperature sintering is described, for example, in the '995 patent to Bhandarkar et al.

In the case of pure SiO_2, the most uniform optical material presently known is by atmospheric pressure thermal oxide (APOX). The APOX process can provide a 13 μm thick silica film having a precise refractive index of 1.4584, at 1550 nm, with a 1σ variance in the refractive index across a 150 mm wafer of $3x10^{-5}$. However, the APOX process does not provide a method of making films with different indices of refraction. It is, therefore, not suitable for forming a waveguide core film with a desired refractive index (n).

Thus, there remains a need for a process to provide optical materials with a specified and uniform index of refraction for planar optical devices. It would be desirable

if the material additionally exhibits high optical transparency, low stress, and high density and is free of structural defects.

SUMMARY

5 A physical vapor deposition process provides optical materials with controlled and uniform refractive index that meet the requirements for active and passive planar optical devices. According to a first aspect of the present invention, radio frequency (RF) sputtering of a wide area target in the presence of a sputtering gas under a condition of uniform target erosion is used to deposit physically and chemically uniform material on a
10 substrate. The substrate is positioned opposite a planar target of the material to be deposited, the area of the target being larger than the area of the substrate. A central area of the target of the same size as the substrate and overlying the substrate is exposed to a uniform plasma condition, which provides a condition of uniform target erosion. A uniform plasma condition can be created without magnetic enhancement, termed diode
15 sputtering, or by providing a time-averaged uniform magnetic field by scanning a magnet across the target in a plane parallel to the plane of the target.

According to an aspect of the present invention, a film deposited on the substrate using a wide area target and uniform target erosion is of uniform thickness for targets with an area at least 1.5 times the area of the substrate. In addition, film deposited on a
20 substrate positioned opposite a central region of the target inside the region providing film thickness uniformity exhibits physical and chemical uniformity useful for fabricating optical devices. The region providing chemical uniformity can be coextensive with the region providing thickness uniformity.

According to another aspect of the present invention, a dual frequency RF
25 sputtering process is used in which the high frequency RF power applied to the target is augmented by applying low frequency RF power to the target, resulting in densification of the deposited film and better coverage of features when deposited over underlying layers. Further, the dual frequency RF process can be used to tune the refractive index of the deposited film. Keeping the total RF power the same, the refractive index tends to increase
30 with the ratio of low frequency to high frequency RF power.

In yet another method, RF power is applied to the substrate resulting in substrate bias. Substrate bias is used with single frequency or with dual frequency RF sputtering to provide improved density and morphology of deposited films and to complete coverage and filling of features on underlying layers. Furthermore, substrate bias contributes to

uniformity of refractive index. Films deposited by diode sputtering including application of substrate bias demonstrate exceptional refractive index uniformity and low average surface roughness.

According to another aspect of the present invention, the refractive index of the
5 material deposited using an RF sputtering process can be deliberately tuned by modifying other plasma processing conditions. First, raising the deposition temperature increases the refractive index of the resulting material. Second, increasing the RF power applied to the target increases the refractive index of the deposited material. Third, a reactive process gas can be added to the sputtering chamber which effectively modifies the chemical
10 composition of the deposited material with a corresponding change in refractive index. Additionally, the refractive index of deposited material can be modified by using a target material in a specific oxidation state. The RF sputtering method is applicable to depositing pure materials and mixed materials including materials containing rare earth dopants for optical amplifier applications. Thus, wide area RF sputtering can be used together with the
15 present refractive index control methods to provide core and cladding materials with a desired difference in refractive index for planar optical waveguides and optical amplifiers.

The present RF sputtering methods for material deposition and refractive index control are combined with processes commonly used in semiconductor fabrication to produce planar optical devices. A surface ridge optical device is produced by using RF
20 sputtering to deposit a stack comprising an upper cladding layer, a middle core layer, and a lower cladding layer on a substrate. A ridge is etched into the upper cladding layer and partway through the thickness of the core layer to produce the surface ridge device. A buried ridge device is produced by etching a ridge into a layer of core material overlying a cladding layer. A top layer of cladding material is deposited over the core ridge by RF
25 sputtering with substrate bias. Use of substrate bias enables the cladding layer to completely cover the exposed ridge without defects. Further, the deposition methods described here are used to fabricate a buried trench device in which RF sputtering with substrate bias completely fills a trench in a layer of cladding material with core material.

Finally, a method for forming composite wide area targets from multiple tiles is
30 provided. The method includes positioning the tiles on a backing plate in a noncontact array.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a is a schematic drawing of a physical vapor deposition apparatus in which wide area target RF sputtering, according to embodiments of the present invention, is performed. FIG. 1b is an expanded view of a portion of the apparatus of FIG. 1a.

5 FIG. 2 is a top down view of the wide area target, scanning magnet, and carrier sheet of the apparatus of FIG. 1.

FIG. 3 is a detail view of a composite target according to an embodiment of the present invention.

FIGS. 4a and 4b are cross section views illustrating a process of fabricating a 10 surface ridge planar optical device, in which processes according to embodiments of the present invention, are used.

FIGS. 5a - 5e are cross section views illustrating a process of fabricating a buried ridge planar optical device, in which processes according to embodiments of the present invention, are used.

15 FIGS. 6a - 6f are cross section views illustrating the process of fabricating a buried trench planar optical device, in which processes according to embodiments of the present invention, are used.

FIG. 7 is a scanning electron micrograph (SEM) of a layer deposited over a substrate patterned with trenches by a RF sputtering process including substrate bias, 20 according to an embodiment of the present invention.

DETAILED DESCRIPTION

A physical vapor deposition process provides optical materials with controlled and uniform refractive index that meet the requirements for active and passive planar optical devices. The process uses radio frequency (RF) sputtering with a wide area target and a 25 condition of uniform target erosion and includes multiple approaches for controlling refractive index.

An apparatus 10 for RF sputtering of controlled refractive index material for planar optical devices is illustrated schematically in FIG. 1a. The apparatus includes a wide area sputter source target 12 which provides material to be deposited on substrate 16. Substrate 30 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when RF power is applied to it and is equivalently termed the cathode. Target 12 is a uniform source of material having a uniform index of refraction. Target 12 is typically composed of pure materials such as quartz, alumina, or sapphire, (the crystalline form of alumina), or mixtures of compounds of optically useful materials. Optically useful materials include

oxides, fluorides, sulfides, nitrides, phosphates, sulfates, and carbonates, as well as other wide band gap semiconductor materials. To achieve uniform deposition, target 12, itself is chemically uniform, flat, and of uniform thickness over an extended area. In practice, target 12 is a composite target fabricated from individual tiles, precisely bonded together
5 on a backing plate with minimal separation. A method of making chemically uniform tiles of mixed materials and attaching them to a backing plate 25, forming target 12, comprises another aspect of the present invention that is described in detail below. The complete target assembly also includes structures for cooling the target as described in U. S. Patent No. 5,565,071 to Demaray et al, and incorporated herein by reference.

10 For fabricating planar optical devices, substrate 16 is a solid, smooth surface. Typically, substrate 16 is a silicon wafer or a silicon wafer coated with a layer of silicon oxide formed by a chemical vapor deposition process or by a thermal oxidation process. Alternatively, substrate 16 is a glass, such as Corning 1737 (Corning Inc., Elmira, NY), a glass-like material, quartz, a metal a metal oxide, or a plastic material. Substrate 16
15 typically is supported on a holder or carrier sheet 17 that may be larger than substrate 16.

An essential feature of the present method is that the area of wide area target 12 is greater than the area on the carrier sheet on which physically and chemically uniform deposition is accomplished. Secondly, it is also essential that a central region on target 12, overlying the substrate 16, be provided with a very uniform condition of sputter erosion of
20 the target material. Uniform target erosion is a consequence of a uniform plasma condition. In the following discussion, all mention of uniform condition of target erosion is taken to be equivalent to uniform plasma condition. Uniform target erosion is evidenced by the persistence of film uniformity throughout an extended target life. A uniform deposited film is defined as a film having a nonuniformity in thickness, when measured at
25 representative points on the entire surface of a substrate wafer, of less than about 5 %. Thickness nonuniformity is defined, by convention, as the difference between the minimum and maximum thickness divided by twice the average thickness. If films deposited from a target from which more than about 20 % of the weight of the target has been removed continue to exhibit thickness uniformity, then the sputtering process is
30 judged to be in a condition of uniform target erosion for all films deposited during the target life.

Thus, it is essential that a uniform plasma condition be created in the region between the target and the substrate overlying the substrate. The region of uniform plasma condition is indicated in the exploded view of FIG. 1b. A plasma is created in the region

denoted 51, which extends under the entire target 12. The central region of the target 52, experiences the condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 will have uniform film thickness.

5 In addition, the region in which deposition provides uniform film thickness is larger than the area in which deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In the present invention it is essential that the target be planar or approximately planar for the formation of a film on a planar substrate which is to be coated with the material of the target. In practice,
10 planarity of the target means that all portions of the target surface in region 52 are within a few millimeters of a planar surface, typically within 0.5 mm.

Multiple approaches to providing a uniform condition of sputter erosion of the target material can be used. A first approach is to sputter without magnetic enhancement. Such operation is referred to as diode sputtering. Using a large area target with a diode
15 sputtering process, a dielectric material can be deposited so as to provide suitably uniform film thickness over a central portion of an adjacent substrate area. Within that area, an area of highly uniform film may be formed with suitable optical uniformity. The rate of formation of films of many microns of thickness by diode sputtering can be slow for small targets. However, in the present method, using large targets, a disadvantage in speed of
20 diode sputtering can be compensated by batch processing in which multiple substrates are processed at once.

Other approaches to providing a uniform condition of sputter erosion rely on creating a large uniform magnetic field or a scanning magnetic field that produces a time-averaged, uniform magnetic field. For example, rotating magnets or electromagnets can be
25 utilized to provide wide areas of substantially uniform target erosion. For magnetically enhanced sputter deposition, a scanning magnet magnetron source is used to provide a uniform, wide area condition of target erosion. Diode sputtering is known to provide uniform films; the magnetron sputtering process described here provides diode-sputtering-like uniformity in a magnetically enhanced sputtering process.

30 As illustrated in FIG. 1a, apparatus 10 also includes a scanning magnet magnetron source 20 positioned above target 12. A scanning magnetron source used for dc sputtering of metallic films is described in U. S. Patent No. 5,855,744 to Halsey, et. al., (hereafter '744), which is incorporated herein by reference, and in references therein. The '744 patent demonstrates the improvement in thickness uniformity that is achieved by reducing

local target erosion due to magnetic effects in the sputtering of a wide area rectangular target. By reducing the magnetic field intensity at these positions, the local target erosion was decreased and the resulting film thickness nonuniformity was improved from 8%, to 4%, over a rectangular substrate of 400 x 500 mm.

5 A top down view of magnet 20 and wide area target 12 is shown in FIG. 2. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to the region of the target indicated by reference numeral 22 has good thickness uniformity. Area 22 is the same size as region 52 of the target, FIG. 1b, that is exposed to a uniform plasma condition. In some implementations, carrier 17 is coextensive with region 22. Reference
10 24 indicates the area below which both physically and chemically uniform deposition is achieved, where physical and chemical uniformity provide refractive index uniformity. FIG. 2 indicates that the region 22 of the target providing thickness uniformity is, in general, larger than the region 24 of the target providing thickness and chemical uniformity. In optimized processes, however, regions 22 and 24 may be coextensive.

15 Magnet 20 extends beyond area 22 in one direction, the Y direction in FIG. 2, so that scanning is necessary in only one direction, the X direction, to provide a time averaged uniform magnetic field. As shown in FIGS. 1a and 1b, magnet 20 is scanned over the entire extent of target 12 which is larger than the region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of the target.

20 Using a wide area target and a scanning magnet to RF sputter a planar silica target 12 of dimension 550 x 650 mm, a film with thickness nonuniformity of ± 5% has been obtained on a substrate placed opposite a region of the target of dimension 300 x 400 mm. The thickness nonuniformity of a 300 mm diameter circular substrate at the center of this region can be less than ±3%. Refractive index nonuniformity at the 150 mm center of the
25 region of less than one part in a thousand has been obtained. The results reported here have been obtained, however, without extensive optimization. Those skilled in the art will recognize that by changing details of the scanning of the magnet, such as the tilt and dwell of the magnet, as described, for example, in '744, further optimization can be achieved. A useful general criterion for the present method of RF sputter deposition, therefore, is that
30 the wide area target be at least 1.5 times the area of the region on the carrier sheet on which physically uniform deposition is obtained. Since the carrier sheet can accommodate a single large substrate or multiple smaller substrates, the criterion can be expressed as the requirement that the area of the target be at least 1.5 times the area of the substrate.

Alternative sputter source designs might be expected to provide a film on a 150 mm wafer with a thickness nonuniformity less than 5%. The results reported for sample C in Example 1 below, demonstrate 4.4% thickness nonuniformity, which corresponds to slightly more than 1.5 % 1 sigma variance. As sample C shows, the nonuniformity of the index of refraction is .067%, or less than 1 part in a thousand. What is not obvious is that a film with more than 1.5 % 1 sigma thickness variance should have a uniformity of index of refraction more than an order of magnitude better. According to one aspect of the present invention, the uniform index of refraction is due to the attributes of the wide area, uniform region of target erosion.

The present method using a wide area target with uniform sputter erosion offers significant advantages over previous deposition approaches. It is possible to form a film with uniform thickness using a target that is smaller in plane area than the substrate. One way to do so is to move the substrate with respect to the source or cathode in such a fashion that the film formed is uniform in thickness. However, such a film will not have been formed under uniform process conditions, such as plasma density, the rate and angle of arrival of the vapor at the substrate, etc. Thus such films will not be uniform in physical properties such as density, refractive index, or resistivity, resulting in nonuniform optical and electrical performance.

It is also well known that it is possible to form a film of uniform thickness from a nonuniform sputter source, say a sputter target with a stationary sputter groove having substantial and increasingly nonuniform erosion through the useful portion of the target life. Such an approach is described, for example, in U.S. Patent No. 5,252,194 to Demaray et al. Similarly, such a nonuniform source of material will not form a film having uniform electrical or optical properties. The example of the ring or cone shaped sputter source illustrates one effect. The anisotropy of the angle of arrival alone can have a substantial effect on the density of the film that is formed. Since the transmission of optical dielectric

uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission or absorptivity.

Returning to FIG. 1a, apparatus 10 includes RF generator 14 for applying RF
5 power to target 12 to generate a plasma in a background gas. RF generator 14 is a high frequency source, conventionally operated at 13.56 MHz. Typical process conditions for RF sputter deposition include applying high frequency RF power in the range of about 500 to 5000 watts. An inert gas, typically, argon, is used as the background sputtering gas. The deposition chamber is operated at low pressure, between about .5 millitorr and 8-10
10 millitorr. Typical process pressure is below about 2 millitorr where there are very few collisions in the gas phase, resulting in a condition of uniform "free molecular" flow. This ensures that the gas phase concentration of a gaseous component is uniform throughout the process chamber.

For example, in the apparatus used in the Examples below, background gas flow
15 rates in the range of about 30 to about 100 sccm, used with a pump operated at a fixed pumping speed of about 50 liters/second, result in free molecular flow conditions. The distance d, in FIG. 1a, between the target and the substrate is varied between about 4 cm and 9 cm. A typical source to substrate distance d is 6 cm. The source to substrate distance is chosen to optimize the thickness uniformity of the film. At large source to substrate
20 distances the film thickness distribution is dome shaped with the thickest region of the film at the center of the substrate. At close source to substrate distance the film thickness is dish shaped with the thickest film formed at the edge of the substrate. The substrate temperature is held constant in the range of about -40 °C to about 550 °C and can be maintained at a chosen temperature to within about 10 °C by means of preheating the substrate and the
25 substrate holder prior to deposition. During the course of deposition, the heat energy impressed upon the substrate by the process must be conducted away from the substrate by cooling the table on which the substrate is positioned during the process, as known to those skilled in the art. The process is performed under conditions of uniform gas introduction, uniform pumping speed, and uniform application of RF power to the periphery of the
30 target as known to skilled practitioners.

The speed at which a scanning magnet 20 is swept over the entire target is determined such that a layer thickness less than about 5 to 10 Å, corresponding roughly to two to four monolayers of material, is deposited on each scan. The rate at which material is deposited depends on the applied RF power and on the distance d, in FIG. 1a, between

the target 12 and the substrate 16. With the silica target described above, scanning speeds between about 2 sec/one-way scan across the target to 20-30 sec/scan provide a beneficial layer thickness. Limiting the amount of material deposited in each pass promotes chemical and physical uniformity. With the typical process conditions, the rate of deposition of pure
5 silica is approximately 0.8 Å/kW-sec. At an applied RF power of 1 kW, the rate of deposition is 0.8 Å/sec. At a magnet scan speed that provides a scan of 2 seconds, a film of 1.8 Å nominal thickness is deposited.

A thickness of 2.4 Å can be associated with one monolayer of amorphous silica film. The impingement rate of process gas equivalent to a monolayer per second occurs at
10 approximately $1x10^{-6}$ torr. The process gas may contain oxygen atoms ejected from the silica during sputtering in addition to the background inert gas. For typical process conditions near 1 millitorr, $4x10^{3}$ monolayers of process gas impinge on the film during the 4 second period of deposition. These conditions provide adequate means for the equilibration of the adsorbed sputtered material with the process gas, if the sputtered
15 material has a uniform composition. Uniform, wide area target erosion is required so as to ensure that the adsorbed sputtered material has a uniform composition.

According to another aspect of the present invention, a dual frequency RF sputtering process, in which low frequency RF power is also applied to the target, is used. Rcturning to FIG. 1a, apparatus 10 includes RF generator 15, in addition to RF generator
20 14 described previously. RF generator 14 is a high frequency source, typically 13.56 MHz, while RF generator 15 provides power at a much lower frequency, typically from about 100 to 400 kHz. Typical process conditions for dual frequency RF deposition include high frequency RF power in the range of about 500 to 5000 watts and low frequency RF power in the range of about 500 to 2500 watts where, for any given
25 deposition, the low frequency power is from about a tenth to about three quarters of the high frequency power. The high frequency RF power is chiefly responsible for sputtering the material of target 12. The high frequency accelerates electrons in the plasma but is not as efficient at accelerating the much slower heavy ions in the plasma. Adding the low frequency RF power causes ions in the plasma to bombard the film being deposited on the
30 substrate, resulting in sputtering and densification of the film.

In addition, the dual frequency RF deposition process generally results in films with a reduced surface roughness as compared with single frequency deposition. For silica, films with average surface roughness in the range of between about 1.5 and 2.6 nm have been obtained with the dual frequency RF process. Experimental results for single and

dual frequency deposition are further described in Example 4 below. As discussed in the co-filed, commonly assigned U.S. application Attorney Docket No. M-11522 US, (the '522 application) which is incorporated herein by reference, reducing surface roughness of core and cladding materials is key to reducing scattering loss in planar optical devices.

5 Further, the dual frequency RF process can be used to tune the refractive index of the deposited film. Keeping the total RF power the same, the refractive index of the deposited film tends to increase with the ratio of low frequency to high frequency RF power. For example, a core layer of a planar waveguide can be deposited by a dual frequency RF process, and the same target 12, can be used to deposit a cladding layer
10 using a single frequency RF process. Introducing low frequency RF power in the core layer deposition process can therefore be used to provide the difference in refractive index between core and cladding layer materials.

It is particularly beneficial to further augment the single frequency or dual frequency RF sputtering process by additionally applying RF power to the substrate 16,
15 using, for example, substrate RF generator 18. Applying power to the substrate, resulting in substrate bias, also contributes to densification of the film. The RF power applied to the substrate can be either at the 13.56 MHz high frequency or at a frequency in the range of the low frequency RF. Substrate bias power similar to the high frequency RF power can be used.

20 Substrate bias has been used previously to planarize sputter deposited quartz films. A theoretical model of the mechanism by which substrate bias operates, has been put forward by Ting et al. (J. Vac. Sci. Technol. 15, 1105 (1978)). When power is applied to the substrate, a so-called plasma sheath is formed about the substrate and ions are coupled from the plasma. The sheath serves to accelerate ions from the plasma so that they
25 bombard the film as it is deposited, sputtering the film, and forward scattering surface atoms, densifying the film and eliminating columnar structure. The effects of adding substrate bias are akin to, but more dramatic than, the effects of adding the low frequency RF component to the sputter source.

Using the bias sputtering process, the film is simultaneously deposited and etched.
30 The net accumulation of film at any point on a surface depends on the relative rates of deposition and etching, which depend respectively, on the power applied to the target and to the substrate, and to the angle that the surface makes with the horizontal. The rate of etching is greatest for intermediate angles, on the order of 45 degrees, that is between about 30 and 60 degrees.

The target and substrate powers can be adjusted such that the rates of deposition and etching are approximately the same for a range of intermediate angles. In this case, films deposited with bias sputtering have the following characteristics. At a step where a horizontal surface meets a vertical surface, the deposited film makes an intermediate angle with the horizontal. On a surface at an intermediate angle, there will be no net deposition since the deposition rate and etch rate are approximately equal. There is net deposition on a vertical surface.

A bias sputtering process without magnetic enhancement has been observed to provide deposited films with exceptionally low surface roughness and exceptional refractive index uniformity. As described in Example 5 below, using substrate bias in a diode sputtering process, a silica film with an average surface roughness of 0.14 nm and a refractive index uniformity of less than $4x10^{-5}$ % has been obtained. Further, as demonstrated in FIG. 7, diode bias sputtering produces structures with the characteristic intermediate angle of the external surface of the film portion covering a raised ridge. Diode bias sputtering therefore, offers particular advantages for forming the core layer of certain waveguide structures, as further discussed in the '522 application.

Dual frequency RF sputter deposition processes or single or dual frequency RF sputtering including substrate bias provide dense films with excellent physical structure for use in planar optical devices. The present processes overcome problems that have been observed in the past in some conventionally deposited, particularly CVD deposited films, which can display so-called "columnar", through thickness structure. In cross section, under magnification, the structure appears like a close packed group of columns or grains. Between the columns, there is often a diffusion path, referred to as "leader" defects. The columnar morphology contributes to the roughness of the surfaces and sidewalls of conventional films after etching during fabrication into devices. The through thickness defects as well as the surface roughness scatters guided light, resulting in insertion and transmission losses. Thus the transparency of materials produced by dual frequency and substrate bias deposition is advantageous for building low loss optical devices.

The use of substrate bias can also influence the refractive index of the deposited film. In the case of an argon gas process, it can be expected that substrate bias will result in densification and etching of the film. An argon bias process can be expected to rise the index of a film deposited from a pure SiO_2 target. However, the rate of etching is proportional to the local plasma density and that density is proportional to the local plasma density at the target cathode. Here again, the uniformity of the target plasma, as

demonstrated by the uniformity of the nearby target erosion is very important for the uniformity of the effect of the substrate bias. Thus, use of substrate bias reinforces the benefits of the wide area target used under condition of uniform target erosion, of the present invention, to provide films with highly uniform optical properties.

5 According to another aspect of the present invention, the refractive index of the material deposited using an RF sputtering process can be deliberately tuned by modifying other plasma processing conditions, provided that such process conditions influence a substantially uniform region of a wide area cathode in a uniform way. First, it has been determined that raising the deposition temperature increases the refractive index of the
10 resulting material. Second, increasing the RF power applied to the target increases the refractive index of the deposited material. Third, a reactive process gas can be added to the sputtering chamber which effectively modifies the chemical composition of the deposited material with a corresponding change in refractive index. In general, adding a reducing gas, such as hydrogen, increases the refractive index and adding an oxidizer, such
15 as oxygen, decreases the refractive index. Nitrogen is also a useful process gas. The direction of the effect on refractive index of replacing some of the argon with nitrogen depends on the chemical composition of the target.

For example, as reported in detail in Example 1, for a pure silica, that is SiO_2, target, increasing the process temperature from 40 °C to 400 °C results in an over 0.7 %
20 increase in refractive index, from 1.438 to 1.449. The process temperature is the temperature at which the substrate carrier 17 is uniformly maintained. All refractive indices reported here are measured at 1550 nm. Increasing the process power from 800 W to 1200 W increases the refractive index of the deposited material by about 0.5 %. Larger changes can be effected by using higher process power or by using reactive process gases
25 in the sputtering chamber. Replacing a third of the argon with nitrogen at 150 °C provides an increase in refractive index of about 7 %. Replacing argon as the sputtering gas with a mixture of 2% H_2 in Ar results in an increase in refractive index of over 2% at 150 °C.

Another approach to providing material with a tailored refractive index is to employ a target material in a specific oxidation state. In the silicon/oxygen system, for
30 example, the refractive index of a bulk SiO_2 target is typically around 1.44. Using the present refractive index control methods with an SiO_2 target, materials with refractive indices between 1.44 and 1.58 have been obtained. Alternatively, as demonstrated in Example 3, target 12 can be composed of silicon monoxide, SiO, which in the bulk state has a refractive index on the order of 1.8. RF sputtered SiO using argon as the sputtering

gas has a refractive index slightly above 2, while SiO that was sputtered using a mixture of argon and nitrogen can have a refractive index lowered by over 15% to below 1.75, depending on the process conditions.

While not bound by any theory, the inventors explain the observed process gas effects on refractive index in the silicon/oxygen system in terms of free electron density on the silicon atoms in the material. Metallic silicon with a high electron density has a high refractive index, about 3.4. Combining silicon atoms with oxygen, which is highly electronegative, that is electron withdrawing, reduces the electron density on silicon, reducing the refractive index to 1.8, for SiO, and to 1.44 for SiO_2. During sputtering of SiO, some of the oxygen is removed by collision with argon ions in the plasma, resulting in sputtered material with a higher refractive index than the SiO target. Nitrogen atoms are electronegative, but not as strongly electronegative as oxygen. When nitrogen is used as a process gas in sputtering of SiO, some nitrogen is added to SiO to form SiON, in which the N adds to withdrawing electrons from Si, lowering the refractive index. However, when nitrogen is used in sputtering of SiO_2, some nitrogen replaces oxygen to form some SiON. In this case, the nitrogen is less electronegative than the oxygen and the refractive index goes up. With this understanding, the practitioner can use reactive process gases to tune refractive index at will.

For passive optical devices, differences in refractive index between the core and the cladding of between about 0.25% and 1.5% are typically required. Thus, wide area RF sputtering can be used together with choice of target oxidation state and refractive index control by varying temperature, power and/or reactive gas to produce both core and cladding materials with a desired Δn. The ability to reproducibly and uniformly provide materials with a range of refractive index enables designers to optimize optical components for geometric or other considerations and specify the desired refractive index of the materials rather than being limited to the values that result from conventional CVD deposition processes.

The specific examples discussed to this point have focused on deposition from targets composed of oxides of silicon. The wide area target RF sputtering process is likewise advantageous for deposition of rare earth doped materials used for the core region of planar optical amplifiers. To deposit rare earth doped materials, a target that is a mixture or compound of the rare earth, typically an oxide, fluoride, sulfide, or nitride, and a suitable oxide host is used. For example, to deposit Er doped SiO, powdered SiO and Er_2O_3 is thoroughly mixed, and formed into tiles by low temperature isostatic pressure.

The present method can be applied to provide rare earth compounds doped in any of the combinations of oxides, including silica and alumina, or silica and alumina augmented by such other host material as yttria, zirconia, titania, or other materials that have been proposed for optical amplifier applications. A mixture of rare earth dopants can be
5 provided, as desired.

Doping oxides of silicon with erbium raises the refractive index of the doped material with respect to the refractive index of the host material. For example, as reported here in sample C of Example 2, a film with an Er concentration of approximately 2×10^{20} atoms/cm^3 in SiO, deposited by RF sputtering, has a refractive index that is 2.3% above
10 that of RF sputtered SiO. The difference in refractive index between the doped core region and the cladding region has an important effect on the performance of planar optical amplifiers. For amplifiers, Δn values between about 0.25% and 15% are typically required. The index control methods described here are beneficially used to provide cladding region materials with a suitable Δn with respect to the doped core region. In the
15 past, additional, so-called tertiary, species such as alkali, phosphorous, boron, and ceria have been introduced into optical layers for refractive index control, raising the index of the core or bringing the refractive index of the cladding up to a desired Δn from the refractive index of the doped core. Such tertiary species can diffuse into the core region and detrimentally interfere with rare earth ion luminescence. Moreover, such tertiary
20 species can raise the coefficient of thermal expansion of the material causing stress and birefringence problems. The present method of wide area target RF sputtering with index control avoids the disadvantages of index modification by tertiary additives.

The chief requirement for applying the present method to deposit doped mixed oxide materials for use in optical amplifiers is that the wide area alloy target be completely
25 uniform in chemical composition, at least to the level of the powder metallurgy utilized to form the powder mixture. Typical powder sizes are between tens and hundreds of microns. In the case of refractory oxide additions, it may be useful to pre-alloy these with the rare earth additions. Plasma spray, transient melting or induction melting may be utilized to form a powder which is a solution or alloy of such materials. In the case of
30 mixed materials containing alumina, for example, the low sputter yield of pure alumina can lead to segregation of the target material during sputtering. This causes the film to be low in aluminum with respect to the alloy target composition. It also can lead to particle production from the cathode. The high solubility of the rare earth material in alumina and the high sputter efficiency of the rare earth doped alumina suggest that practical formation

of a sputter target material proceed through a first step of alloying the rare earth dopant and one or more of the host oxide additions to form a first powder material. The remainder of the host materials can be added prior to consolidation of the alloy target material. With this understanding the practitioner can fabricate alloy tiles of uniform composition.

5 According to yet another aspect of the present invention, a method of forming targets 12 composed of individual tiles is provided. In order to form a wide area target of an alloy target material, the consolidated material must first be uniform to the grain size of the powder from which it is formed. It also must be formed into a structural material capable of forming and finishing to a tile shape having a surface roughness on the order of 10 the powder size from which it is consolidated. As an example, the manufacture of indium tin oxide targets for wide area deposition has shown that it is impractical to attempt to form a single piece, wide area target of fragile or brittle oxide material. The wide area sputter cathode is therefore formed from a close packed array of smaller tiles. A target of a size used in the Examples herein may have from 2 to 20 individual tiles. The tiles are finished 15 to a size so as to provide a margin of non-contact, tile to tile, 29 in FIG. 3, less than. 0.010" to 0.020" or less than half a millimeter so as to eliminate plasma process between the tiles. The distance of the target tile assembly comprising target 12 to the dark space anode or ground shield 19, in Figs. 1a and 1b can be somewhat larger so as to provide non contact assembly or provide for thermal expansion tolerance during process chamber conditioning 20 or operation.

The low thermal expansion and fragile condition of ideal optical dielectric tile material can be a cause of great difficulty in bonding and processing a wide area array of such tiles. The bonding process according to the present invention that overcomes these difficulties is illustrated in FIG. 3. Sputter coating a side of such a tile in region 26 prior to 25 bonding with backing plate 25 can be accomplished with a layer of a material such as chrome or nickel as a diffusion layer. Such a metallurgical layer acts as a wetting layer to be tinned with a suitable solder material such as indium or an indium alloy. The backing plate 25 should be made of titanium or molybdenum or other low expansion metal so as to provide a good match with the thermal expansion of the tile material. A very important 30 aspect of the formation of a tiled target is the finishing and coating of the backing plate prior to the solder bonding of the array of tiles. The portion 27 of the backing plate to be exposed to vacuum, either between the tiles or about the periphery or dark space region of the tile assembly should be bead blasted and plasma spray coated with a material such as alumina or silica to prevent contamination of the process by the target backing plate

material. The portion 26 of the backing plate beneath the tile should be sputter coated with a material such as nickel or chrome to enable solder bonding. Pure indium solder, although it has a higher melting point than alloys such as indium-tin, is much more ductile. This allows the solder to yield during cooling of the solder bonded assembly relieving stress on
5 the bonded tiles.

It is useful to provide an outer frame fixture which is located precisely for the location of the outer tiles. It is also useful to provide shim location, tile to tile, while the assembly is at temperature. The actual solder application and lay up procedure can be devised by those versed in solder assembly. It is essential for reasons of heat transfer that
10 the solder forms a full fill of the volume between the tile and the backing plate. It is also essential that the solder not be exposed to the plasma. There should not be any visible solder in the region between the tiles or on the backing plate. To enable this condition it is useful to sputter coat the wetting layer area with an offset 28 of several millimeters on both the tile and the backing plate. It is also useful to pre-solder or tin both the tiles and the
15 backing plate prior to final assembly. The solder material will not wet region 28 upon assembly. A mask for the sputter deposition of the diffusion barrier/wetting layer film is useful. Finally, cleaning of the bonded target tile assembly should utilize anhydrous cleaning rather than aqueous based cleaning methods.

The RF sputtering methods for material deposition, described here, are combined
20 with processes commonly used in semiconductor fabrication, such as photo-lithographic patterning and etching, to produce planar optical devices. A process to produce a surface ridge device is illustrated schematically in the device cross sections of Figs. 4a and 4b. RF sputtering is used to deposit a layer of cladding material 34 on a substrate 32. A layer of core material 36, having a higher index of refraction than the cladding layer is then
25 deposited by RF sputtering on the cladding layer 34, followed by another layer 34 of the cladding material, as shown in FIG. 4a. A ridge structure 31 is then formed in the upper cladding layer and a portion of the core material, as required by the design of the waveguide, by means of lithography and etching, FIG. 4b. The ridge 31, serves to guide the light in the core material. In the case that the core material is doped with a
30 photoluminescent active material and the conditions for amplification are met, such a structure may be used as a planar waveguide amplifier device.

Figs. 5a-5e illustrate the steps of forming a buried ridge planar wave-guide. FIG. 5a shows the same sequence of films as FIG. 4a without the upper cladding layer. FIG. 5b shows a ridge 37 that has been formed by lithography and etching from the core layer 36.

The ridge is shown as unity aspect ratio but might have another aspect in cross section. Fig 5c illustrates the conformity or ridge coverage shape 38 of an overlayer of the cladding material formed by means of standard RF sputtering. The line of sight arrival of the sputtered cladding material results in poor step coverage of those portions of the ridge
5 having low solid angle exposure to the sputter cathode source. The film grows in a lateral direction from the upper corners of the ridge resulting in a 'bread loaf' shape. The overhang of the lateral growth causes the rate of deposition to decrease at the lower corner of the ridge. A 'bird's beak' shaped defect in the coverage is formed in the covering film. In micro-electronic applications, such a 'bird's beak', or leader, defect is the cause of
10 electrical breakdown of an insulating dielectric layer. In the present optical application, a buried ridge wave-guide having an upper cladding as shown in FIG. 5c would demonstrate poor single mode confinement and substantial polarization dependence for the guided light due to the 'bird's beak defect. Substantial insertion loss would result from the roughness introduced by the defect in the longitudinal direction of the wave-guide.
15 FIG. 5d illustrates the effect of dual frequency RF deposition on the formation of the coverage of the ridge. Using dual RF frequencies, a small amount of ion bombardment of the cladding layer 39 can be achieved during deposition, providing a small etch rate to reduce the lateral growth of the deposition on the top corners of the ridge. The small etch rate during deposition reduces the shadowing at the lower corner of the ridge and increases
20 the step coverage. The low amount of ion bombardment also acts to densify the film by forward scattering of the adsorbed, sputtered material and provides for increased mobility of the sputtered material on the surface of the film. Both effects act to reduce the leader defect shown in FIG. 5c. FIG. 5d shows the improved step coverage 39 that can result from the application of dual frequency power for the sputter deposition of the upper
25 cladding. Due to the fact that the lower frequency, of the dual frequency process, is applied to the cathode, the deposition rate will increase with the addition of the second frequency power. Thus, the positive effect of the second frequency can not be isolated from the deposition rate. However, the structure, shown in FIG. 5d, is not an ideal structure for the formation of a light wave guiding device because the step coverage defect has not been
30 eliminated.

FIG. 5e shows the effect of the addition of substrate bias during the sputter deposition of the upper cladding layer. The substrate bias power is independent of the source power. The addition of further bias power to the substrate will increase the etch rate. In practice it may be equal to the source power. The rate of deposition of the film

will be significantly greater on the horizontal features of the substrate then the rate of etching. However, due to the efficiency of ion etching of a feature of the film inclined near 45 degrees from the horizontal surface, the net accumulation at that angle may be very low. By adjusting the ratio of the bias to the sputter power, an angle of constant repose can be
5 impressed upon the accumulation shape of the deposited cladding layer.

FIG. 5e shows schematically the step coverage that can be obtained in the cladding layer 40 by bias sputtering. FIG. 7 demonstrates that the smooth, straight sidewalls and characteristic 45 degree angles depicted schematically in FIG. 5e are achieved in practice. In particular, the leader defect and the shadowing effect of unbiased deposition can be
10 completely eliminated. The step coverage can be increased by increasing the thickness of layer 40. While the discussion above has emphasized the beneficial geometrical effects of bias sputtering deposition of cladding layer 40, it is also useful to use bias sputtering to deposit all the layers of planar optical devices because of the increased transparency of bias sputtered materials. Also, since bias sputtering affects refractive index, it is desirable
15 to use bias sputtering for both lower and upper cladding layers in order for the cladding layers to have the same refractive index.

A wave guide device 30, as shown in FIG. 5e, with very low polarization dependence and high quality mode containment can be obtained in a material such as pure silica. If such a device is realized in pure silica without the use of dopants, substantial
20 improvement in thermal stability over present devices can be achieved. Device 30 may be used as a wave-guide or splitter. When the core is rare earth doped, it may be utilized to form an active device such as an optical amplifier. When formed by thin film methods, arrays of such devices may be created. Exemplary dimensions of the cross section of ridge 31 or 37 or core 46, discussed below, are from about 2 x 2 μm to about 9 x 9 μm.
25 Exemplary dimensions for cladding layer 34 is between about 10 and 25 μm thick.

The process of forming a trench device 50 is shown schematically in Figs. 6a – 6f. First, a thick layer 41 of cladding material is deposited by RF sputtering on substrate 32, FIG. 6a. Next a trench 42 is formed by photo-lithographic patterning and etching in cladding layer 41, FIG. 6b. Core material 43 may be RF sputtered into the trench, FIG. 6c.
30 As in the case of covering a ridge, the lateral growth of the surface film shadows the line of sight coverage of the trench. The maximum thickness of the bottom fill of an aspect one trench with a film of unity thickness may be less than 10 to 20 %. In practice, the core layer can close off, leaving a void in the trench. The best prior art, teaches that the film 43 should be etched back. An etch back process removes the surface layer, opens the void if

one has formed and leaves the partial fill in the trench, (see H. Ohkubo, et. al. "Polarization-Insensitive Arrayed-Waveguide Grating Using Pure SiO_2 Cladding, Proc. OECC 2000, Technical Digest, July 2000, Makuhari Messe, Japan.). A second deposition can fill the partially filled trench. In contrast, FIG. 6d shows the cladding layer applied by means of a dual frequency process. Using dual frequency, layer 44 remains open due to the etching influence of the second lower frequency. The bottom fill can increase to as much as 60 to 80 %. While dual RF deposition is more successful at filling the trench than single frequency deposition, the process is not ideal for fabrication of buried trench waveguides.

According to the present invention, a trench can be filled in a single process step using bias sputtering. FIG. 6e schematically shows core material deposited by means of RF bias sputtering of layer 45. FIG. 7 demonstrates complete trench fill has been achieved in practice with bias sputtering. The structure of FIG. 6e can be etched back by means of a bias process with the net rate of bias etching greater than the rate of deposition on the horizontal surface. It can also be mechanically polished or etched back. Deposition of a cladding layer by means of RF sputtering results in device 50 shown in FIG. 6f. Device 50 can be used as a polarization independent wave guide. In the prior art, Ohkubo, et. al., the core material was doped with germania to raise the index of refraction. In the present invention, the control of the index of deposited pure silica can be used to provide the higher index material of the core as a uniform layer. The wide area magnetron RF source will also provide a uniform plasma condition for the application of the uniform bias sputtering.

In the case of wave length division, Ohkubo, et. al. utilize a three step process of deposition, etch back and deposition to fill a trench between two ridge waveguide structures. In the design of planar waveguide structures there are many instances in which two core waveguide structures, formed either by etching a ridge or filling a trench, are brought together either to merge, thus forming a so called '3 dB' junction, or into close proximity so as to form a coupler. In these cases, narrow, deep structures are formed. In all these cases it is necessary to fill these structures of adjacency between nearby wave-guides. According to the present invention, the trench fill, the ridge coverage and the adjacent structure fill can be accomplished uniformly in the subject wide area RF bias sputtering process. In all cases, it is also necessary to adjust the index of refraction difference to a precise value. Such a value of Δn may be chosen from 0.1 to 0.8 percent for the purpose of weak mode confinement at a wavelength or for control of the numerical

aperture of a waveguide device. The index difference may need to be uniform to ±5% of the difference for each film. The overall nonuniformity of each film, 1 percent of 5 percent is $5x10^{-4}$. Evaluated at a nominal index of 1.50, such a nonuniformity corresponds to a variance of 0.00075 for each film. The nonuniformity of index reported here and achieved
5 by means of wide area RF sputtering is, on first result, very close to the estimated value required for each film.

The features and benefits of the present methods of wide area target RF sputtering to provide materials for planar optical devices are further illustrated in the following examples which are offered by way of illustration, but not of limitation.

10

EXAMPLE 1: DEPOSITION OF SiO_2

An AKT 1600 series PVD production reactor (Applied Komatsu Technology, Santa Clara, CA) modified for RF application with custom ceramic tile targets was used for RF sputter deposition of SiO_2. A wide area target of dimension 550 x 650 mm was fabricated
15 from four quartz tiles, each 4 mm thick, Corning code 9780 glass (Corning Inc. Elmira, NY). The tiles were finished to a smooth surface, chemically cleaned, rinsed with hot deionized water, dried, and sputter coated with several microns of chrome. The chrome coated sides were bonded to a thin plate of titanium as described above. The titanium backing plate was prepared for bonding by bead blasting, chemical cleaning, and plasma
20 coating with silicon. The tiles and the backing plate were heated to approximately 180 °C and regions were coated with a layer of liquid indium. The tiles were precisely placed on the backing plate such that they were separated by no more than 0.02 inches from each other and from the edges of the region exposed to the plasma.

A 150 mm p-type silicon wafer substrate was placed in the center of a 400 x 500
25 mm glass carrier sheet. 800 watts of power was applied to the target at 13.56 MHz. A race-track shaped magnet of approximate dimension 150 mm x 600 mm was swept over the face of the target at a rate of 4 seconds per one-way scan (8 seconds per complete cycle.) Substrate temperature was uniformly held at 40 °C and the sputter gas was 99.99999% pure argon at a flow rate of 60 sccm. The target to substrate distance was 6.5
30 cm. Deposition efficiency was approximately 0.8 Å/kW-sec. Film thickness and index of refraction were measured at five equally spaced points over the full face of the wafer using a FilmTek 4000 interferometer. Refractive index at 1550 nm was 1.437998 ± 0.001297 (0.09%); film thickness was 9227.66 nm with a nonuniformity of 6.8 %. Results are included as Sample A in Table 1 below.

EXAMPLE 2: DEPOSITION OF SiO_2 WITH INDEX MODIFICATION

SiO_2 films were deposited by processes analogous to that described in Example 1, varying deposition temperature, applied power, and process gas. Results are tabulated in Table 1 below.

5 Table 1: SiO_2 Thickness and Refractive Index as Function of Deposition Conditions

	Power (watts)	Temperature (°C)	Sputtering gas/ Flow rate (sccm)	Refractive index* at 1550 nm	Thickness (nm)#
A	800	40	Ar/60	1.437998 (0.001297)	9227.66 (6.8%)
B	800	150	Ar/60	1.440923 (0.001979)	3133.25
C	800	400	Ar/60	1.450126 (0.000726)	9295.86 (4.8%)
D	1200	150	Ar/60	1.448610 (0.000976)	9.2×10^3
E	800	150	2%H_2 in Ar/60	1.462198 (0.001809)	1287.15
F	800	150	N_2/20, Ar/40	1.580249 (0.008346)	608.87
G	1400	150	N_2/20, Ar/40	1.548439 (0.006499)	2354.80
H	800	400	Ar/60	1.450036 (0.000702)	9295.84 (4.8%)

* Standard deviation (1σ) in parentheses

\# Thickness nonuniformity

10 EXAMPLE 3: DEPOSITION OF SiO AND ERBIUM DOPED SiO

Target tiles of SiO were prepared from a powder of SiO by low temperature isostatic pressure. The tiles were cut and bonded to a backing plate as described above. Mixed oxide tiles used to deposit erbium doped SiO were prepared by mixing powdered Er_2O_3 and SiO in a ratio of 2 molar cation percent erbia. SiO and Er doped SiO films were

15 deposited as in Examples 1 and 2 above. Refractive index and thickness are tabulated for SiO in Table 2 and for Er doped SiO (SiO:Er) with an Er concentration of approximately 2×10^{20} Er atoms/ cm^3, in Table 3.

Table 2: SiO Thickness and Refractive Index as Function of Deposition Conditions

	Power (watts)	Temperature (°C)	Sputtering gas/ Flow rate (sccm)	Refractive index* at 1550 nm	Thickness (nm)
J	1000	150	Ar/60	2.084500	691.78
K	1000	150	N_2/10, Ar/50	1.736693 (0.010250)	1000.96
L	1000	150	N_2/25, Ar/50	1.740680	770.08

* Standard deviation (1σ) in parentheses

Table 3: SiO:Er Thickness and Refractive Index as Function of Deposition Conditions

	Power (watts)	Temperature (°C)	Sputtering gas/ Flow rate (sccm)	Refractive index* at 1550 nm	Thickness (nm)
M	1000	150	Ar/60	2.132870	791.35
N	1000	150	N_2/10, Ar/50	1.740480 (0.017838)	1501.04
O	1000	150	N_2/25, Ar/50	1.750910	1400.11
P	1000	150	N_2/50, Ar/25	1.792790	786.78
Q	800	400	O_2/3, Ar/57	1.454825 (0.005425)	1159.50

* Standard deviation (1σ) in parentheses

5 EXAMPLE 4: SINGLE AND DUAL FREQUENCY RF SPUTTER DEPOSITION OF SILICA

An AKT 1600 series PVD production reactor and wide area target as described in Example 1 was used. High frequency (13.56 MHz) and low frequency (about 350 kHz) process powers are listed along with surface roughness and refractive index (RI) of the
10 deposited films in Table 4 below. Depositions were all conducted at Ar flow rates of 40 standard cubic centimeters per minute (sccm) and at or near room temperature, except as noted below. Refractive index at 1.5 µm was measured using a Film Tek 4000 normal incidence interferometer (SCI, Encinitas, CA). Average surface roughness, R_a, was determined from Atomic Force Microscopy (AFM) measurements using a NanoScope III
15 5000 instrument (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA)

Table 4. Average Surface Roughness and Refractive Index of RF Sputtered Silica

EXAMPLE	HF Power (kW)	LF Power (kW)	R_a (nm)	RI	Total Power	LF/HF Power Ratio
A	2.3	--	2.988	1.4492	2.300	0
B	2.3	--	2.804	1.4494	2.300	0
C	2.3	--	3.412	1.4473	2.300	0
D	2.0	0.350	1.818	1.4538	2.350	0.175
E	2.0	0.350	1.939	1.4533	2.350	0.175
F	2.0	0.350	2.007	1.4547	2.350	0.175
G	2.0	0.350	2.571	1.4520	2.350	0.175
H	1.7	0.600	1.729	1.4560	2.300	0.353
I	1.7	1.000	1.445	1.4617	2.700	0.588
J	3.0	0.525	2.359	1.4542	3.525	0.175
K*	2.0	0.350	3.419	1.4523	2.350	0.175
L#	3.0	0.525	4.489	1.4449	3.525	0.175

* Deposition temperature 225 °C

Ar flow rate 120 sccm

Films deposited with a single frequency RF process (Examples A-C) had average
5 surface roughness values in the range of 2.8 to 3.4 nm while the dual frequency process produced films with systematically lower average surface roughness of between 1.4 and 2.6 nm. Keeping other process conditions the same, increasing the ratio of low frequency to high frequency power is seen to result in decreasing surface roughness. Refractive index is observed to have the opposite proportional dependence on power ratio; increasing
10 the low frequency power contribution results in films with higher refractive index. Beneficially, the higher refractive index material has the lower average surface roughness. Thus, in similar processes, core layer material can be obtained by using dual frequency deposition without use of dopants to modify the index of either layer, while using only the high frequency component produces a material of lower refractive index suitable for the
15 cladding layer.

EXAMPLE 5: RF SPUTTER DEPOSITION OF SILICA WITH SUBSTRATE BIAS

An AKT 4300 series PVD production reactor (Applied Komatsu Technology, Santa Clara, CA) modified to accept custom ceramic tile targets and modified to induce a voltage on the substrate was used to deposit silica on planar and patterned 100 mm silicon wafers.
5 A wide area target of dimension 750 x 870 mm was fabricated as described in Example 1. The wafers were placed in the center of a Corning code 1739 glass carrier sheet opposite the target. The reactor was operated in the diode sputtering mode, without magnetic enhancement, at a high frequency RF power of 2500 W and an induced voltage of -400V. A bias voltage of -125 V at 2 MHz and 250 W was induced on the substrate. An argon gas
10 flow rate of 160 sccm was used.

Average surface roughness of a 0.75 μm thick film deposited on a planar wafer, determined as in Example 4, was 0.14 nm. The refractive index determined as the average of measurements at 12 points on the surface was 1.4622 with a uniformity, defined as the difference of the minimum and maximum values divided by twice the average, of 3.4×10^{-5}
15 percent. To the best knowledge of the inventors, the exceptional uniformity reported here exceeds that of any vacuum deposited film reported previously.

FIG. 7 shows an SEM image of a silica film deposited over a patterned substrate. The trenches in the patterned substrate are seen to be completely and uniformly filled and the ridges are uniformly covered. The top surface of the layer overlying the ridges is flat
20 and the sloping sides of the layer overlying the ridges are nominally at 45 degree angles. All of the foregoing geometric features are characteristic of bias sputtering deposition. As reported above, for trench features with unit aspect ratio, the maximum thickness at the bottom of the trench of films deposited by conventional RF sputtering is less than about 10-20%.

25 Although the present invention has been described in terms of specific materials and conditions, the description is only an example of the invention's application. Various adaptations and modifications of the processes disclosed are contemplated within the scope of the invention as defined by the following claims.

CLAIMS

We claim:

1. A method of making a material layer used in forming planar optical devices, the method comprising:

5 positioning a substrate opposite a planar target, the target having an area larger than the area of the substrate; and

applying radiofrequency power at a first frequency to the target in the presence of a gas, under a condition wherein a central portion of the target overlying the substrate is exposed to a uniform plasma condition, whereby a

10 material layer is formed on the substrate.

2. The method of Claim 1 wherein the uniform plasma condition is created by applying a time-averaged uniform magnetic field.

15 3. The method of Claim 2 wherein the uniform magnetic field is applied by moving a magnet positioned proximate to the target across the target in a plane parallel to the plane of the target.

4. The method of Claim 3 wherein moving a magnet across the target is

20 moving a magnet in a first direction, the magnet extending beyond the target, in a second direction perpendicular to the first direction.

5. The method of Claim 1 wherein the area of the planar target is at least 1.5 times greater than the area of the substrate.

25

6. The method of Claim 5 wherein the material layer deposited on the substrate has a thickness nonuniformity of less than 5 percent.

7. The method of Claim 6 wherein the material layer deposited on the

30 substrate has a nonuniformity in an optical property that is smaller than a nonuniformity in thickness.

8. The method of Claim 1 further comprising applying radiofrequency power at a second frequency to the target wherein the second frequency is lower than the first frequency.

5 9. The method of Claim 1 further comprising applying radiofrequency power to the substrate.

10. The method of Claim 8 further comprising applying radiofrequency power to the substrate.

10

11. The method of Claim 1 wherein the uniform plasma condition is created without use of a magnet and further comprising applying radiofrequency power to the substrate.

15 12. The method of Claim 1 wherein the target comprises refractory oxides.

13. The method of Claim 12 wherein the target comprises oxides of silicon.

14. The method of Claim 13 wherein the target comprises silicon monoxide.

20

15. The method of Claim 12 wherein the target further comprises compounds of rare earths.

16. The method of Claim 8 wherein the refractive index of a first material layer
25 deposited with the radiofrequency power at the second frequency at a first power level is higher than the refractive index of a second material layer deposited with the radiofrequency power at the second frequency at a second power level, wherein the first power level is higher than the second power level and wherein the sum of the power levels of the first frequency and the second frequency are the same during deposition of the first
30 material layer and the second material layer.

17. The method of Claim 1 wherein the refractive index of a first material layer deposited with the substrate held at a first temperature is higher than the refractive index of

a second material layer deposited with the substrate held at a second temperature wherein the first temperature is higher than the second temperature.

18. The method of Claim 1 wherein the refractive index of a first material layer
5 deposited at a first radiofrequency power is higher than the refractive index of a second material layer deposited at a second radiofrequency power wherein the first power is higher than the second power.

19. The method of Claim 1 wherein the gas comprises an inert gas.

10

20. The method of Claim 1 wherein the gas further comprises a reactive gas whereby the refractive index of the material layer is modified compared with the refractive index of a material layer formed in the absence of the reactive gas.

15 21. The method of Claim 20 wherein the reactive gas is a reducing gas and wherein the refractive index of the material layer is greater than the refractive index of a material layer formed in the absence of the reducing gas.

22. The method of Claim 20 wherein the reactive gas is an oxidizing gas and
20 wherein the refractive index of the material layer is smaller than the refractive index of a material layer formed in the absence of the oxidizing gas.

23. The method of Claim 1 wherein the target comprises a plurality of tiles.

25 24. The method of Claim 23 wherein the tiles comprise an alloy material.

25. A method of making a planar optical device, the method comprising:

depositing a first layer of cladding material having a first refractive index on a substrate by physical vapor deposition to form a first structure, wherein
30 radiofrequency power is applied to a planar source of cladding material positioned opposite the substrate, the source having an area greater than the area of the substrate, the power applied in the presence of a gas and under a condition wherein a central portion of the source overlying the substrate is exposed to a uniform plasma condition; and

depositing a layer of core material on the cladding material to form a second structure, the core material having a second refractive index greater than the first refractive index, the core material deposited by physical vapor deposition, wherein radiofrequency power is applied to a planar source of core material positioned opposite the first structure, the source of core material having an area greater than the area of the first structure, the power applied in the presence of a gas and under a condition wherein a central portion of the source of core material overlying the first structure is exposed to a uniform plasma condition;

26. The method of Claim 25 further comprising:

depositing a second layer of cladding material on the layer of core material by physical vapor deposition wherein radiofrequency power is applied to the planar source of cladding material positioned opposite the second structure under a condition wherein a central portion of the source overlying the second structure is exposed to a uniform plasma condition; and

etching regions of the second layer of the cladding material and a portion of the thickness of the layer of core material to produce a ridge structure in the second layer of cladding material and in a portion of the layer of core material.

27. The method of Claim 25 further comprising;

etching regions of the layer of core material to produce a ridge structure in the layer of core material, forming a third structure; and

depositing a second layer of cladding material over the ridge structure by physical vapor deposition wherein

radiofrequency power is applied to the planar source of cladding material positioned opposite the third structure, under a condition wherein the central portion of the source of cladding material overlying the third structure is exposed to a uniform plasma condition, and

radiofrequency power is applied to the third structure.

28. The method of Claim 27 wherein depositing the first layer of cladding material further comprises applying radiofrequency power to the substrate.

29. The method of Claim 28 wherein depositing the layer of core material further comprises applying radiofrequency power to the second structure.

30. A method of making a planar optical device, the method comprising:

5 depositing a first layer of cladding material having a first refractive index on a substrate by physical vapor deposition, wherein radiofrequency power is applied to a planar source of cladding material positioned opposite the substrate, the source having an area greater than the area of the substrate, the power applied in the presence of a gas and under a condition wherein a central portion of the

10 source overlying the substrate is exposed to a uniform plasma condition;

forming a trench in the first layer of cladding material to form a first structure;

depositing a layer of core material on the cladding material completely filling the trench, the core material having a second refractive index greater than

15 the first refractive index, the core material deposited by physical vapor deposition, wherein radiofrequency power is applied to the first structure and radiofrequency power is applied to a planar source of core material positioned opposite the first structure, the source of core material having an area greater than the area of the substrate, the power applied in the presence of a gas and under a condition wherein

20 a central portion of the source of core material overlying the first structure is exposed to a uniform plasma condition;

removing core material overlying the first layer of cladding material exposing the cladding material except in the area of the trench to provide a cladding layer with filled trench; and

25 depositing a layer of cladding material on the cladding layer with filled trench by physical vapor deposition wherein radiofrequency power is applied to the planar source of cladding material positioned opposite the cladding material with filled trench.

30 31. The method of Claim 30 wherein depositing a first layer of cladding material further comprises applying radiofrequency power to the substrate, and wherein depositing a layer of cladding material on the cladding layer with filled trench further comprises applying radiofrequency power to the cladding layer with filled trench.

32. A method of making a composite sputtering target comprising a plurality of tiles, the target used for physical vapor deposition of material, the method comprising:

sputter coating a side of each of the plurality of tiles with a wetting layer material to within an offset of the edge of each tile;

5 providing a backing plate composed of a metal with thermal expansion coefficient similar to the thermal expansion coefficient of the plurality of tiles;

plasma spray coating the backing plate with a ceramic material so as to cover the regions of the backing plate exposed during physical vapor deposition;

sputter coating regions of the backing plate corresponding in placement to

10 the wetted regions of the tiles with a wetting layer;

wetting the sputtered regions of the plurality of tiles and of the backing plate with solder material; and

assembling the plurality of tiles on the backing plate so as to form a solder bonded non contacting array of uniformly spaced tiles.

15

33. The method of Claim 32 wherein the plurality of tiles comprise an alloy material.

34. The method of Claim 32 wherein the wetting layer material comprises

20 chrome or nickel or mixtures thereof.

35. The method of Claim 32 wherein the ceramic material comprises alumina or silica.

25 36. The method of Claim 32 wherein the solder material is indium.

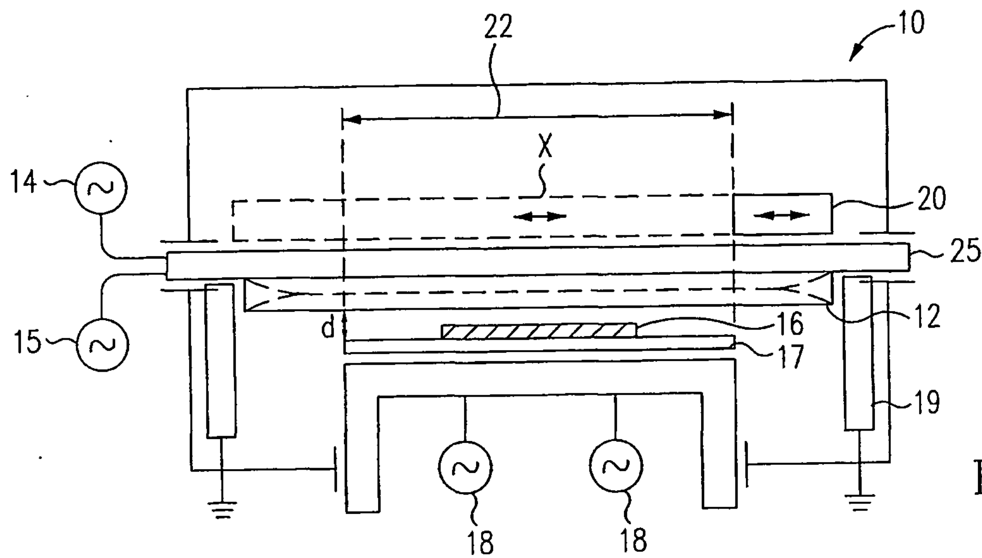


FIG. 1a

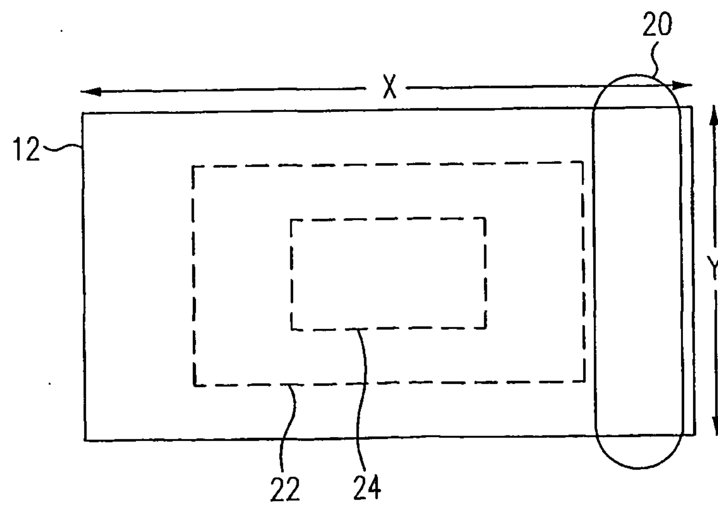


FIG. 2

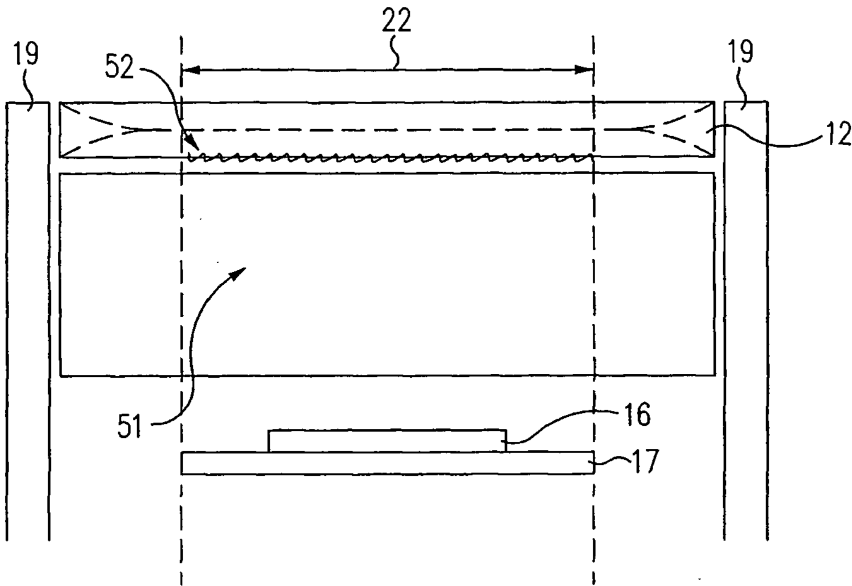


FIG. 1b

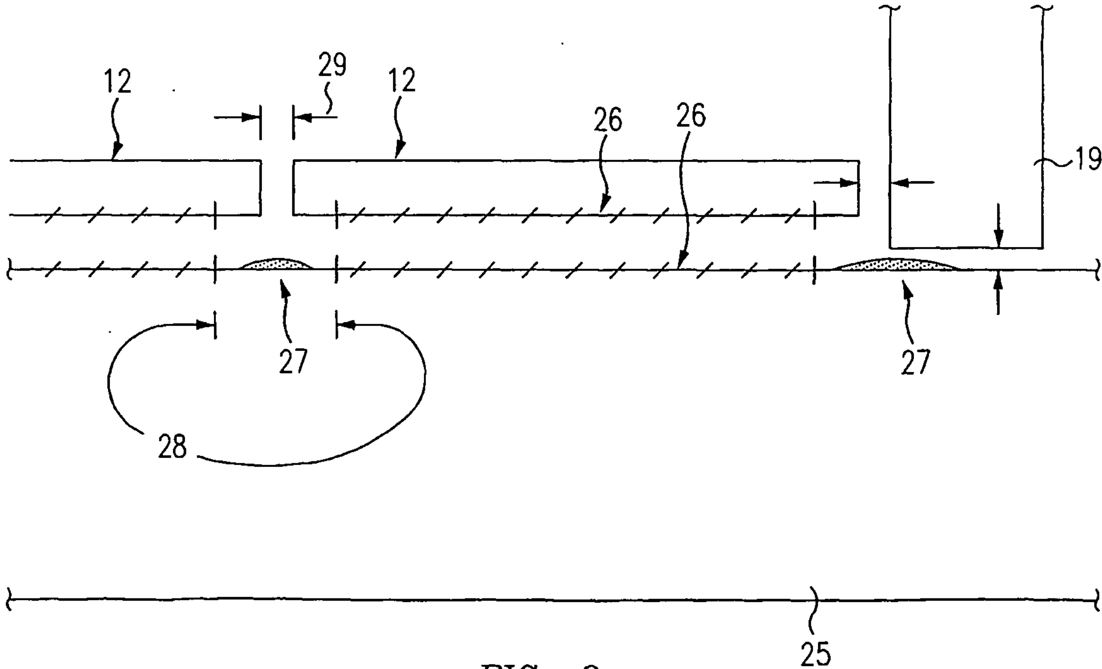


FIG. 3

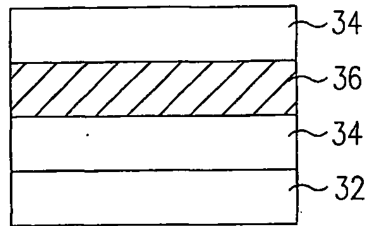


FIG. 4a

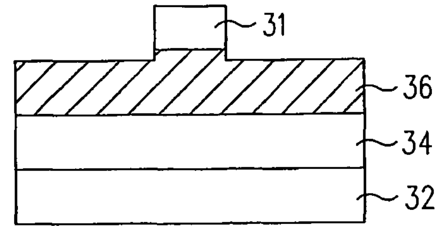


FIG. 4b

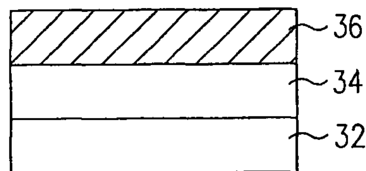


FIG. 5a

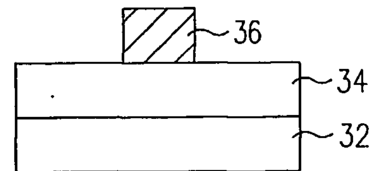


FIG. 5b

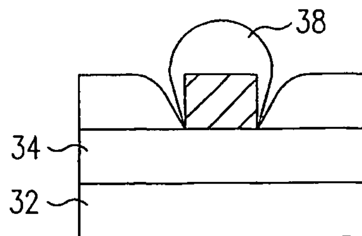


FIG. 5c

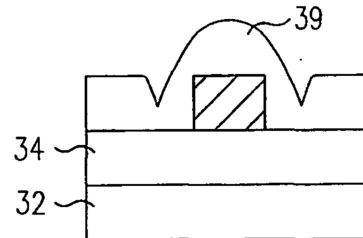


FIG. 5d

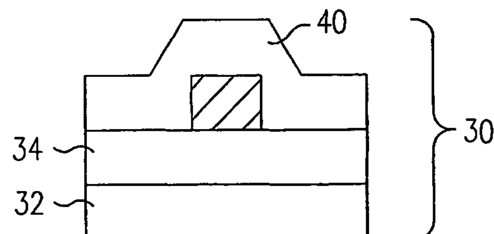


FIG. 5e

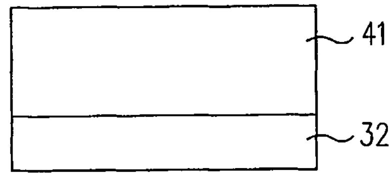


FIG. 6a

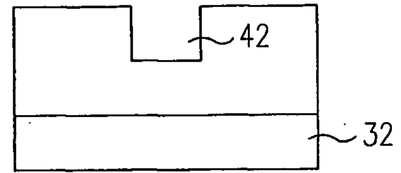


FIG. 6b

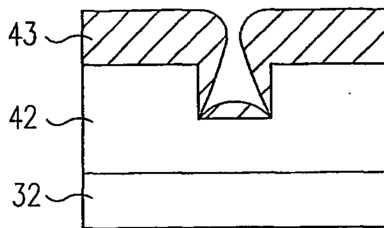


FIG. 6c

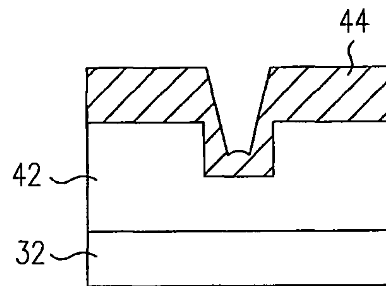


FIG. 6d

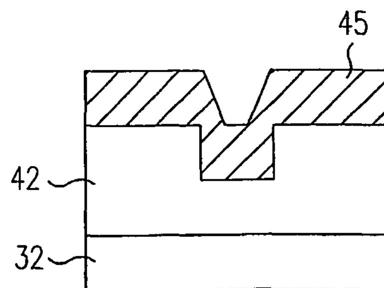


FIG. 6e

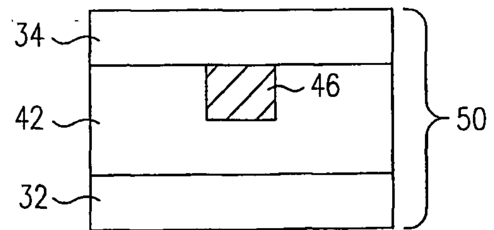


FIG. 6f

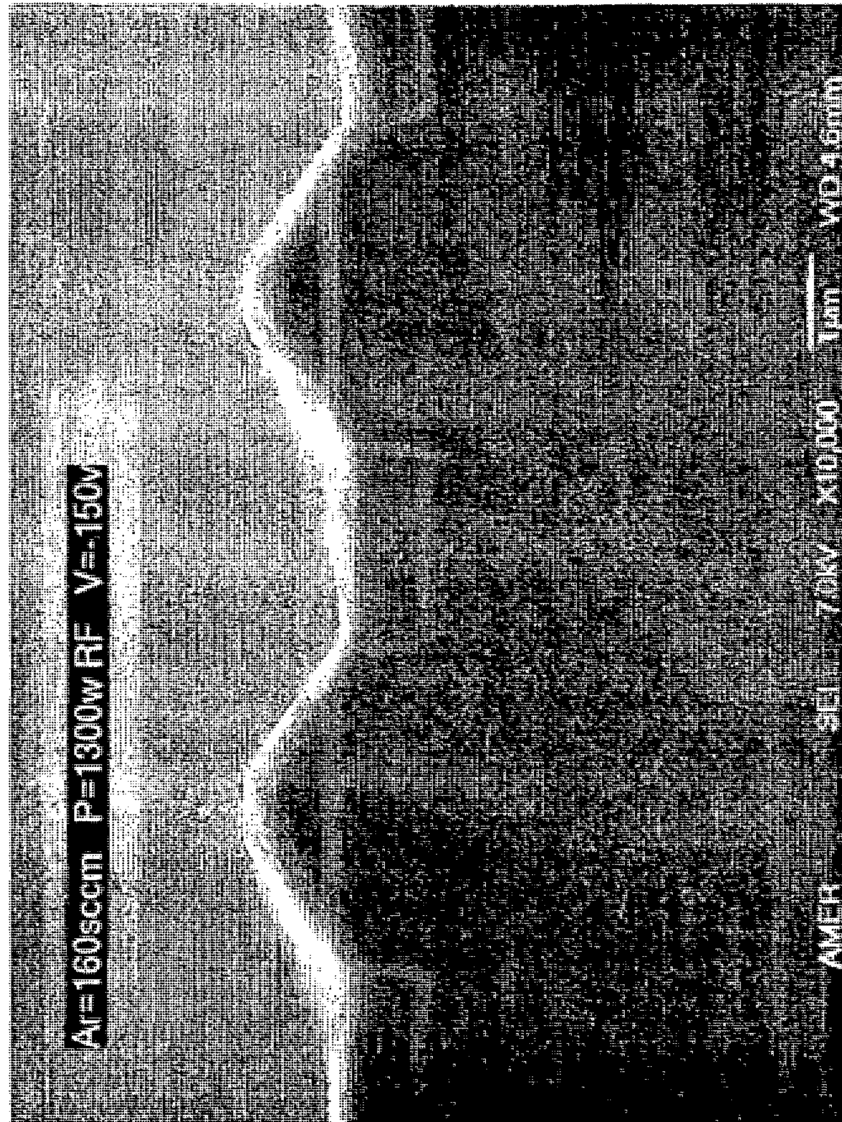


FIG. 7

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/012932 A3

(51) International Patent Classification[7]: C23C 14/34, 14/35

(21) International Application Number: PCT/US01/22750

(22) International Filing Date: 18 July 2001 (18.07.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/633,307 7 August 2000 (07.08.2000) US
09/903,050 10 July 2001 (10.07.2001) US

(71) Applicant: SYMMORPHIX, INC. [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventors: DEMARAY, Richard, E.; 190 Fawn Lane, Portola Valley, CA 94028 (US). WANG, Kai-An; 1082 West Hill Court, Cupertino, CA 95014 (US). MULLAPUDI, Ravi, B.; 2117 Shiangzone Court, San Jose, CA 95121 (US). STADTLER, Douglas, P.; 18509 Murphy Court, Morgan Hill, CA 95037 (US). ZHANG, Hongmei; 1330 Rodney Drive, San Jose, CA 95118 (US). PETHE, Rajiv; 3680 Springbrook Avenue, San Jose, CA 95148 (US).

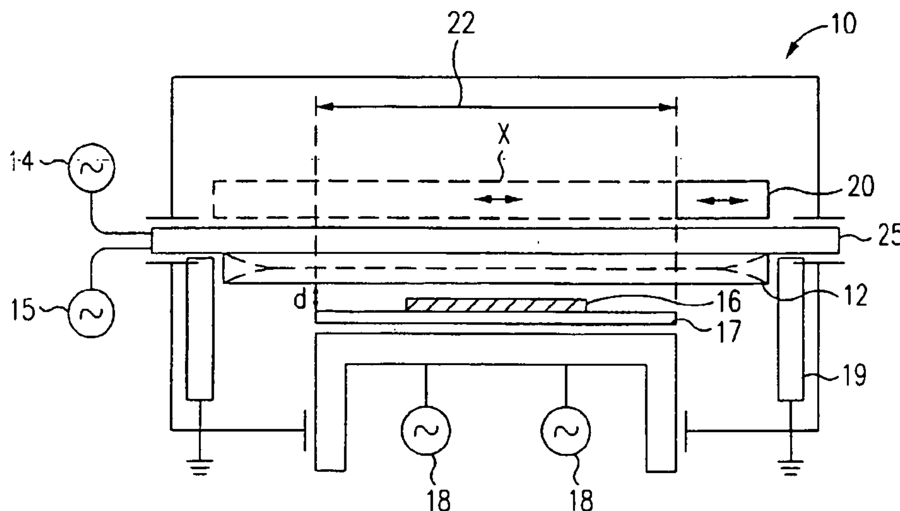
(74) Agents: SAXON, Roberta, P. et al.; Skjerven Morrill MacPherson LLP, 25 Metro Drive, Suite 700, San Jose, CA 95110 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHODS FOR MANUFACTURING PLANAR OPTICAL DEVICES



WO 02/012932 A3

(57) Abstract: Physical vapor deposition processes provide optical materials with controlled and uniform refractive index that meet the requirements for active and passive planar optical devices. All processes use radio frequency (RF) (14) sputtering with a wide area target (12), larger in area than the substrate (16) on which material is deposited, and uniform plasma conditions which provide uniform target erosion. In addition, a second RF (15) frequency can be applied to the sputtering target and RF power (18) can be applied to the substrate (16) producing substrate bias. Multiple approaches for controlling refractive index are provided. The present RF sputtering methods for material deposition and refractive index control are combined with processes commonly used in semiconductor fabrication to produce planar optical devices such surface ridge devices, buried ridge devices and buried trench devices. A method for forming composite wide area targets from multiple tiles is also provided.

WO 02/012932 A3

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report: 3 October 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/22750

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C14/34 C23C14/35

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, IBM-TDB, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 97 35044 A (MATERIALS RESEARCH CORP) 25 September 1997 (1997-09-25) page 1, line 28 -page 3, line 7; figure 1	1 2-7, 12-15,19
Y	EP 0 510 883 A (AMERICAN TELEPHONE & TELEGRAPH) 28 October 1992 (1992-10-28) cited in the application column 7, line 45 -column 9, line 11	12-15,19
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 215 (C-1191), 18 April 1994 (1994-04-18) & JP 06 010127 A (ULVAC JAPAN LTD), 18 January 1994 (1994-01-18) abstract	2-4

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 February 2002	19.07.2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	EKHULT, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/22750

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 437 966 A (HOPE LAWRENCE L ET AL) 20 March 1984 (1984-03-20) column 2, line 50 -column 4, line 54; figures 2-4 ---	5-7
A	EP 0 820 088 A (APPLIED KOMATSU TECHNOLOGY INC) 21 January 1998 (1998-01-21) cited in the application column 1, line 1 -column 4, line 13; figures 1-6 column 6, line 10 - line 19 -----	6,7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 01/22750

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-7,12-15,19

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

International Application No. PCT/US 01/22750

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-7,12-15,19

   Sputtering method using a time averaged uniform magnetic field.

2. Claims: 1,8,10,16

   Sputtering method using dual frequency.

3. Claims: 1,9,11

   Sputtering method using RF substrate bias.

4. Claims: 1,17,18,20-22

   Sputtering method using sputtering parameters to influence the refractive index of the coating.

5. Claims: 25-31

   Methods for making optical devices.

6. Claims: 1,23,24,32-36

   Method for making a composite target.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/22750

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9735044	A	25-09-1997	AU	1978497 A	10-10-1997
			WO	9735044 A1	25-09-1997
EP 0510883	A	28-10-1992	US	5119460 A	02-06-1992
			DE	69212207 D1	22-08-1996
			DE	69212207 T2	06-02-1997
			EP	0510883 A2	28-10-1992
			JP	2501395 B2	29-05-1996
			JP	5160498 A	25-06-1993
			US	5200029 A	06-04-1993
JP 06010127	A	18-01-1994	NONE		
US 4437966	A	20-03-1984	CA	1206914 A1	01-07-1986
			DE	3378710 D1	19-01-1989
			EP	0105407 A2	18-04-1984
			JP	4002667 B	20-01-1992
			JP	59116379 A	05-07-1984
EP 0820088	A	21-01-1998	US	5855744 A	05-01-1999
			EP	0820088 A2	21-01-1998
			JP	10096078 A	14-04-1998
			TW	425590 B	11-03-2001

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 14/34, H01J 37/34 | A1

(11) International Publication Number: WO 96/23085

(43) International Publication Date: 1 August 1996 (01.08.96)

(21) International Application Number: PCT/US95/01089

(22) International Filing Date: 25 January 1995 (25.01.95)

(71) Applicant *(for all designated States except US)*: APPLIED KOMATSU TECHNOLOGY, INC. [JP/JP]; c/o Applied Komatsu Technology America, Inc., 3050 Bowers Avenue, M/S 02634, Santa Clara, CA 95054 (US).

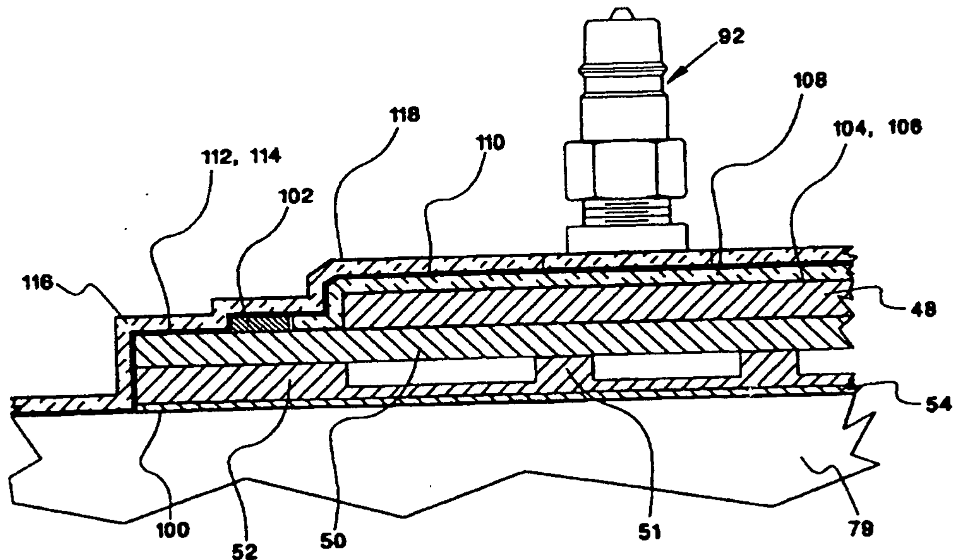
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: DEMARAY, Richard, Ernest [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). HERRERA, Manuel [US/US]; 1583 Brandywine Road, San Mateo, CA 94402 (US).

(74) Agent: STERN, Robert, J.; Legal/Patent Dept., Applied Materials, Inc., 3050 Bower Avenue, M/S 2634, Santa Clara, CA 95054 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
With amended claims and statement.

(54) Title: AUTOCLAVE BONDING OF SPUTTERING TARGET ASSEMBLY



(57) Abstract

Fabrication techniques for an integrated sputtering target assembly include pressure assisted bonding of soldered layers of material, in particular, soldering of the target material to its backing plate; pressure assisted curing of structural adhesives used to join a finned cover plate (52) to a backing plate (50) which between them form passages for fluid cooling; and bonding an electrical insulating layer to the back surface of the backing plate. The pressure to assist in bonding is typically applied by an autoclave. The cooling fluid passages disposed between a cover and a finned backing plate can be sealed by using laser welding or electron beam welding rather than closing the cooling passages with structural adhesives.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	Country	Code	Country	Code	Country
AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

AUTOCLAVE BONDING OF SPUTTERING TARGET ASSEMBLY

5

Field of the Invention

This invention relates to techniques used to fabricate internally cooled sputtering target assemblies generally used in planar magnetron sputtering, and in
10 particular to fabrication techniques used to enhance and assure parallelism between the surface of a target material and the substrate being sputter deposited.

Background of the Invention

Sputtering describes a number of physical techniques commonly used in,
15 for example, the semiconductor industry for the deposition of thin films of various metals such as aluminum, aluminum alloys, refractory metal silicides, gold, copper, titanium-tungsten, tungsten, molybdenum, tantalum, indium-tin-oxide (ITO) and less commonly silicon dioxide and silicon on an item (a substrate), for example a wafer or glass plate being processed. In general, the techniques involve
20 producing a gas plasma of ionized inert gas "particles" (atoms or molecules) by using an electrical field in an evacuated chamber. The ionized particles are then directed toward a "target" and collide with it. As a result of the collisions, free atoms are released from the surface of the target as atom sized projectiles, essentially converting the target material to its gas phase. Most of the free atoms
25 which escape the target surface condense (the atomic sized projectiles lodge on the surface of the substrate at impact) and form (deposit) a thin film on the surface of the object (e.g. wafer, substrate) being processed, which is located a relatively

short distance from the target.

One common sputtering technique is magnetron sputtering. When processing wafers using magnetron sputtering, a magnetic field is used to concentrate sputtering action in the region of the magnetic field so that sputtering
5 occurs at a higher rate and at a lower process pressure. The target itself is electrically biased with respect to the wafer and chamber, and functions as a cathode. The magnetic field's influence on the ions is proportional to its distance from the front of the target. Optimally a target assembly (the target and its backing plate) is thin to allow the magnetic field to have the greatest influence.

10 In generating the gas plasma and creating ion streams impacting on the cathode, considerable energy is used. This energy must be dissipated to avoid melting or nearly melting the structures and components involved. A technique used for cooling sputtering target assemblies is to pass water or other cooling liquid through fixed internal passages of the sputtering target assembly.

15 An example is shown in the simplified perspective sketch of Figure 1, a sputtering system designed for large rectangular substrates, which includes a relatively thin sputtering target assembly with internal cooling passages. (Details of the chamber and its operation are described in earlier U.S. Patent Applications of the inventors: U.S. Serial No. 08/157,763 filed 11-24-93 and U.S. Serial No.
20 08/236,715 filed 4-29-94, now hereby incorporated by reference herein.) The processing/sputtering chamber 30 encloses a dark space ring 31 surrounding a substrate 32 to be sputter deposited. The upper flange of the sputtering chamber 30 supports a lower insulating ring 33 supporting a sputtering target assembly 40. The target material on the sputtering target assembly is facing toward the substrate
25 32 to be sputtered. The target assembly is negatively biased relative to the substrate to effect the sputtering. Inlet cooling lines 36 and outlet cooling lines 37 connect to cooling passages in the sputtering target assembly 40 to cool the assembly during sputtering. The top of the sputtering target assembly 40 is enclosed by a top chamber 35 supported on the back of the sputtering target
30 assembly by an upper insulating ring 34. As fully discussed in the references

previously cited, the top chamber 35 can house a moveable magnetron in an evacuated top chamber. The top chamber can be evacuated so that its pressure approaches the pressure of the process chamber. The force exerted on the area of the target assembly due to differential pressure between the process chamber and
5 the top chamber is then minimal and easily restrained by the thin sputtering target assembly 40.

A multi-layered sputtering target assembly 40, as shown in Figures 2 and 3, is typically assembled according to the above mentioned patent applications using a two step process. In one step, a target material 48 is solder bonded to the
10 backing plate 50. In another step, a finned (or grooved) cover plate 52 is bonded to the back of the backing plate 50 using a structural epoxy based adhesive. The structural epoxy based adhesive is cured by putting it in position and raising the temperature of the pieces to be joined while at the same time applying a pressure to keep the parts in intimate contact throughout the heating cycle. The order in
15 which the two steps are done is dependent on the melting temperature of the solder and the curing temperature of the structural epoxy. The higher temperature bonding process is done first so that the integrity of the first formed bond is not affected by the subsequent process.

The process and materials used in producing a structural epoxy bond
20 generally create a good bond; however, the cooling fluid occasionally leaks due to imperfections in bonding thereby causing such sputtering target assemblies to be rejected. The factors affecting the structural epoxy bond integrity are 1) surface treatment of the pieces to be joined, 2) epoxy selection and curing procedure, and 3) mechanical fitting or mating of the surfaces being joined prior to adhesive cure.
25 Surface treatment removes mechanically weak or non-adherent surface film on the metal. For example, surface treatment may simply consist of mechanically abrading the surface to be bonded in order to obtain a "clean" metal surface. Or, for superior results, the procedure may involve a) degreasing, followed by b) an acid etch to remove any visible oxide film or scale, c) rinsing to remove all traces
30 of the acid, d) a surface-conditioning step to deliberately form a corrosion film of

controlled chemical composition and thickness which promotes primer adhesion, e) drying, and f) priming within an hour to seal the surface from atmospheric oxygen and moisture.

Epoxy selection is based on several factors including: type of carrier,
5 strength of the adhesive, adhesion to the primed surface, curing temperature and pressure procedure, and ability of the adhesive to flow to create a leak-free joint.

Surface treatment, epoxy selection, and curing procedures are factors controlled by manufacturing rigor. However, good mechanical fitting or mating of the surfaces being joined is also required to achieve leak-free joints. Distortion
10 and voids are introduced by the two-step soldering process presently used to join large areas (e.g. 643mm x 550mm target material dimension) of a) dissimilar metals and/or b) non-uniformly heated or cooled similar metals. The present process includes the solder wetting of the two surfaces to be bonded. The target material is then heated and a pool of solder is created at the soldering location.
15 The backing plate, also heated, is then slid into the pool of solder to avoid trapping the solder oxide that normally floats over the molten solder, and the weight of the piece and a light pressure cause the solder in the pool to spread out over the surfaces to be soldered and bring the two materials generally in close contact. The pieces are held aligned one to the other until the solder cools below
20 its melting temperature and the two pieces are bonded.

For example, when solder bonding indium-tin-oxide (ITO) to a commercially pure titanium backing plate, during cooling from the soldering temperature (e.g., 156°C for pure indium solder) to ambient temperature, the differential thermal contraction of the soldered connection tends to cause bending
25 of the pieces. The edges of the target material, being the first to cool, initially form a stronger bond than the higher temperature center of the target. As a result, the strong connection between pieces of the outer edge of the target material causes the center of the target material to buckle and lift from the backing plate at the center of the target, by as much as 0.125" (3.175 mm), as the target material
30 and backing plate continue to contract at different rates. In the subsequent

structural epoxy bond step (the finned cover 52 is bonded to this highly distorted target/backing plate assembly), mechanical fitting or mating of the surfaces being joined is difficult. Poor mating results in uneven bond thickness which can cause the cooling fluid to leak resulting in rejection of the sputtering target assembly.

5 In addition, if such a sputtering target assembly is not flattened, the non-parallelism between the target material and the substrate being sputtered creates non-uniform films on the substrate. Raised areas at the center of the target material may create a void behind the raised area, or the target material may fracture. Such voids change the thermal conductivity between the target and 10 backing plate and the temperature distribution across its face. Since the distribution of sputtered material and the rate of sputtering of the target are directly dependent respectively on the target material distance from the substrate and on its temperature, variations in the gap (distance) between the target and substrate and in the temperature of the target material will also change the 15 uniformity of target material sputter deposited on the substrate.

Since the object of large area sputtering chambers, as described above, includes uniform film thickness across the entire area of the substrate being sputter deposited, variations in film thickness due to variable properties in the target surface of the sputtering target assembly are a great impediment to improving 20 processing efficiency and sputter depositing a uniform film thickness over the whole surface.

Summary of the Invention

A method according to the present invention includes overcoming the 25 distortion and imperfections introduced by the sputtering target assembly fabrication techniques described above to provide generally uniform target properties across the surface of the target. Specifically, the improved fabrication techniques include: pressure-assisted bonding when using solder and/or structural adhesives to bond the material layers making up a sputtering target assembly; and 30 enclosing cooling passages in the target backing plate by laser welding or electron

beam welding one or more cover plates over the void in the backing plate forming the cooling passages. Variations of both techniques are discussed.

These techniques according to the invention, reduce the number of steps in the fabrication process and reduce, if not eliminate, distortion due to differences in
5 coefficients of thermal expansion of adjacent layers. They also virtually eliminate the possibility of cooling fluid leakage due to the failure of cured adhesive based structural bonds.

In one method (or technique), the sputtering target assembly (comprised principally of backing plate, finned cover (plate), insulating sheet, and target
10 material layers) is, as required, machined, ground, lapped, chem-cleaned, primed, and polished prior to assembly. The final step of bonding the layers together under pressure is performed inside a gas-tight fabric bag (preferably in an oxygen-depleted environment) inside an autoclave. The pressurized autoclave exerts a uniform force on the surface of the bag to keep the layers in tight contact
15 throughout the thermal cycling of bond formation and/or curing. During the cooling cycle, the exerted pressure forces the solder layer to plastically flow or yield preventing the assembly from distorting. Spacers, disposed between the target material and backing plate and interspersed in the solder layer control the thickness, uniformity, and integrity of the joint created by the solder layer.

20 In the bonding step, pressure (preferably provided in an autoclave) bonding the target to the backing plate using solder, and bonding the finned (grooved) cover plate to the backing plate using a structural adhesive are performed in one step. The electrical insulating layer can be bonded to the back surface of the target assembly using a structural adhesive during this same step. To perform this
25 bonding step, the target assembly is partially double vacuum bagged to isolate the solder bonding process from the structural bonding process. One (the lower) vacuum bag configuration (system) is attached to the backing plate and encloses only the target material to be solder bonded to the backing plate. The second (the upper) vacuum bag configuration (system) generally encloses the lower bag
30 system, the backing plate, the finned cover, and the electrical insulating sheet and

provides a pass through gas connection to the lower vacuum bag. An epoxy based structural adhesive laminate placed between the backing plate and finned cover plate and between the finned cover plate and the electrical insulation sheet bonds these layers together.

5 The vacuum bags are first evacuated and the autoclave pressure is increased to approximately 15 psi above atmospheric. The vacuum bags are then backfilled with a moisture-free inert or oxygen absorbing gas to approximately one atmosphere to eliminate the possibility (in the event of bag failure) that a vacuum system evacuating the bag will suddenly receive high pressure gas from the 10 autoclave environment. The autoclave pressure is then increased to provide the desired pressure on the unbonded target assembly layers. The assembly is then heated and cooled according to a predefined procedure.

A variation of this method is to solder bond the target to the backing plate first, then enclose the whole assembly in a vacuum bag system and cure the 15 structural adhesive bonded pieces in an autoclave while, at the same time, stress relieving and flattening the target backing plate sub-assembly.

In another variation of this method, the target is solder bonded in the autoclave first, then the cover to hold the cooling fluid is attached by means of fasteners sealed by gasket type (preferably O-ring) seals.

20 A second method according to the invention, involves construction and closure of the void forming the cooling fluid passages in the backing plate and cover assembly. The backing plate includes a recess to receive the cover configured to fit in the recess. The cover and backing plate are joined by laser welding around the edge between the recess and the cover and by spot or seam 25 welding across the field of the cover at generally regularly spaced locations corresponding to the ends of fins (or walls between grooves) in the finned backing plate. A variation would be to use electron beam welding (a low input of heat to avoid material distortion due to welding is desired). The target material can then be solder bonded to the welded assembly by a) solder bonding the target to the 30 welded backing plate using a single vacuum-bagged autoclave procedure, or b)

solder bonding the target to the welded backing plate first, then enclosing the whole assembly in a vacuum bag to stress relieve and flatten the target assembly in the autoclave.

5 Brief Description of the Drawings

Figure 1 is a perspective view of a simplified sputtering chamber system using a sputtering target assembly 40 fabricated according to the invention;

Figure 2 is a plan view of a target side of a sputtering target assembly according to the invention;

10 Figure 3 is a side cross-section view of Figure 2 taken at 3-3;

Figure 4 is a side cross-sectional exploded view showing one embodiment of the layers of material involved in assembling a target assembly such as the one shown in Figure 3;

Figure 5 is a side cross-sectional exploded view showing a second 15 embodiment of layers of material used in assembling a target assembly such as the one shown in Figure 3;

Figure 6 shows a close-up view of the assembled target assembly as pictured in Figure 3;

Figure 7 shows a panel of target material consisting of three tiles used with 20 the sputtering target assembly according to the invention;

Figure 8 shows a tape a) wrapped around the tiles to cover the joints between the tiles of the target panel, and b) covering the target side of the tiles of Figure 7;

Figures 8A and 8B show a pre-assembly perspective view and a final 25 configuration cross sectional view of a joint between adjacent tiles as shown in Figs. 8, 9 and 10;

Figure 9 shows the assembly of the target panel of Figure 8 on a base plate according to the invention;

Figure 10 shows a perspective view of the assembled sputtering target 30 assembly of Figure 9;

Figure 11 shows a partial cutaway view of a bottom of a target backing plate utilizing two welded cover panels covering the cooling passage void in the backing plate;

Figure 12 shows a cross-section of Figure 11 taken at 12-12;

5 Figure 13 shows a target backing plate having the cooling passage void covered by a single cover plate;

Figure 14 shows a close-up cross-sectional view of typical welds at the edge of the cover plate and along the tops of the fins for finned backing plate assemblies with welded cover plates as shown in Figures 11, 12, 13, and 15;

10 Figure 15 shows another embodiment of a target backing plate with two separate cover plates;

Figure 16 shows an overall side cross-sectional view of the material layers used to envelope and create bags around the target assembly being processed in an autoclave;

15 Figure 17 shows a simplified perspective view of the layers of Figure 16, but not showing gas connection fittings;

Figure 18 shows a plan view of the polyamide tape layer on the backing plate surrounding the target material used when processing the target assembly according to the invention;

20 Figure 19 shows a side cross-sectional view of the items of Figure 16 in position for processing;

Figure 20 shows a close-up view of the material layers of Figure 19 surrounding the gas fitting 92;

Figure 21 shows a close-up view of the edge seal of the outside bag shown

25 in close proximity to the gas fitting 90;

Figure 22 shows a configuration for providing thermocouple wiring into the vacuum bag enclosures to monitor the temperature of the target material and/or backing plate;

Figure 23 is a side view of a typical gas fitting connection through a

30 barrier film of a vacuum bag;

Figure 24 is a side cross-sectional exploded view of a single vacuum bag bonding system according to the invention;

Figure 25 is a side cross-sectional view of the material layers of Figure 24 ready to be bonded according to the invention;

5 Figure 26 is a plan view of the sputtering target assembly as pictured in Figure 9; it clearly shows one example of the possible locations for gas connections to the gas barrier layers of the vacuum bags; and

Figure 27 is a perspective view showing a typical configuration of a gas connection through the outer (upper) bag barrier to the inner (lower) bag barrier of 10 the dual bag configuration as pictured in Figures 16, 19, 20, and 26.

Detailed Description

Figure 1, as discussed above, shows a sputtering process system which uses a sputtering target assembly 40 fabricated according to the invention.

15 A general configuration of an embodiment according to the invention is shown in Figure 2. The integrated sputtering target assembly 40 is shown in plan view with its target side up. The sputtering target material 48 is bonded to the backing plate 50. Bonds can be made by soldering, diffusion bonding, or other techniques which provide and maintain satisfactory bonds between dissimilar 20 metals at process temperatures. In other instances (e.g., aluminum or titanium) the target 48 and backing plate 50 may be a monolith of a single material requiring no bonding. In general, it is preferable to machine, grind, lap and polish the target side of the backing plate to form a highly polished vacuum sealing surface 77 (preferably polished to a surface finish of 8μin (0.20μm) Ra, a 25 mirror finish), on the backing plate border 78, circumscribing the target area prior to bonding the target material 48. This surface 77 provides an exceptional leak-tight seal when an O-ring is placed against it. The backing plate 50 includes inlet water fitting ports 67 and 68, outlet water fitting ports 69 and 71, and a rough vacuum port 75 which are preferably machined into the backing plate 50 30 prior to bonding according to the invention.

Figure 3 is a cross-sectional view of Figure 2 taken at 3-3 showing target material 48 attached to backing plate 50 which, in turn, is attached to a finned cover plate 52 which is covered on its outside surface by an electrical insulating sheet 54.

5 Figure 4 is an exploded view of an embodiment of the configuration as typically shown by Figure 3 showing a first structural adhesive laminate 60 disposed between the electrical insulating sheet 54 and finned cover plate 52. The first adhesive laminate 60 is trimmed to match the outline of the finned cover plate 52 to bond the insulating sheet 54 to the cover plate 52. A second layer of 10 structural adhesive laminate 58 is disposed between the top of the finned cover plate 52 and the back of the backing plate 50. The second laminate layer 58 has been trimmed (typically suspended from a carrying screen or mesh not shown) to match the surface pattern of the top of the fins 59 of the cooling passages so that only the surfaces intended to be in contact with each other are bonded (i.e., the 15 top of the fins 59 and the border of the finned side of the cover plate 52). A solder layer 56 consisting of solder-material strips 0.010"-0.020" (0.25 mm-0.51mm) thick is disposed between the target material 48 and front of the backing plate 50. The solder layer 56 may also be formed by pre-wetting the target material 48 and front of the backing plate 50 using other means such as a) a 20 hot plate to dip the surfaces to be bonded in a pool of solder, b) brushing on the solder over the surfaces to be bonded, or c) sputter coating the surfaces to be bonded with a solder layer.

Figure 5 is an exploded view of another configuration as typically shown by Figure 3 showing another embodiment according to the invention. In some 25 instances, to improve surface adhesion or wetting prior to attempting to make a solder bond, the surfaces to be solder bonded can be cleaned by sputter etching (bombarded with ions), and one or more layers of sputter coating material 65 can be sputter coated (deposited) onto the bonded side of the target material 48 and the backing plate 50 to pre-wet or tin their surfaces in preparation for soldering. 30 Another less reliable procedure involves conventionally pre-wetting the surfaces to

be solder bonded and scuffing the wetted solder prior to bonding to remove surface oxides. Once the surfaces to be bonded are tinned (pre-wetted), solder material strips 56, e.g. pure indium, and spacers 63 (e.g., pre-wetted 0.001"-0.010" (0.025mm-0.25mm) diameter copper wires) are positioned between
5 the target material 48 and the backing plate 50 in preparation for solder bonding.

Figure 6 shows a close-up of a cross-section of Figure 3 near its edge consisting of the layers as shown in the embodiment of the invention shown in Figure 5. The backing plate 50 is a rectangular monolith, as generally described above, having a top target surface and a back surface. The top target surface,
10 after having been sputter coated with an adhesion layer, can be wetted by sputtering pure indium on the backing plate 50 made of, for example, titanium. A target material 48 made of, for example, indium-tin-oxide (ITO) is also coated with an adhesion layer and can be wetted with a coating (e.g., pure indium) on its back surface. A series of alternating strips of solder 56 (e.g., strips
15 0.010"-0.020" (0.25 mm-0.51mm) thick of pure indium) and spacer 63 (e.g, pre-wetted 0.005"-0.010" (0.13mm-0.25mm) diameter copper wires) are positioned between the target material 48 and the backing plate 50. While a series of alternating spacers 63 and solder regions 56 with a high concentration are shown in Figure 6, such a high frequency of spacers 63 is not required. The
20 spacers 63 provide a vertical spacing (preferably approximately 0.010" (0.25 mm)) so that after bonding of the target plate 48 to the backing plate 50, a spacer thickness solder joint is maintained. This extra thickness of the solder joint allows the solder material to readily plastically yield when subjected to a clamping pressure during the solder cooling cycle. The solder yielding avoids excessive
25 distortion of the surface of the target material 48 due to a differential thermal expansion. Without spacers 63, the solder joint would have a much reduced thickness, e.g., less than 0.005" (0.13 mm), and thickness uniformity could not be controlled. Also, the excess solder from the thicker solder strips permits the surface oxide, which floats over the molten solder, to be forced out of the joint
30 resulting in excellent solder bond coverage.

The finned cover plate 52 is covered with a layer of structural adhesive laminate 58 which has been trimmed with, for example, a razor blade to match the top of the exposed surfaces which will contact the back side of the backing plate 50. When the structural adhesive laminate 58 is cured, a good bond will create a
5 tight seal between the cooling passages of the finned cover plate 52 and the backing plate 50. Thorough bonding of the ends of the fins of the cover plate 52 to the backing plate 50 will prevent ballooning of the cooling passages when cooling liquids under pressure are introduced into the cooling passages. An electrical insulating sheet 54 is bonded to the backside of the finned cover plate 52
10 by a structural adhesive laminate 60 similar to the structural adhesive laminate 58 used for the bond between the finned cover plate 52 and the backing plate 50.

Figures 7, 8, 9, and 10 provide easy visualization of the steps taken to position a multi-tiled target material (e.g., ITO) to be bonded to a backing plate 50 made of a material (e.g., titanium) with qualities compatible with the sputtering
15 target material. As shown in Figure 7, because indium-tin-oxide is difficult to produce in large plates, when large plates of ITO are needed for sputtering, several tiles 49a, 49b, 49c are positioned adjacent to one another to provide full coverage for sputtering. The tiles are held adjacent to one another by an assembly frame (not shown). In Figure 8 the edges of the tiles and the target side of the
20 tiles are covered with a high temperature polyamide flash breaker tape 43 to prevent the solder from wetting these surfaces. Also, the flash breaking tape 43 facilitates removal of solder material from the spaces between the panels thereby avoiding solder contamination when sputtering the finished target assembly 40.

Fig. 8A shows each tile's perimeter edge wrapped with polyimide tape 43a,
25 43b having a width equal to the thickness of the tile. The tiles (e.g. 49a, 49b) are placed adjacent to one another with a shim 45 maintaining the space between tiles. A joint forming flash breaker tape 43z is laid across two adjacent tiles 49a, 49b whose edges have been taped with polyamide tape 43a, 43b.

Fig. 8B shows the tiles 49a and 49b positioned in a plane ready to be
30 mounted on the backing plate 50. A joint shim 47 positioned between tiles 49a,

49b maintains uniform spacing between tiles as the joint forming flash breaker tape 43z is bent around the joint shim 47 to a position where the tiles are adjacent to one another in a plane. Typically the thickness of the tape 43a, 43b, and 43z is 0.003" (0.076mm). Four layers of this tape, as seen in Figure 8B, provide a built-up thickness of 0.012" (0.30mm). Since it is desired that the final space between tiles be 0.015"-0.020" (0.38-0.51mm) when all tape and shims are removed, the thickness of the shim 47 should be between 0.003" and 0.008" (0.076" and 0.20mm). The shim 47 can be held in place until soldering is complete to assure uniform spacing between tiles. The height of the shim 47 is typically approximately 0.003" (0.076mm) less than the thickness of the tile. Once soldering is complete the shim 47 and all tape layers (43z, 43a, 43b) are removed to leave a 0.015"-0.020" (0.38-0.51mm) gap. Sputtering does not occur in this gap as it acts as a dark space shielded from the effects of sputtering.

Wetting or tinning of the back of the tiles 49a, 49b, and 49c can also take place, if necessary, at this time. A frame around the tiles is used to align and handle them before soldering takes place.

As can be seen in Figure 9, the target backing plate is prepared by positioning a series of solder panels 56 and spacers 63 adjacent to one another such that when the panels 49a, 49b, 49c are positioned over the solder panels (or strips) 56a and spacers 63 and heat is applied, the solder strips 56a will melt and solder will readily flow and bond the backing plate 50 to the target panel material 48 consisting of the tiles 49a, 49b, and 49c. Figure 10 shows the three-tile ITO target material 48 in position on the backing plate 50. The same process can be performed for monolithic target materials without joints. The number of spacers 63 and solder material strips 56 shown in Figure 9 is representative of the kind of spacing that is expected to be needed in order to maintain a generally uniform top surface without excessive deflection of the target material in the face of a uniform clamping pressure exerted by an autoclave. In the case of each pictured ITO tile (49a, b, c), the outer two spacers 63 would act as a bridge across which the tile, for example 49a, would span and deflect. Excessive deflection is not acceptable.

Therefore a middle spacer is provided. Further adjustments to the configuration can be made based on empirical measurements as needed.

A structural configuration for a finned backing plate 50a without epoxy cured bonds is shown in Figure 11. The finned backing plates 50a, 50b, 50c as
5 shown in Figures 11, 12, 13, 14, and 15 include cover receiving recesses as, for example, can be seen in Figure 14 extending down from the top surface in the finned area. The cover plates 53a, b, c, d, or e match the size and thickness of the recess covering the cooling passages and fins 51 dividing and directing the cooling liquid flow from the inlet cooling passage openings to the outlet cooling
10 passage openings. Figure 11 shows a two-piece cover, 53a and 53b, each panel symmetrical to the other along their common edge. Two separate cooling passage cavities are provided. Each cooling passage cavity and cover plate is separately welded by an edge weld (for example, 78) and a seam weld or a series of intermediate plug (or spot) welds 80 regularly located along the top of the fins 51
15 and the intermediate barrier 55 between adjacent cavities, although, it is possible to weld only some of the fins. Typically a seam weld is provided on the top of each fin 51. The finned plate 50a also includes a rough vacuum port 75, a power interlock port 74, and a power attachment fixture 76.

Figure 12 provides a cross-section of Figure 11 taken at 12-12.

20 Figure 13 provides an alternate configuration for a finned backing plate using a one-piece cover plate 53c. A welded finned backing plate 50b and cover 53c form a set of cooling fluid passages. A recess is made on the backing plate 50b to accept the thin cover 53c to hold the cooling fluid and all seams are welded shut. The one piece cover plate 53c is welded around its perimeter by a weld 72
25 and on the top of each fin, from end to end, by a seam weld 70.

Figure 14 is a close-up cross-sectional view of Figures 11, 13, and 15 showing typical weld locations and configurations.

Figure 15 shows an alternate configuration of a finned backing plate 50c where the cooling passages are separated by a thicker intermediate wall than in the
30 prior embodiments, and are covered by separate cover plates 53d and 53e. A

perimeter weld 61 now also passes down the center axis of the finned backing plate 50c. Seam welds 62 are provided on the top of each cooling-passage fin. Seam welds are made over the fins to prevent the cover 53c from ballooning under pressure.

5 When using a backing plate (i.e., 50a, 50b, or 50c) of a weldable aluminum (e.g., aluminum alloy 6061), the recommended material for the thin cover (i.e., 53a, 53b, 53c, 53d, or 53e) is a silicon rich (9%-13% Si) aluminum alloy (e.g., aluminum alloy 4047 containing 11%-13% Si, an aluminum alloy used in the hybrid-package industry). Silicon rich aluminum is used to prevent

10 fractures in the thin cover along the heat affected zone of the welds. Commercially pure titanium backing plates are welded to a thin cover of the same alloy.

The preferred method of bonding the sputtering target assembly involves vacuum autoclave pressure bonding using two bags. Figure 16 is an exploded

15 view showing the different layers included in a two vacuum (flexible) bag system configuration for bonding the target assembly. Figure 17 is a perspective view of the items of Figure 16 without showing the gas connectors. A bead of vacuum bag sealant 98, e.g., General Sealants, Inc. part no. 213 which is a high-temperature (350°F or 177°C) synthetic rubber tape, is attached to a tool (or

20 support) plate 79. A sheet of non-perforated release film 100 is laid inside the area enclosed by the sealant 98 and is used to prevent the part (the sputtering target assembly 40) from bonding to the tool plate 79. Examples of the release film 100 are Airtech International, Inc. part no. Wrightlease 5900, a high-temperature PTFE release film used up to 650°F or 340°C, or Wrightlon

25 5200 Blue, a fluorocarbon release film used up to 450°F or 230°C.

The sputtering target assembly 40 is assembled as an unbonded sandwich according to Figure 16, with the side edges of the insulator sheet 54 wrapped with a flash breaker tape 49, the edges of the finned cover plate 52 wrapped with a flash breaker tape 44, the edges of the backing plate 50 wrapped with a flash

30 breaker tape 42, and the backing plate border 78 up to the edge of the target

material 48 masked with a polyamide high-temperature tape coating 46. A plan view of the border coating 46 is shown in Figure 18.

Examples of flash breaker tapes that may be employed are the high tensile polyester films of fully cured silicon adhesive marketed by Airtech International,
5 Inc. as Flashbreaker 1, 2, 5, the numerical designations referring to the thickness of the film (1, 2, and 5 mils thick respectively), and rated up to 400°F (205°C). Examples of polyamide tapes to mask the target material are manufactured by 3M under Scotch® brand 5413 and 5419 (low static) rated up to 500°F (260°C).

The assembled sputtering target assembly 40 is then placed over the release
10 film 100 lying on the tool plate 79.

To form the lower vacuum bag system, a bead of vacuum bag sealant 102 is laid over the tape coating 46 covering the border of the backing plate 50 (target side). General Sealants, Inc. part no. 213 may be used; however, General Sealants, Inc. manufactures a variety of vacuum bag sealants rated by tackiness,
15 ability to remove clean after bonding, and temperature, whose use might be explored.

Inside the area enclosed by sealant 102, a release film 104, a bleeder film 106 and a breather mat 108 are laid over the target material 48.

Examples of the release film 104 that may be used are oil-free aluminum
20 foil per ASTM B479 and uncoated polyamide film. These release films are used to protect the target surface from contaminants and to prevent bonding of the other films.

Examples of the bleeder film 106 are marketed by Airtech International, Inc. under Release Ply A and B, which are heat set and scoured uncoated nylon
25 fabrics that can absorb excess bonding material. Their counterparts, Bleeder Lease A and B, are not used here in order to prevent contamination from a release agent used in these films.

Examples of the breather mat 108 are marketed by Airtech International, Inc. under Airweave N7 (a 7-oz. polyester breather and resin absorber) and
30 Ultraweave 715 (a nylon 6-6 non-woven breather that does not seal off on

350°F/177°C cures). The breather material is required to facilitate nearly complete air evacuation from the vacuum bag.

Vacuum fitting bases 120 are laid over the breather mat 108 near the border of the backing plate 50 (see Figure 26 for a plan view of the locations of
5 the gas connections). Nylon bag film 110, extending beyond the peripheries of a) the release and bleeder films 104 and 106, and b) mat 108, is laid over the assembly and pressed against vacuum sealant 102 to complete the lower vacuum bag system. Holes are made in the nylon bag film 110 to mate the vacuum fittings 92 and 94 to the bases 120.

10 Examples of nylon bag film 110 are marketed by Airtech International, Inc. under KM1300 rated 390°F/199°C and Wrightlon 7400 rated at the same temperature. These nylon films exhibit 300%+ elongation at break which allows the films to conform to the shape of the part without bridging, which can cause the bag to rupture and defeat the necessary pressure differential. Alternatively, a
15 reusable silicon sheeting bag marketed by, for example, Zip-Vac, Inc., may be substituted for the vacuum bag film.

A typical vacuum fitting, e.g. 90 as shown in Figures 16, 21, and 23, is comprised of a base 120, and an upper assembly comprised of a seal 136 attached to a pressure plate 138, a male quick disconnect fitting 140, and a centrally
20 located T-shaped pin 144 extending downwardly. The pin 144 of the upper assembly extends through a hole in the base and the arms of the pin engage opposite circular ramps on the bottom of the base as the upper assembly is twisted to tighten and seal the fitting 90 to the bag film 110.

The lower vacuum bag system is covered and enclosed with an upper
25 vacuum bag system comprised principally of a release film 112, a bleeder film 114, a breather mat 116 and a vacuum bag film 118. The release and bleeder films 112 and 114, and the breather mat 116 extend beyond the periphery of the target assembly 40 but are laid inside the area enclosed by the bag sealant 98.

An example of release film 112 that may be used is marketed by Airtech
30 International, Inc. under Release Ease 234 TFP, a porous release coated fiberglass

film rated at 550°F/285°C that will, according to the manufacturer, release from all commercial resin systems.

Examples of a bleeder film 114 are Release Ply A and B or Bleeder Lease A and B previously discussed.

5 Examples of a breather mat 116 are Airweave and Ultraweave 715 previously discussed.

Examples of a nylon bag film 118 are KM1300 and Wrightlon 7400, or the reusable silicon sheeting bag previously discussed.

During assembly of the upper vacuum bag system, bases 120 for the
10 fittings 90 and 96 are laid over the breather mat 116 away from the side of the sputtering target assembly 40 (see location pictured in Figure 26), and nylon bag film 118 is laid over the assembly and pressed against vacuum bag sealant 98 to complete the upper vacuum bag system. Holes are made in the nylon bag film 118 to mate the fittings 90 and 96 to the bases 120.

15 Holes are provided in the upper bag system to allow the gas connections from the lower bag system to pass through the upper bag system while maintaining a separation between the upper and lower bag systems. Beads 119 and 121 (identified as 146 in Figure 27) of vacuum bag sealant (e.g., items 98 and 102 described above), applied inside the periphery of each opening, seal the openings
20 and can expose the lower bag system around the gas fittings 92, 94 to the autoclave 88 pressure.

The tool plate 79 and attached elements are then placed into an autoclave 88 enclosure and the vacuum and gas supply fittings 81, 83, 85, 87 are connected. For example, vacuum disconnect fitting 87 connects to the male fitting 96 to pull a
25 vacuum on the upper bag. Vacuum female fitting 81 connects to male fitting 90 to backfill the upper vacuum bag system with clean dry nitrogen when the autoclave pressure reaches approximately 1 atmosphere.

Figure 19 is a cross-sectional view of the double bagged layup (sandwich) after vacuum has been pulled inside the bags. All layers are now fully compressed
30 against the contours of the sputtering target assembly (i.e., the part to be bonded);

no bridging exists. The sputtering target assembly 40 is disposed between a "Blanchard" ground tool plate 79 (to maintain flatness) and the double bagged vacuum system. Figures 20 and 21 provide a detailed close-up view of the features of Figure 19.

5 The autoclave 88 consists of a pressure vessel equipped with an internal heater and fan (not shown). The fan helps maintain a nearly constant fluid temperature inside the autoclave. Thermocouples 142 attached to the part 40 and tool plate 79 monitor the temperature inside the autoclave and provide input to a temperature controller (not shown) located outside the autoclave. This controller 10 cycles the heater on and off in order to reach the desired temperature. The autoclave is pressurized by pumping nitrogen using a compressor (not shown) also located outside the autoclave. Vacuum lines, attached to a vacuum pump(s), enter the autoclave walls through sealed ports and provide vacuum to the bag(s) system. Similarly, gas lines, attached to gas bottle(s) on one end, enter the autoclave walls 15 through sealed ports and are used to backfill the vacuum bag(s) system.

The autoclave "press" principle is to maintain a pressure differential, while heating or cooling, between the part 40, which starts under vacuum, and the outside atmosphere, which is at the autoclave pressure. The part 40, supported on one side by the tool plate 79, is subjected to a uniform autoclave pressure pressing 20 against the vacuum bag. When the autoclave pressure reaches about 15 psi above atmosphere, enough pressure difference exists across the vacuum bag, vacuum pumping is stopped and the vacuum bag is backfilled with, for example, clean, dry nitrogen to avoid ingress of moist air or contaminants inside the bag. Alternately, a reducing, oxygen absorbing gas (i.e., carbon monoxide) can be used to eliminate 25 the possibility of oxidizing parts at elevated temperatures. The autoclave pressure will continue to rise to the bonding pressure recommended by the specifications for use of the structural adhesives. The external side of the vacuum bag is pressurized at the autoclave pressure, for example 60 psi or whatever pressure is recommended, while the inside of the bag is maintained at atmospheric pressure 30 (~15 psi). This pressure differential creates the pressure necessary to maintain

the parts to be bonded in intimate contact while the adhesive is curing. Usually, when the recommended curing pressure is reached, the autoclave will then be heated to the recommended curing temperature of the adhesive. For example:

1) Cytec Engineered Materials, Inc. which manufactures Cybond EF-9500
5 recommends a cure cycle having a 30 minute ramp at 6°F (3.3°C) per minute to go from ambient to 250°F ±5°F (120°C ±3°C), then holding for 90 minutes at 250°F ±5°F (120°C ±3°C) while the pressure is maintained at 60 psi ±5 psi (0.28 MPa ±0.03 MPa).

2) 3M Aerospace Materials which manufactures AF-191, a modified epoxy
10 structural adhesive film, recommends a 4°F to 5°F (2°C to 3°C) per minute temperature rise to the cure temperature of 350°F ±5°F (177°C ±3°C), then holding for 60 minutes at 350°F ±5°F (177°C ±3°C) while the pressure is maintained at 45 psi ±5 psi.

Preferably, parts are to be cooled below 160°F (71°C) before removing
15 from the autoclave 88 or venting to atmosphere.

The structural adhesive film and the components comprising the double bagged vacuum system are selected to withstand the melting point of the solder. For example, when indium solder is used (melting point of 156°C), the adhesive system is selected to withstand up to 350°F/177°C cure. Also, the vacuum bag
20 components are selected to withstand 350°F/177°C, a temperature sufficiently high to ensure melting of the solder material.

Using a double bagged vacuum system, the target assembly 40 is fabricated by solder bonding and structural epoxy bonding in a single autoclave run. The manufacturer's cure procedure for the adhesive film is modified to accommodate
25 the solder process. For example, when using indium solder and the above described Cybond EF-9500 structural adhesive, the autoclave is heated at a rate of 6°F (3.3°C) per minute to go from ambient to 350°F ±5°F (177°C ±3°C). This temperature will be maintained for approximately one minute to insure melting the indium solder strips 56 (shown in Figure 9). The autoclave is then cooled at a
30 rate of approximately 9°F (5°C) per minute to 250°F ±5°F (120°C ±3°C) to

freeze the solder, then held for 60 minutes at 250°F ±5°F (120°C ±3°C) to fully cure the structural adhesive. The pressure is maintained at 60 psi ±5 psi (0.28 MPa ±0.03 Mpa) during the entire heating and cooling cycles. The lower vacuum bag system enclosing the solder is purged with a reducing gas (i.e.,
5 carbon monoxide) to help reduce or eliminate the presence of oxygen and to improve the solder joint integrity (i.e., to avoid formation of indium oxide in the molten solder). In order to minimize oxidizing the solder, the solder strips 56, spacers 63, target material 48 and backing plate 50 (sides to be bonded only) are stripped of surface oxides and maintained in an inert gas atmosphere during the
10 layup process. Other techniques such as ion bombardment (remove surface oxides) followed by sputtering a thin layer (one or two monolayers) of, for example, carbon may also be used. The carbon layer can react with oxygen to form a gas that can be pumped by the vacuum system attached to the lower vacuum bag.

15 Vacuum male fitting 94 (attached to the lower vacuum bag system) and vacuum female fitting 85 (attached to male fitting 94 and to a hose which exits the autoclave 88 and attaches to a line that splits into two valved lines -- one going to a vacuum pump and the other to a vent) connect to the lower vacuum bag system enclosing the target material 48, a portion of the backing plate 50, and the solder
20 material 56 disposed between them (refer to Figure 5). Similarly, mating fittings 92 and 83 connect to a valved gas supply outside the autoclave 88. Although not shown, more than one set of vacuum lines may be attached to each vacuum bag system to increase vacuum pumping or purging of the bag.

Vacuum male fitting 96 (attached to the upper vacuum bag system) and
25 vacuum female fitting 87 (attached to male fitting 96 and to a hose which exits the autoclave and attaches to a line that splits into two valved lines -- one going to a vacuum pump and the other to a vent) connect to the upper vacuum bag system enclosing a) the target backing plate assembly (enclosed by the lower vacuum bag), the finned cover 52 and the adhesive 58 disposed between them; and b) the
30 finned cover 52, the electrical insulating sheet 54 and the adhesive 60 disposed

between them.

When the pressure in the autoclave 88 reaches 15 psi (for reasons previously described), the valves to the vacuum pump(s) are closed and the valves to the gas lines are opened to bring the pressure inside the vacuum bag to
5 approximately 15 psi or 1 atmosphere of the appropriate gas, i.e., an inert or oxygen-absorbing (getter) gas. When pressure inside the vacuum bag reaches approximately 1 atmosphere, the vent valves on the vacuum pump hoses are opened once and then closed to purge the vent lines and leave the vacuum bags saturated with the vent/purge gas.

10 For example, carbon monoxide gas may be introduced into the lower vacuum bag system via a hose attached to female fitting 83 which attaches to male fitting 92. As previously discussed, carbon monoxide is used here to absorb free oxygen and to maintain the cleanest possible environment for the solder bond. Clean, dry nitrogen is introduced into the upper vacuum bag system via a hose
15 attached to female fitting 81 which attaches to male fitting 90 to avoid ingress of moist air or contaminants while the structural adhesive laminates cure.

Figure 22 shows an example of routing a thermocouple wire 142 through the bag seal 98 of a vacuum bag system barrier film 118. Typically at least two thermocouples are provided to each target assembly in an autoclave 88 and the
20 temperature of the target material 48 serves as input to the temperature controller to cycle the autoclave heater on and off.

Figure 23 shows a side view of a typical male fitting (i.e., items 90, 92, 94, and 96) connection through a barrier film of a vacuum bag (i.e., items 110 or 118). Using, for example, a razor blade, a hole is made on the vacuum bag to
25 permit pin 144 extending downwardly to engage the base 120. A seal is made by the rubber seal 136; however, leaky connections are often repaired by sealing the connection using vacuum sealant (e.g., items 98 or 102.)

Figure 24 is an exploded view showing the different layers comprising a single vacuum bag system. Vacuum bag sealant 98 is pressed against tool plate 79
30 (it will later form a vacuum seal with the nylon bag film 118). The assembled

sputtering target assembly 40 is placed over the release film 100 lying on the tool plate 79 and enclosed by the sealant 98. A release film 112, a bleeder film 114 and a breather mat 116 are laid over the sputtering target assembly 40. Vacuum fitting bases 120 are laid over the breather mat 116 away from the sputtering
5 target assembly 40, and nylon bag film 118 is laid over the assembly and pressed against vacuum sealant 98 to complete the vacuum bag system. Holes are made in the nylon bag film 118 to mate the fittings 90 and 96 to the bases 120, all similar to the two bag system described above.

Figure 25 is a cross-sectional view of a single bagged vacuum system layup
10 described in Figure 24 after vacuum has been pulled inside the bags. A double bagged system is useful for solder and epoxy bonding in a single autoclave run; but a single bagged system is useful for: (a) enclosing the whole assembly in a vacuum bag system to cure the adhesive bonded surfaces in the autoclave 88 while, at the same time, stress relieving and flattening the previously soldered
15 target/backing plate sub-assembly; (b) solder bonding the target/backing plate sub-assembly in the autoclave first; the cover to hold the cooling fluid may be attached later by means of fasteners sealed by O-ring seals; (c) solder bonding the target/backing plate sub-assembly in the autoclave after a finned backing plate and cover which holds the cooling fluid have been welded (e.g., laser or electron beam
20 welded); or (d) solder bonding a new target material 48 to refurbish a target assembly 40 ("backing plate" recycle method) fabricated by any of the previously described methods.

Figure 26, as discussed above when discussing Figure 16, shows the location of the sputtering target assembly 40 on the tool plate 79 showing the
25 routing of the sealant 98 and 102 on the tool plate 79 and the border of the backing plate 50, respectively. The hoses connecting to the gas passage fittings 81, 83, 85 and 87 are also shown.

Figure 27, as previously discussed when discussing Figure 16, shows a typical opening in the barrier film 118 of the upper bag sealed by a bead of sealant
30 146 to expose the gas connection fitting 92 to the lower bag film barrier 110.

Autoclaving is a well-known and economical technology. Nonetheless, the autoclave processes described above provide a unique, dependable, and efficient method of producing a sputtering target assembly. It is of course possible to achieve the required temperature and pressure by means other than an autoclave.

5 While the invention has been described with regard to specific embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention.

CLAIMS

1. A method for producing a sputtering target assembly, comprising the steps of:

providing the components of a sputtering target assembly assembled in an
5 unbonded sandwich, at least two layers of said unbonded sandwich being separated by a bonding layer;

pressing the layers of the unbonded sandwich together using a source of pressure which provides a generally uniform pressure distribution across the top and bottom surfaces of said unbonded sandwich;

10 raising the temperature of the unbonded sandwich above a predetermined bonding temperature of said bonding layer while maintaining pressure on said layers;

maintaining the temperature and pressure on the layers of said unbonded sandwich above said bonding temperature for the duration of a predetermined bond
15 curing time; and

maintaining the pressure on the unbonded sandwich while the temperature of the unbonded sandwich falls to a predetermined process completion temperature.

20 2. A method for producing a sputtering target assembly as in Claim 1 further comprising,

enclosing the unbonded sandwich in a flexible vacuum tight enclosure;

creating a vacuum pressure within the flexible vacuum tight enclosure, thus forming a vacuum encapsulated unbonded sandwich assembly; and

25 wherein the pressing step includes pressurizing the flexible vacuum tight enclosure and vacuum encapsulated unbonded sandwich assembly in a pressure chamber; and

wherein the steps of raising the temperature, maintaining the temperature, and maintaining the pressure are all performed in a pressure chamber.

30

3. A method for producing a sputtering target assembly as in Claim 2, wherein the enclosing step includes supporting said unbonded sandwich on a support plate and covering and sealing the unbonded sandwich with a flexible vacuum tight covering sealed to the support plate.

5

4. A method of producing a sputtering target assembly as in Claim 2, wherein the enclosing step includes a target backing plate supporting a target member of said unbonded sandwich on a target backing plate and sealing a flexible vacuum tight covering covering the target member of said unbonded sandwich to the target backing plate.

10

5. A method for producing a sputtering target assembly, comprising the steps of:

laminating the components of a sputtering target assembly in an unbonded sandwich on a support plate, at least two layers of said unbonded sandwich being separated by a bonding layer;

15

covering the unbonded sandwich on the support plate with an upper flexible vacuum tight covering sealed to the support plate thus forming a vacuum encapsulated unbonded sandwich assembly;

20

creating a vacuum pressure within the upper flexible vacuum tight covering over the unbonded sandwich and the support plate;

pressurizing the support plate and vacuum encapsulated unbonded sandwich assembly in a pressure chamber;

raising the temperature of the vacuum encapsulated unbonded sandwich assembly in the pressure chamber above a predetermined bonding temperature of said bonding layer;

25

maintaining the temperature and pressure on the vacuum encapsulated unbonded sandwich assembly in the pressure chamber above the bonding temperature for the duration of a predetermined bond curing time;

30

maintaining the pressure on the support plate and vacuum encapsulated

unbonded sandwich assembly while the temperature of the vacuum encapsulated unbonded sandwich assembly falls to a predetermined process completion temperature.

5 6. A method for producing a sputtering target assembly, as in Claim 5, wherein the step of covering the unbonded sandwich further includes covering a target material with a lower flexible vacuum tight covering and sealing the lower covering to a target backing plate of said unbonded sandwich inside said upper flexible vacuum tight covering;

10 wherein the step of creating a vacuum pressure includes creating a vacuum pressure within the lower flexible vacuum tight covering over the target material and the target backing plate.

7. A method for producing a sputtering target assembly, as in Claim 5,

15 wherein the laminating step includes disposing a release film between the unbonded sandwich and the support plate.

8. A method for producing a sputtering target assembly as in Claim 5; wherein the laminating step includes placing a solder material in spaces

20 between spacer members disposed to maintain a predefined clearance between a sputtering target material and the backing plate when the solder melts.

9. A method for producing a sputtering target assembly as in Claim 6; wherein the laminating step includes placing a solder material in spaces

25 between spacer members disposed to maintain a predefined clearance between a sputtering target material and the backing plate when the solder melts.

10. A method for producing a sputtering target assembly as in Claim 5 further comprising;

30 wherein activity prior to the laminating step includes sputter depositing the

back side of a target material with a solder material to act as tinning in preparation for subsequent solder bonding of said target to a backing plate when a bonding temperature is achieved in the subsequent step of raising the temperature of the vacuum encapsulated unbonded sandwich assembly.

5

11. A method for producing a sputtering target assembly as in Claim 6; wherein activity prior to the laminating includes sputter depositing the back side of a target material with a solder material to act as tinning in preparation for subsequent solder bonding of said target to a backing plate when a bonding
10 temperature is achieved in the subsequent step of raising the temperature of the vacuum encapsulated unbonded sandwich assembly.

12. A method for producing a sputtering target assembly as in Claim 10; wherein prior to sputter depositing the back side of a target material with a
15 solder material, the back side is sputter etched.

13. A method for producing a sputtering target assembly as in Claim 11; wherein prior to sputter depositing the back side of a target material with a solder material, the back side is sputter etched.

20

14. A method for producing a sputtering target assembly, as in Claim 7, wherein the step of providing the components of a sputtering target assembly further includes providing a breather mat film over said unbonded sandwich disposed between the unbonded sandwich and the upper flexible vacuum
25 tight covering.

15. A method for producing a sputtering target assembly, as in Claim 7, wherein the step of providing the components of a sputtering target assembly further includes sequentially providing a release film, a bleeder film, and
30 a breather mat film over said unbonded sandwich disposed between the unbonded

sandwich and the upper flexible vacuum tight covering.

16. A method for producing a sputtering target assembly as in Claim 1, wherein the step of providing the components includes a target backing plate as a component of the unbonded sandwich said backing plate having been produced by a method including the steps of:

providing a finned target backing plate including a void forming a set of cooling fluid passages in said plate, said void including a series of fins, each fin having a top surface;

putting a cover in place over said void;

seal welding the edges of said cover to said backing plate to seal said void; and

spot or seam welding said cover to the tops of said fins in a predetermined weld pattern.

17. A method for producing a sputtering target assembly, comprising the steps of:

providing a finned target backing plate including a void forming a set of cooling fluid passages in said plate, said void including a series of fins, each fin having a top surface;

putting a cover in place over said void;

seal welding the edges of said cover to said backing plate to seal said void; and

spot or seam welding said cover to the tops of said fins in a predetermined weld pattern.

18. A method for producing a sputtering target assembly as in Claim 17, wherein said cover is a silicon rich (7%-14% Si) aluminum alloy.

19. A method for producing a sputtering target assembly as in Claim 17,

wherein said backing plate is a weldable aluminum alloy.

20. A method for producing a sputtering target assembly as in Claim 17, wherein said backing plate and cover are a weldable titanium alloy or
5 commercially pure titanium.

21. A method of fabricating a sputtering target assembly, comprising the steps of:

applying a bonding agent to a surface of a first of a plurality of generally
10 planar panels, one of which comprises a sputtering target;

laminating together said plurality of panels, said surface of said first panels facing a surface of a second of said panels, said first and second panels constituting a first pair of panels;

a first step of exerting a differential hydrostatic pressure across at least
15 some of said laminated panels including said first pair pressing a first of said panels toward said second of said panels; and

during said first exerting step, heating said laminated panels to a first temperature, whereby said bonding agent causes said first pair of panels to be bonded together.

20

22. A method as recited in Claim 21, wherein said bonding agent is a solder.

23. A method as recited in Claim 22, wherein said bonding agent is an adhesive.

25

24. A method as recited in Claim 21, wherein said plurality of panels comprises at least three of said panels and wherein said first exerting step exerts said differential hydrostatic pressure across only some of said panels including said first pair.

30

25. A method as recited in claim 24,

wherein said bonding agent comprises a solder; and

further comprising applying an adhesive to a third surface of one of said second pair of panels, said third surface facing the other of said second pair of
5 panels; and

wherein said first exerting step exerts said differential hydrostatic pressure across said first pair; and

further comprising:

a second step of exerting said differential hydrostatic pressure across at
10 least some of said panels including said second pair; and

during said second exerting step, heating said laminated panels to a second temperature lower than said first temperature, whereby said adhesive causes said second pair of panels to be bonded together.

15 26. A method as recited in Claim 21, wherein said differential hydrostatic pressure is a differential gaseous pressure.

26. A method as recited in Claim 21, wherein one of said first pair of panels includes a surface having grooves for forming fluid cooling channels in said
20 sputtering target assembly.

27. A method of Claim 1;

wherein the sputtering target material includes tiles with one or more joints between them and the joints are sealed during soldering by use of a flexible tape
25 sealed to an edge of each tile and bridging said one or more joints to prevent solder from flowing from the backing plate surface into said one or more joints.

AMENDED CLAIMS

[received by the International Bureau on 12 April 1996 (12.04.96); original claims 1-27 replaced by amended claims 1-46 (11 pages)]

1. A method for producing a sputtering target assembly, comprising the steps of:

providing the components of a sputtering target assembly assembled in an
5 unbonded sandwich, at least two layers of said unbonded sandwich being separated by a bonding layer;

pressing the layers of the unbonded sandwich together using a source of pressure which provides a generally uniform pressure distribution across the top and bottom surfaces of said unbonded sandwich;

10 raising the temperature of the unbonded sandwich above a bonding temperature of said bonding layer while maintaining pressure on said layers;

maintaining the temperature and pressure on the layers of said unbonded sandwich above said bonding temperature for the duration of a bond completion time; and

15 maintaining the pressure on the unbonded sandwich while the temperature of the unbonded sandwich falls to a process completion temperature.

2. A method for producing a sputtering target assembly as in Claim 1 further comprising,

20 enclosing the unbonded sandwich in a flexible vacuum tight enclosure;

creating a vacuum pressure within the flexible vacuum tight enclosure, thus forming a vacuum encapsulated unbonded sandwich assembly; and

wherein the pressing step includes pressurizing the flexible vacuum tight enclosure and vacuum encapsulated unbonded sandwich assembly in a pressure
25 chamber; and

wherein the steps of raising the temperature, maintaining the temperature, and maintaining the pressure are all performed in a pressure chamber.

3. A method for producing a sputtering target assembly as in Claim 2,
30 wherein the enclosing step includes supporting said unbonded sandwich on a

3. A method for producing a sputtering target assembly as in Claim 2, wherein the enclosing step includes supporting said unbonded sandwich on a support plate and covering and sealing the unbonded sandwich with a flexible vacuum tight covering sealed to the support plate.

5

4. A method of producing a sputtering target assembly as in Claim 2, wherein the enclosing step includes a target backing plate supporting a target member of said unbonded sandwich on a target backing plate and sealing a flexible vacuum tight covering covering the target member of said unbonded

10 sandwich to the target backing plate.

5. A method for producing a sputtering target assembly, comprising the steps of:

laminating the components of a sputtering target assembly in an unbonded

15 sandwich on a support plate, at least two layers of said unbonded sandwich being separated by a bonding layer;

covering the unbonded sandwich on the support plate with an upper flexible vacuum tight covering sealed to the support plate thus forming a vacuum encapsulated unbonded sandwich assembly;

20 creating a vacuum pressure within the upper flexible vacuum tight covering over the unbonded sandwich and the support plate;

pressurizing the support plate and vacuum encapsulated unbonded sandwich assembly in a pressure chamber;

raising the temperature of the vacuum encapsulated unbonded sandwich

25 assembly in the pressure chamber above a predetermined bonding temperature of said bonding layer;

maintaining the temperature and pressure on the vacuum encapsulated unbonded sandwich assembly in the pressure chamber above the bonding temperature for the duration of a predetermined bond curing time;

30 maintaining the pressure on the support plate and vacuum encapsulated

6. A method for producing a sputtering target assembly, as in Claim 5, wherein the step of covering the unbonded sandwich further includes covering a target material with a lower flexible vacuum tight cover and sealing the lower flexible vacuum tight cover to a target backing plate of said unbonded
5 sandwich inside said upper flexible vacuum tight cover;

wherein the step of creating a vacuum pressure includes creating a vacuum pressure within the lower flexible vacuum tight cover over the target material and the target backing plate.

10 7. A method for producing a sputtering target assembly, as in Claim 5, wherein the laminating step includes disposing a first release film between the unbonded sandwich and the support plate.

8. A method for producing a sputtering target assembly as in Claim 5;
15 wherein the laminating step includes placing a solder material in spaces between spacer members disposed to maintain a predefined clearance between a sputtering target material and the backing plate when the solder melts.

9. A method for producing a sputtering target assembly as in Claim 6;
20 wherein the laminating step includes placing a solder material in spaces between spacer members disposed to maintain a predefined clearance between the sputtering target material and the backing plate when the solder melts.

10. A method for producing a sputtering target assembly as in Claim 5 further
25 comprising;

wherein activity prior to the laminating step includes sputter depositing the back side of a target material with a solder material to act as tinning in preparation for subsequent solder bonding of said target to a backing plate when a bonding temperature is achieved in the subsequent step of raising the temperature of the
30 vacuum encapsulated unbonded sandwich assembly.

11. A method for producing a sputtering target assembly as in Claim 6; wherein activity prior to the laminating includes sputter depositing the back side of a target material with a solder material to act as tinning in preparation for subsequent solder bonding of said target to a backing plate when a bonding
5 temperature is achieved in the subsequent step of raising the temperature of the vacuum encapsulated unbonded sandwich assembly.

12. A method for producing a sputtering target assembly as in Claim 10; wherein prior to sputter depositing the back side of a target material with a
10 solder material, the back side is sputter etched.

13. A method for producing a sputtering target assembly as in Claim 11; wherein prior to sputter depositing the back side of a target material with a solder material, the back side is sputter etched.

15

14. A method for producing a sputtering target assembly, as in Claim 7, wherein the step of providing the components of a sputtering target assembly further includes providing a breather mat film over said unbonded sandwich disposed between the unbonded sandwich and the upper flexible vacuum
20 tight cover.

15. A method for producing a sputtering target assembly, as in Claim 7, wherein the step of providing the components of a sputtering target assembly further includes sequentially providing a second release film, a bleeder
25 film, and a breather mat film over said unbonded sandwich disposed between the unbonded sandwich and the upper flexible vacuum tight cover.

16. A method for producing a sputtering target assembly as in Claim 1, wherein the step of providing the components includes a target backing
30 plate as a component of the unbonded sandwich said backing plate having been

produced by a method including the steps of:

providing a finned target backing plate including a void forming a set of cooling fluid passages in said plate, said void including a series of fins, each fin having a top surface;

5 putting a cover in place over said void;

seal welding the edges of said cover to said backing plate to seal said void; and

spot or seam welding said cover to the tops of said fins.

10 17. A method for producing a sputtering target assembly, comprising the steps of:

providing a finned target backing plate including a void forming a set of cooling fluid passages in said plate, said void including a series of fins, each fin having a top surface;

15 putting a cover in place over said void;

seal welding the edges of said cover to said backing plate to seal said void; and

spot or seam welding said cover to the tops of said fins.

20 18. A method for producing a sputtering target assembly as in Claim 17, wherein said cover is a silicon rich (7%-14% Si) aluminum alloy.

19. A method for producing a sputtering target assembly as in Claim 17, wherein said backing plate is a weldable aluminum alloy.

25

20. A method for producing a sputtering target assembly as in Claim 17, wherein said backing plate and cover are a weldable titanium alloy or commercially pure titanium.

30 21. A method of fabricating a sputtering target assembly, comprising the steps

of:

applying a bonding agent to a surface of a first of a plurality of generally planar panels, one of which comprises a sputtering target;

locating said plurality of panels together, said surface of said first of said
5 plurality of panels facing a surface of a second of said plurality of panels, said first and second of said plurality of panels constituting a first pair of panels;

exerting a first pressure across at least two or more of said plurality of panels including said first pair, said first pressure pressing said first of said panels toward said second of said panels; and

10 simultaneously with exerting said first pressure, heating at least said first and second of said plurality of panels to a first temperature at which said bonding agent causes said first pair of panels to be bonded together.

22. A method as recited in Claim 21, wherein said bonding agent is a solder.

15

23. A method as recited in Claim 22, wherein said bonding agent is an adhesive.

24. A method as recited in Claim 21, wherein said plurality of panels comprises
20 at least three of said panels and wherein said first pressure exerts pressure across at least two of said panels including said first pair.

25. A method as recited in claim 24,

wherein said bonding agent comprises a solder; and

25 further comprising applying an adhesive to a third surface of one of a second pair of panels, said second and a third of said plurality of panels comprising said second pair, said third surface facing a fourth surface of said second pair of panels; and

wherein said first pressure exerts a first force pressing said first pair of
30 panels together; and

further comprising:

exerting a second pressure across at least two of said panels including said second pair; and

simultaneously with exerting said second pressure, heating at least said
5 second and third of said plurality of panels to a second temperature lower than said first temperature, at which said adhesive causes said second pair of panels to be bonded together.

26. A method as recited in Claim 21, wherein said differential hydrostatic
10 pressure is a differential gaseous pressure.

27. A method of Claim 1;

wherein at least one of said layers includes a set of tiles with one or more joints between them and the joints are sealed during soldering by use of a flexible
15 tape sealed to an edge of each tile and bridging said one or more joints to prevent solder from flowing from the backing plate surface into said one or more joints.

28. A method for producing a sputtering target assembly, comprising the steps of:

20 providing the components of a sputtering target assembly assembled in an bonded sandwich, at least two layers of said bonded sandwich being separated by a bonding layer;

pressing the layers of the unbonded sandwich together using a source of pressure which provides a generally uniform pressure distribution across the top
25 and bottom surfaces of said bonded sandwich;

raising the temperature of the bonded sandwich to a stress relieving temperature of said bonding layer;

continuing pressing the layers together and maintaining the temperature of said unbonded sandwich at said stress relieving temperature for the duration of a
30 stress relieving time; and

continuing pressing the layers of the bonded sandwich together while the temperature of the bonded sandwich falls to a stress relief process completion temperature.

5 29. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, and maintaining the temperature; said components are exposed to a substantially inert gas environment.

10 30. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, and maintaining the temperature; said components are exposed to a substantially moisture free and inert gas environment.

15 31. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, and maintaining the temperature; said components are exposed to a substantially oxygen absorbing gas environment.

20 32. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, maintaining the temperature, and maintaining the pressure; said components are enclosed in a gas tight enclosure having a flexible wall, said enclosure containing a substantially inert gas environment.

25

33. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, maintaining the temperature, and maintaining the pressure; said components are enclosed in a gas tight enclosure having a flexible wall, said enclosure containing a substantially

30 moisture free inert gas environment.

34. A method for producing a sputtering target assembly, as in Claim 1, wherein during the steps of: providing, pressing, raising, maintaining the temperature, and maintaining the pressure; said components are enclosed in a gas tight enclosure having a flexible wall, said enclosure containing a substantially
5 oxygen absorbing gas environment.

35. A method for producing a sputtering target assembly, as in Claim 34, wherein the substantially oxygen absorbing gas environment is formed primarily with carbon monoxide.

10

36. A method for producing a sputtering target assembly, as in Claim 32, wherein before providing a substantially inert gas environment to the gas tight enclosure said enclosure has been substantially evacuated.

15 37. A method for producing a sputtering target assembly, as in Claim 33, wherein before providing a substantially inert gas environment to the gas tight enclosure said enclosure has been substantially evacuated.

38. A method for producing a sputtering target assembly, as in Claim 34,
20 wherein before providing a substantially inert gas environment to the gas tight enclosure said enclosure has been substantially evacuated.

39. A method for producing a sputtering target assembly, as in Claim 1, wherein the step of providing the components includes providing a surface
25 of at least one of the faces of said layers facing one another and being separated by a bonding layer having been coated by sputter depositing a layer of said bonding material thereon.

40. A method for producing a sputtering target assembly, as in Claim 29,
30 wherein the step of providing the components includes providing a surface

of at least one of the faces of said layers facing one another and being separated by a bonding layer having been coated by sputter depositing a layer of said bonding material thereon.

5 41. A method for producing a sputtering target assembly, as in Claim 30, wherein the step of providing the components includes providing a surface of at least one of the faces of said layers facing one another and being separated by a bonding layer having been coated by sputter depositing a layer of said bonding material thereon.

10

42. A method for producing a sputtering target assembly, as in Claim 31, wherein the step of providing the components includes providing a surface of at least one of the faces of said layers facing one another and being separated by a bonding layer having been coated by sputter depositing a layer of said bonding

15 material thereon.

43. A method as recited in Claim 21, wherein one of said first pair of panels includes a surface having grooves for forming fluid cooling channels in said sputtering target assembly.

20

44. A method for producing a sputtering target assembly as in Claim 1; wherein the step of providing the components for the bonding layer includes placing a solder material in spaces between spacer members disposed to maintain a predefined clearance between at least two layers of said unbonded sandwich when

25 the solder melts.

45. A method for producing a sputtering target assembly as in Claim 1; wherein activity prior to the step providing the components includes sputter depositing bonding side of a first of said at least two layers with a solder material

30 to act as tinning in preparation for subsequent solder bonding of said first of said at

STATEMENT UNDER ARTICLE 19

- Claims 1 and 5 the word "predetermined" has been deleted from before the words "bonding temperature"; the words "predetermined bond curing" have been replaced by the words "bond completion"; and the word "predetermined" has been deleted from before the words "process completion."

- Once in each Claim 3, 4, 14, and 15; twice in Claim 5; and three times in Claim 6 the words "flexible vacuum tight covering" have been changed to "flexible vacuum tight cover" to increase clarity and avoid confusion with the method step of "covering" (a verb). The noun "covering" in the specification and in the claims is considered synonymous with the noun "cover."

- In Claim 6 the wording "lower covering" has been changed to "lower flexible vacuum tight cover."

- In Claim 7 the word "first" has been inserted before the words "release film."

- In Claim 9 the words "between a" have been revised to "between the."

- In Claim 15 the word "second" has been inserted before the words "release film."

- In Claims 16 and 17 the words "in a predetermined weld pattern" have been deleted.

- In Claim 21, 24, 25, and 27 numerous changes in wording have made. Portions of the changes to the text are shown as follows <u>added text is shown underlined</u>, while [deleted text is shown in brackets].

21. . . .
<u>locating</u> [laminating together] said plurality of panels <u>together</u>, . . . first <u>of</u>

21. . . .

locating [laminating together] said plurality of panels together, . . . first of said plurality of panels . . . said plurality of panels, . . . second of said plurality of panels . . .

exerting a first [step of exerting a differential hydrostatic] pressure across at least [some] two or more of said [laminated] plurality of panels including said first pair, said first pressure pressing [a] said first . . .

[during said first] simultaneously with exerting said first pressure [step], heating at least said first and second of said [laminated] plurality of panels to a first temperature[, whereby] at which said bonding . . ..

25. . . . .

. . . one of [said] a second pair of panels, said second and a third of said plurality of panels comprising said second pair, said third surface facing a fourth [the other] surface of said . . .

wherein said first pressure [said first exerting step] exerts [said differential hydrostatic pressure across] a first force pressing said first pair of panels together . . .

. . .

exerting a second [step of exerting said differential hydrostatic] pressure . . . least [some] two of said . . .

[during said second] simultaneously with exerting said second pressure [step], heating at least said second and third of said [laminated] plurality of panels . . . temperature, [whereby] at which said adhesive . . ..

27. . . .

wherein at least one of said layers [the sputtering target material] includes a set of tiles . . ..

- Two Claims numbered 26 were initially submitted. The first remains unchanged. The second has been cancelled.
- Claims 28 to 46 are new.

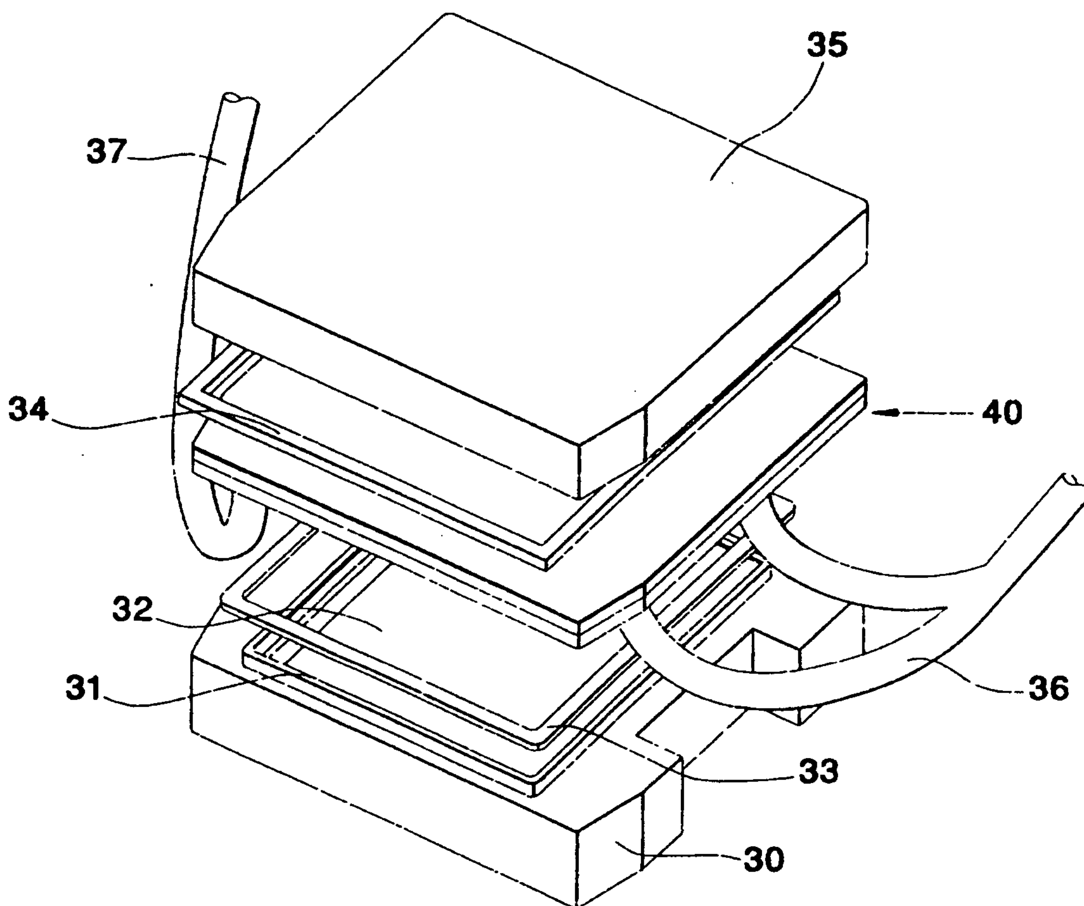


Fig. 1

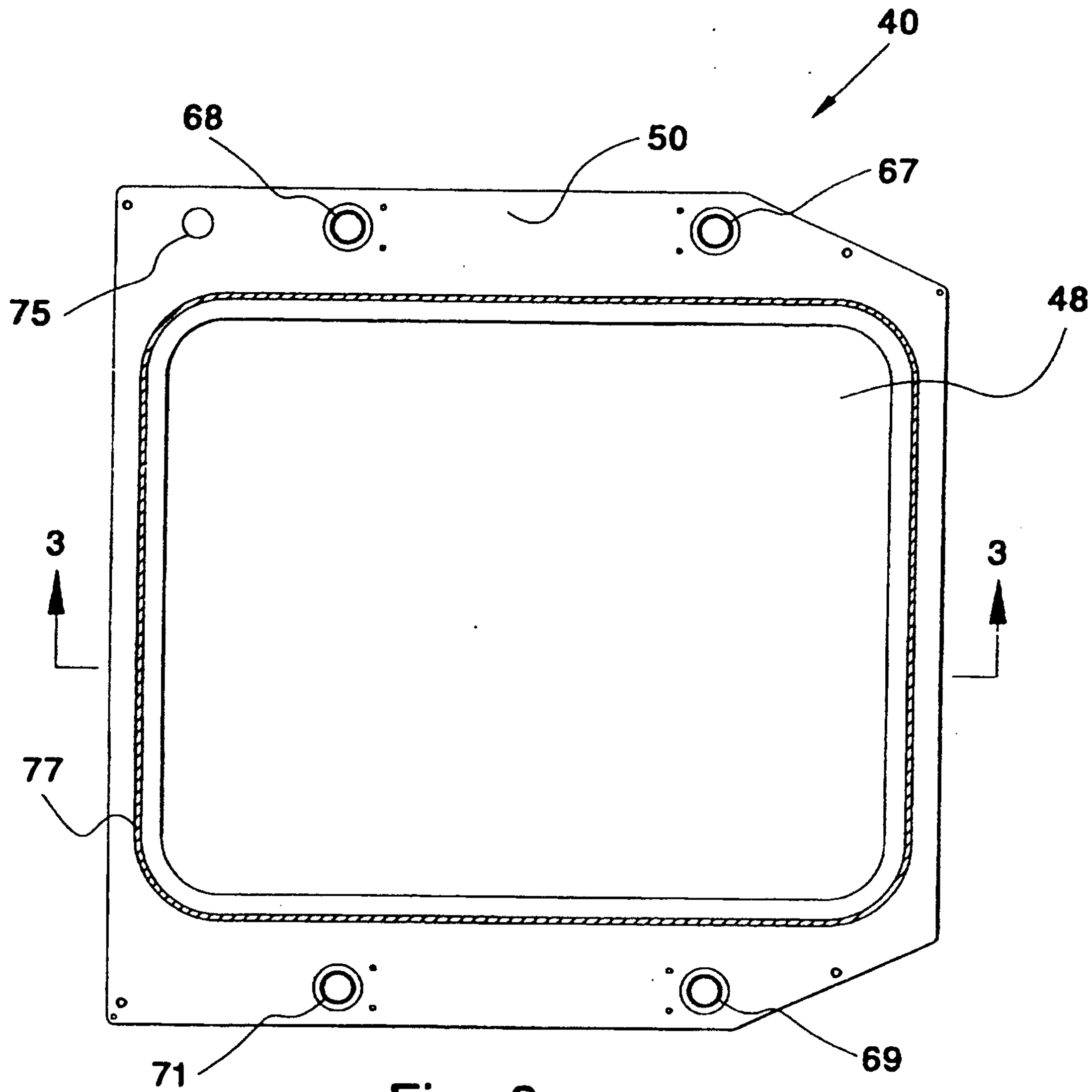


Fig. 2

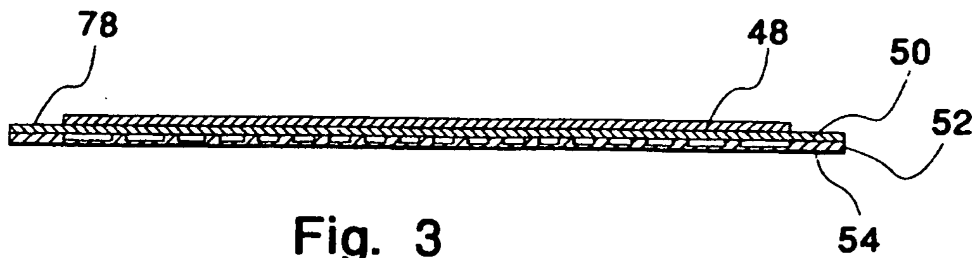


Fig. 3

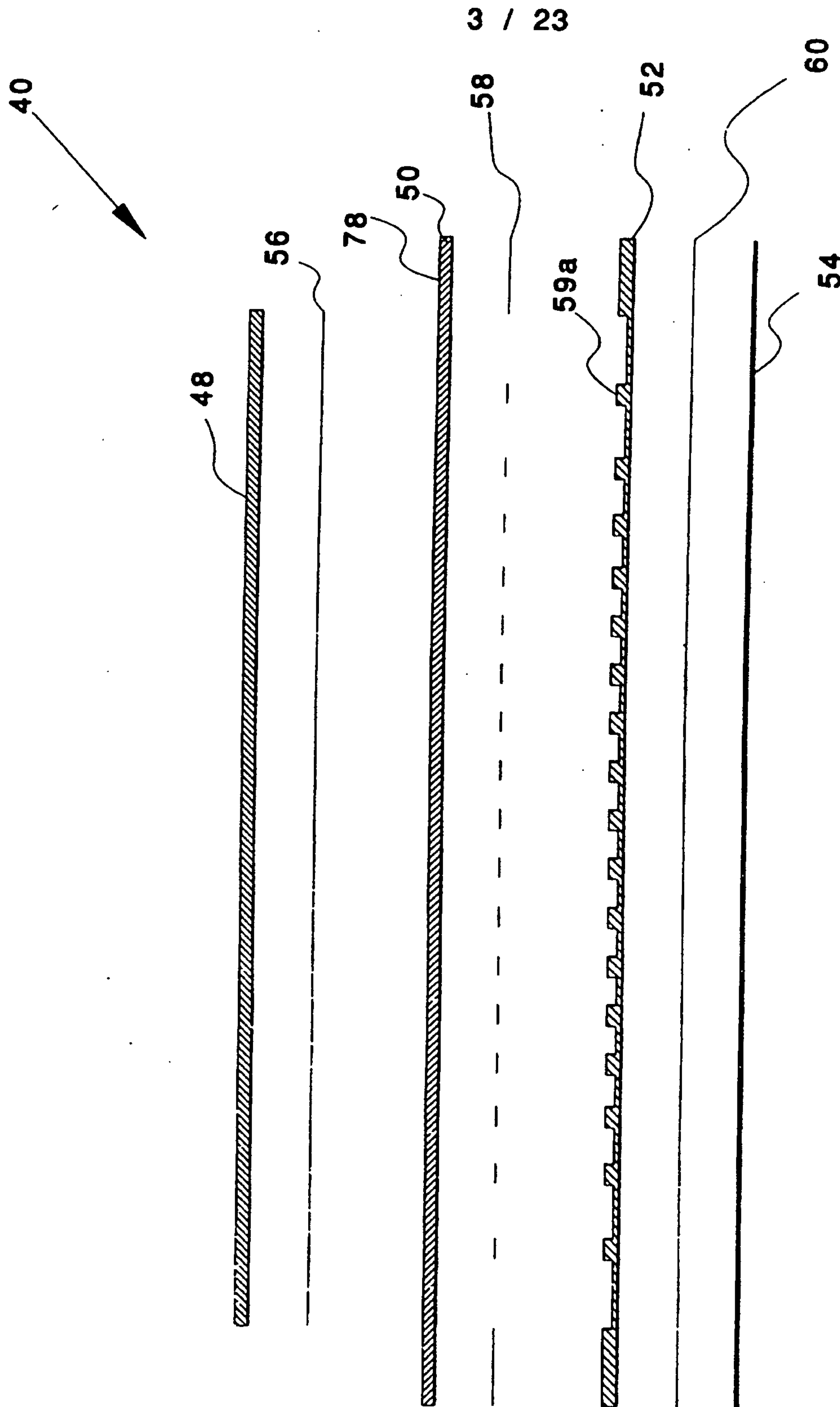
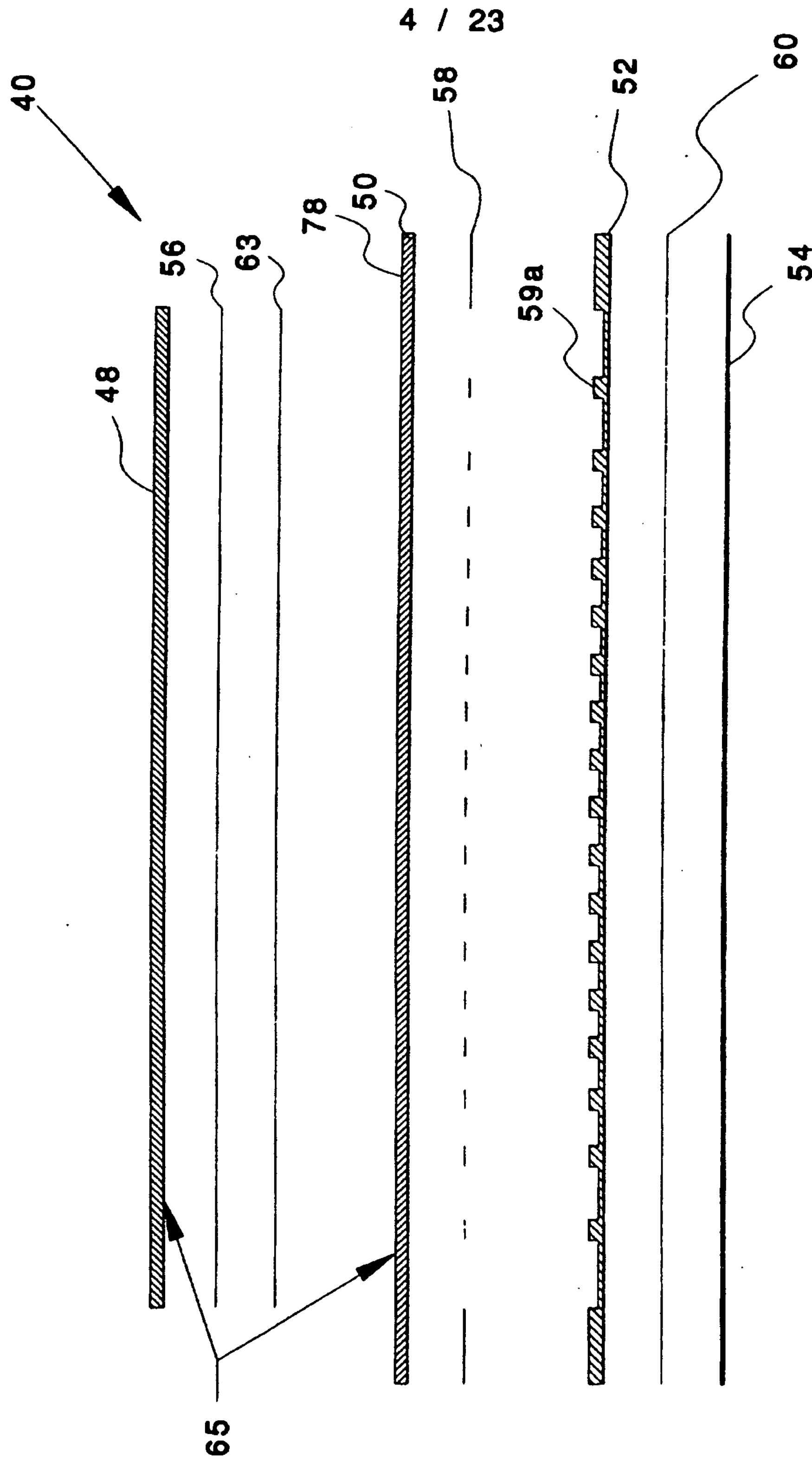


Fig. 4


40
58
52
60
50
78
56
63
54
59a
48
65
Fig. 5

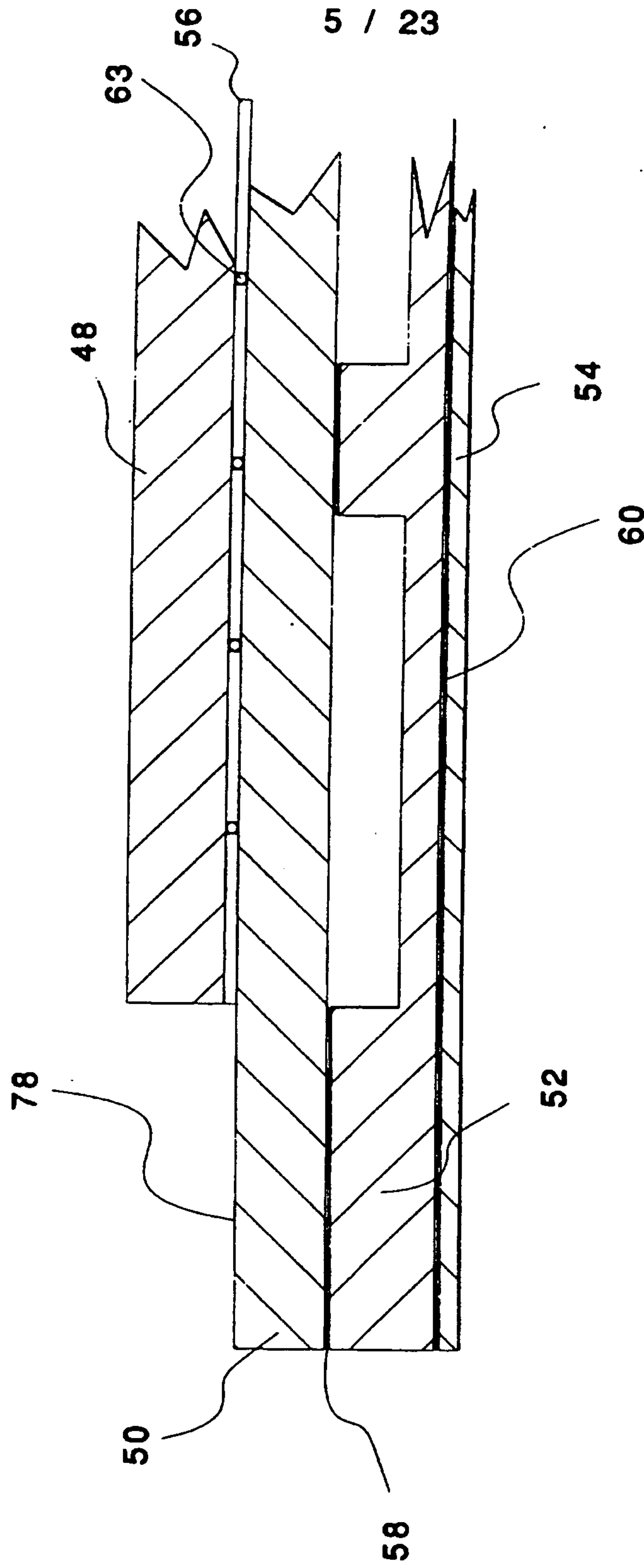


Fig. 6

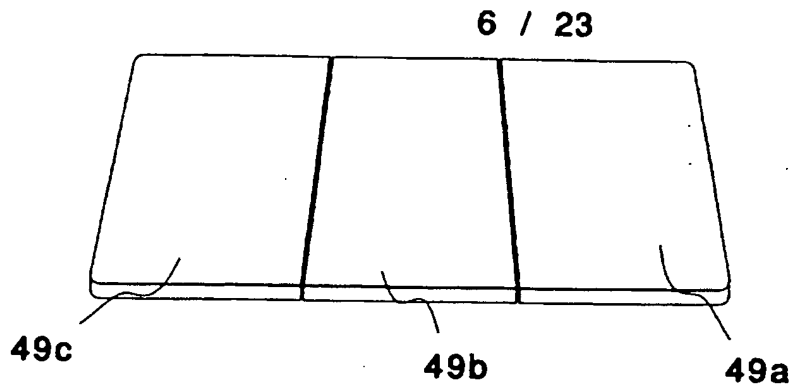


Fig. 7

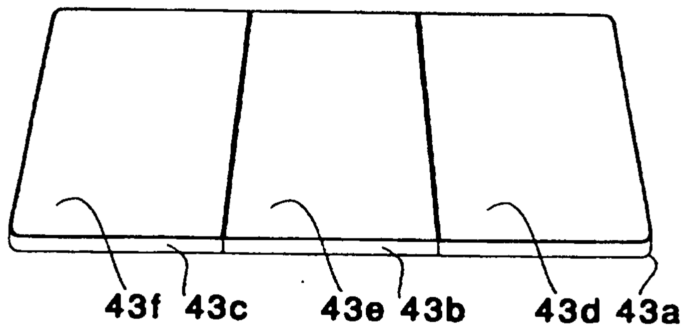


Fig. 8

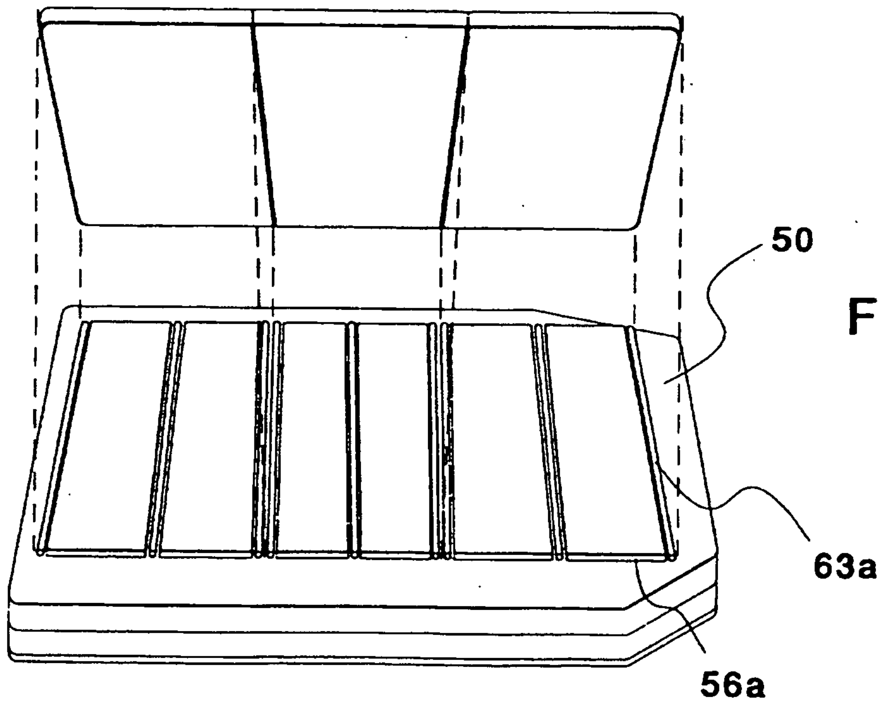


Fig. 9

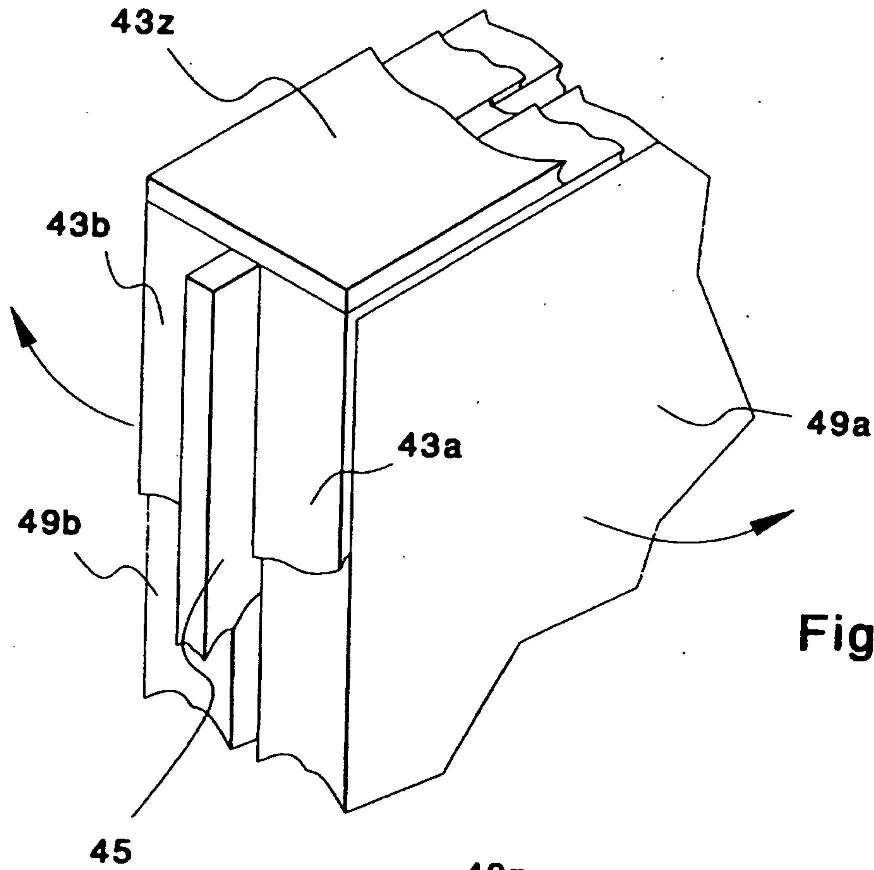


Fig. 8A

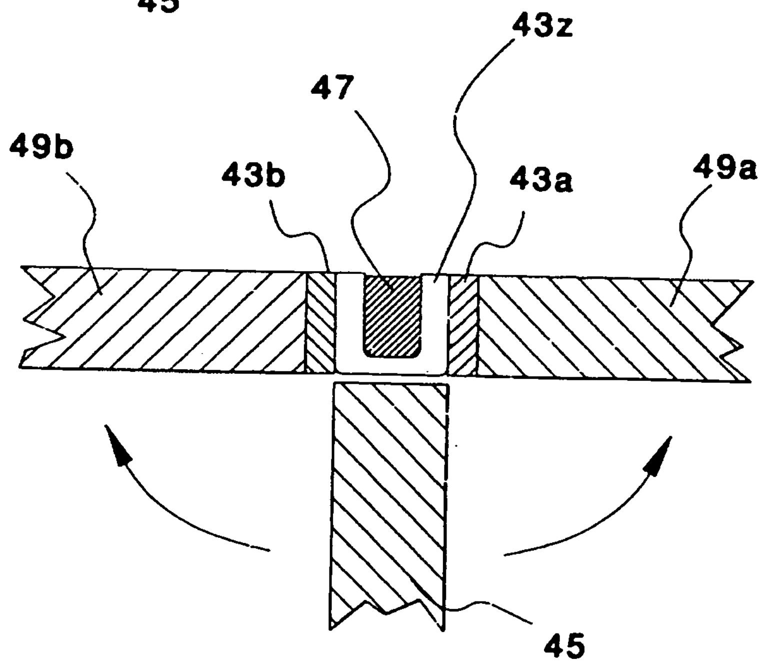


Fig. 8B

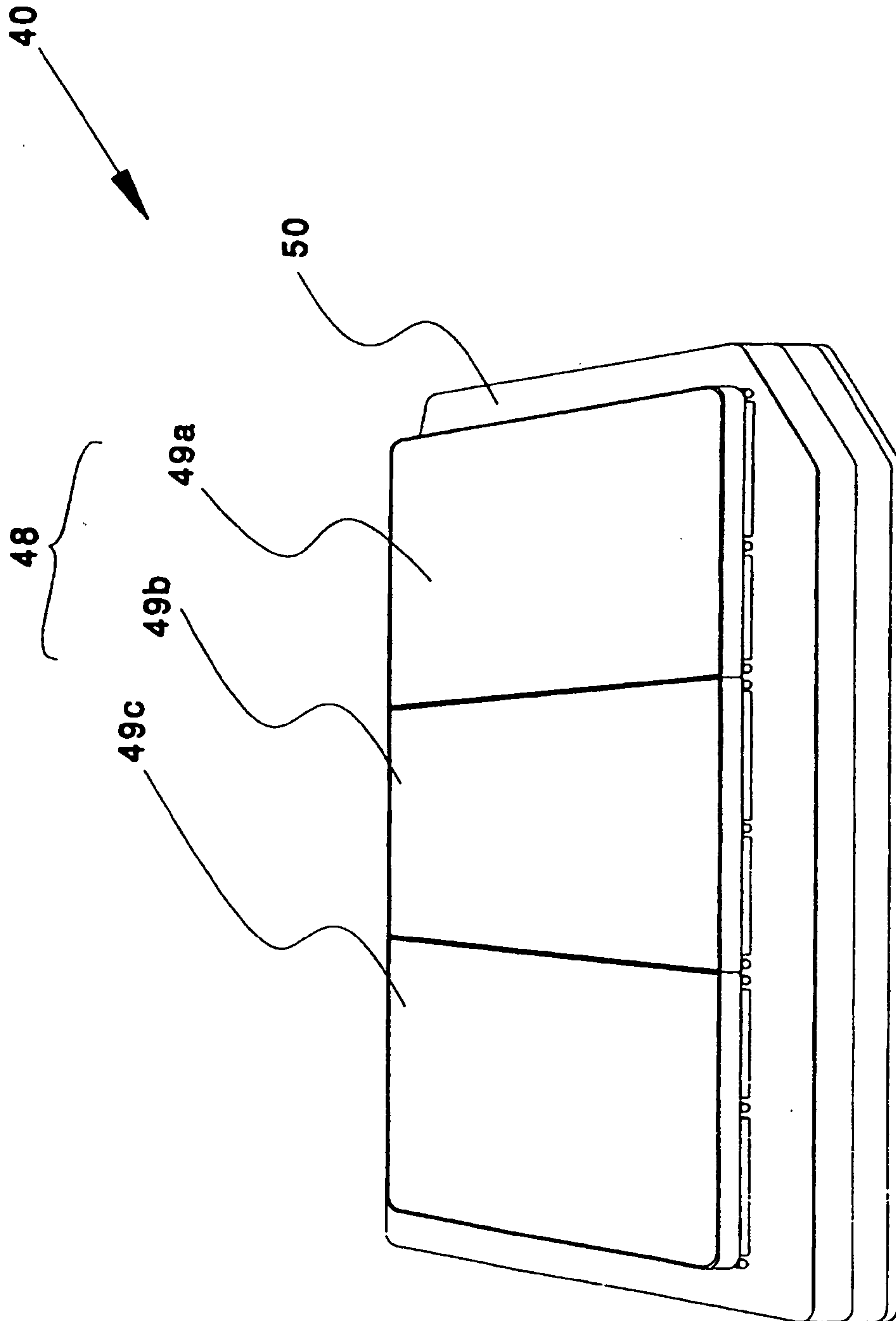


Fig. 10

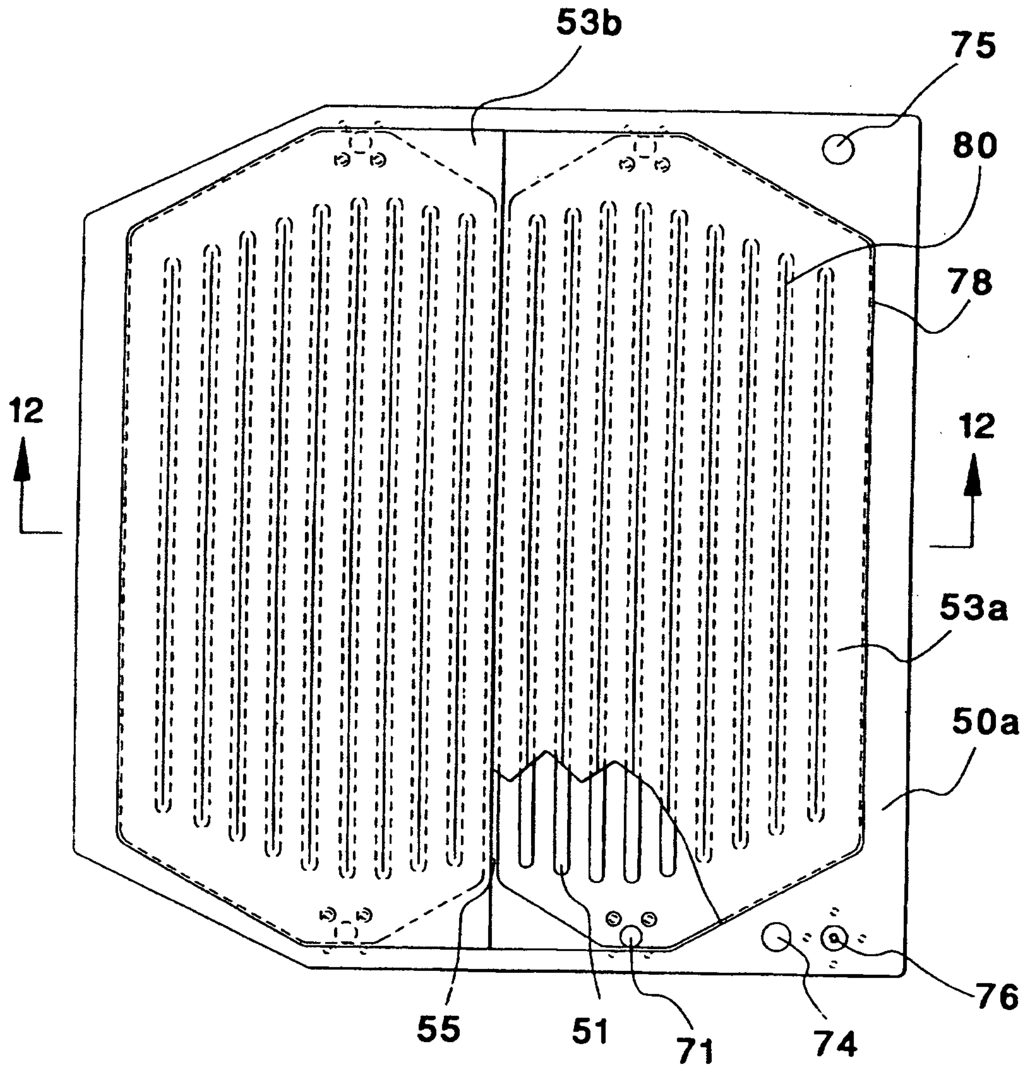


Fig. 11

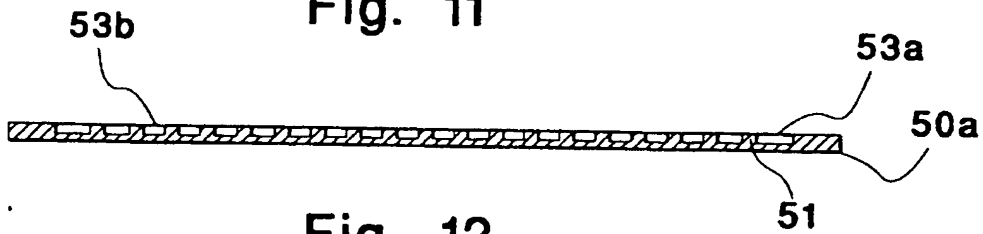


Fig. 12

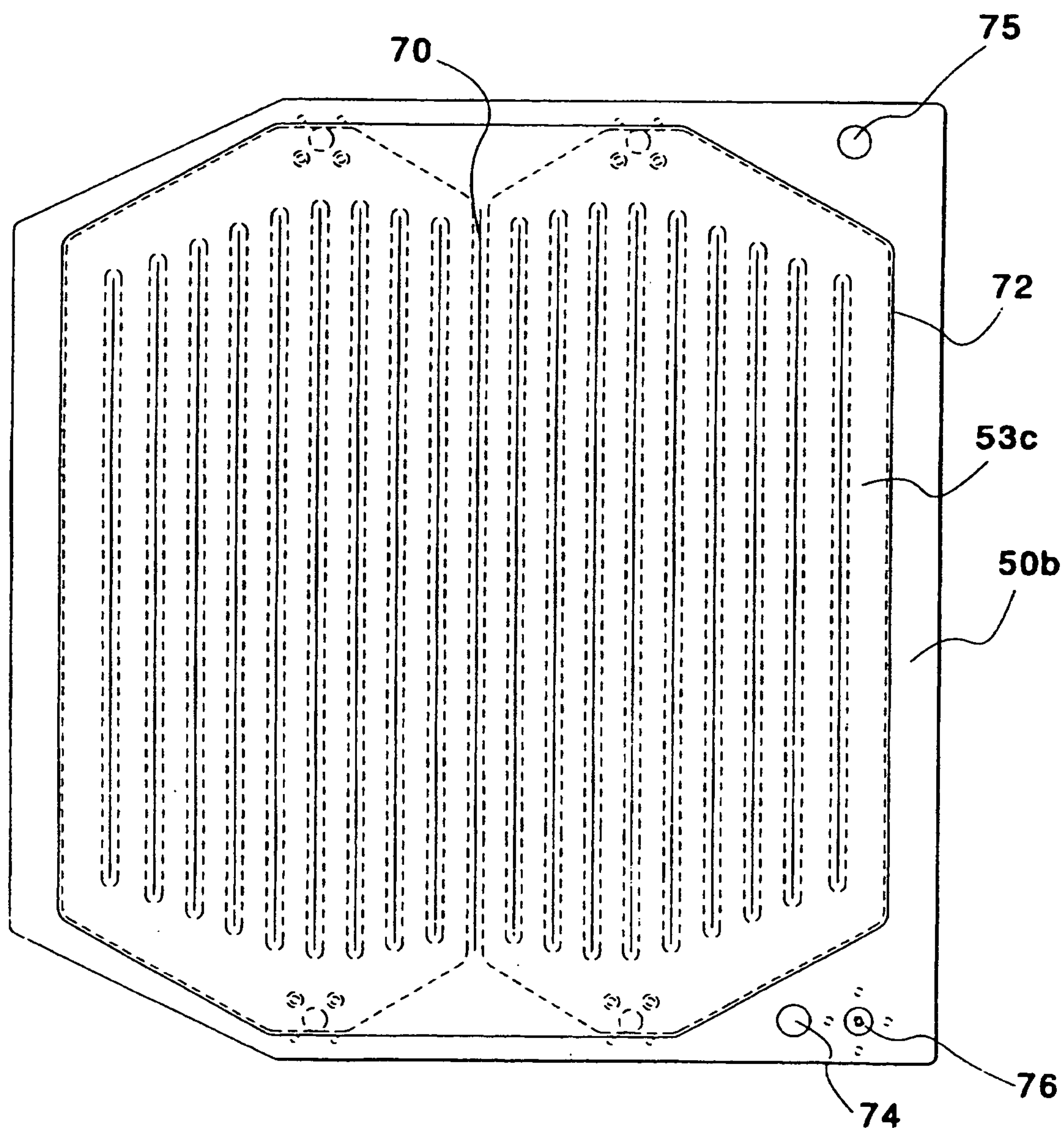


Fig. 13

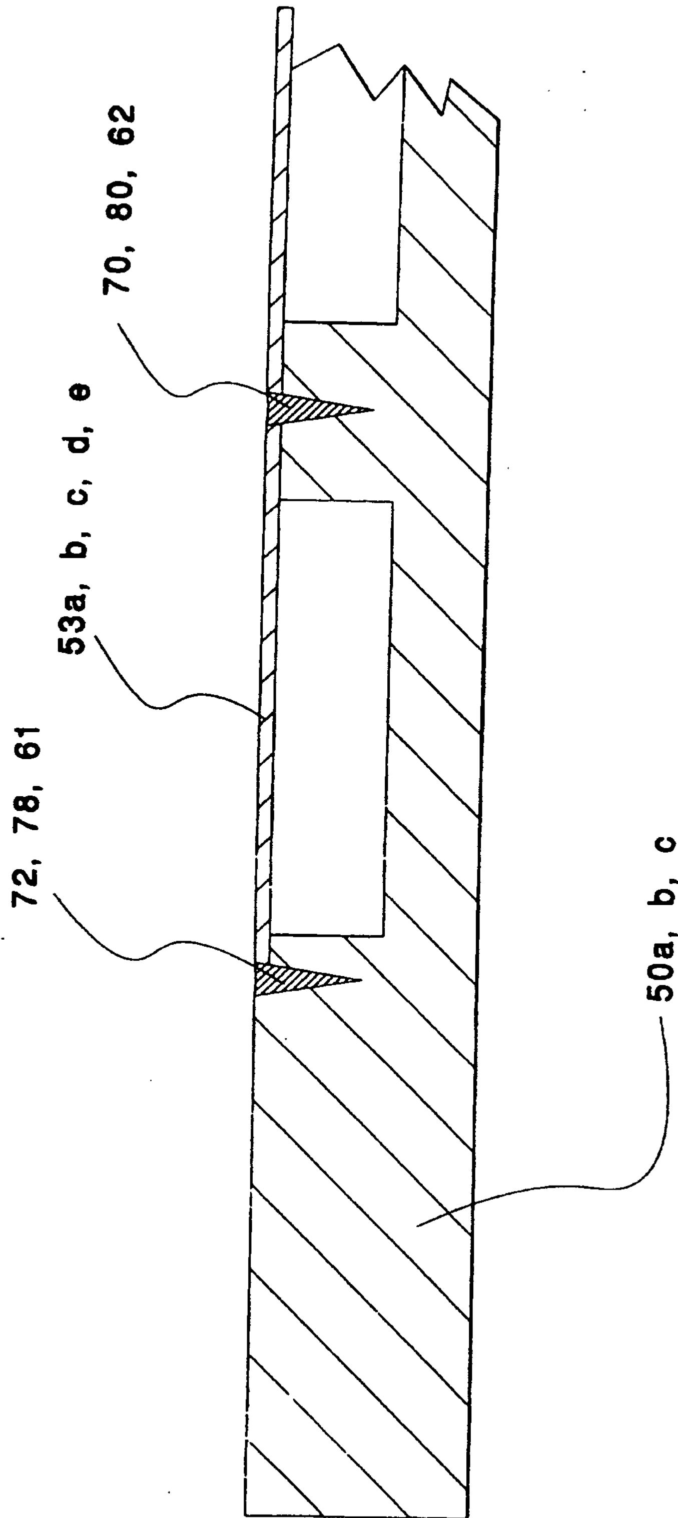


Fig. 14

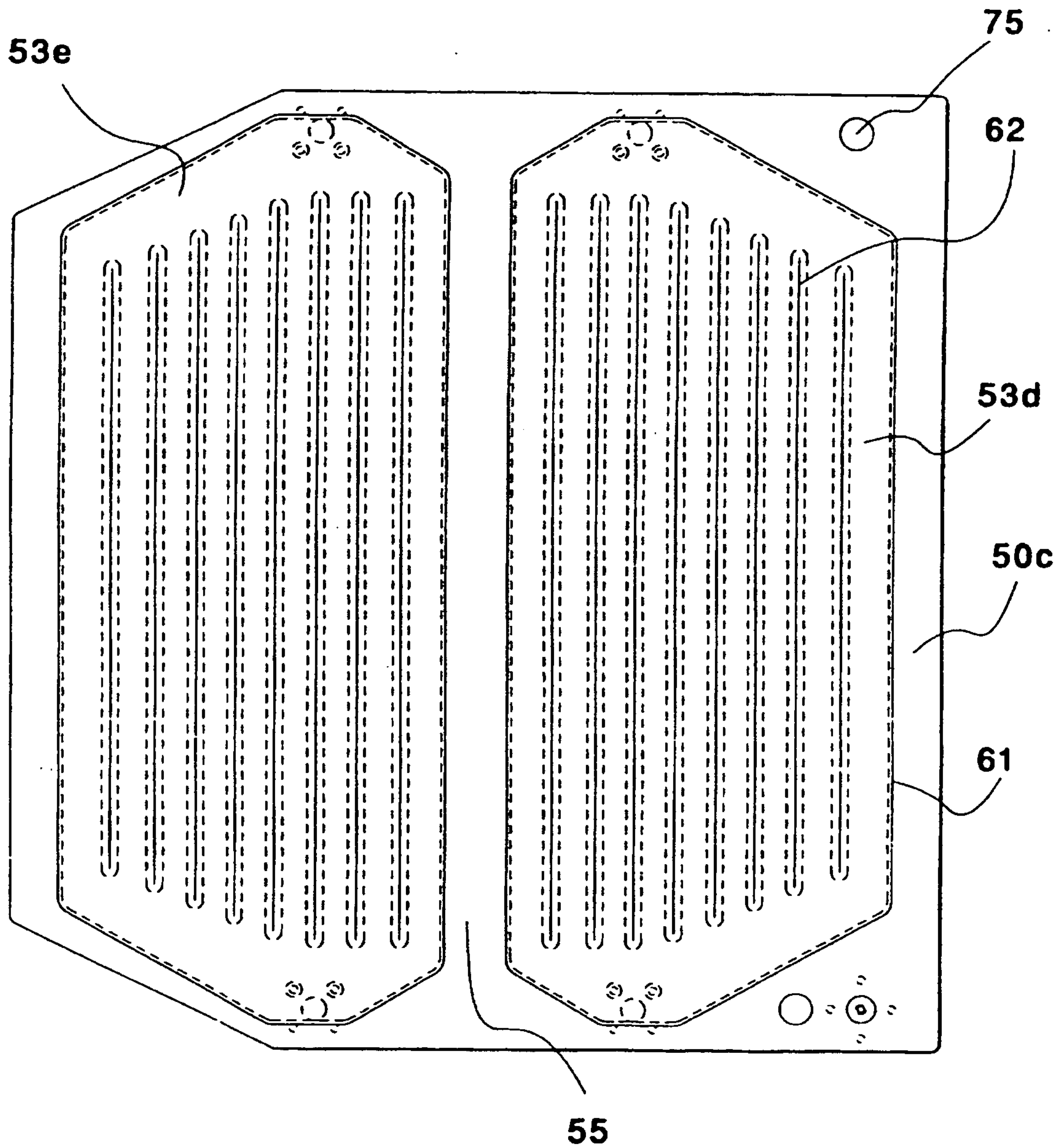


Fig. 15

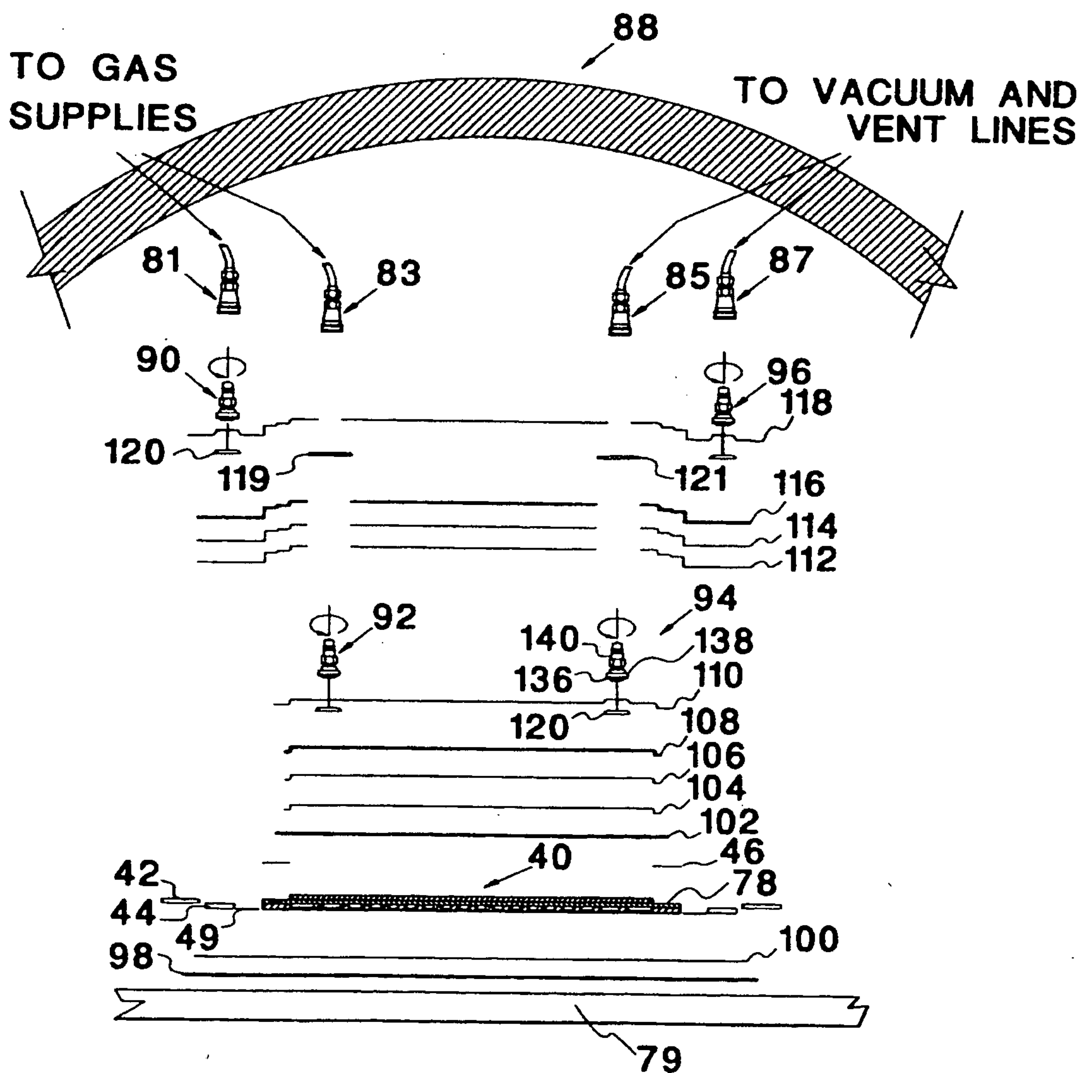


Fig. 16

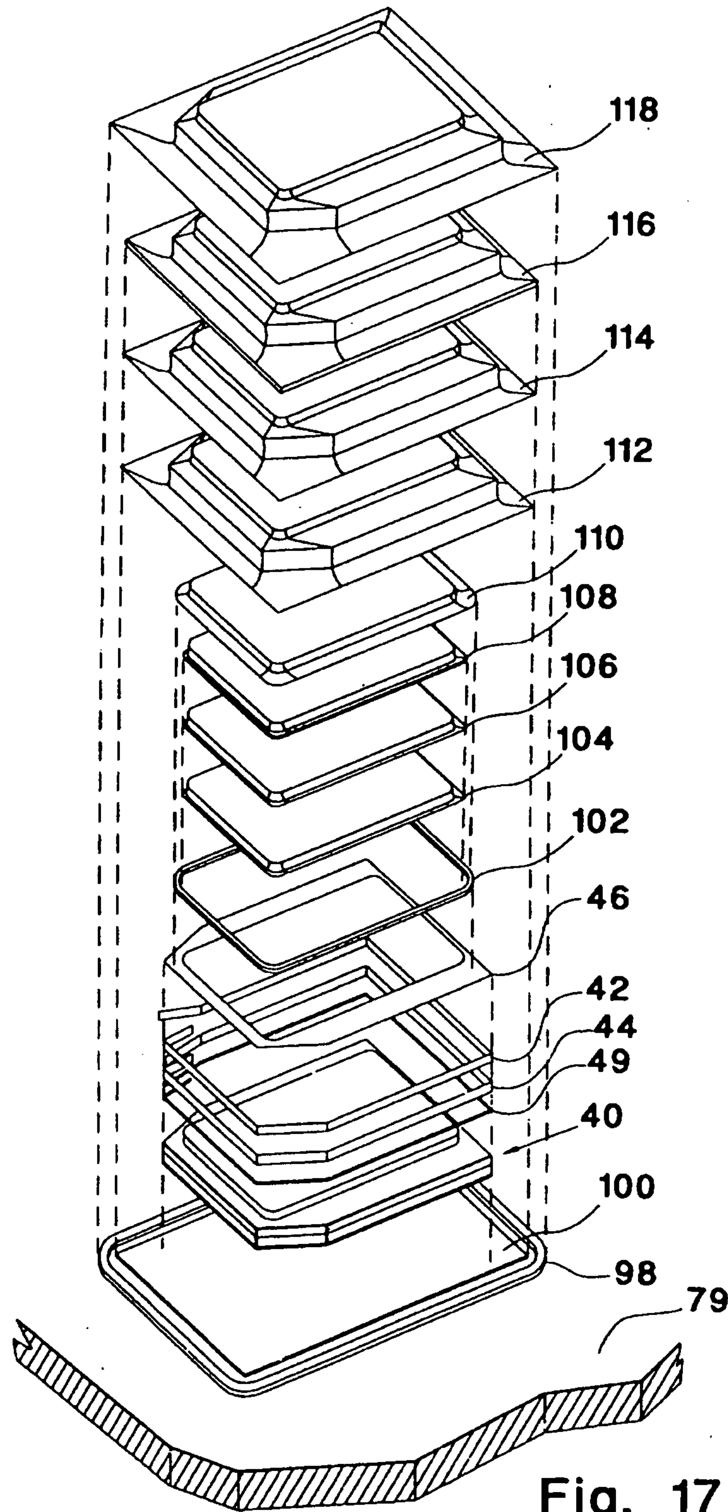


Fig. 17

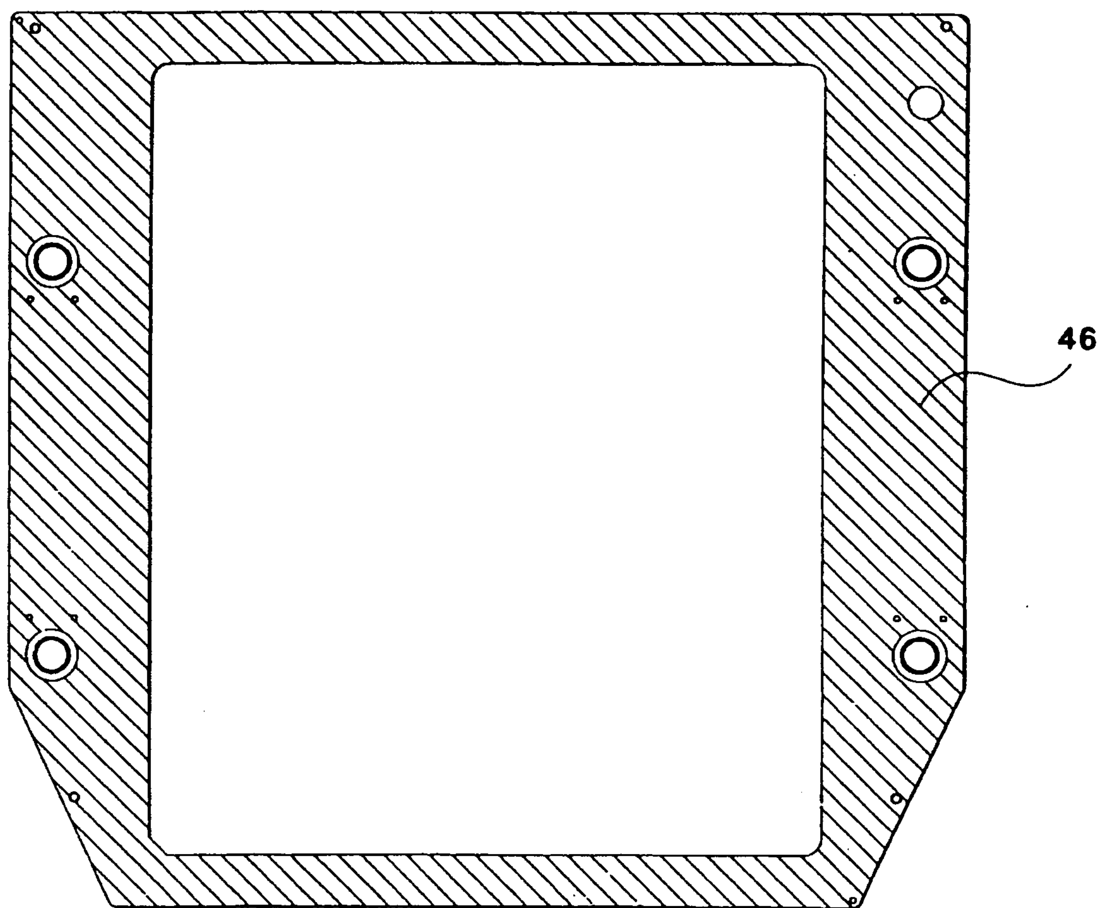


Fig. 18

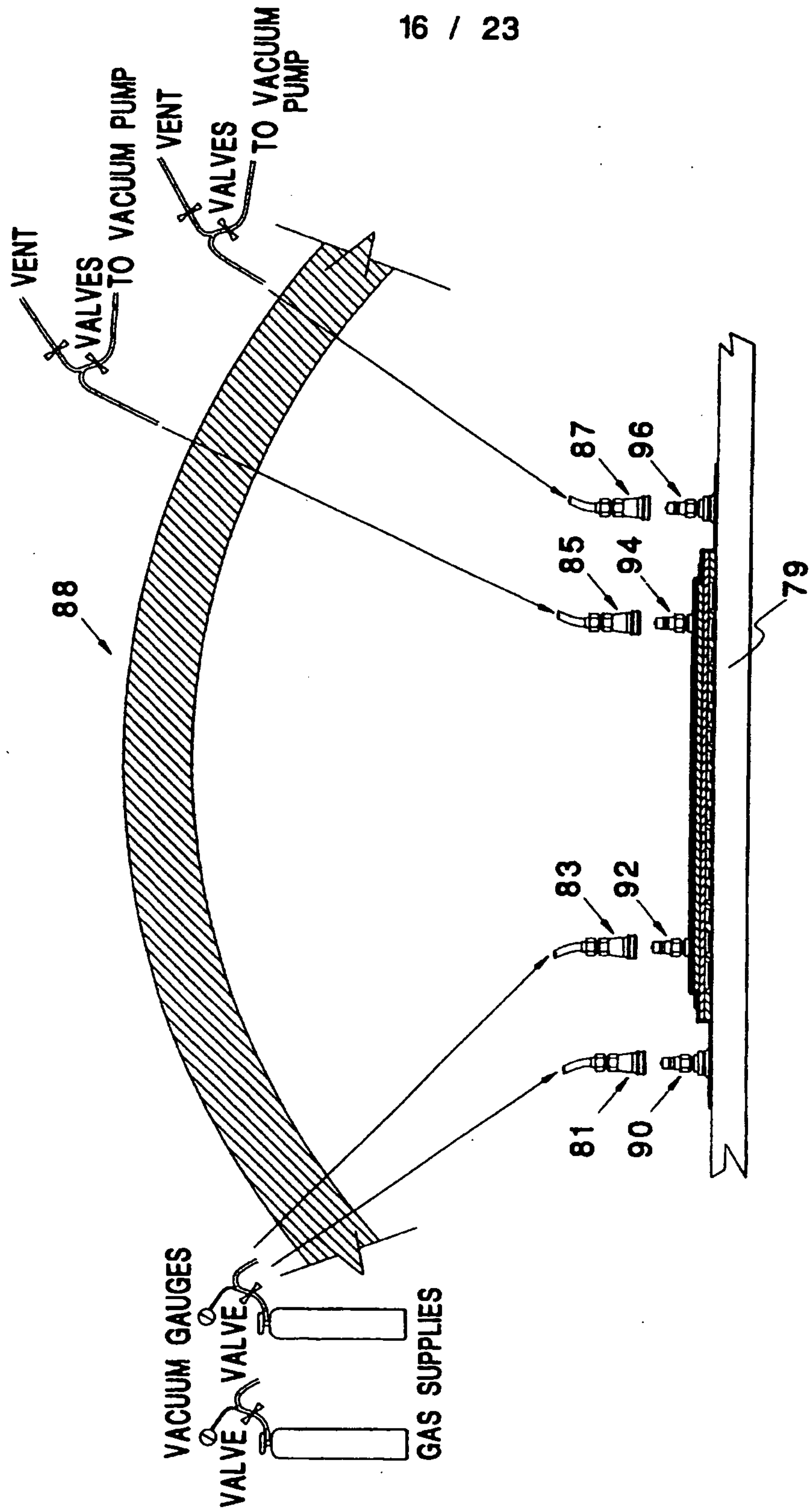


Fig. 19

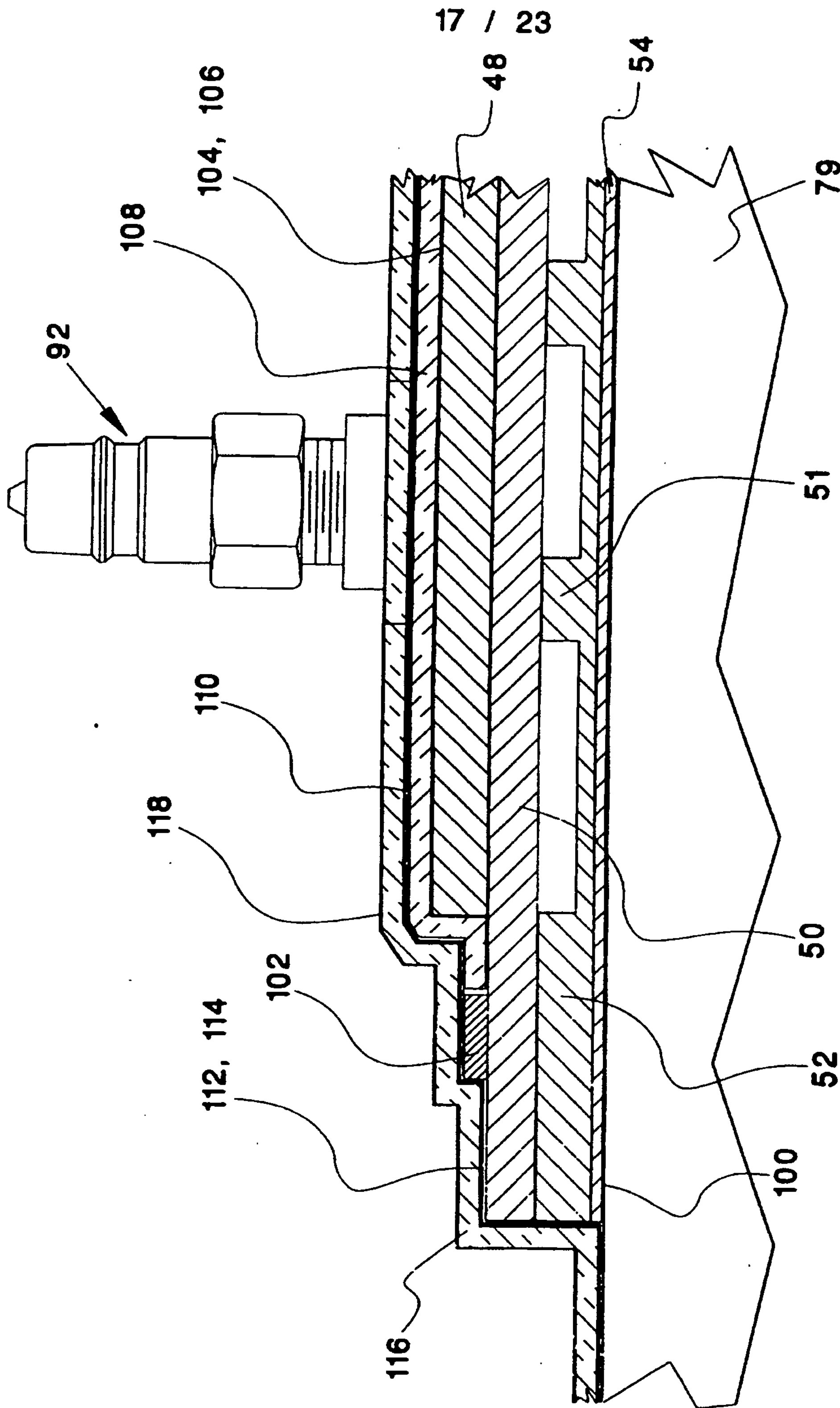


Fig. 20

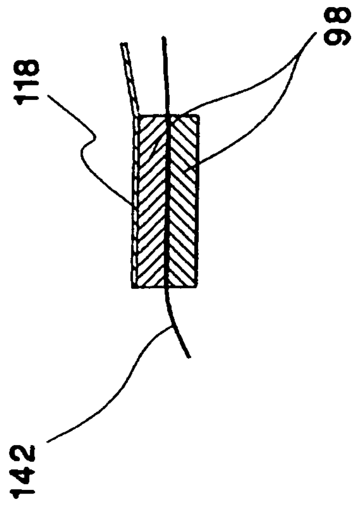


Fig. 22

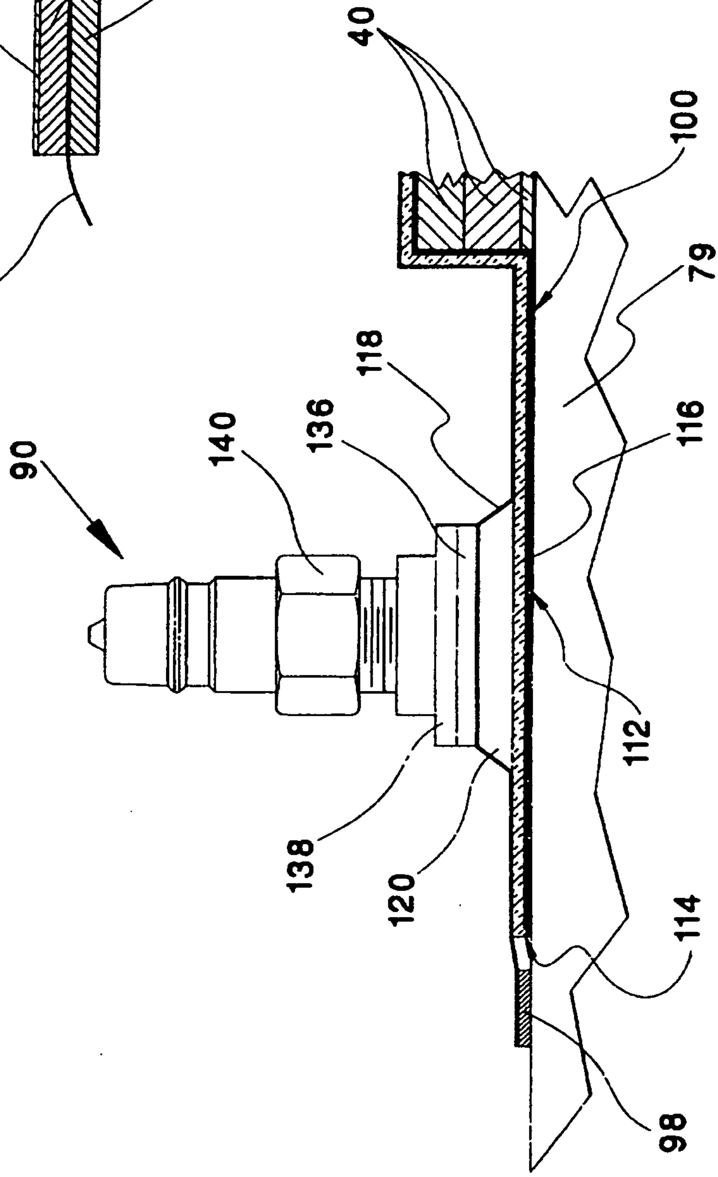


Fig. 21

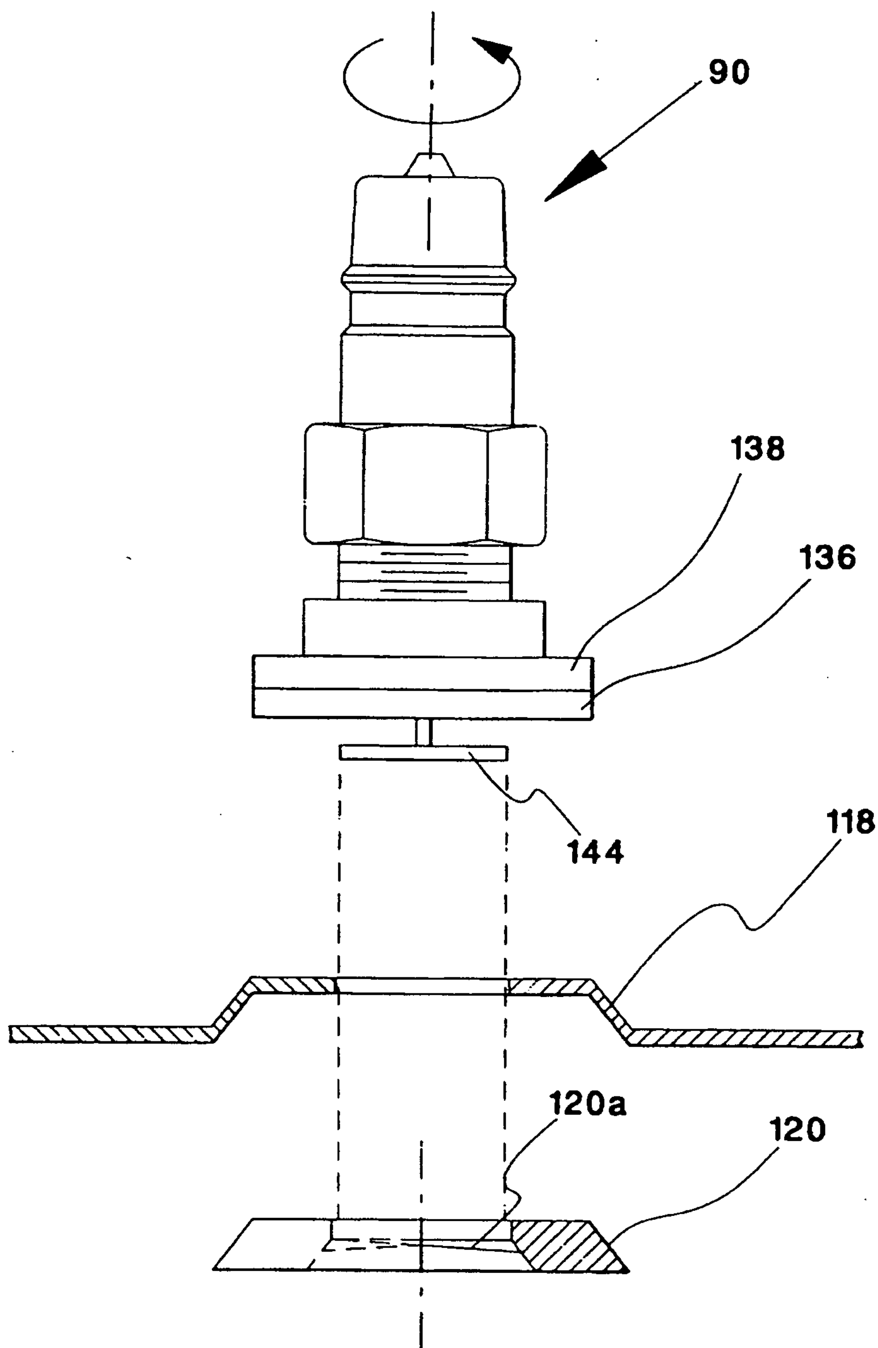


Fig. 23

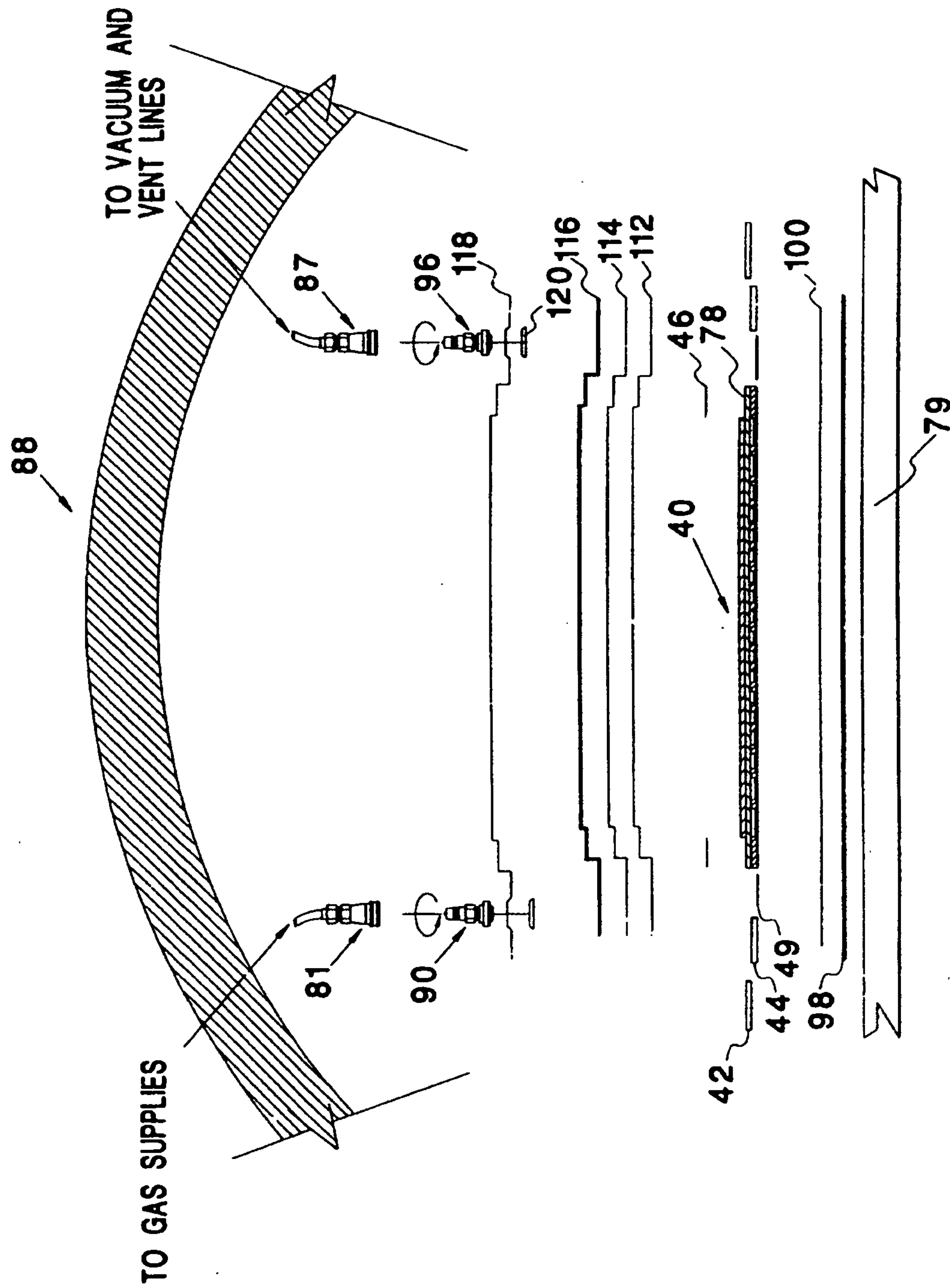


Fig. 24

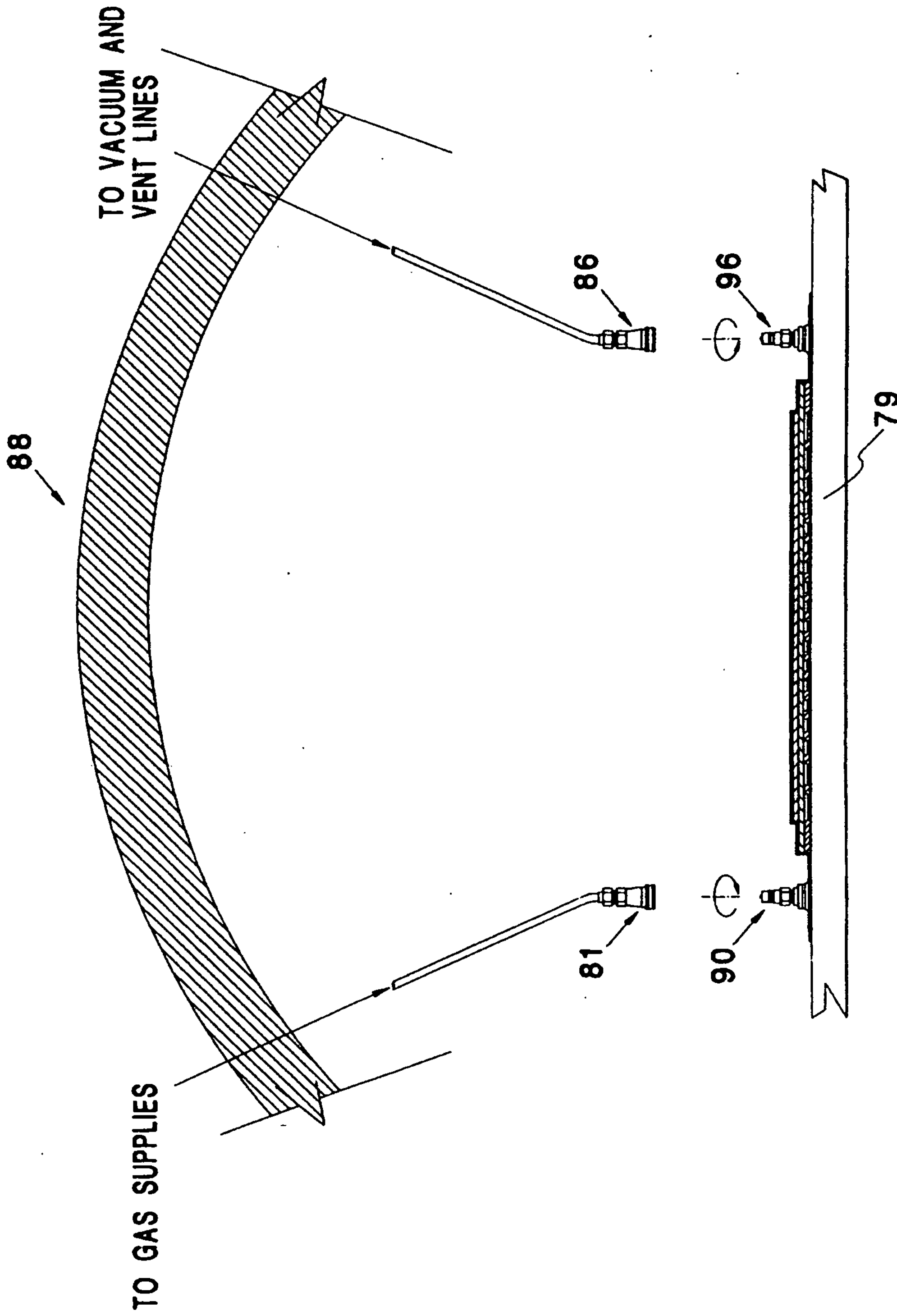


Fig. 25

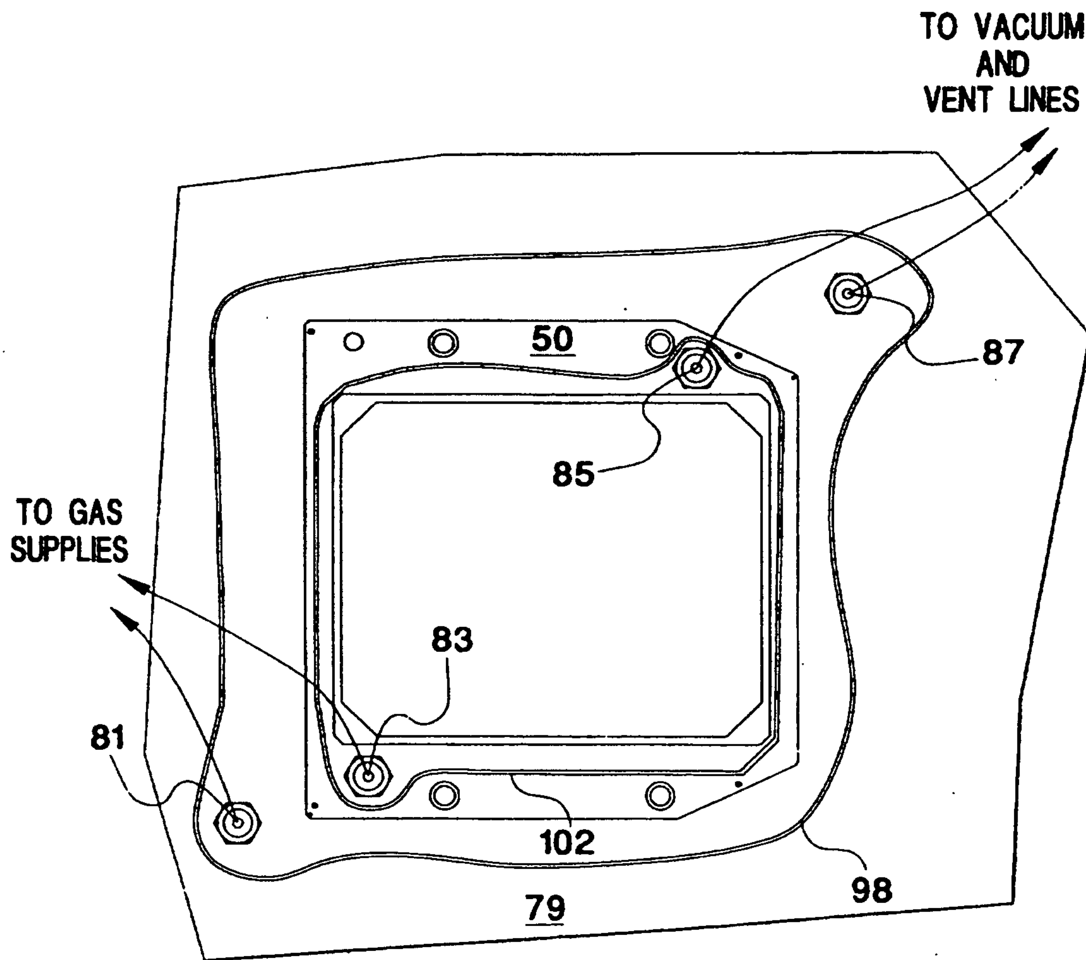


Fig. 26

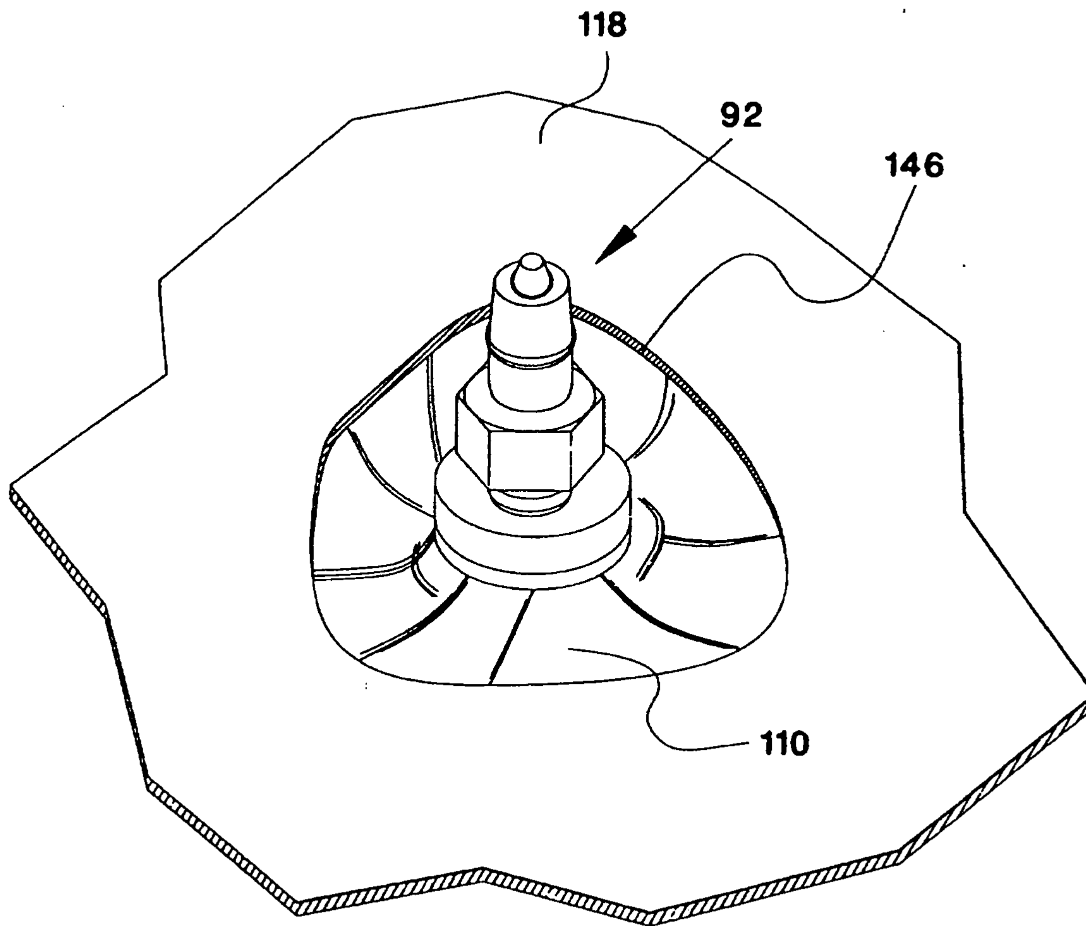


Fig. 27

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/01089

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C14/34 H01J37/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 013 no. 384 (C-629) ,24 August 1989 & JP,A,01 132758 (HITACHI METALS LTD) 25 May 1989, see abstract ---	1-27
A	PATENT ABSTRACTS OF JAPAN vol. 013 no. 084 (C-572) ,27 February 1989 & JP,A,63 270459 (MATSUSHITA ELECTRIC IND CO LTD) 8 November 1988, see abstract ---	1-27
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
2 October 1995	24.10.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ekhult, H

INTERNATIONAL SEARCH REPORT

Inter. ...al Application No
PCT/US 95/01089

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	REVIEW OF SCIENTIFIC INSTRUMENTS, APRIL 1973, USA, vol. 44, no. 4, ISSN 0034-6748, pages 522-523, TERHUNE C 'Target bonding (for sputtering)' see page 523, right column, line 4 - line 19 ---	1-27
A	PATENT ABSTRACTS OF JAPAN vol. 015 no. 357 (C-0866) ,10 September 1991 & JP,A,03 140464 (KOBE STEEL LTD) 14 June 1991, see abstract ---	1-27
A	GB,A,2 255 105 (ION COAT LIMITED) 28 October 1992 see page 7, line 16 - line 22 -----	1-27

1

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 14/40 — A1

(11) International Publication Number: WO 97/35044

(43) International Publication Date: 25 September 1997 (25.09.97)

(21) International Application Number: PCT/US97/03047

(22) International Filing Date: 4 March 1997 (04.03.97)

(30) Priority Data:
08/620,650 22 March 1996 (22.03.96) US

(71) Applicant: MATERIALS RESEARCH CORPORATION [US/US]; 560 Route 303, Orangeburg, NY 10962 (US).

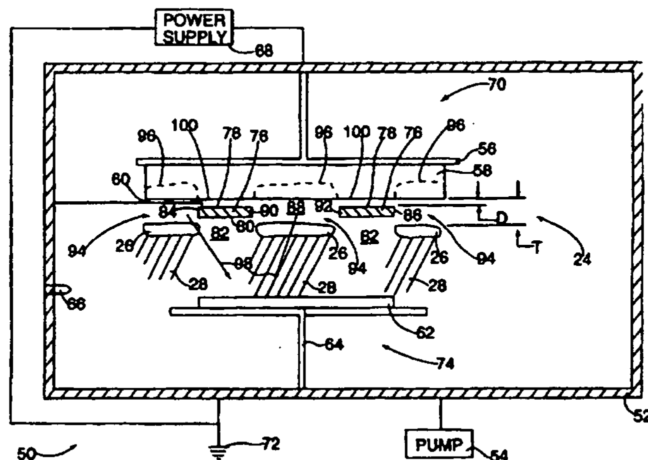
(72) Inventor: HURWITT, Steven; 159 Pascack Road, Park Ridge, NJ 07656 (US).

(74) Agents: MILLER, Jerry, A. et al.; 1 Sony Drive, MD #T1-1, Park Ridge, NJ 07656 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD AND APPARATUS FOR RF DIODE SPUTTERING



(57) Abstract

A sputtering system (50) includes an evacuatable chamber (52) having a target (58) which includes a sputtering surface (60). The target (58) is biased to form a cathode element (70) which causes the emission of electrons. The system (50) further includes an anode element (74) which includes the substrate (62). In use, a sputtering gas is ionized in response to the electrons to form a plasma. The plasma includes a cathode dark space (24) having a first thickness (T) wherein ionization does not occur. A plate element (76) having a bottom surface (80) is positioned a first distance (D) from the sputtering surface (60). Electrons emitted from the target (58) are absorbed by the plate element (76) to inhibit plasma formation in a first area (82) adjacent the bottom surface (60) such that target material (58) is not eroded opposite the first area (82). Further, plasma is formed in a second area (94) adjacent an edge (84, 86, 90, 92) to cause target material (58) to be eroded from the second area (94).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	State
AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

METHOD AND APPARATUS FOR RF DIODE SPUTTERING

FIELD OF THE INVENTION

This invention relates to RF diode sputtering, and more particularly, to a plate positioned within a cathode dark space which serves to selectively inhibit plasma formation in order to be able to selectively erode areas of a sputtering surface to provide a desired non-uniform erosion pattern for improving thickness uniformity for a film formed on a substrate.

BACKGROUND OF THE INVENTION

An integrated circuit (IC) is manufactured by a process which utilizes planar technology. Generally, this process includes subjecting a substrate, such as a silicon wafer or a ceramic plate, to a sputtering process in which a thin layer or film of material is deposited on the substrate. A common type of sputtering is known as magnetron sputtering. In this type of sputtering, a sputter deposition system is used which includes a chamber having a sputtering target. The target is fabricated from a desired source material and includes a sputtering surface from which material is removed for forming the film. In operation, a substrate which is to be sputtered is positioned within the chamber opposite the sputtering surface. A process gas, such as argon, is introduced into the chamber between the sputtering surface and the substrate. The target is then negatively energized so as to cause electrons to be emitted from the target. The electrons strike and ionize the gas particles to cause the formation of a plasma having positively charged argon ions. The ions then bombard the sputtering surface, which causes the removal of target material. The removed target material is then ultimately deposited onto the substrate to form the film.

A magnetic field for confining and shaping the plasma into a desired configuration is positioned near the sputtering surface. In particular, the plasma is shaped such that a desired non-uniform pattern of erosion is formed on the sputtering surface. This serves to ensure that all areas of the substrate receive substantially equal amounts of sputtered material, thus enabling a substantially uniform film thickness to be formed on the substrate.

In an alternative form of sputtering, which is known as radio frequency (RF) diode sputtering, a magnetic field is not utilized to confine or shape the plasma. This type of sputtering

is frequently used for the sputtering of electrically insulating target materials, and for sputtering targets of magnetic material. In addition, RF diode sputtering is also used where the presence of magnetic fields generated by the sputtering cathode may undesirably affect properties of the deposited film. However, since a magnetic field is not used to confine and shape the plasma in RF diode sputtering, the erosion pattern of the sputtering surface cannot be controlled as desired. As a result, an undesirable uniform erosion pattern forms on the sputtering surface which results in the formation of a film thickness that is not uniform. Further, reduced deposition occurs near the substrate edge due to the shape of the plasma, which also undesirably affects film thickness uniformity.

Referring now to FIGURE 1, an illustrative depiction of a plasma 10 is shown located between a target 12 having an initial sputtering surface 14 and a substrate 18 which is supported by support 16. The plasma 10 includes several different functional zones which are formed during the sputtering process. In use, the target 12 is negatively energized and the support 16 is grounded to form a cathode element 20 and an anode element 22, respectively. This causes electrons to be emitted from the target 12 which travel through a cathode dark space 24 and then collide with gas molecules to cause the formation of ions in a negative glow area 26 and a positive column 28. In the cathode dark space 24, ionization does not occur since the emitted electrons typically do not possess sufficient energy. Further, the cathode dark space 24 has a thickness T which depends primarily on the voltage applied to the target 12 and the type and pressure of the sputtering gas utilized. The ions are then accelerated towards cathode element 20 by a high voltage gradient across the cathode dark space 24.

A device known as a dark space shield 30 is located adjacent to a rear surface 32 of the target 12. The shield 30 is spaced apart from the rear surface 32 by a distance X which is less than thickness T. As such, the shield 30 is located in a region where ionization does not occur. The shield 30 is connected to ground 34 and serves to absorb electrons which are emitted, thus inhibiting the formation of plasma adjacent the rear surface 32. The shield 30 is utilized in configurations wherein sputtering on the rear surface 32 is not desired such as when a structural backing plate is used to support the cathode element 20. For plasmas which are not magnetically confined, thickness T is typically between approximately 0.25 to 0.75 inches under commonly used sputtering conditions.

One method of improving film thickness uniformity in RF diode sputtering is to increase the size of the target 12 relative to the substrate 18. This has been found to reduce the effect of reduced deposition near the substrate edge. However, a disadvantage of this method is that larger and more costly targets are needed. This results in the need for correspondingly larger processing
5 chambers to hold the targets and larger power supplies to energize the targets, which also increases costs. Moreover, the use of larger targets results in reduced utilization of target material.

Another method for improving film thickness uniformity includes the positioning of an object, such as an aperture plate, between the target and substrate. The aperture plate serves to
10 intercept a percentage of sputtered material to prevent its deposition on the substrate. This method is described in U. S. Patent No. 5,415,753, which issued to Hurwitt, et al. and is assigned to Materials Research Corporation, an assignee herein. Referring to FIGURE 2, an illustrative cross sectional view of a portion of an aperture plate 36 having an aperture 38 in accordance with U.S. Patent No. 5,415,753 is shown. The aperture plate 36 is located between the target 12 and
15 the substrate 18 which is to be sputtered. In RF diode sputtering, wherein a magnetic field is not used to control the plasma, the initial sputtering surface 14 is eroded in an undesirable uniform pattern to form a new sputtering surface 40 (shown as dashed lines) which is generally flat and parallel to the initial sputtering surface 14. The design of the aperture plate 36 and its spacing from target 12 and substrate 18 is calculated so as to intercept controlled amounts of material
20 emitted from target 12. In particular, a portion of sputtered material (illustrated by arrow 42 which depicts a flight path of a first particle) emitted from the target 12 passes through or around the aperture plate 36 and is deposited on substrate 18. Another portion of sputtered material (illustrated by arrow 44 which depicts a flight path of a second particle) is intercepted by the aperture plate 36 and forms a deposit 46 on the aperture plate 36. As such, this technique
25 improves thickness uniformity by intercepting material emitted from target 12 and not by controlling the shape of the plasma.

However, this technique has disadvantages. One disadvantage is that extended spacing is needed between target 12 and substrate 18 to permit proper placing of target 12 to avoid a shadow of the aperture plate 36 from forming in the deposited film. Another disadvantage is that

as more material is sputtered, the deposit 46 increases in size and forms flakes or microscopic particles which fall on or become imbedded in the film that is formed on the substrate.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a sputtering system for improving thickness uniformity of a film sputtered on a substrate.

It is a further object of the present invention to selectively inhibit the formation of plasma by absorbing electrons emitted from a target in order to provide a desired non-uniform erosion pattern suitable for improving film thickness uniformity.

The present invention relates to a sputtering system for depositing a thin film on a substrate. In particular, the system includes an evacuatable chamber having a target. The target includes a sputtering surface which is biased to form a cathode element which emits electrons. The system further includes an anode element which includes the substrate. The substrate is positioned opposite the cathode element in the chamber. In use, a sputtering gas is ionized in response to the electrons to form a plasma for eroding target material from the sputtering surface which is then deposited on the substrate to form the film. In addition, the plasma includes a cathode dark space having a first thickness wherein ionization does not occur.

A plate element having a bottom surface and at least one edge is positioned a first distance, which is less than the first thickness, from the sputtering surface. Electrons emitted from the target are absorbed by the plate element so as to selectively inhibit plasma formation in a first area adjacent the bottom surface such that target material is not eroded from a predetermined first portion of the sputtering surface opposite the first area. Further, plasma is formed in a second area adjacent the edge to cause target material to be eroded from a predetermined second portion of the sputtering surface opposite the second area. This forms a desired non-uniform erosion pattern on the sputtering surface for improving thickness uniformity of the film.

BRIEF DESCRIPTION OF THE FIGURES

FIGURE 1 depicts a conventional plasma formed during a sputtering process.

FIGURE 2 is a cross section view of a portion of an aperture plate for intercepting material sputtered from a sputtering surface.

FIGURE 3 depicts a sputtering system having a plate element positioned within a cathode dark space in accordance with the present invention.

5

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

While this invention is susceptible of embodiment in many different forms, there is shown in the drawings and will herein be described in detail specific embodiments, with the understanding that the present disclosure is to be considered as an example of the principles of the invention and intended to limit the invention to the specific embodiments shown and described. In the
10 description below, like reference numerals are used to describe the same, similar or corresponding parts in FIGURES 1-3.

Referring to FIGURE 3, a sputtering system 50 in accordance with the present invention is shown. The system 50, which may be an RF diode sputtering system, includes a chamber 52 which is evacuated by a vacuum pump 54 to a vacuum level suitable for sputtering. The chamber
15 52 includes a target mounting element 56 for holding a target 58. The target 58 includes a sputtering surface 60 from which target material is removed, or sputtered, which is ultimately deposited on a substrate 62 to form a thin film. The system 50 further includes a support 64 for holding the substrate 62 in a position generally opposite the sputtering surface 60. In use, a sputtering gas, such as argon, is introduced into the chamber 52 through a nozzle 66. The target
20 58 is then negatively energized by a power supply 68 to cause an emission of electrons from the target 58, thus forming a cathode element 70. Further, the support 64 and substrate 62 are connected to ground 72, thus forming an anode element 74.

A plate element 76 (shown as a cross section) is positioned between the cathode 70 and anode 74 elements. The plate element 76 includes a top surface 78 which is spaced apart from
25 the sputtering surface 60 by a distance D which is less than thickness T. This serves to locate the plate element 76 within the cathode dark space 24. The plate element 76 further includes a bottom surface 80 which faces the substrate 62. The plate element 76 is connected to ground and thus serves to attract and absorb electrons which are emitted from the target 58. In accordance

with the present invention, this inhibits the formation of plasma in first areas 82 adjacent the bottom surface 80. Alternatively, it is noted that the plate element 76 and/or the substrate 62 may be subjected to a desired voltage by an alternate power supply rather than being connected to ground.

5 The plate element 76 further includes left 84 and right 86 outer vertical edges and a hole 88 which defines left 90 and right 92 inner vertical edges. In use, normal plasma formation occurs in second areas 94 which are adjacent the vertical edges 84, 86, 90, 92 and wherein electrons are not absorbed by plate element 76. As a result, first portions 96 of the sputtering surface which are directly opposite the second areas 94 are eroded. Some of the material removed from 10 portions 96 (illustrated by arrow 98 which depicts flight paths of removed material) is then ultimately deposited on the substrate to form the film.

In accordance with the present invention, second portions 100 of the sputtering surface 60 which are opposite the first areas 82 do not erode due to the absence of plasma in these areas. This results in a desired non-uniform pattern of erosion on the sputtering surface 60 which 15 provides a film on the substrate 62 having a substantially uniform thickness. Consequently, the present invention provides a uniform film thickness by selectively inhibiting the formation of plasma. In addition, since target material is not sputtered from second portions 100, the amount of target material that is accumulated on the top surface 78 is substantially reduced. Thus, contamination of the film due to the formation of flakes and particles on the top surface 78 is also 20 substantially reduced.

The shape and dimensions of plate element 76 are each chosen to provide a desired erosion shape on target 58 which will produce a desired film profile on substrate 62. Several factors affect the configuration of plate element 76 such as the size of the target 56 and the substrate 62 and the distance between the target 58 and substrate 62. For typical sputtering 25 conditions, it has been found that acceptable results are obtained when dimension D is between approximately 0.05 inch to 1.0 inch, wherein 1/8 to 3/8 of an inch is preferred. It is further noted that plate element 76 may also be configured in various other shapes and sizes so as to provide a desired film profile on substrate 62. For example, plate element 76 may be configured to include more than one hole. Alternatively, plate element 76 may be a solid plate. In addition, a series 30 of concentric rings may be used in place of plate element 76.

Thus it is apparent that in accordance with the present invention, an apparatus that fully satisfies the objectives, aims and advantages is set forth above. While the invention has been described in conjunction with specific embodiments, it is evident that many alternatives, modifications, permutations and variations will become apparent to those skilled in the art in light 5 of the foregoing description. Accordingly, it is intended that the present invention embrace all such alternatives, modifications and variations are far within the scope of the appended claims.

What Is Claimed Is:

1. A sputtering system for depositing a thin film on a substrate, said system including an evacuatable chamber which includes said substrate, comprising:

a target positioned within said chamber, said target including a sputtering surface;

biasing means for biasing said target to form a cathode element which emits electrons;

an anode element which includes said substrate, wherein said substrate is positioned opposite said cathode element in said chamber;

ionization means for ionizing a sputtering gas, in response to said electrons, to form a plasma for eroding target material from said sputtering surface which is then deposited on said substrate to form said film, said plasma including a cathode dark space having a first thickness wherein ionization does not occur; and

a plate element having a bottom surface and at least one edge, said plate element being spaced apart from said sputtering surface by a first distance which is less than said first thickness, wherein electrons emitted from said target are absorbed by said plate element to selectively inhibit plasma formation in a first area adjacent said bottom surface such that target material is not eroded from a predetermined first portion of said sputtering surface opposite said first area, and wherein plasma is formed in a second area adjacent said edge to cause target material to be eroded from a predetermined second portion of said sputtering surface opposite said second area, thereby forming a desired non-uniform erosion pattern on said sputtering surface for improving thickness uniformity of said film.

2. The system according to claim 1, wherein said plate includes at least one hole for forming associated inner edges.

3. The system according to claim 1, wherein said plate element includes at least two concentric rings.

4. The system according to claim 1, wherein said plate element is a solid plate.

5. The system according to claim 1, wherein said plate element is maintained at a potential which is positive relative to said target.

6. The system according to claim 1, wherein said plate element is grounded.

7. The system according to claim 1, wherein said first distance is between approximately 0.05 and 1.0 inches.

8. A method for sputtering a thin film on a substrate, comprising the steps of:

biasing a target having a sputtering surface to form a cathode element which emits electrons;

providing an anode element which includes said substrate, wherein said substrate is positioned opposite said cathode element;

forming a plasma, in response to said electrons, for eroding target material from said sputtering surface which is then deposited on said substrate to form said film, said plasma including a cathode dark space having a first thickness;

positioning a plate element a first distance from said sputtering surface, said first distance being less than said first thickness and said plate element including a bottom surface and at least one edge;

inhibiting plasma formation in a first area adjacent said bottom surface by absorbing electrons emitted from said target such that target material is not eroded from a predetermined first portion of said sputtering surface opposite said first area;

forming plasma in a second area adjacent said edge to cause target material to be eroded from a predetermined second portion of said sputtering surface opposite said second area, thereby forming a desired non-uniform erosion pattern on said sputtering surface for improving thickness uniformity of said film.

9. The method according to claim 8, wherein said plate includes at least one hole to form first and second edges.

10. The method according to claim 8, wherein said plate element includes at least two concentric rings.

11. The method according to claim 8, wherein said plate element is a solid plate.

12. The method according to claim 8, wherein said plate element is maintained at a potential which is positive relative to said target.

13. The method according to claim 8, wherein said plate element is grounded.

14. The method according to claim 8, wherein said first distance is between approximately 0.05 and 1.0 inches.

15. A sputtering system for depositing a thin film on a substrate, comprising:

an evacuatable chamber;

a target positioned within said chamber, said target including a sputtering surface;

biasing means for biasing said target to form a cathode element which emits electrons;

an anode element which includes said substrate, wherein said substrate is positioned opposite said cathode element in said chamber;

ionization means for ionizing a sputtering gas, in response to said electrons, to form a plasma for eroding target material from said sputtering surface which is then deposited on said substrate to form said film, said plasma including a cathode dark space having a first thickness wherein ionization does not occur; and

a plate element having first and second outer edges and at least one hole to form first and second inner edges and first and second bottom surfaces, said plate element being grounded and spaced apart from said sputtering surface by a first distance which is between approximately 0.05 and 1.0 inches and which is less than said first thickness, wherein electrons emitted from said target are absorbed by said plate element to selectively inhibit plasma formation in first areas adjacent said first and second bottom surfaces such that target material is not eroded from predetermined first portions of said sputtering surface opposite said first areas, and wherein plasma is formed in a second areas adjacent said first and second inner and outer edges to cause

target material to be eroded from predetermined second portions of said sputtering surface opposite said second areas, thereby forming a desired non-uniform erosion pattern on said sputtering surface for improving thickness uniformity of said film.

16. The system according to claim 15, wherein said plate element includes at least two concentric rings.

17. The system according to claim 15, wherein said plate element is a solid plate.

18. The system according to claim 15, wherein said plate element is maintained at a potential which is positive relative to said target.

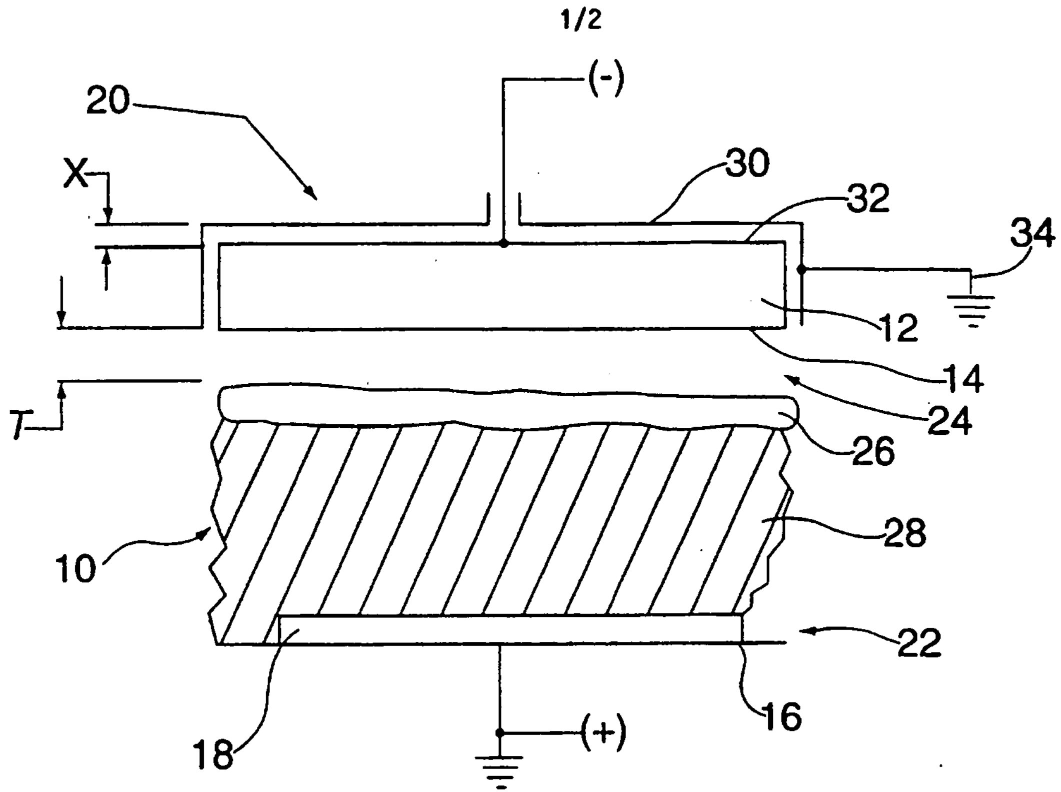


FIG. 1

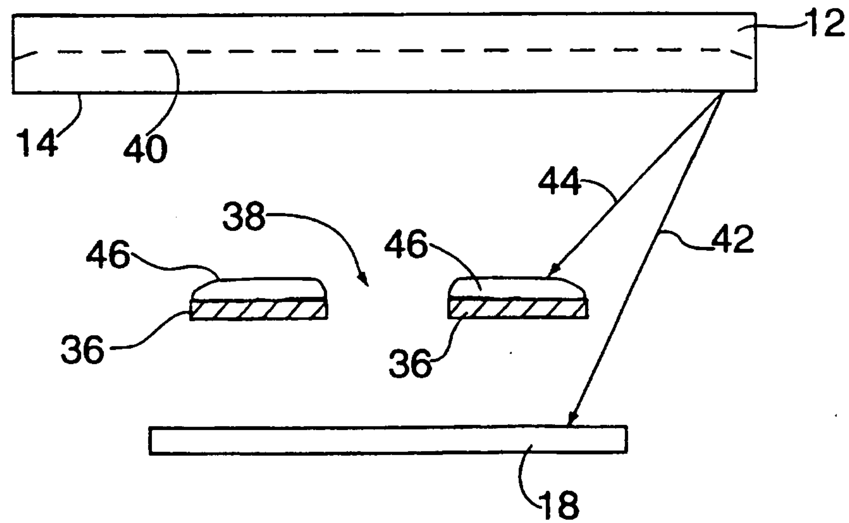


FIG. 2

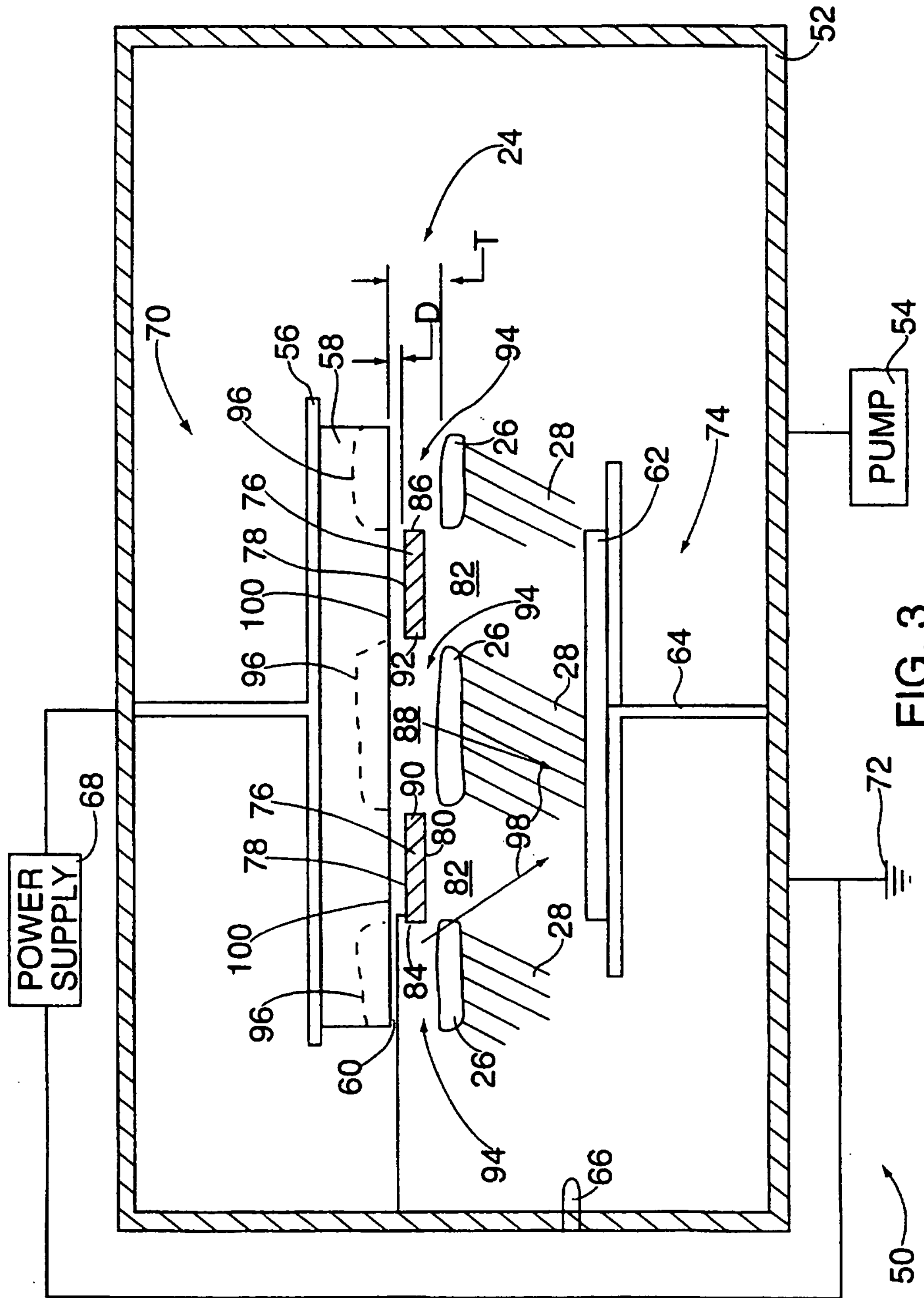


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/03047

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C23C 14/40
US CL : 204/192.12, 298.06, 298.11, 298.14, 298.15
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/192.12, 298.06, 298.11, 298.14, 298.15

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,824,544 A (MIKALESEN et al) 25 April 1989, Column 4 lines 64-68; Column 5 lines 1-5, lines 10-13, lines 54-65, lines 66-68; Column 6 lines 1-3.	1-18
Y	US 4,508,612 A (BLACKWELL et al) 02 April 1985, Column 3 lines 49-52; Column 5 lines 16-25, lines 26-36; Column 7 lines 21-27; Figure 2.	1-18
Y	US 3,985,635 A (ADAM et al) 12 October 1976, Column 2 lines 37-44, lines 45-50, lines 51-68; Column 3 lines 1-22, lines 60-63; Column 4 lines 18-23, lines 33-55; Column 6 lines 9-24.	1-18

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 MARCH 1997	13.05.97

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	RODNEY MCDONALD
Facsimile No. (703) 305-3230	Telephone No. (703) 308 - 3807

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/03047

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,361,659 A (BERTELSEN) 02 January 1968, Column 3 lines 50-57, lines 63-68; Column 4 lines 60-75; Column 5 lines 1-17, lines 27-30; Column 6 lines 32-34.	1-18

PATENT APPLICATION FEE DETERMINATION RECORD
Effective October 1, 2001

Application or Docket Number

CLAIMS AS FILED - PART I

	(Column 1)	(Column 2)
TOTAL CLAIMS	39	
FOR	NUMBER FILED	NUMBER EXTRA
TOTAL CHARGEABLE CLAIMS	39 minus 20=	* 19
INDEPENDENT CLAIMS	5 minus 3 =	* 2
MULTIPLE DEPENDENT CLAIM PRESENT		☐

* If the difference in column 1 is less than zero, enter "0" in column 2

SMALL ENTITY TYPE ☐ OR OTHER THAN SMALL ENTITY

RATE	FEE		RATE	FEE
BASIC FEE	370.00	OR	BASIC FEE	740.00
19 X$ 9=	171	OR	X$18=	
2 X42=	84	OR	X84=	
+140=		OR	+280=	
TOTAL	625	OR	TOTAL	

Amdt 7-23-04

CLAIMS AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	* 19	Minus	** 39	= —
Independent	* 2	Minus	*** 5	= —
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

SMALL ENTITY OR OTHER THAN SMALL ENTITY

RATE	ADDI-TIONAL FEE		RATE	ADDI-TIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

RATE	ADDI-TIONAL FEE		RATE	ADDI-TIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT C

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM ☐				

RATE	ADDI-TIONAL FEE		RATE	ADDI-TIONAL FEE
X$ 9=		OR	X$18=	
X42=		OR	X84=	
+140=		OR	+280=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

BEST AVAILABLE COPY

ISSUE SLIP STAPLE AREA (for additional cross-references)

ISSUING CLASSIFICATION

BEST AVAILABLE COPY

ORIGINAL		CROSS REFERENCE(S)						
CLASS	SUBCLASS	CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					
INTERNATIONAL CLASSIFICATION								
	/							
	/							
	/							
	/							
	/							

^ Continued on Issue Slip Inside File Jacket

INDEX OF CLAIMS

✓ .... Rejected - (Through numeral) ... Canceled N .... Non-elected A .... Appeal
= .... Allowed + ... Restricted I .... Interference O .... Objected

Claim Final	Claim Original	Date 03/12/04
	1	✓
	2	|
	3	|
	4	|
	5	|
	6	✓
	7	O
	8	✓
	9	|
	10	|
	11	|
	12	|
	13	✓
	14	N
	15	|
	16	|
	17	|
	18	|
	19	N
	20	✓
	21	O
	22	O
	23	O
	24	O
	25	N
	26	|
	27	|
	28	|
	29	|
	30	|
	31	|
	32	|
	33	|
	34	|
	35	|
	36	|
	37	|
	38	|
	39	N
	40	
	41	
	42	
	43	
	44	
	45	
	46	
	47	
	48	
	49	
	50	

Claim Final	Claim Original	Date
	51	
	52	
	53	
	54	
	55	
	56	
	57	
	58	
	59	
	60	
	61	
	62	
	63	
	64	
	65	
	66	
	67	
	68	
	69	
	70	
	71	
	72	
	73	
	74	
	75	
	76	
	77	
	78	
	79	
	80	
	81	
	82	
	83	
	84	
	85	
	86	
	87	
	88	
	89	
	90	
	91	
	92	
	93	
	94	
	95	
	96	
	97	
	98	
	99	
	100	

Claim Final	Claim Original	Date
	101	
	102	
	103	
	104	
	105	
	106	
	107	
	108	
	109	
	110	
	111	
	112	
	113	
	114	
	115	
	116	
	117	
	118	
	119	
	120	
	121	
	122	
	123	
	124	
	125	
	126	
	127	
	128	
	129	
	130	
	131	
	132	
	133	
	134	
	135	
	136	
	137	
	138	
	139	
	140	
	141	
	142	
	143	
	144	
	145	
	146	
	147	
	148	
	149	
	150	

If more than 150 claims or 9 actions staple additional sheet here

BEST AVAILABLE COPY

21823 IDS

IFW

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
H. Zhang, et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: Michelle Estrada
	)	
Filed: March 16, 2002	)	Confirmation No.: 6938
	)	
For: BIASED PULSED DC REACTIVE SPUTTERING OF OXIDE FILMS	)	

Mail Stop AMENDMENTS
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants brings to the attention of the Examiner the documents listed on the attached PTO 1449. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), this Information Disclosure Statement is accompanied by a fee of $180.00 as specified by Section 1.17(p).

Copies of the listed documents are attached.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

09/03/2004 SDIRETA1 00000004 10101863

01 FC:1806 180.00 OP

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

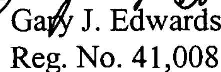
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

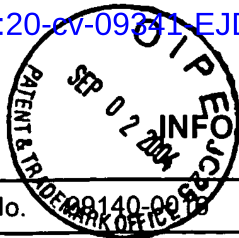
If there is any additional fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: September 1, 2004

By: 
Gary J. Edwards
Reg. No. 41,008



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No. 09140-0018	Appln. No. 10/101,863
Applicant ZHANG et al.	
Filing Date March 16, 2002	Group: 2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
		3,616,403	Oct. 26, 1971	Collins et al.	204	192	
		3,850,604	Nov. 26, 1974	Klein	65	32	
		4,111,523	Sep. 5, 1978	Kaminow et al.	350	96.14	
		4,619,680	Oct. 28, 1986	Nourshargh et al.	65	3.12	
		5,196,041	Mar. 23, 1993	Tumminelli et al.	65	30.1	
		5,287,427	Feb. 15, 1994	Atkins et al.	385	124	
		6,511,615 B1	Jan. 28, 2003	Dawes et al.	264	1.21	
		6,563,998 B1	May 13, 2003	Farah et al.	385	131	
		6,605,228 B1	Aug. 12, 2003	Kawaguchi et al.	216	24	
		6,615,614 B1	Sep. 9, 2003	Makikawa et al.	65	386	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

Examiner	Date Considered
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

7590 10/06/2004

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

DATE MAILED: 10/06/2004

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No.	Applicant(s)	
	10/101,863	ZHANG ET AL.	
	Examiner	**Art Unit**	
	Michelle Estrada	2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *23 July 2004*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-14 and 20-24* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-13 and 20* is/are rejected.

7)☒ Claim(s) *7,14 and 21-24* is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *7/23/04,9/2/04*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____.

DETAILED ACTION

Claim Objections

Claim 14 is objected to because of the following informalities: in line 2, it appears that "12" should be deleted. Appropriate correction is required.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-13 and 20 are rejected under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938).

With respect to claim 1, Le et al. disclose providing pulsed DC power (22) to a target (14) (Page 4, Paragraph [0070]); providing bias power to a substrate (16) positioned opposite the target (Page 5, lines 13-14); providing process gas between the target and the substrate (Page 4, Paragraph [0067]).

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

With respect to claim 8, Le et al. disclose wherein the process gas includes a mixture of oxygen and argon (Page 4, Paragraph [0067]).

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

With respect to claim 10, Le et al. disclose wherein the process gas further includes nitrogen (Page 5, Paragraph [0074]).

With respect to claim 11, Le et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 3).

With respect to claim 12, Le et al. disclose further including uniformly sweeping the target with a magnetic field (Page 5, Paragraph [0073]).

With respect to claim 13, Le et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Page 5, Paragraph [0073]).

With respect to claim 20, Le et al. disclose conditioning a target (Page 4, Paragraph [0070]); preparing the substrate (Page 3, Paragraph [0065]); adjusting the bias power to the substrate (Page 4, Paragraph [0041]); setting the process gas flow (Page 4, Paragraph [0067]); and applying pulsed DC power to the target to deposit the film (Page 4, Paragraph [0071]).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range

of values disclosed. Furthermore, Le et al. disclose that sets of process parameters depend on the specific process chamber (Page 6, Paragraph [0081]).

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Le et al. do not disclose providing a DC power through a filter.

With respect to claims 1 and 5, Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form the DC power supply (Col. 6, lines 32-37).

Allowable Subject Matter

Claims 7, 14 and 21-24 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Response to Arguments

Applicant's arguments filed 7/23/04 have been fully considered but they are not persuasive. Applicant argues that Le et al. do not disclose a bias applied to the substrate. However, Applicant is directed to Page 5, lines 13-14, wherein Le et al. disclose applying a RF energy (bias) to the gas supplied to the substrate.

Applicant argues that Fukui does not teach a pulsed DC power supply. However, Fukui was not relied on upon for that purpose. Fukui teaches supplying power from a DC supply through a filter to the target. Fukui was relied on for the use of a filter to supply a power to the target.

In response to applicant's argument that the examiner's conclusion of obviousness is based upon improper hindsight reasoning, it must be recognized that any judgment on obviousness is in a sense necessarily a reconstruction based upon hindsight reasoning. But so long as it takes into account only knowledge which was within the level of ordinary skill at the time the claimed invention was made, and does not include knowledge gleaned only from the applicant's disclosure, such a reconstruction is proper. See *In re McLaughlin*, 443 F.2d 1392, 170 USPQ 209 (CCPA 1971).

Applicant argues that utilizing a filter provided for a DC power supply is not obvious and may not be necessary in the system taught by Le because of the lack of a bias. However, Le discloses applying a bias to energize the gas being applied to the substrate, as explained above. Therefore, a filter may be used to provide the pulsed DC power through the filter since a bias is being applied.

Applicant argues that there is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply with a pulsed DC power supply. However, the Examiner is not substituting the pulsed DC power supply for the

RF power supply coupled to the target. The rejection is based on utilizing the filter of Fukui to be used in the pulsed DC power supply of Le.

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

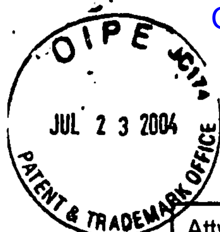
Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri can be reached on 571-272-1855. The fax phone numbers for the organization where this application or proceeding is assigned are 703-308-7722 for regular communications and 703-308-7724 for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

MEstrada
October 4, 2004

Olik Chaudhuri
Supervisory Patent Examiner
Technology Center 2800



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

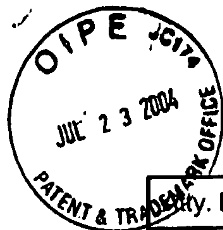
U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
ME		2002/0106297		Ueno et al.	419	12	Aug. 08, 2002
ME		2003/0019326		Han et al.	45	245	Jan. 30, 2003
ME		2003/0063883		Demaray et al.	385	129	Apr. 3, 2003
ME		2003/0175142		Milonopoulou et al.	419	49	Sep. 18, 2003
ME		4,437,966	Mar. 7, 1961	Hope et al	204	298	
ME		4,915,810	Apr. 10, 1990	Kestigian et al.	204	298.04	
ME		4,978,437	Dec. 18, 1990	Wirz	204	192.	
ME		5,174,876	Dec. 29, 1992	Buchal et al.	427	526	
ME		5,200,029	Apr. 6, 1993	Bruce et al.	156	657	
ME		5,206,925	Apr. 27, 1993	Nakazawa et al.	385	142	
ME		5,225,288	Jul. 6, 1993	Beeson et al.	428	475.5	
ME		5,237,439	Aug. 17, 1993	Misono et al.	359	74	
ME		5,252,194	Oct. 12, 1993	Demaray et al.	204	298	
ME		5,303,319	Apr. 12, 1994	Ford et al.	385	131	
ME		5,381,262	Jan. 10, 1995	Arima et al.	359	341	
ME		5,427,669	Jun. 27, 1995	Drummond	204	298.2	
ME		5,475,528	Dec. 12, 1995	LaBorde	359	341	
ME		5,483,613	Jan. 9, 1996	Bruce et al.	385	129	
ME		5,555,127	Sep. 10, 1996	Abdelkader et al.	359	341	
ME		5,565,071	Oct. 15, 1996	Demaray et al.	204	192	
ME		5,603,816	Feb. 18, 1997	Demaray et al.	204	298	

Examiner Michelle Estrada	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 Patent and Trademark Office - U.S. Department of Commerce



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

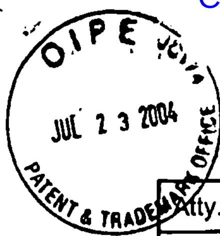
Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS								
Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MLE		5,613,995	Mar. 25, 1997	Bhandarkar et al.	65	384	
MLE		5,654,054	Aug. 5, 1997	Tropsha et al.	428	36.6	
MLE		5,693,956	Dec. 2, 1997	Shi et al.	257	40	
MLE		5,718,813	Feb. 17, 1998	Drummond	204	192.2	
MLE		5,719,976	Feb. 17, 1998	Henry et al.	385	50	
MLE		5,792,550	Aug. 11, 1998	Phillips et al.	428	336	
MLE		5,841,931	Nov. 24, 1998	Foresi et al.	385	131	
MLE		5,847,865	Dec. 8, 1998	Gopinath et al.	359	343	
MLE		5,855,744	Jan. 5, 1999	Halsey et al.	204	192	
MLE		5,948,215	Sep. 7, 1999	Lantsman	204	192.12	
MLE		5,961,682	Oct. 5, 1999	Lee et al.	65	384	
MLE		5,977,582	Nov. 2, 1999	Fleming et al.	257	310	
MLE		6,001,224	Dec. 14, 1999	Drummond	204	192.12	
MLE		6,024,844	Feb. 15, 2000	Drummond et al.	204	192.12	
MLE		6,051,114	Apr. 18, 2000	Yao et al.	204	192.3	
MLE		6,093,944	Jul. 25, 2000	VanDover	257	310	
MLE		6,162,709	Dec. 19, 2000	Raux et al.	438	513	
MLE		6,176,986	Jan. 23, 2001	Watanabe et al.	204	298.13	
MLE		6,248,291	Jun. 19, 2001	Nakagama et al.	419	46	
MLE		6,280,585 B1	Aug. 28, 2001	Obinata et al.	204	298.19	
MLE		6,287,986	Sep. 11, 2001	Mihara	438	763	

Examiner *Michelle Estrada*	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 — Patent and Trademark Office - U.S. Department of Commerce



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MYE		6,290,822	Sep. 18, 2001	Fleming et al.	204	192.22	
MYE		6,344,419	Feb. 5, 2002	Forster et al.	438	758	
MYE		6,350,353	Feb. 26, 2002	Gopalraja et al.	204	192.3	
MYE		6,358,810	Mar. 19, 2002	Dornfest et al.	438	396	
MYE		6,409,965	Jun. 25, 2002	Nagate et al.	419	26	
MYE		6,413,382	Jul. 2, 2002	Wang et al.	204	192.12	
MYE		6,537,428	Mar. 25, 2003	Xiong et al.	204	192.13	
MYE		6,602,338	Aug. 5, 2003	Chen et al.	252	301.4	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No
MYE		EP 0 820 088	01/21/98	Europe	H 01 J	37/34	
MYE		EP 0 867 985 A1	09/01/98	Europe	H 01 S	3/06	
MYE		JP 6-010127	01/18/94	Japan	C 23 C	14/35	Abstract
MYE		JP 6-100333	12/04/94	Japan	C 03 C	21/00	Abstract
MYE		WO 00/22742	04/01/00	PCT	H O4 B		
MYE		WO 00/36665	06/22/00	PCT	H 01 L	51/20	
MYE		WO 02/12932	02/14/02	PCT	H 01 S	3/16	
MYE		WO 96/23085	08/01/96	PCT	C 23 C	14/34	
MYE		WO 97/35044	09/25/97	PCT	C 23 C	14/40	

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

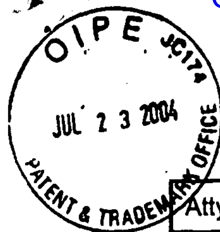
OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
ME	BARBIER, Denis, "Performances and potentioal applications of erbium doped planar waveguide amplifiers and lasers," GeeO, pp. 58-63.
ME	BELKIND et al., "Using pulsed direct current power for reactive sputtering of Al_2O_3," *J. Vac. Sci. Technol.* A 17(4), pp. 1934-40 (Jul. 1999).
ME	BYER et al., "Nonlinear Optics and Solid-state Lasers," *IEEE Journal on Selected Topics in Quantum Electronics*, Vol. 6, No. 6, pp. 921-929 (Nov. 2000).
ME	FUJII et al, "1.54 mm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals for Er^{3+}", *Appl. Phys. Lett.*, 71 (9), pp. 1198-1200 (September, 1997).
ME	KELLY et al., "Reactive pulsed magnetron sputtering process for alumina films," *J. Vac. Sci. Technol.* A 18(6), pp. 2890-96 (Nov. 2000).
ME	KELLY et al., "Control of the structure and properties of aluminum oxide coatings deposited by pulsed magnetron sputtering," *J. Vac. Sci. Technol.* A 17(3), pp. 945-953 (May 1999).
ME	PAN et al., "Planar Er3+-doped aluminosilicate waveguide amplifier with more than 10 dB gain across C-band," Optical Society of America, 3 pages (2000).
ME	ROBERTS et al., "The Photoluminescence of Erbium-doped Silicon Monoxide," Department of Electronics and Computer Science, 7 pages (June 1996).
ME	SCHILLER et al. "PVD Coating of Plastic Webs and Sheets with High Rates on Large Areas," European Materials Research Society 1999 Spring Meeting, Strasbourg, France (June 1-4, 1999).
ME	SHAW et al. "Use of Vapor Deposited Acrlate Coatings to Improve the Barrier Properties of MetallizedFilm," Society of Vacuum Coaters 505/856-7168, 37th Annual Technical Conference Proceedings, pp. 240-244 (1994).
ME	SHIN et al. "Dielectric and Electrical Properties of Sputter Grown (Ba,Sr)TiO_3 Thin Films," *J. Appl. Phys.*, Vol. 86, No. 1, pp. 506-513, (July 1, 1999).
ME	SHMULOVICH et al., "Recent progress in Erbium-doped waveguide amplifiers," Bell Laboratories, 3 pages (1999).
ME	TING et al., "Study of planarized sputter-deposited SiO2," *J. Vac. Sci. Technol.*, 15(3) pp. 1105-1112 (May/Jun. 1978).

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



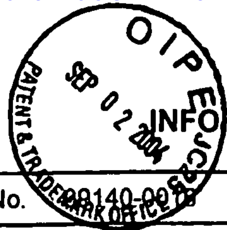
OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
[initials]	VAN DOVER, R.B. "Amorphous Lanthanide-Doped TiO_x Dielectric Films," *Appl. Phys. Lett.*, Vol. 74, No. 20, pp. 3041-3 (May 17 1999).
[initials]	WESTLINDER et al. "Simulation and Dielectric Characterization of Reactive dc Magnetron Cosputtered $(Ta_2O_5)_{1-x}(TiO_2)_x$ Thin Films," *J. Vac. Sci. Technol.* B, Vol 20, No. 3, pp. 855-861 (May/Jun 2002).
[initials]	YOSHIKAWA, K. et al., "Spray formed aluminium alloys for sputtering targets," *Power Metallurgy*, Vol. 43, No. 3, pp. 198-99 (2000)
[initials]	ZHANG, Hongmei et al. "High Dielectric Strength, High k TiO_2 Films by Pulsed DC, Reactive Sputter Deposition," (2002).

Examiner [signature]	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No. 09140-0016	Appln. No. 10/101,863
Applicant ZHANG et al.	
Filing Date March 16, 2002	Group: 2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MLE		3,616,403	Oct. 26, 1971	Collins et al.	204	192	
MLE		3,850,604	Nov. 26, 1974	Klein	65	32	
MLE		4,111,523	Sep. 5, 1978	Kaminow et al.	350	96.14	
MLE		4,619,680	Oct. 28, 1986	Nourshargh et al.	65	3.12	
MLE		5,196,041	Mar. 23, 1993	Tumminelli et al.	65	30.1	
MLE		5,287,427	Feb. 15, 1994	Atkins et al.	385	124	
MLE		6,511,615 B1	Jan. 28, 2003	Dawes et al.	264	1.21	
MLE		6,563,998 B1	May 13, 2003	Farah et al.	385	131	
MLE		6,605,228 B1	Aug. 12, 2003	Kawaguchi et al.	216	24	
MLE		6,615,614 B1	Sep. 9, 2003	Makikawa et al.	65	386	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

Examiner Michelle Estrada	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 — Patent and Trademark Office - U.S. Department of Commerce

ISSUE SLIP STAPLE AREA (for additional cross-references)

ISSUING CLASSIFICATION

ORIGINAL		CROSS REFERENCE(S)	
CLASS	SUBCLASS	CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)
INTERNATIONAL CLASSIFICATION			
/			
/			
/			
/			
/			

^ Continued on Issue Slip Inside File Jacket

BEST AVAILABLE COPY

BEST AVAILABLE COPY

INDEX OF CLAIMS

✓ .... Rejected - (Through numeral) ... Canceled N .... Non-elected A .... Appeal
= .... Allowed + ... Restricted I .... Interference O .... Objected

Claim (Original)	Date	Date	Claim (Original)	Date	Claim (Original)	Date
1	✓	✓	51		101	
2			52		102	
3			53		103	
4			54		104	
5			55		105	
6	✓	✓	56		106	
7	O	O	57		107	
8	✓	✓	58		108	
9			59		109	
10			60		110	
11			61		111	
12			62		112	
13	✓	✓	63		113	
14	N	O	64		114	
15			65		115	
16			66		116	
17			67		117	
18			68		118	
19	N		69		119	
20	✓	✓	70		120	
21	O	O	71		121	
22	O	O	72		122	
23	O	O	73		123	
24	O	O	74		124	
25	N		75		125	
26			76		126	
27			77		127	
28			78		128	
29			79		129	
30			80		130	
31			81		131	
32			82		132	
33			83		133	
34			84		134	
35			85		135	
36			86		136	
37			87		137	
38			88		138	
39	N		89		139	
40			90		140	
41			91		141	
42			92		142	
43			93		143	
44			94		144	
45			95		145	
46			96		146	
47			97		147	
48			98		148	
49			99		149	
50			100		150	

If more than 150 claims or 9 actions staple additional sheet here

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

7590 10/06/2004

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

EXAMINER	
ESTRADA, MICHELLE	

ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 10/06/2004

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No. 10/101,863	Applicant(s) ZHANG ET AL.
	Examiner Michelle Estrada	Art Unit 2823

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *23 July 2004*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-14 and 20-24* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-13 and 20* is/are rejected.

7)☒ Claim(s) *7,14 and 21-24* is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *7/23/04,9/2/04*.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

DETAILED ACTION

Claim Objections

Claim 14 is objected to because of the following informalities: in line 2, it appears that "12" should be deleted. Appropriate correction is required.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-13 and 20 are rejected under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938).

With respect to claim 1, Le et al. disclose providing pulsed DC power (22) to a target (14) (Page 4, Paragraph [0070]); providing bias power to a substrate (16) positioned opposite the target (Page 5, lines 13-14); providing process gas between the target and the substrate (Page 4, Paragraph [0067]).

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

With respect to claim 8, Le et al. disclose wherein the process gas includes a mixture of oxygen and argon (Page 4, Paragraph [0067]).

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

With respect to claim 10, Le et al. disclose wherein the process gas further includes nitrogen (Page 5, Paragraph [0074]).

With respect to claim 11, Le et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 3).

With respect to claim 12, Le et al. disclose further including uniformly sweeping the target with a magnetic field (Page 5, Paragraph [0073]).

With respect to claim 13, Le et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Page 5, Paragraph [0073]).

With respect to claim 20, Le et al. disclose conditioning a target (Page 4, Paragraph [0070]); preparing the substrate (Page 3, Paragraph [0065]); adjusting the bias power to the substrate (Page 4, Paragraph [0041]); setting the process gas flow (Page 4, Paragraph [0067]); and applying pulsed DC power to the target to deposit the film (Page 4, Paragraph [0071]).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range

of values disclosed. Furthermore, Le et al. disclose that sets of process parameters depend on the specific process chamber (Page 6, Paragraph [0081]).

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Le et al. do not disclose providing a DC power through a filter.

With respect to claims 1 and 5, Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form the DC power supply (Col. 6, lines 32-37).

Allowable Subject Matter

Claims 7, 14 and 21-24 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Response to Arguments

Applicant's arguments filed 7/23/04 have been fully considered but they are not persuasive. Applicant argues that Le et al. do not disclose a bias applied to the substrate. However, Applicant is directed to Page 5, lines 13-14, wherein Le et al. disclose applying a RF energy (bias) to the gas supplied to the substrate.

Applicant argues that Fukui does not teach a pulsed DC power supply. However, Fukui was not relied on upon for that purpose. Fukui teaches supplying power from a DC supply through a filter to the target. Fukui was relied on for the use of a filter to supply a power to the target.

In response to applicant's argument that the examiner's conclusion of obviousness is based upon improper hindsight reasoning, it must be recognized that any judgment on obviousness is in a sense necessarily a reconstruction based upon hindsight reasoning. But so long as it takes into account only knowledge which was within the level of ordinary skill at the time the claimed invention was made, and does not include knowledge gleaned only from the applicant's disclosure, such a reconstruction is proper. See *In re McLaughlin*, 443 F.2d 1392, 170 USPQ 209 (CCPA 1971).

Applicant argues that utilizing a filter provided for a DC power supply is not obvious and may not be necessary in the system taught by Le because of the lack of a bias. However, Le discloses applying a bias to energize the gas being applied to the substrate, as explained above. Therefore, a filter may be used to provide the pulsed DC power through the filter since a bias is being applied.

Applicant argues that there is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply with a pulsed DC power supply. However, the Examiner is not substituting the pulsed DC power supply for the

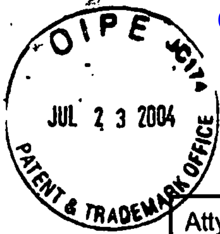
RF power supply coupled to the target. The rejection is based on utilizing the filter of Fukui to be used in the pulsed DC power supply of Le.

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri can be reached on 571-272-1855. The fax phone numbers for the organization where this application or proceeding is assigned are 703-308-7722 for regular communications and 703-308-7724 for After Final communications.



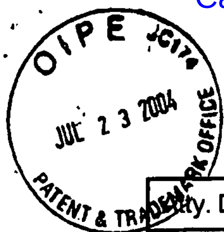
OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS							
Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
ME		2002/0106297		Ueno et al.	419	12	Aug. 08, 2002
ME		2003/0019326		Han et al.	45	245	Jan. 30, 2003
ME		2003/0063883		Demaray et al.	385	129	Apr. 3, 2003
ME		2003/0175142		Milonopoulou et al.	419	49	Sep. 18, 2003
ME		4,437,966	Mar. 7, 1961	Hope et al	204	298	
ME		4,915,810	Apr. 10, 1990	Kestigian et al.	204	298.04	
ME		4,978,437	Dec. 18, 1990	Wirz	204	192.	
ME		5,174,876	Dec. 29, 1992	Buchal et al.	427	526	
ME		5,200,029	Apr. 6, 1993	Bruce et al.	156	657	
ME		5,206,925	Apr. 27, 1993	Nakazawa et al.	385	142	
ME		5,225,288	Jul. 6, 1993	Beeson et al.	428	475.5	
ME		5,237,439	Aug. 17, 1993	Misono et al.	359	74	
ME		5,252,194	Oct. 12, 1993	Demaray et al.	204	298	
ME		5,303,319	Apr. 12, 1994	Ford et al.	385	131	
ME		5,381,262	Jan. 10, 1995	Arima et al.	359	341	
ME		5,427,669	Jun. 27, 1995	Drummond	204	298.2	
ME		5,475,528	Dec. 12, 1995	LaBorde	359	341	
ME		5,483,613	Jan. 9, 1996	Bruce et al.	385	129	
ME		5,555,127	Sep. 10, 1996	Abdelkader et al.	359	341	
ME		5,565,071	Oct. 15, 1996	Demaray et al.	204	192	
ME		5,603,816	Feb. 18, 1997	Demaray et al.	204	298	

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
[initials]		5,613,995	Mar. 25, 1997	Bhandarkar et al.	65	384	
[initials]		5,654,054	Aug. 5, 1997	Tropsha et al.	428	36.6	
[initials]		5,693,956	Dec. 2, 1997	Shi et al.	257	40	
[initials]		5,718,813	Feb. 17, 1998	Drummond	204	192.2	
[initials]		5,719,976	Feb. 17, 1998	Henry et al.	385	50	
[initials]		5,792,550	Aug. 11, 1998	Phillips et al.	428	336	
[initials]		5,841,931	Nov. 24, 1998	Foresi et al.	385	131	
[initials]		5,847,865	Dec. 8, 1998	Gopinath et al.	359	343	
[initials]		5,855,744	Jan. 5, 1999	Halsey et al.	204	192	
[initials]		5,948,215	Sep. 7, 1999	Lantsman	204	192.12	
[initials]		5,961,682	Oct. 5, 1999	Lee et al.	65	384	
[initials]		5,977,582	Nov. 2, 1999	Fleming et al.	257	310	
[initials]		6,001,224	Dec. 14, 1999	Drummond	204	192.12	
[initials]		6,024,844	Feb. 15, 2000	Drummond et al.	204	192.12	
[initials]		6,051,114	Apr. 18, 2000	Yao et al.	204	192.3	
[initials]		6,093,944	Jul. 25, 2000	VanDover	257	310	
[initials]		6,162,709	Dec. 19, 2000	Raux et al.	438	513	
[initials]		6,176,986	Jan. 23, 2001	Watanabe et al.	204	298.13	
[initials]		6,248,291	Jun. 19, 2001	Nakagama et al.	419	46	
[initials]		6,280,585 B1	Aug. 28, 2001	Obinata et al.	204	298.19	
[initials]		6,287,986	Sep. 11, 2001	Mihara	438	763	

Examiner Michelle Estrada	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

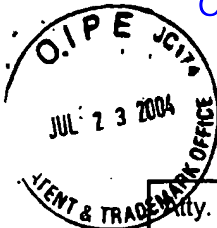
INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS							
Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MAE		6,290,822	Sep. 18, 2001	Fleming et al.	204	192.22	
MAE		6,344,419	Feb. 5, 2002	Forster et al.	438	758	
MAE		6,350,353	Feb. 26, 2002	Gopalraja et al.	204	192.3	
MAE		6,358,810	Mar. 19, 2002	Dornfest et al.	438	396	
MAE		6,409,965	Jun. 25, 2002	Nagate et al.	419	26	
MAE		6,413,382	Jul. 2, 2002	Wang et al.	204	192.12	
MAE		6,537,428	Mar. 25, 2003	Xiong et al.	204	192.13	
MAE		6,602,338	Aug. 5, 2003	Chen et al.	252	301.4	

FOREIGN PATENT DOCUMENTS							
		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No
MAE		EP 0 820 088	01/21/98	Europe	H 01 J	37/34	
MAE		EP 0 867 985 A1	09/01/98	Europe	H 01 S	3/06	
MAE		JP 6-010127	01/18/94	Japan	C 23 C	14/35	Abstract
MAE		JP 6-100333	12/04/94	Japan	C 03 C	21/00	Abstract
MAE		WO 00/22742	04/01/00	PCT	H O4 B		
MAE		WO 00/36665	06/22/00	PCT	H 01 L	51/20	
MAE		WO 02/12932	02/14/02	PCT	H 01 S	3/16	
MAE		WO 96/23085	08/01/96	PCT	C 23 C	14/34	
MAE		WO 97/35044	09/25/97	PCT	C 23 C	14/40	

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



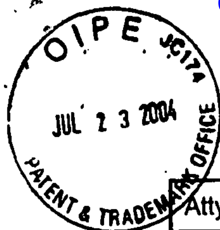
OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No. 09140-0016	Appln. No. 10/101,863
Applicant ZHANG et al.	
Filing Date March 16, 2002	Group: 2823

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)	
ME	BARBIER, Denis, "Performances and potentioal applications of erbium doped planar waveguide amplifiers and lasers," GeeO, pp. 58-63.
ME	BELKIND et al., "Using pulsed direct current power for reactive sputtering of Al_2O_3," *J. Vac. Sci. Technol.* A 17(4), pp. 1934-40 (Jul. 1999).
ME	BYER et al., "Nonlinear Optics and Solid-state Lasers," *IEEE Journal on Selected Topics in Quantum Electronics*, Vol. 6, No. 6, pp. 921-929 (Nov. 2000).
ME	FUJII et al, "1.54 mm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals for Er^{3+}", *Appl. Phys. Lett.*, 71 (9), pp. 1198-1200 (September, 1997).
ME	KELLY et al., "Reactive pulsed magnetron sputtering process for alumina films," *J. Vac. Sci. Technol.* A 18(6), pp. 2890-96 (Nov. 2000).
ME	KELLY et al., "Control of the structure and properties of aluminum oxide coatings deposited by pulsed magnetron sputtering," *J. Vac. Sci. Technol.* A 17(3), pp. 945-953 (May 1999).
ME	PAN et al., "Planar Er3+-doped aluminosilicate waveguide amplifier with more than 10 dB gain across C-band," Optical Society of America, 3 pages (2000).
ME	ROBERTS et al., "The Photoluminescence of Erbium-doped Silicon Monoxide," Department of Electronics and Computer Science, 7 pages (June 1996).
ME	SCHILLER et al. "PVD Coating of Plastic Webs and Sheets with High Rates on Large Areas," European Materials Research Society 1999 Spring Meeting, Strasbourg, France (June 1-4, 1999).
ME	SHAW et al. "Use of Vapor Deposited Acrlate Coatings to Improve the Barrier Properties of MetallizedFilm," Society of Vacuum Coaters 505/856-7168, 37th Annual Technical Conference Proceedings, pp. 240-244 (1994).
ME	SHIN et al. "Dielectric and Electrical Properties of Sputter Grown (Ba,Sr)TiO_3 Thin Films," *J. Appl. Phys.*, Vol. 86, No. 1, pp. 506-513, (July 1, 1999).
ME	SHMULOVICH et al., "Recent progress in Erbium-doped waveguide amplifiers," Bell Laboratories, 3 pages (1999).
ME	TING et al., "Study of planarized sputter-deposited SiO2," *J. Vac. Sci. Technol.*, 15(3) pp. 1105-1112 (May/Jun. 1978).

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



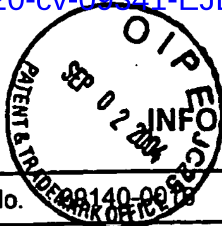
OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
ME	VAN DOVER, R.B. "Amorphous Lanthanide-Doped TiO_x Dielectric Films," *Appl. Phys. Lett.*, Vol. 74, No. 20, pp. 3041-3 (May 17 1999).
ME	WESTLINDER et al. "Simulation and Dielectric Characterization of Reactive dc Magnetron Cosputtered $(Ta_2O_5)_{1-x}(TiO_2)_x$ Thin Films," *J. Vac. Sci. Technol.* B, Vol 20, No. 3, pp. 855-861 (May/Jun 2002).
ME	YOSHIKAWA, K. et al., "Spray formed aluminium alloys for sputtering targets," *Power Metallurgy*, Vol. 43, No. 3, pp. 198-99 (2000)
ME	ZHANG, Hongmei et al. "High Dielectric Strength, High k TiO_2 Films by Pulsed DC, Reactive Sputter Deposition," (2002).

Examiner *Michelle Estrada*	Date Considered *9/28/04*
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No. 08140-00	Appln. No. 10/101,863
Applicant ZHANG et al.	
Filing Date March 16, 2002	Group: 2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MK		3,616,403	Oct. 26, 1971	Collins et al.	204	192	
MK		3,850,604	Nov. 26, 1974	Klein	65	32	
MK		4,111,523	Sep. 5, 1978	Kaminow et al.	350	96.14	
MK		4,619,680	Oct. 28, 1986	Nourshargh et al.	65	3.12	
MK		5,196,041	Mar. 23, 1993	Tumminelli et al.	65	30.1	
MK		5,287,427	Feb. 15, 1994	Atkins et al.	385	124	
MK		6,511,615 B1	Jan. 28, 2003	Dawes et al.	264	1.21	
MK		6,563,998 B1	May 13, 2003	Farah et al.	385	131	
MK		6,605,228 B1	Aug. 12, 2003	Kawaguchi et al.	216	24	
MK		6,615,614 B1	Sep. 9, 2003	Makikawa et al.	65	386	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

Examiner Michelle Estrada	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 Patent and Trademark Office - U.S. Department of Commerce

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

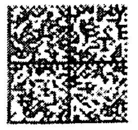
MEstrada
October 4, 2004

Olik Chaudhuri
Supervisory Patent Examiner
Technology Center 2800

Organization TC2800 Bldg./Room Jeff

U. S. DEPARTMENT OF COMMERCE
COMMISSIONER FOR PATENTS
P.O. BOX 1450
ALEXANDRIA, VA 22313-1450
IF UNDELIVERABLE RETURN IN TEN DAYS

OFFICIAL BUSINESS



UNITED STATES POSTAGE
U.S. OFFICIAL MAIL
PENALTY FOR PRIVATE USE $300
PITNEY BOWES
$ 01.06⁰
02 1A
0004202245 OCT 19 2004
MAILED FROM ZIPCODE 22202

AN EQUAL OPPORTUNITY EMPLOYER

ORDER EXPIRED

RECEIVED
OCT 28 2004
TECHNOLOGY CENTER 2800

2823

PATENT
Customer No. 22,852
Attorney Docket No. 09140-0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	
ZHANG et al.	Group Art Unit: 2823
Application No.: 10/101,863	Examiner: Michelle Estrada
Filed: March 16, 2002	Confirmation No.: 6938
For: BIASED PULSED DC REACTIVE SPUTTERING OF OXIDE FILMS	

Mail Stop AMENDMENTS
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SECOND SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents listed on the attached Form PTO/SB/08. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), this Information Disclosure Statement is accompanied by a fee of $180.00 as specified by Section 1.17(p).

These documents, as summarized in the chart below, are U.S. patents and applications that are possibly related to the pending application by subject matter. This submission should not be construed, however, as an admission of relatedness.

12/08/2004 HDEMESS1 00000109 10101863
01 FC:1806 180.00 OP

Attorney Docket Number	U.S. Patent/ Serial No.	U.S./PCT Publication No.	Title	Examiner
09140-0001-00	10/291,179	US 2003/0134054 A1	Low temperature zirconia based thermal barrier layer by PVD	Rodney McDONALD
09140-0002-01	6,506,289	US 2002/0033330 A1	Planar optical devices and methods for their manufacture	Steven H. VERSTEEG
09140-0002-02	6,827,826	US 2003/0127319 A1	Planar optical devices and methods for their manufacture	Steven H. VERSTEEG
09140-0004-00	6,533,907	US 2002/0134671 A1	Method of Producing amorphous silicon for hard mask and waveguide applications	Steven H. VERSTEEG
09140-0014-00	09/903,081	US 2003/0063883 A1	As-deposited planar optical waveguides with low scattering loss and methods for their manufacture	John M. HOFFMANN
09140-0015-00	10/101,492	US 2003/0173208 A1	Mode size converter for a planar waveguide	Steven H. VERSTEEG
09140-0016-00 (present application)	10/101,863	US 2003/0173207 A1	Biased pulse DC reactive sputtering of oxide films	Michelle ESTRADA
09140-0016-01	10/954,182		Biased pulse DC reactive sputtering of oxide films	Not Yet Assigned
09140-0017-00	10/101,341	US 2003/0175142 A1	Rare-earth pre-alloyed PVD targets for dielectric planar applications	Daniel J. JENKINS
09140-0021-00 (abandoned)	10/101,493	US 2003/0174391 A1	Gain flattened optical amplifier	Deandra M. HUGHES
09140-0025-00	10/650,461	US 2004/0105644 A1 WO 2004/021532 A1	Optical Coupling into Highly Uniform Waveguides	Scott A. KNAUSS
09140-0030-00	10/789,953	WO 2004/077519 A2	Dielectric Barrier Films	Not Yet Assigned

Attorney Docket Number	U.S. Patent/ Serial No.	U.S./PCT Publication No.	Title	Examiner
09140-0033-00	10/851,542		Energy Conversion and Storage Devices by Physical Vapor Deposition of Titanium and Titanium Oxides and Sub-Oxides	Not Yet Assigned
09140-0034-00	10/850,968		Transparent Conductive Oxides from a Metallic Target	Not Yet Assigned

U.S. Patent Application No. 10/954,182 (Attoney Docket No. 09140-0016-01) is a continuation of the present application and has the same specification.

For U.S. Patent Application No. 10/789,953 (Attorney Docket No. 09140-0030-00) the Applicants submit corresponding PCT publication.

For U.S. Patent Application No. 10/851,542 (Attorney Docket No. 09140-0033-00) and U.S. Patent Application No. 10/850,968 (Attorney Docket No. 09140-0034-00), that have not been published yet, the Applicants submit copies of specifications as filed.

The Applicants submit office actions issued by the U.S. Patent and Trademark Office in the above-listed applications.

The Applicants also submit International Search Reports and Written Opinions issued in the Patent Cooperation Treaty applications corresponding to the U.S. Patent Applications listed above.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form. Should

the Examiner conclude that any of these claims form the basis of a rejection, the Examiner is invited to contact the undersigned.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the Office the relevant facts and law regarding the appropriate status of such documents.

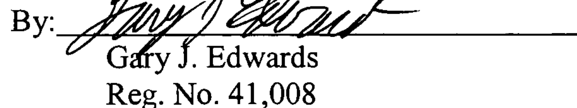
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

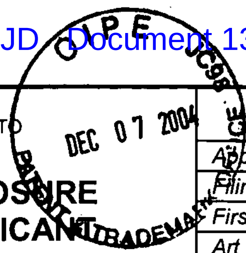
If there is any additional fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 7, 2004

By: 
Gary J. Edwards
Reg. No. 41,008



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG et al.
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	Michelle ESTRADA
Sheet	1	of	2	*Attorney Docket Number*	09140-0016-00000

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 2002/0033330 A1	Mar. 21, 2002	Demaray et al.	
		US 2002/0134671 A1	Jul. 17, 2003	Demaray et al.	
		US 2003/0063883 A1	Apr. 3, 2003	Demaray et al.	
		US 2003/0127319 A1	Jul. 10, 2003	Demaray et al.	
		US 2003/0134054 A1	Jul. 17, 2003	Demaray et al.	
		US 2003/0173207 A1	Sep. 18, 2003	Zhang et al.	
		US 2003/0173208 A1	Sep. 18, 2003	Pan et al.	
		US 2003/0174391 A1	Sep. 18, 2003	Pan et al.	
		US 2003/0175142 A1	Sep. 18, 2003	Milonopoulou et al.	
		US 2004/0105644 A1	Jun. 3, 2004	Dawes	
		US 6,506,289	Jan. 14, 2003	Demaray et al.	
		US 6,533,907	Mar. 18, 2003	Demaray et al.	
		US 6,827,826	Dec. 7, 2004	Demaray et al.	

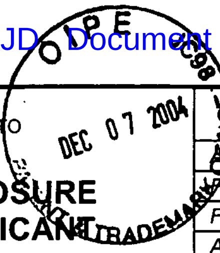
Note: Copies of the U.S. Patent Documents are not Required in IDS filed after October 21, 2004

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		WO 2004/021532 A1	Mar. 11, 2004	Symmorphix, Inc.		
		WO 2004/077519 A2	Sep. 10, 2004	Narasimhan et al.		

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
				Application Number	10/101,863
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Filing Date	March 16, 2002
				First Named Inventor	ZHANG et al.
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	Michelle ESTRADA
Sheet	2	of	2	Attorney Docket Number	09140-0016-00000

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Office Action issued on September 27, 2004 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Office Action issued on November 28, 2001 in U.S. Patent No. 6,506,289 (Attorney Docket No. 09140-0002-01).	
		Office Action issued on April 17,2002 in U.S. Patent No. 6,506,289 (Attorney Docket No. 09140-0002-01).	
		Quayle Action issued on November 10, 2003 in U.S. Patent No. 6,827,826 (Attorney Docket No. 09140-0002-02).	
		Office Action issued on May 2, 2002 in U.S. Patent No. 6,533,907 (Attorney Docket No. 09140-0004-00).	
		Office Action issued on February 12, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on September 10, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on September 3, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Office Action issued on October 22, 2003 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on June 10, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on May 4, 2004 in U.S. Serial No. 10/101,493 (Attorney Docket No. 09140-0021-00).	
		International Search Report issued on November 21, 2003 in PCT/US03/24809 (Attorney Docket No. 09140-0025-00).	
		International Search Report issued on October 11, 2004 in PCT/US2004/005531 (Attorney Docket No. 09140-0030-00)	
		Written Opinion issued on October 11, 2004 in PCT/US2004/005531 (Attorney Docket No. 09140-0030-00)	
		Patent Application No. 10/851,542 for ENERGY CONVERSION AND STORAGE DEVICES BY PHYSICAL VAPOR DEPOSITION OF TITANIUM AND TITANIUM OXIDES AND SUB-OXIDES filed on May 20, 2004. (Attorney Docket No. 09140-0033-00)	
		Patent Application No. 10/850,968 for TRANSPARENT CONDUCTIVE OXIDES FROM A METALLIC TARGET filed on May 20, 2004. (Attorney Docket No. 09140-0034-00)	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 March 2004 (11.03.2004)

PCT

(10) International Publication Number
WO 2004/021532 A1

(51) International Patent Classification[7]: H01S 3/16, 3/063, 3/0933

(21) International Application Number: PCT/US2003/024809

(22) International Filing Date: 27 August 2003 (27.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/406,451 27 August 2002 (27.08.2002) US

(71) Applicant *(for all designated States except US)*: **SYMMORPHIX, INC.** [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **DAWES, David** [US/US]; 5861 Castleknock Road, Dublin,OH 43016, (US).

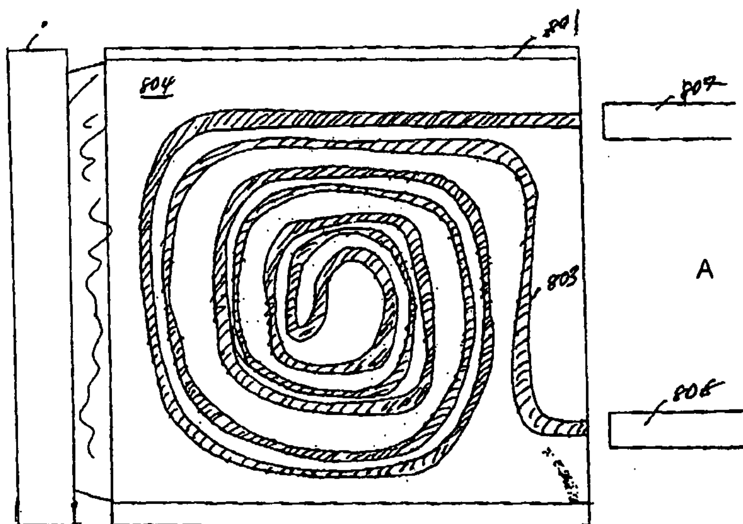
(74) Agent: **GARRETT, Arthur, S.**; Finnegan, Henderson, Farabow, Garrett & Dunner L.L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

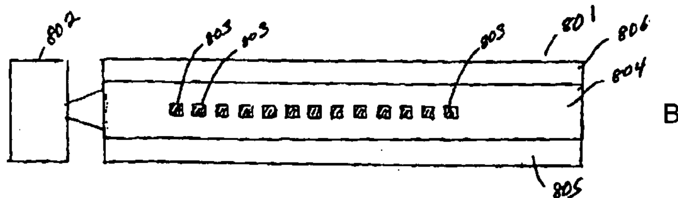
(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,

[Continued on next page]

(54) Title: OPTICALLY COUPLING INTO HIGHLY UNIFORM WAVEGUIDES



(57) Abstract: In accordance with the present invention, one or more laser diodes (802) are efficiently coupled into a waveguide amplifier (801) in order to provide either an efficient amplifier or a laser. Light from one or more laser diodes (802) is efficiently coupled into one or more waveguides (803) through the effects in the refractive index between the core material of the waveguide and the cladding material (804) around the waveguide. Both the core material (803) and the cladding material (804) can be deposited with a high degree of uniformity and control in order to obtain the coupling.



WO 2004/021532 A1

BEST AVAILABLE COPY

WO 2004/021532 A1

SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

OPTICALLY COUPLING INTO HIGHLY UNIFORM WAVEGUIDES

Background

1. Technical Area

[0001] The present invention relates to coupling of pump light into an optical amplifier or a laser and, in particular, to coupling from a multimode laser diode in order to optically pump an optical amplifier or laser.

2. Discussion of Related Art

[0002] Use of directed energy beams, such as those produced by amplifiers or lasers, are diverse and include applications in a wide range of fields, including biotechnology, medicine, semiconductor processing, manufacturing, image recording and defense. In biotechnology, directed energy beams are used, for example, in flow cytometry, DNA sequencing, confocal microscopy, and hematology. Medical applications include use in ophthalmology, non-invasive surgery, and photodynamic therapy. In the semiconductor industry, applications include wafer inspection, rapid thermal processing, and scribing or marking. Image recording applications include, for example, high-speed printing, photo-processing, film subtitling and holography. Industrial applications include, for example, rapid prototyping, materials processing and scribing or marking. Additionally, military applications include range finding, target designation, lidar, and chemical or biological threat detection. The graphics and printing industry, one of the largest businesses in the world, has a need for inexpensive laser systems for use in applications such as thermal graphics. Such applications require a highly reliable, low noise laser or optical amplifier at a low cost.

[0003] Typically, applications for directed energy beams require a laser or optical amplifier. An optical amplifier differs from a laser by the absence of a laser cavity. Both devices typically require an active optical material, for example rare-earth doped YAG, ruby (Al_2O_3:Cr), or other material, which can be optically "pumped," such that energy can be stored in the excited states of the active atoms or molecules by an optical pump source. Amplification of input optical radiation or stimulated emission for lasing then occurs when the same optical energy stored in

the excited states is coupled to the incident optical beam.

[0004] **Figure 1A** shows an example of a side-pumped laser 100. Laser material 101 is positioned in a laser cavity defined by mirrors 102 and 103 and is pumped by diode array 104. Diode array 104 includes a series of laser diodes 105-1 through 105-N positioned to illuminate all or most of laser material 101. There are a variety of choices for laser diodes and laser diode arrays available to pump Nd or Yb doped YAG, for example. In most applications, Nd:YAG is pumped at about 808 nm and Yb:YAG is pumped at about 940 nm. Choices for diode array 104 include 10-40W arrays, 40-50W single bars, and 240-600W stacked bars, for example. Arrays can also be formed from readily available 1-2W single laser diodes.

[0005] **Figure 1B** illustrates the optical density in a cross section of laser material 101 in side-pumped laser 100 of **Figure 1A**. As is shown in **Figure 1B**, the optical density is greatest in the center of laser material 101 where the laser beam is located. However, much of the pump energy is dissipated in areas of laser material 101 that are not actively involved in the lasing process. Therefore, side pumping techniques are inherently inefficient.

[0006] As is illustrated in **Figure 1A**, the laser beam is directed between mirrors 102 and 103, where a percentage of the beam is transmitted through mirror 103. **Figure 2** illustrates the shape of a laser beam in a laser cavity such as in laser 100. The closer the laser beam is to its diffraction limit in laser material 101, the greater the depth of field and the smaller the diameter of beam handling optics (for example mirrors 102 and 103) required to transmit the beam. The ratio of the divergence of the laser beam to that of a theoretically diffraction limited beam of the same waist size in the TEM_{00} mode is usually given as $M^2=(\Theta/\theta)$, where Θ is the divergence angle of the laser beam and θ is the divergence angle of the theoretical laser beam. The angular size of the laser beam in the far field will be M^2 times the size calculated for a perfect Gaussian beam, i.e. $\Theta=M^2(2\lambda/W_0)$ for a beam waist diameter of $2W_0$.

[0007] **Figure 1C** illustrates an end-pumping arrangement for pumping laser material 101. In the arrangement shown in **Figure 1C**, laser material 101 is again placed in a laser cavity formed by mirrors 102 and 103. The laser optical energy transmitted through mirror 103 is reflected by a dichroic beam splitter 114 to form the beam. Optical energy from pump source 116 is incident on lens 115 and passes through dichroic beam splitter 114 and mirror 103 to focus in a nearly diffraction limited region of laser material 101. The beam from pump source 116 is reduced to a size and shape that resembles the shape of the laser beam shown in **Figure 2**

in active material 101. Additionally, a second pump source 110 can be focused by lens 113 through mirror 102 and into laser material 101. In some embodiments, additional optical energy can be coupled into laser material 101 from pump source 111 using a polarizing beam splitting cube 112, which transmits light from pump source 110 while reflecting light from pump source 111.

[0008] A cross section of laser material 101 illustrating optical power concentration is shown in **Figure 1D**. As can be seen in **Figure 1D,** nearly all of the pump power, as well as the laser beam, is focused in the active region of laser material 101, where the laser beam produced by laser 117 is produced.

[0009] As is pointed out in U.S. Patent 4,710,940 to D. L. Sipes, Jr, issued on December 1, 1987, to a first approximation, and not being limited by theory, the higher the pump power density the more efficient is the use of pump power. This concept is illustrated in the graphs shown in **Figures 1E and 1F**. **Figure 1E** shows the photon conversion efficiency (i.e., the number of pump photons versus the number of output laser light photons) with increasing mirror reflectivity at various input optical power densities. Higher mirror reflectivity increases the optical power density within the laser cavity. At higher pump power densities, higher efficiencies result. **Figure 1F** shows photon conversion efficiencies as a function of pump power for various spot sizes, which shows the same trend of higher efficiency with optical density as does the graph shown in **Figure 1E**. Spot size refers to the diameter of the optical pump in the optically active laser material.

[0010] Table I shows typical power usage and lifetime characteristics for a side pumped laser 100 as shown in **Figure 1A**, an end-pumped laser 117 as is shown in **Figure 1C,** and a lamp pumped laser. As expected, the diode end-pumped laser 117 has the greater efficiency. However, end-pumped laser systems have more optical components and therefore are difficult to align.

[0011] Typically, the optical beam from a laser diode outputs is highly assymmetric. Therefore, light from the diodes is difficult to couple into the active material, e.g. laser material 101, of an optical amplifier or a laser. However, as shown in Table I, the lifetimes, efficiency, and expense of various laser diode configurations make them very attractive as pump sources for optically active devices.

Table I

	Lamp Pumped	Diode End-Pumped	Diode Side-Pumped
Power to Pump Source	5000W	2.5W	50W
Power to Cooling System	500W	2.5 W	50W
Power from Pump Source	3500W	1.25W	20W
Single-Mode Power from Laser	10W	0.8W	10W
Wall-Plug Efficiency	0.2%	16%	10%
Cooling	Water	Free Air	Forced Air
Power Consumed/Output kW-hr	500 kW-hr	6.5 kW-hr	10 kW-hr
Cost of Light Source	$200	$400	$1000
Lifetime of Light Source	200 hrs	20,000 hrs	10,000 hrs

[0012] Multimode laser diodes are highly desirable optical pump sources as they are inexpensive to manufacture and are capable of producing much higher power levels than single mode lasers. Multimode lasers are more reliable than single-mode lasers as they have lower output power densities reducing the risk of catastrophic facet damage, the primary cause of laser diode failure. However the light emitted by a multimode laser diode is very asymmetric. Typically, the laser diode emitting aperture has dimensions on the order of 1μm x 100μm. It is very difficult and costly to collect and couple light emitted by a multimode laser diode into the end facet of a single-mode optical waveguide or fiber.

[0013] Most conventional waveguide amplifiers and lasers include one or more waveguide cores doped with active elements, such as Er, Yb, Nd and Tm, and are designed such that the waveguide can support coaxially propagating single-mode output and pump light. The output power of a single-mode, single laser pumped amplifier or laser is often limited to about 20dBm (100mW) by the power levels of available single-mode pump lasers. Single-mode pump lasers require more precision manufacturing tolerances and are consequently more expensive to produce than multimode lasers. As a result complex and costly schemes are required to pump arrays of waveguide optical amplifiers and lasers. Pump light has to be distributed to each amplifier channel or laser element, requiring combinations of splitters, combiners, taps, monitors

and associated control electronics to effectively manage the distribution. Polarization sensitivity of waveguide elements further complicates the distribution process.

[0014] Therefore, there is a need for optical laser devices capable of efficiently coupling light from a laser diode into the active region of a laser cavity that is cost effective and reliable, and that produces high optical output power.

Summary

[0015] In accordance with the present invention, an optical waveguide device that couples light from at least one laser diode into a high refractive index contrast slab waveguide is presented. In some embodiments, the high refractive index contrast slab waveguide includes a light duct in a horizontal plane in order to receive light from the at least one laser diode. In some embodiments, the high refractive index contrast slab waveguide includes a high refractive index active waveguide and an intermediate refractive index passive cladding.

[0016] In some embodiments, the high refractive index contrast slab waveguide is folded in a horizontal axis. In some embodiments, the intermediate passive cladding is thick enough in the vertical axis to capture a substantial amount of light from the at least one laser diode in the vertical direction. In some embodiments, light transmitted from the optical waveguide device is efficiently coupled into single mode optical fibers by mode size converters.

[0017] These and other aspects of the present invention are further described in the following figures.

Short Description of the Figures

[0018] **Figures 1A and 1B** illustrate a side-pumped solid-state laser.

[0019] **Figures 1C and 1D** illustrate an end-pumped solid-state laser.

[0020] **Figures 1E and 1F** show graphs illustrating higher pump efficiency with higher optical densities.

[0021] **Figure 2** illustrates the characteristics of a typical laser beam in a laser cavity.

[0022] **Figures 3A and 3B** illustrate integration of photodetectors and laser diodes with planar waveguides.

[0023] **Figure 4** illustrates a butt-coupling technique for optically coupling between a laser diode and a waveguide.

[0024] **Figures 5A, 5B and 5C** illustrate integrated coupling chips for coupling optical energy from a single mode laser diode chip.

[0025] **Figures 6A and 6B** illustrate a coupling chip for coupling optical energy from a multi-mode laser diode array to a multi-mode optical fiber in accordance with the present invention.

[0026] **Figures 7A and 7B** illustrate a coupling chip for coupling optical energy from a multi-mode laser diode array to a single mode optical fiber in accordance with the present invention.

[0027] **Figures 8A and 8B** illustrate an embodiment of an amplifier chip according to the present invention.

[0028] **Figure 9** illustrates the optical materials utilized in waveguides according to the present invention.

[0029] **Figures 10A, 10B, and 10C** illustrate an efficient mode size conversion for vertical

pumping of an amplifier core.

[0030] **Figure 11** illustrates a monolithic array beam concentrator chip according to the present invention.

[0031] **Figures 12A and 12B** illustrate the mode images for two example waveguides according to the present invention.

[0032] **Figure 13** illustrates a Vertical Cavity Surface Emitting Laser (VCSEL) pumped microchip laser according to the present invention.

Detailed Description

[0033] Lasers and other light sources have great utility when able to produce high optical power densities The speed and effectiveness of the interaction of laser power or energy with materials is in direct proportion to the brightness and intensity of the power or energy that the laser can deliver to the material. The highest brightness or intensity of a laser output beam is obtained when the beam is confined to the fundamental, lowest order transverse electromagnetic mode (TEM_{00}). Therefore, single transverse mode is the highest brightness form of a laser's output, which is the laser's most desirable property.

[0034] In accordance with some embodiments of the present invention, a high refractive refractive index contrast multimode slab waveguide of an appropriate design to collect and contain a high proportion of the light emitted by a single or multi-element multi-mode pump laser diode and efficiently couple that light into an assembly of actively doped single-mode waveguides embedded within the slab is presented. The light from the pump source, then, is efficiently coupled into one or more active regions through the effects of the differences in refractive index between the slab material of the waveguide and the cladding material around the slab. Both the slab material and the cladding material can be deposited with a high degree of uniformity and control in order to obtain the coupling. Further, the embedded active core material of the waveguide can also be manufactured with a high degree of uniformity and control.

[0035] In some embodiments of the invention, long, single-mode waveguides are folded many times to accommodate lengths greater than the dimensions of the pumped, encapsulating

multimode slab waveguide. The single-mode waveguide cores can be folded in such a manner as to optimize the effective absorption cross-section they present to the guided multimode pump light flux while minimizing losses due to bending experienced by propagating single-mode signal light. The efficiency of absorption of pump light from the multimode laser diodes by single-mode actively doped waveguide cores is a function of the ratio of the effective cross-section areas of the single-mode and multimode waveguides.

[0036] In some embodiments of the invention, the multimode slab waveguide itself is pumped. This effect can result in a slap light source.

[0037] In some embodiments, the dimension of the multimode slab waveguide enables conservation of high power densities of the light emitted by the pump laser diode elements, while not increasing the difficultly and reducing the effectiveness of direct coupling between the laser diodes and the edge facet of the slab waveguide. High pump power densities are particularly important for three-level active systems where natural ground state absorption must first be bleached out before gain can be achieved.

[0038] In some embodiments single-mode light emitted by the laser diode in its fast axis direction (i.e., the direction of larger laser beam divergence) is converted to multiple-mode light immediately after the light enters a slab waveguide, thereby limiting the return path for pump energy to the pump laser source. Such an arrangement increases the pumping efficiency because more light is available for pumping.

[0039] Lasing and optical amplification processes are processes of energy conversion. Energy is pumped into exciting active elements in the active material, where the energy is stored, from any energy source, commonly optical, which is capable of exciting the active elements. Energy stored in the excited active elements, then, is released when the excited active element is induced by a signal, such as when the active element is perturbed by presence of another photon, into releasing the energy in the form of an optical photon. For example, energy from the excited states of a laser material is released in a highly coherent form by stimulated emission. The efficiency of the conversion process is a key factor in determining the cost-effectiveness of a particular laser or optical amplification or conversion process.

[0040] Planar waveguide forms of optical amplifiers and lasers are desirable as they are very compact compared to other forms of optical amplifiers and lasers. In addition, a planar

waveguide form potentially allows the integration of diverse optical and electronic functions on, for example, silicon wafers which can be manufactured in high volumes and at low cost with processes commonly used in the semiconductor-industry. In addition to waveguides, slab emitters are desirable as efficient light sources.

[0041] **Figure 3A**, for example, illustrates integration of an optical waveguide 301 with a photodetector (PD) 302. Photodetector 302 is formed on semiconducting layer 305. An optical layer 303 is formed over photodiode 302 and waveguide 301 is formed on optical layer 303. Light traveling through waveguide 301 can be coupled onto photodetector 302 at coupler 306.

[0042] **Figure 3B** illustrates integration of pump laser diodes 310 with an active material waveguide 311. As shown in **Figure 3B**, laser waveguide 311 is formed on an optical layer 313. Optical layer 313 is formed over laser diodes 310, which are formed on semiconducting layer 312. In some embodiments, laser diodes 310 can be formed to the side of optical waveguide 311, over optical waveguide 311, or in any other orientation with respect to optical waveguide 311 that allows pumping of the active dopant ions of optical waveguide 311.

[0043] **Figure 4** illustrates coupling of a laser diode chip 410 with a high refractive index contrast (Δn) waveguide 411. The method of coupling illustrated in **Figure 4** is referred to as "butt coupling," where laser diode 410 is a single-mode semiconductor laser diode output facet positioned to within about 5 μm of high Δn rectangular waveguide 411 in order to correct for mode astigmatism, thereby reducing coupling loss. In some embodiments, about a 50% coupling can be achieved with this method utilizing uncoated facets. Unfortunately, customer demand is for greater than 80-85% coupling efficiency for laser diodes with complex, non-gaussian mode output profiles. Therefore, conventional butt-coupling techniques are not meeting customer demand.

[0044] **Figure 5A** illustrates a laser coupling chip 501 that couples light from a laser diode 506 to an optical fiber 507. Coupling chip 501 includes a waveguide 502 with an integrated photodiode 503 to allow for down-stream power monitoring. In some embodiments, photodiode 503 may couple about 0.02 dB to about 0.05 dB of the optical power in waveguide 502 to provide optical coupling. A dual-core mode size converter 504 can be formed in coupling chip 501 to optimize for efficient optical coupling to optical fiber 507. Dual-core mode size converter 504 can couple light to optical fiber with a coupling loss of about 0.25 dB. The resulting total loss of less than 1 dB in laser coupling chip 501 results in a greater than 80% coupling efficiency

between laser diode 506 and optical fiber 507. However, there remains the problem that the coupling efficiency between laser diode 506 and coupling chip 501 is less than 80%.

[0045] In some embodiments, coupling chip 501 can be formed on a millimeter-scale chip sized to fit a standard 14-pin butterfly package. Further, in order to achieve optimum coupling efficiencies, the slow-axis and fast-axis alignment between laser diode 506 and coupling chip 501 requires sub-micron positioning precision.

[0046] **Figure 5B** shows a single mode laser diode array coupler chip 508. Light from laser diode array 520 is coupled into waveguides 521, 522, 523, and 524. Waveguides 521, 522, 523 and 524 are each integrated with a photodetector 525, 526, 527, and 528, respectively, as is discussed above with regard to **Figure 5A**. Further, mode size converters 529, 530, 531, and 532 formed in waveguides 521, 522, 523, and 524, respectively, efficiently couple light into optical fibers 533, 534, 535, and 536, respectively. Light from diode array 520, then, is coupled through optical fibers 521, 522, 523, and 524 into optical fibers 533, 534, 535, and 536. **Figure 5C** shows a single mode laser diode array coupler chip 509 similar to diode array coupler chip 508 with a pitch size converter 540, which provides for closer packing of optical fibers 533, 534, 535, and 536.

[0047] Other pumping schemes are described, for example, in U.S. Patent 6,236,793, issued to Lawrence et al. on May 22, 2001; U.S. Patent 4,710,940, issued to Sipes; U.S. Patent 4,785,459 issued to Baer on November 15, 1988; and at Lawrence Livermore National Labs. In a system proposed by Lawrence, et al., the pump light is reflected into the active waveguide core by reflecting the pump beam from a prism. Signal power is then transmitted through the prism into the waveguide core. However, in this configuration alignment of the optics directing the pump power into the waveguide core for efficient pumping needs to be arranged such that the waist of the beam is incident on the waveguide core. This results in a large alignment problem for efficiently coupling the pump power into the waveguide core. The arrangement proposed by Sipes involves an array of laser diodes arranged along the corners of a pumping path, for example a zig-zag pattern, such that pump power from multiple laser diodes are coupled into an active waveguide. The arrangement proposed by Baer includes a side pumped active material block with zig-zagging of the signal bea, through the active material for maximum interaction.

[0048] Lawrence Livermore National Labs has proposed a high output Yb:YAG laser system that utilizes a diode bar stack and a lens duct that brings the pump light from the diode bar stack

into a Yb:YAG laser rod. About an 80% coupling efficiency can be achieved in this fashion. However, this solution requires a bulk laser rod and a large lens duct to direct light from the diode bar stack into the laser rod.

[0049] Some embodiments of the present invention can utilize multimode laser diodes in the form of single elements or arrays, to efficiently pump compact, single-mode, planar waveguide optical amplifiers, lasers, and slab devices, which can be integrated with other optical and electronic functions and manufactured inexpensively in high volumes with semiconductor industry techniques. As shown in **Figures 6A and 6B,** the output light from a multimode laser diode 610 is single-mode in the vertical plane (the fast axis) and multimode in the horizontal plane (the slow axis). Therefore, the output beam diverges very rapidly in the vertical axis (the fast axis) but slowly diverges in the horizontal plane (the slow axis).

[0050] **Figures 6A and 6B** illustrate coupling of light from a laser diode array into a planar waveguide in accordance with the present invention. As shown in **Figures 6A and 6B,** the light beam from multimode laser diode array 610 diverges less in the slow axis direction (shown in **Figure 6A**) than it does in the fast axis direction (shown in **Figure 6B**). The output beams from laser diode array 610 diverge more in the vertical axis (shown in **Figure 6B**) than in the horizontal axis (shown in **Figure 6A**). Embodiments of the present invention take advantage of the slow divergence in the horizontal axis to increase the optical density in high refractive index waveguide 612. Coupling chip 611 can include a large lens duct 613 to direct light into high refractive index waveguide 612. The material of waveguide 612 and lens duct 613 can be the same material and can be deposited and patterned on a substrate in the same series of processing steps. Light from waveguide 612 can then be coupled into multimode fiber 614.

[0051] A higher optical power density, then, can be achieved utilizing less expensive multimode laser diode bars, rather than single mode laser diode arrays, and coupling the optical output from multiple ones of the laser diodes in diode array 610 into waveguide 612. Higher coupling efficiency is achieved by utilizing a light duct 613 formed with waveguide 612. Further, the horizontal alignment between diode array 610 and coupling chip 611 is not critical, so long as the light beams are directed toward duct 613. As shown in **Figure 6B,** alignment in the vertical axis (i.e., the fast axis) is somewhat critical because of the large divergence of the light output from diode array 610 in that direction.

[0052] The pump light from the laser diode can be constrained within the confines of the

high Δn slab waveguide and therefore no critical alignment exists between the laser diode and the active waveguide, as would be true for conventional pumping configurations as has been discussed above. Further, there is no need to maintain single-mode propagation in the horizontal direction, as alignment tolerance are relaxed in the horizontal plane. In the vertical plane, a single optical mode can be excited to obtain maximum power density by using more precise alignment. When maximize power density is not required, the alignment tolerances in the vertical plane can also be relieved by using a thicker high refractive index contrast slab waveguide and allowing the light to propagate multimode in the vertical direction as well.

[0053] **Figures 7A and 7B** illustrate coupling utilizing a double-clad core. As shown in **Figure 7A,** light from one or more laser diodes 710 of multimode pump diode array 702 is coupled into waveguide 703 of coupling chip 701. Again, a lens duct 704 can be formed with waveguide 703 to direct light from laser diodes 710 in diode array 702 into waveguide 703. In coupling chip 701, light from waveguide 703 can be coupled into single-mode fiber 705.

[0054] **Figure 7B** shows a cross-section of waveguide 703. Waveguide 703 includes a single-mode core 706. Single-mode core 706 can be formed, for example, from rare-earth doped Al_2O_3, Y_2O_3, or TiO_2 to form a high refractive index core. Single-mode core 706 can be surrounded by a multi-mode cladding 707 having a lower refractive index than that of single-mode core 706, which can be formed from an intermediate refractive index contrast material such as Al_2O_3 or Y_2O_3. In some embodiments, the dimensions of multi-mode cladding 707 can capture most or all of the light output from laser diode array 702. Waveguide 703 can be formed on, for example, a silica or aluminasilicate buffer layer 709 deposited on a substrate. A second buffer layer 708 can be formed over waveguide 703.

[0055] In this way, coupling chip 701 can provide efficient conversion of low optical power density light emitted from directly-coupled multimode laser diode bars to high optical power density. Where high-refractive index contrast core 706 is optically active, a laser can be formed by including a laser cavity, which can be formed by depositing mirrors on the ends of chip 701.

[0056] Very high optical-to-optical efficiencies (e.g., greater than 80%) can be achieved in coupling chip 701. For example, a multimode laser diode operating at a wavelength of 920 nm, is efficiently coupled into a single-mode output laser at about 1100 nm utilizing an active waveguide 706 formed from double-clad Yb-doped silica, for example.

[0057] Having efficiently coupled the multimode pump light into a high refractive index slab waveguide which is multimode in the horizontal plane and may or may not be single mode in the vertical plane, a single mode active waveguide located in the high refractive index portion of the slab will be efficiently pumped. Such active areas are shown, for example, in **Figures 8A and 8B**. In some embodiments, the active region of the waveguide can be "folded" or routed through many loops in order to increase the length of active material pumped and thereby increase the amplification in the waveguide.

[0058] An embodiment of a folded active region embedded within the large high refractive index slab is shown in **Figures 8A and 8B**. One skilled in the art will recognize that any appropriate configuration or routing of active area waveguide within the slab can be utilized. For example, zig-zag configurations may also be utilized in addition to the spiral configuration shown in **Figure 8A**. Additionally, linear arrays of active regions may be utilized.

[0059] **Figure 8A** shows the slow axis view (i.e., the horizontal view) and **Figure 8B** shows the fast-axis view (i.e., the vertical cross section) of an active waveguide amplifier or laser chip 801 pumped by a multimode laser diode array in accordance with the present invention. As shown in **Figure 8A,** a single mode high refractive index contrast core 803 is arranged on chip 801. Although a spiral arrangement is shown in **Figure 8A,** any arrangement that provides a long signal path between a single mode input fiber 807 and a single mode output fiber 808 can be implemented. Light output from laser diode array 802 is captured by an intermediate refractive index contrast cladding layer 804 in which the single-mode high refractive index contrast active waveguide 803 is embedded. **Figure 8B** shows a cross section of an area of chip 801 with multiple crossings of single-mode high refractive index contrast active waveguide 803. As an example, active waveguide 803 can be formed from Yb-doped Al_2O_3, Y_2O_3 or TiO_2. Intermediate refractive index contrast cladding 804 can be formed from Al_2O_3 or Y_2O_3. In this arrangement, a high pump-power density can be achieved in multi-mode cladding 804, which results in highly efficient pumping of active waveguide 803.

[0060] Multi-port amplifiers can be obtained by routing multiple folded regions of active waveguide such as waveguide 803 within the high Δn slab 804 of chip 801. For example, multiple active cores may be routed together as shown in **Figure 8A**. A single multimode pump, therefore, can be shared among several single-mode active amplifying waveguides without the need to split the pump light and separately distribute the light to activate the single-mode

amplifying waveguides separately. There is, therefore, no need for pump splitters or multiplexers. Further, the higher area of the active region increases absorption of the pump light, reducing the need for mirrors to rout the pump light through the active regions multiple times.

[0061] **Figure 9** illustrates material depositions that provide high grade, optically transparent, highly uniform slab waveguides with highly controllable Δn values. The production of such waveguides is further discussed in U.S. Application Serial No. 09/903081, "As-Deposited Optical Waveguides with Low Scattering Loss and Methods for Their Manufacture," by Demaray et al, filed on July 10, 2001; U.S. Application Serial No. 10/101863, "Biased Pulse DC Sputtering of Oxide Films, by Zhang et al., filed on March 16, 2002; U.S. Application Serial No. 10/101,341, "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," by Milonopoulou et al., filed on March 16, 2002; and Application Serial No. 09/633307, "Planar Optical Devices and Methods for their Manufacture," by Demaray et al., filed on August 7, 2000, each of which is incorporated by reference herein in its entirety.

[0062] Waveguide materials used to form active core waveguides, passive waveguides, and claddings consistent with embodiments of the present invention can be deposited by biased pulsed DC plasma vapor deposition (PVD), as described in U.S. Application Serial No. 10/101,341 (the '341 application). The physical characteristics of the optical material deposited by biased pulsed DC PVD depends on various process parameters, as discussed in the '341 application. A device, including photodetectors and other electronics, such as those shown in Figures 3A through 8B and discussed above, can be fabricated by depositing one or more active or passive optical layers and patterning the optical layers to form the waveguides and lens ducts as shown. In some applications, several deposition and patterning steps may be applied to form the desired structures.

[0063] As shown in **Figure 9**, which shows active and passive waveguide materials of highly amorphous, defect free films of aluminasilicated deposited by biased pulsed DC PVD. Further, the films have very high optical transparency, for example below 0.3 db/cm loss and, in some deposited films, less than about 0.1 db/cm loss. Therefore, deposition of films utilizing biased pulsed-DC PVD are useful for providing structures for optical coupling devices, optical amplifiers, and optical laser structures for highly efficient coupling of pump sources as has been discussed above.

[0064] In biased pulsed DC PVD, deposition is performed in a vacuum deposition chamber.

A substrate is mounted on a support which also provides an RF bias voltage to the substrate. RF power is supplied to a target formed from material to be deposited as gas is allowed into the chamber. A plasma is excited in the gas and the material is deposited on the substrate. Further, a pulsed DC signal is provided to the target. Further details regarding the deposition process are provided in the '341 application.

[0065] Coupling of light, for example from optical fiber 807 into waveguide 803, through efficient mode size conversion is illustrated in **Figures 10A, 10B, and 10C.** Vertically tapered mode-size conversion is further discussed in U.S. Application Serial No. 10/101492, "Mode Size Converter for a Planar Waveguide," by Tao et al, filed on March 16, 2002, herein incorporated by reference in its entirety. A very smooth vertical taper can efficiently couple light from optical fiber 807 into high refractive index contrast, core waveguide 803 very efficiently. **Figure 10B** shows the mode size of an optical beam at a point where light enters waveguide 803. **Figure 10B** shows a significantly smaller mode size in the region of waveguide 803 after the adiabatic S-taper mode size converter 1001. Mode size converter 1001 can be produced in a biased pulsed-DC PVD process with a shadow mask.

[0066] Table II shows modeling of mode diameter at the output facet of a mode converter for various core/cladding refractive index contrasts Δn. The dimensions in Table II refer to the dimensions of the output facet of the rectangular mode converter.

Table II

Δn	1.0 μm x 1.0 μm	1.5 μm x 1.5 μm	2.0 μm x 2.0 μm	2.5 μm x 2.5 μm
0.43%	38 μm	35 μm	14 μm	6 μm
0.3%		36 μm	20 μm	16 μm
0.2%			32 μm	24 μm

[0067] **Figure 11** illustrates an image concentrator 1101 for adiabatically compressing the diameter of the mode output by a passively Q-switched microchip laser array. Image concentrator 1101 employs a reverse taper 1106, such as that first disclosed in U.S. Application Serial No. 10/101492 to Tao et al. Reverse taper 1106 can be formed vertically and/or horizontally and thereby provides coupling into a smaller mode size. A further embodiment includes a pitch size conversion such as that illustrated in **Figure 5C.** Embodiments of the

invention enable the mode size and pitch size conversion of individually addressable microchip laser array, so as to be tailored to standard print pixel densities for use in direct printing and micromaching applications.

[0068] Image concentrator 1101 can include an addressable array pump bar 1102 which is capable of addressing and exciting individual pixels of a microchip bar 1103. Array pump bar 1102 includes an array of laser diodes which produce light when individually addressed. Microchip bar 1103, which provides amplification as was discussed in **Figures 6-8**. Beam concentrator chip 1104 can include light ducts or vertical tapers in order to collect a substantial amount of light from microchip bar 1103. Further, a vertical reverse taper 1106, as is described in U.S. Application Serial No. 10/101,492, allows for a compressed output mode. As shown in **Figure 11**, the mode of the beam output by beam concentrator chip 1104 is much smaller than the mode of the beam in microchip bar 1103. In some embodiments, a monolithic array beam concentrator chip can convert 50 μm or 90 μm diameter single mode spots from microchip bar 1103 into 20 to 25 μm diameter spots.

[0069] **Figures 12A and 12B** show mode sizes for some weakly-confined mode propagation in waveguides. **Figure 12A** illustrates a 6.2 μm mode diameter at the output facet of a 1.5 μm x 3.5 μm waveguide for 980 nm light with a refractive index contrast Δn between the core and the cladding of about 1%. **Figure 12B** illustrates a 7.6 μm mode diameter at the output facet of a 1.25 μm x 3.5 μm waveguide for 980 nm light with a refractive index contrast of about 1%. As is shown in **Figures 12A and 12B**, the optical energy is concentrated in the center of the facet.

[0070] Table III illustrates facet damage considerations in a image concentrator such as image concentrator 1101 shown in **Figure 11**. Table III illustrates, for representative pixel densities, the mode size required, the distance between modes, and the resulting power density in image concentrator 1101. The value of 14.2 for power density shown for 2400 dpi pixel density exceeds the damage threshold of Quartz.

Table III

Pixel Density (dpi)	Mode Pitch/Mode Size	Power Density at Facet (GWcm^{-2})	Collimation Distance (μm)
600	42	0.9	842
1200	21	3.6	210
2400	11	14.2	53

[0071] **Figure 13** illustrates a vertical cavity surface emitting laser (VCSEL)-pumped microchip 1401 according to the present invention. VCSELs 1401 can be deposited on a GaAs substrate 1402. VCSELs 1401 include a dichroic output facet coating. An active gain medium 1404 can be deposited directly over VCSELs 1403. Active gain medium 1404 can be, for example, Nd, Yb, Er, Tm, Ho, Pr, or Ce doped silica. A saturable absorber 1405 can be deposited over gain medium 1404. Saturable absorber 1405 can be, for example, a Cr4+ or Co2+ doped silica film. A VCSEL pumped microchip 1401 can be fabricated using high volume wafer-scale semiconductor manufacturing techniques. The doped silica used for saturable absorber 1405 and active gain medium 1404, for example, can be deposited by biased pulsed-DC PVD processing techniques.

[0072] The embodiments discussed here are examples only and are not intended to be limiting of the invention. One skilled in the art will recognize multiple variations that are intended to be within the spirit and scope of the present disclosure.

I claim:

1. An optical waveguide device, comprising,

at least one laser diode; and

at least one high refractive index contrast slab waveguide coupled to receive light from the at least one laser diode,

wherein the slab waveguide is deposited by biased pulsed DC plasma vapor deposition.

2. The optical waveguide device of claim 1, wherein the slab waveguide is formed from a highly amorphous film.

3. The optical waveguide device of claim 1, wherein the slab waveguide is highly optically transparent.

4. The optical waveguide device of claim 1, wherein the slab waveguide has a high surface smoothness.

5. The optical waveguide device of claim 1, wherein the high-refractive index contrast slab waveguide includes a lens duct.

6. The optical waveguide device of claim 1, wherein the at least one laser diode comprises a diode array.

7. The optical waveguide device of claim 1, wherein the high refractive index contrast slab waveguide includes a high refractive index active waveguide and an intermediate refractive index passive cladding.

8. The optical waveguide device of claim 7, wherein the high refractive index contrast slab waveguide is folded in the plane of the slab.

9. The optical waveguide device of claim 7, wherein the intermediate passive cladding is thick enough in the vertical axis to capture a substantial amount of light emitted from the at least one laser diode.

10. The optical waveguide device of claim 1, wherein the high refractive index contrast slab waveguide includes a mode-size converter.

11. The optical waveguide device of claim 1, wherein the at least one laser diode is a vertical cavity surface emitting laser and the high refractive index contrast waveguide is deposited over the vertical cavity surface emitting laser.

12. The optical waveguide device of claim 1, wherein the high refractive index contrast slab waveguide includes an array of waveguides.

13. The optical waveguide device of claim 11, wherein a mode size of an optical beam transmitted by the high refractive index contrast slab waveguide is less than a mode size of an incident optical beam.

14. The optical waveguide device of claim 12, wherein the high refractive index contrast slab waveguide includes at least one vertical reverse taper.

15. A method of coupling pump light into a gain medium, comprising:

depositing the gain medium by a biased pulsed-DC plasma vapor deposition process;

forming a high refractive index contrast waveguide from the gain medium; and

directing pump light into the high refractive index contrast waveguide.

16. The method of claim 15, wherein forming a high refractive index contrast waveguide includes patterning the gain medium.

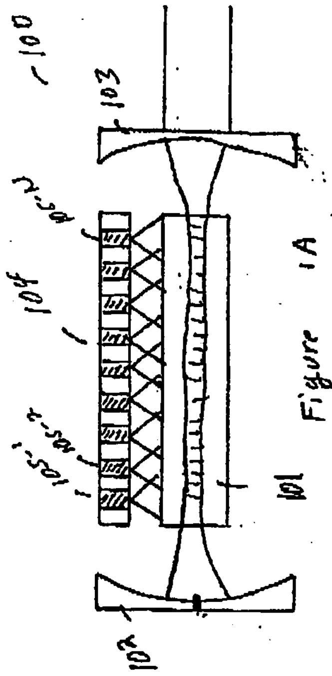
17. The method of claim 16, further including depositing an intermediate refractive index contrast material over the high refractive index contrast waveguide.

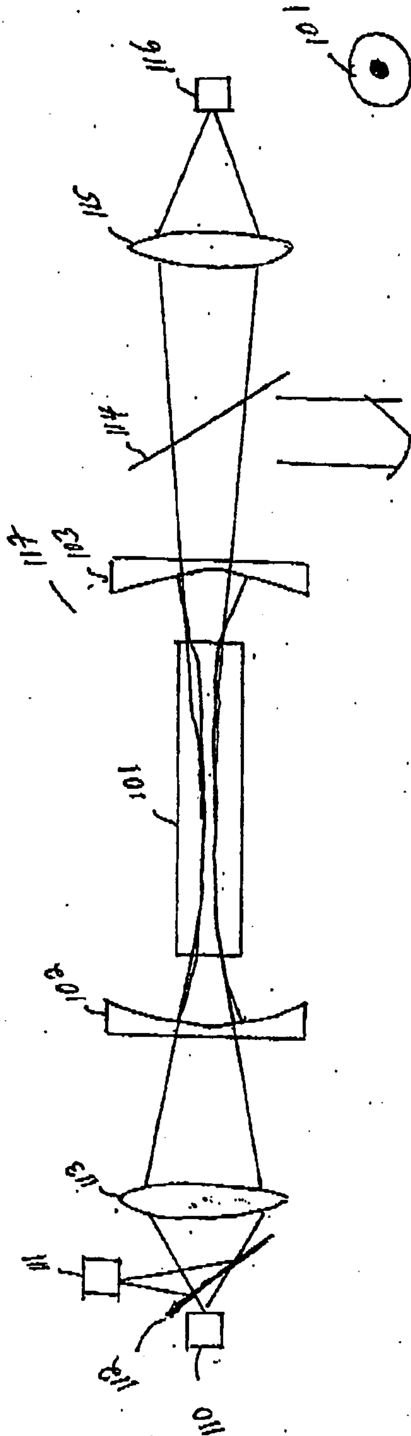
18. The method of claim 16, wherein patterning the gain medium includes forming a lens duct.

19. The method of claim 16, wherein patterning the gain medium includes forming a horizontal taper.

20. The method of claim 16, wherein depositing the gain medium includes forming a vertical taper.

101
Figure 1B


100
103
104
101
102
Figure 1A


116
115
114
117
103
101
102
113
111
112
110
Figure 1C

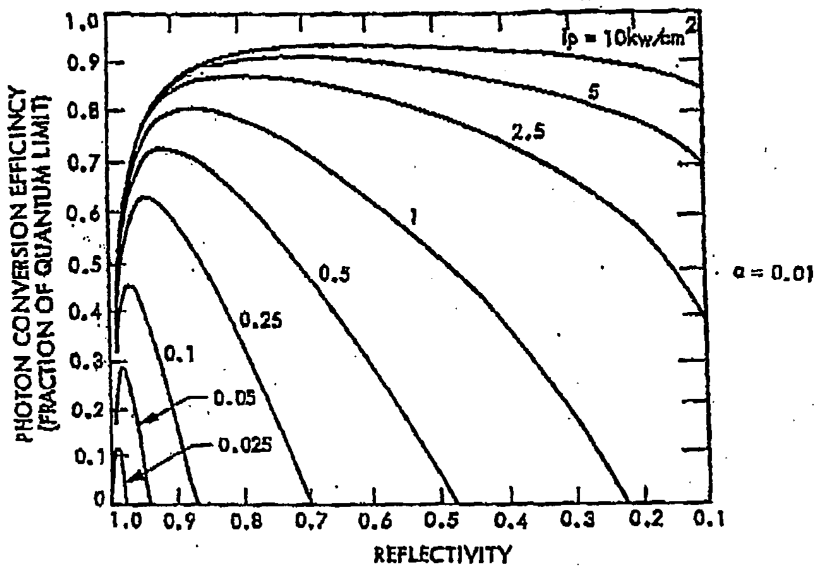


Figure 1E

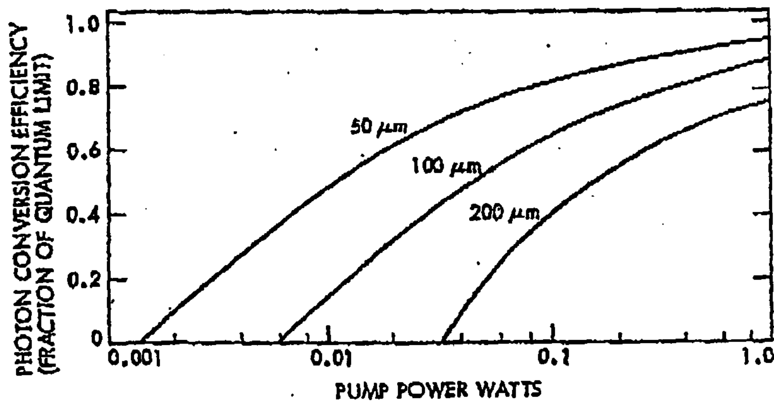


Figure 1F

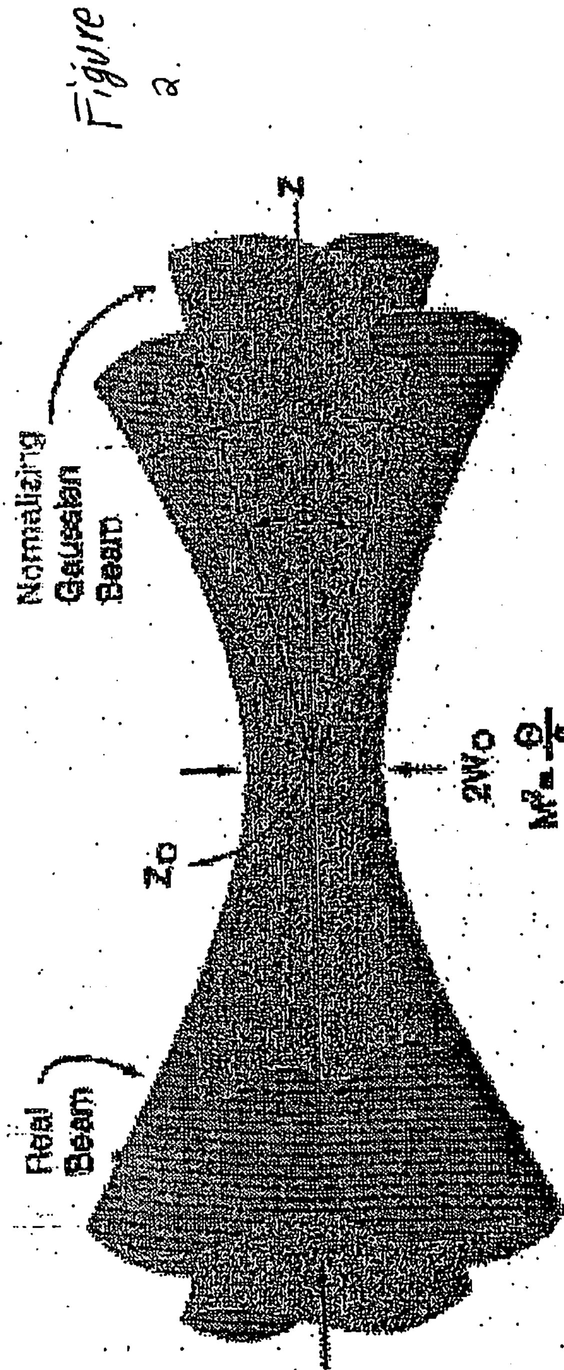


Figure 2.
Z
Normalizing Gaussian Beam
Zo
2Wo
Real Beam

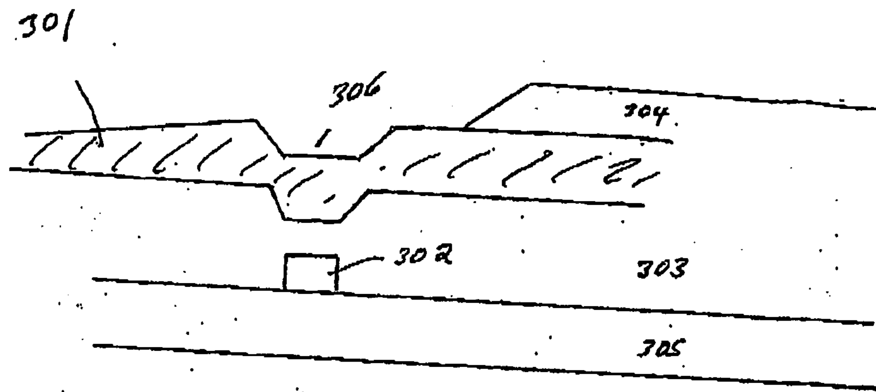


Figure 3A

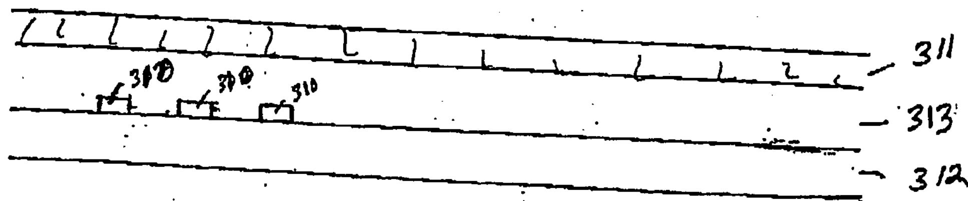


Figure 3B

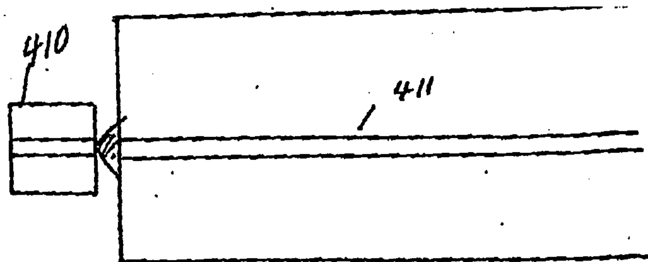


Figure 4

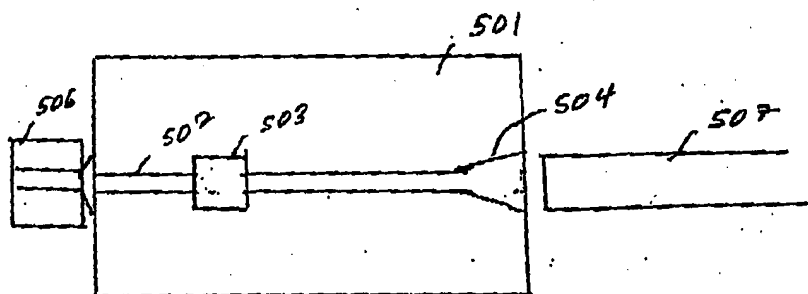


Figure 5A

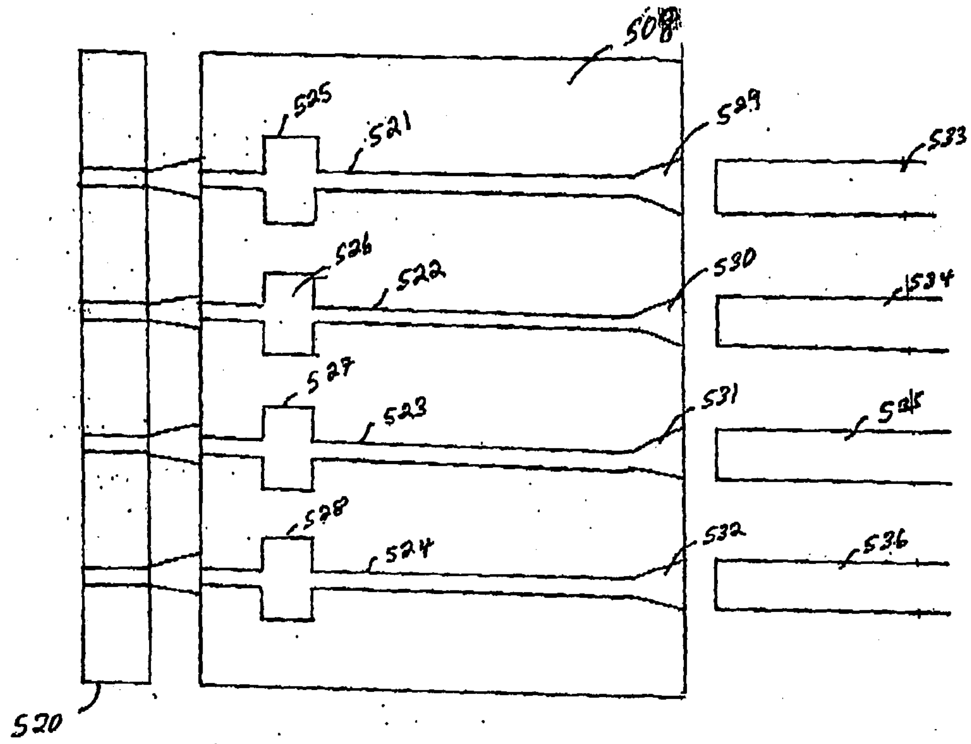


Figure 5.B

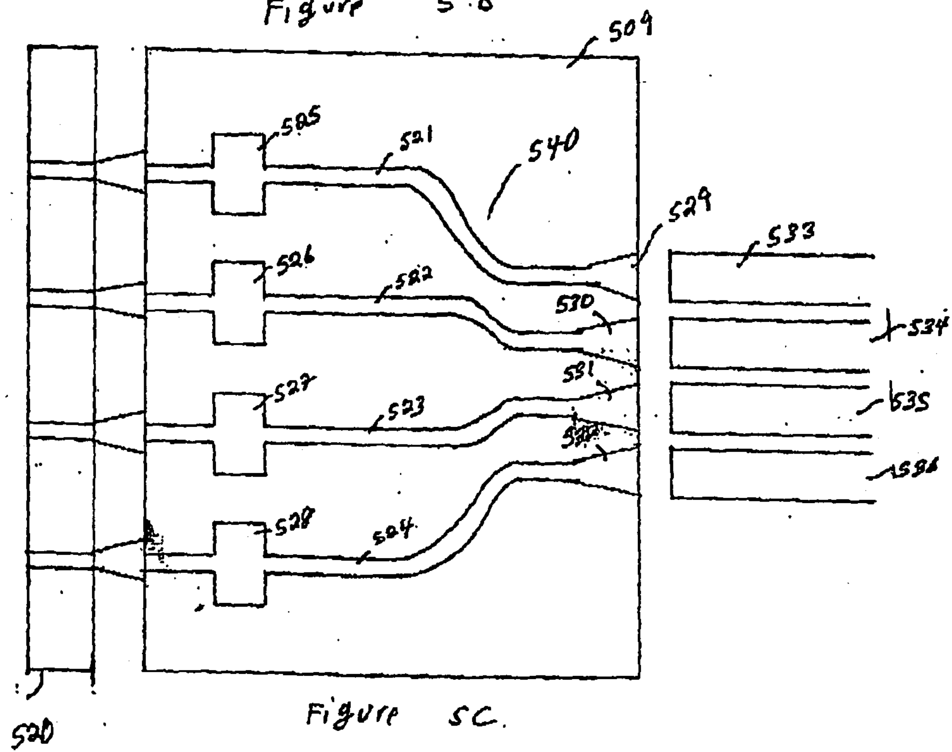


Figure 5C.

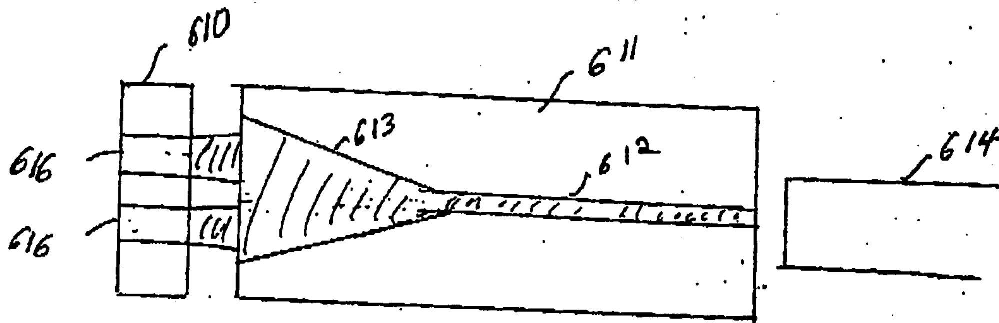


Figure 6A

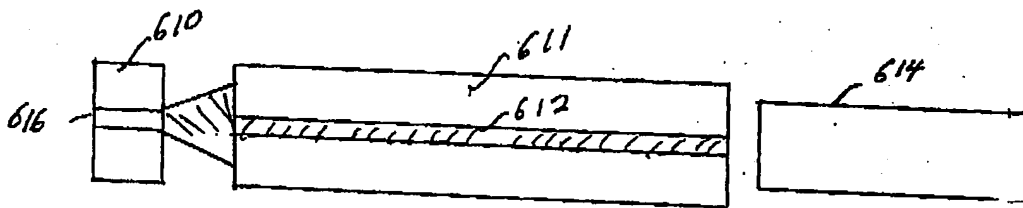


Figure 6B

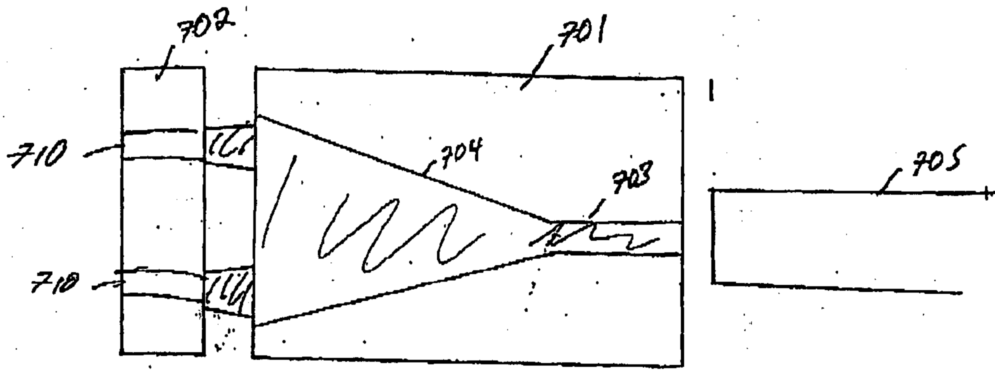


Figure 7A

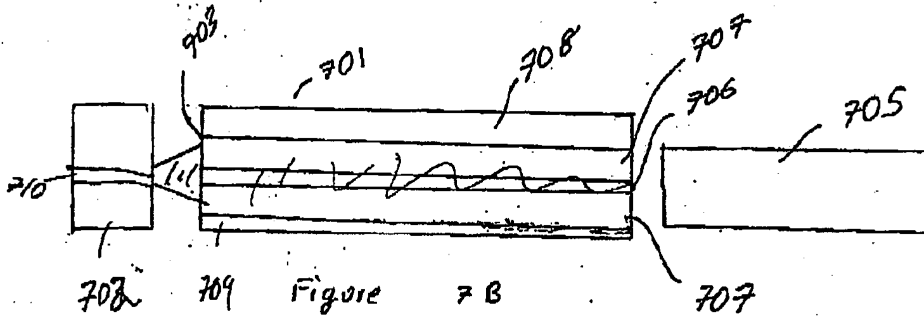


Figure 7 B

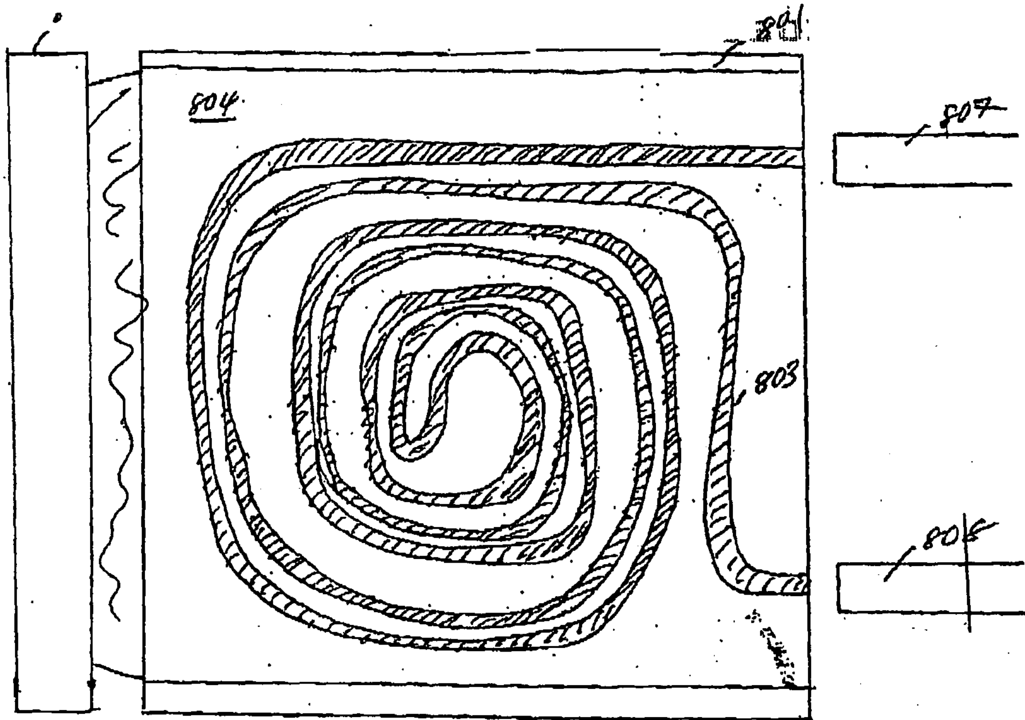


Figure 8A

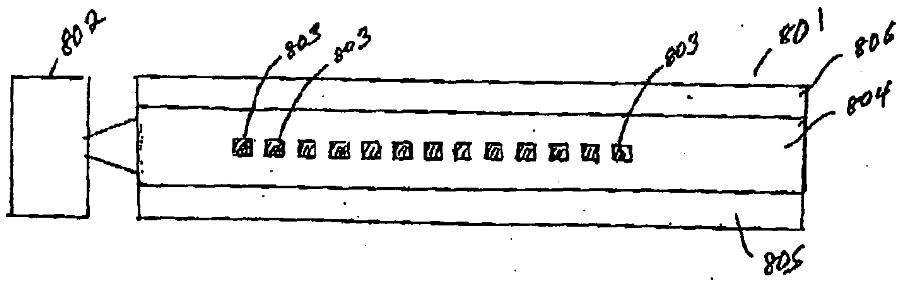
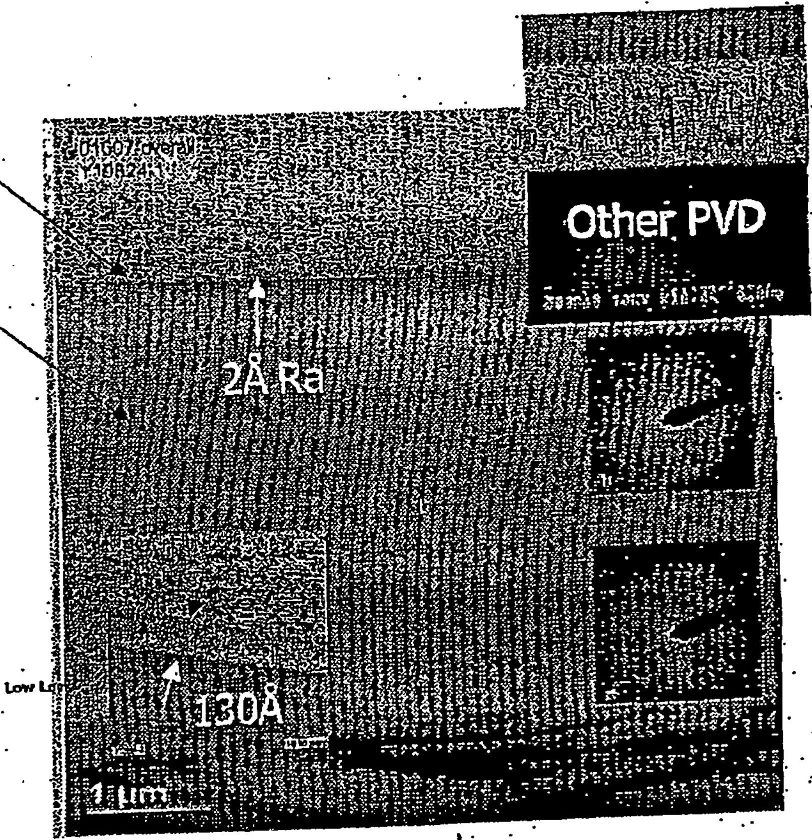
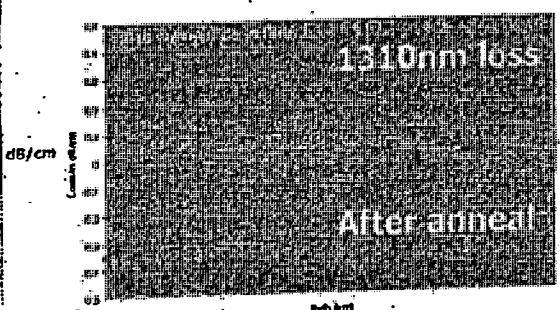


Figure 8B

- Smooth surface indicates defect free film
- Diffraction shows amorphous film through thickness
- High optical transparency





Film transparency below 0.1dB detection sensitivity

Figure 9

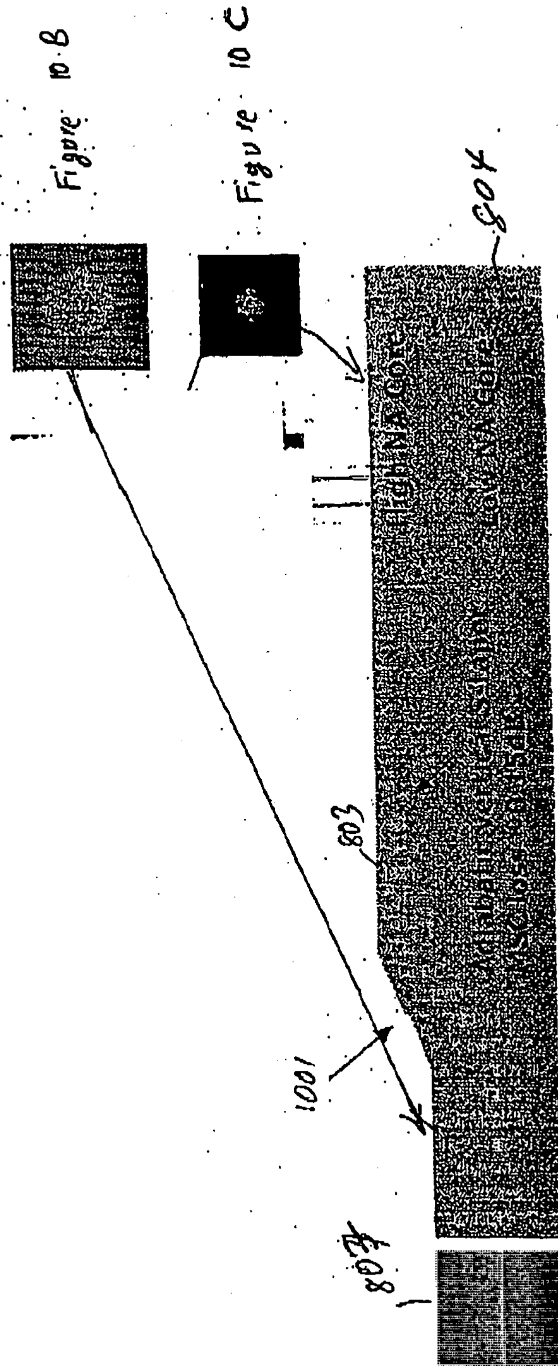
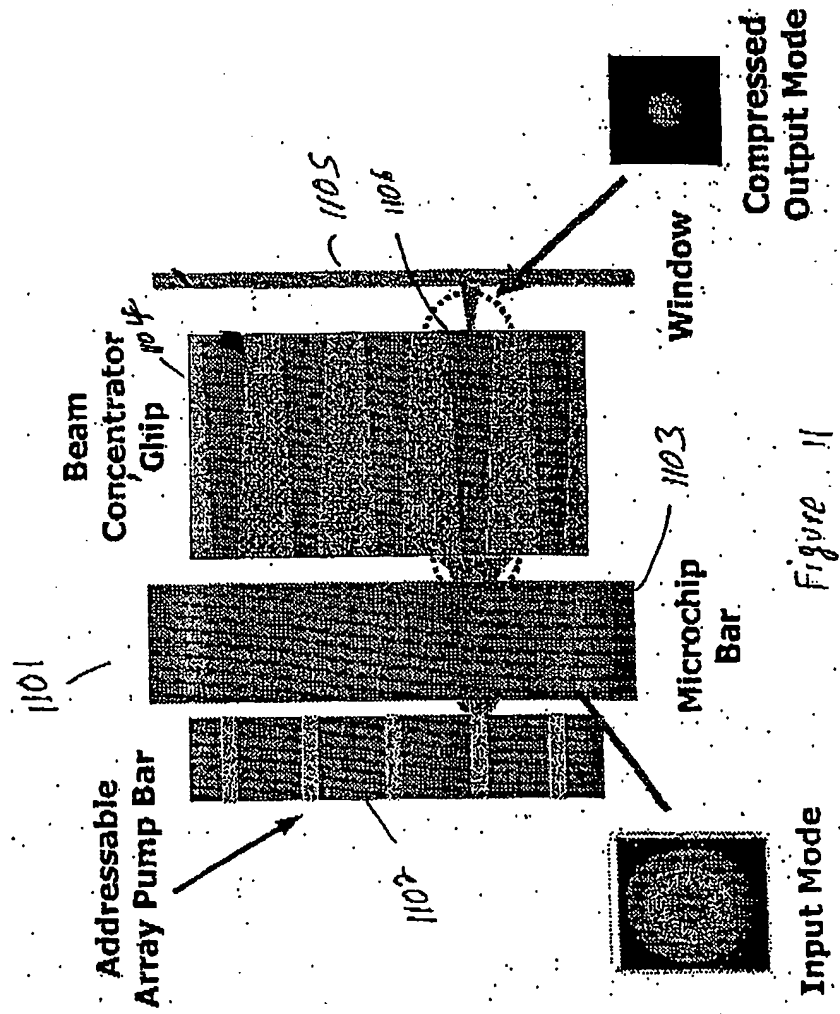


Figure 10A


Addressable
Array Pump Bar
1101
1102
Beam
Concentrator
Chip
1104
1105
1106
Window
Compressed
Output Mode
1103
Microchip
Bar
Input Mode
Figure 11

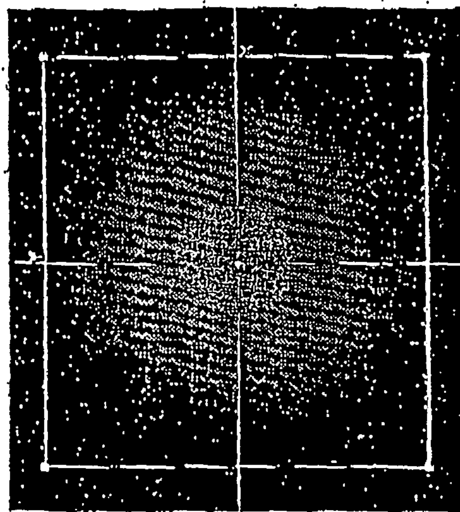


Figure 12B

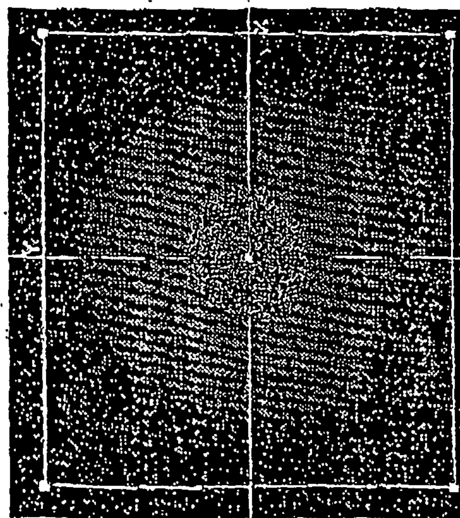


Figure 12A

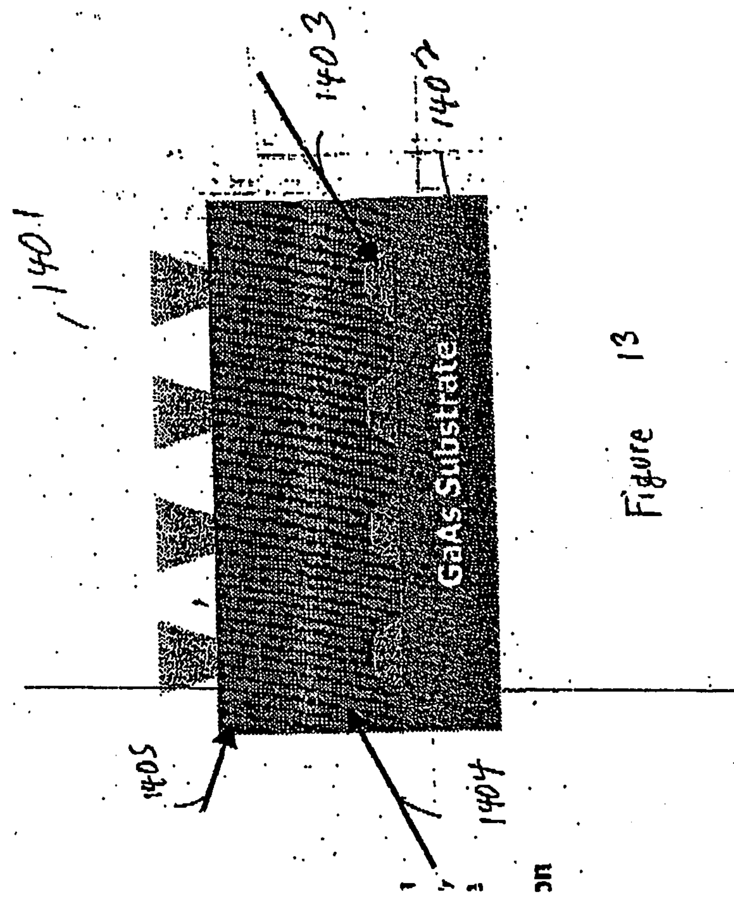


Figure 13

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/24809

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01S3/16 H01S3/063 H01S3/0933

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01S

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 12932 A (SYMMORPHIX INC) 14 February 2002 (2002-02-14) cited in the application page 5, line 22-26; figure 5	1-20
A	JONSSON L B ET AL: "Frequency response in pulsed DC reactive sputtering processes" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 365, no. 1, April 2000 (2000-04), pages 43-48, XP004195125 ISSN: 0040-6090 paragraph '0001!	1,15
A	US 5 689 522 A (BEACH RAYMOND J) 18 November 1997 (1997-11-18) column 3, line 41-52	5,6,18

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2003	12/12/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Jobst, B

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/24809

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 052 397 A (JEON HEONSU ET AL) 18 April 2000 (2000-04-18) column 2, line 66 -column 3, line 4 ---	10,11, 13,14, 19,20
A	BEACH R J: "Theory and optimization of lens ducts" APPLIED OPTICS, 20 APRIL 1996, OPT. SOC. AMERICA, USA, vol. 35, no. 12, pages 2005-2015, XP002262395 ISSN: 0003-6935 the whole document ---	5,6,18
P,X	US 2003/063883 A1 (DEMARAY RICHARD E ET AL) 3 April 2003 (2003-04-03) cited in the application paragraphs '0044!,'0045! -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/24809

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0212932	A	14-02-2002	US	2002033330 A1	21-03-2002
			AU	7700201 A	18-02-2002
			TW	520450 B	11-02-2003
			WO	0212932 A2	14-02-2002
			US	2003127319 A1	10-07-2003
US 5689522	A	18-11-1997	NONE		
US 6052397	A	18-04-2000	US	6174748 B1	16-01-2001
US 2003063883	A1	03-04-2003	NONE		

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 September 2004 (10.09.2004)

PCT

(10) International Publication Number
WO 2004/077519 A2

(51) International Patent Classification[7]: H01L

(21) International Application Number: PCT/US2004/005531

(22) International Filing Date: 26 February 2004 (26.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/451,178 27 February 2003 (27.02.2003) US
60/506,128 25 September 2003 (25.09.2003) US

(71) Applicants and
(72) Inventors: **NARASIMHAN, Mukundan** [IN/US]; 293 Bluefield Drive, San Jose, CA 91536 (US). **DEMARAY, Richard, E.** [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). **BROOKS, Peter** [US/US]; 611 Glen Alto Drive, Los Altos, CA 94024 (US).

(74) Agent: **GARRETT, Arthur, S.**; Finnegan, Henderson, Farabow Garrett & Dunner, L. L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIELECTRIC BARRIER LAYER FILMS

(57) Abstract: In accordance with the present invention, a dielectric barrier layer is presented. A barrier layer according to the present invention includes a densified amorphous dielectric layer deposited on a substrate by pulsed-DC, substrate biased physical vapor deposition, wherein the densified amorphous dielectric layer is a barrier layer. A method of forming a barrier layer according to the present inventions includes providing a substrate and depositing a highly densified, amorphous, dielectric material over the substrate in a pulsed-dc, biased, wide target physical vapor deposition process. Further, the process can include performing a soft-metal breath treatment on the substrate. Such barrier layers can be utilized as electrical layers, optical layers, immunological layers, or tribological layers.

WO 2004/077519 A2

BEST AVAILABLE COPY

TITLE OF THE INVENTION

DIELECTRIC BARRIER LAYER FILMS

RELATED APPLICATIONS

[001] The present application claims priority to U.S. Provisional Application 60/451,178, "Dielectric Barrier Film," filed on February 27, 2003, by Richard E. Demaray, Mukundan Narasimhan, and Hongmei Zhang, herein incorporated by reference in its entirety, and to U.S. Provisional Application 60/506,128, "Indium Nucleation Layer," filed on September 25, 2003, by Mukundan Narasimhan and Peter Brooks, herein incorporated by reference in its entirety.

BACKGROUND

1. Field of the Invention

[002] The present invention is related to dielectric barrier films and, in particular, dielectric barrier films formed from high-density optical material layers for utilization in optical, electrical, tribological, and bio-implantable devices.

2. Discussion of Related Art

[003] Dielectric barrier layers are becoming increasingly important as protective layers for organic light emitting diodes (OLEDs) and other optical or opto-electronic devices. Typically, dielectric barrier layers are deposited thin films with the appropriate electrical, physical, and optical properties to protect and enhance the operation of other devices. Dielectric barrier layers can be utilized in optical, electrical, or tribological devices. For example, touch screen displays require

optically transparent protective layers to protect against transmission of atmospheric contaminants as well as to protect against physical wear.

[004] Many thin film deposition technologies that may be utilized to form such dielectric layers include some form of ion densification or substrate bias densification. The densification process eliminates the columnar thin film structure that is typical of vacuum deposited chemical vapor (CVD) or physical vapor deposition (PVD) thin films. It is well known that such densification can be achieved by a secondary ion source arranged to "bombard" the film during deposition. *See, e.g.*, W. Essinger "Ion sources for ion beam assisted thin film deposition," Rev. Sci. Instruments (63) 11-5217 (1992). *See, also,* Hrvoje Zorc, et al. Proceedings of the Society of Vacuum Coaters, 41st Annual Technical Conference Proceedings, 243-247, 1998, which discusses the effects of moisture exposure on wavelength shift for electron beam evaporated films (e-beams). In particular, Zorc et al. demonstrated a factor of 15 or so improvement in wavelength shift for electron beam evaporated films (e-beam) as compared to e-beam films deposited with a directed ion beam source after exposure to 30% humidity at 25 °C.

[005] D. E. Morton, et al. demonstrated wide-band dielectric pass filters comprised of alternating layers of SiO_2 and TiO_2 deposited using a "cold cathode ion source" to produce oxygen ions for the purpose of providing "moisture stable stacks of dense optical films of silicon dioxide as the low index material and either titanium dioxide, tantalum pentoxide or niobium pentoxide." D. E. Morton, et al. Proceedings of the Society of Vacuum Coaters, 41st annual Technical Conference, April 18-23, 1998. The results described by Morton, et al., indicated that room temperature

resistance to humidity up to 100% humidity was attained, as measured by the optical performance of single dielectric layers deposited on substrates mounted on a rotating platen. Optical extinction coefficients for the six samples tested in Morton, et al., varied from 0.1 to 1.6 ppt, indicating the presence of significant concentrations of defects or absorption centers in the dielectric layers. Additionally, no film thickness or film thickness uniformity data was reported by Morton, et al., for ion beam energies between 134 and 632 Volts and ion beam current up to 5 amps. Morton, et al., therefore fail to describe a film that would operate as a good barrier layer for optical devices.

[006] Self biased physical vapor deposition, such as ion coating or activated reactive deposition, are well-known means of providing hard wear resistant coatings. However, these coatings are either deposited at several hundred Volts of bias voltage and form penetrating surface treatments with the ion flux penetrating the surface to react with the substrate material, or they are ion assisted for the purpose of decreasing the columnar structure of the film. A "filtered cathodic vacuum arc" (FCVA-reference - http://www.nanofilm-systems.com /eng/fcva_technology.htm) has been used to form a dense film from an ion flux. In this case, ions are created and separated from the neutral vapor flux by a magnetic vector so that only species having a positive charge impinge the substrate. The bias voltage can be preset so that average translational energy ranges from about 50 to several hundred Volts are available. Lower ion energies are not reported due to the problem of extracting and directing a lower energy ion flux with a useful space charge density. Although quite rough due to re-sputtering at the high ion energies, hard protective layers of alumina,

and other materials such as tetrahedral carbon, can be deposited with this process on cutting tools and twist drills with commercial levels of utility. Due to the limitation of the coating species to the ion flux, coating rates are low. The best or hardest carbon films are often deposited with the lowest rate of deposition, e.g., 0.3 nanometers per second on substrates up to 12" in diameter.

[007] Transmission of a ZnO film deposited by FCVA at 600 nm wavelength is increased from about 50% at room temperature to above 80% for single films by increasing the temperature of deposition to above 230 °C, with the best transmission at 600 nm of about 90% at a deposition temperature of 430 °C and a substrate bias voltage not greater than about 50 Volts. This high temperature processing indicates the use of a thermal anneal process for repair of ion-induced damage to the films. For FCVA deposition with a 200 Volt bias the transmission is much reduced. FCVA films deposited in this fashion have been shown to be polycrystalline. The defect structures exhibited in the FCVA layer are too large for formation of effective optical barrier layers. Additionally, ion sputtering of crystalline films is dependent on the crystal orientation, leading to higher surface roughness. Defect structures formed in a protective layer can degrade the optical quality of the layer and also provide paths for diffusion of atmospheric contaminations through the layer, compromising the protective properties of the layer.

[008] Ion biased films have shown significant progress toward the goal of providing a satisfactory barrier for protection of electronic and optical films, such as, for example, photovoltaic, semiconducting and electroluminescent films. Particularly organic light emitting diodes, which utilize calcium or other very reactive metal

doped electrodes and other hydroscopic or reactive materials, can be protected by such films. However, the most biased process to date, the filtered Cathodic Vacuum Arc Coating Technology or FCVAC process, is reported to produce films with a particle density greater than about 1 defect per square centimeter. It may be that the high resputtering rate at the high voltages used in this process cause surface roughening. Certainly, the presence of a particle represents a defect through which diffusion of water vapor or oxygen can proceed. Also, the roughness of the surface formed by the FCVAC process impacts the stress and morphology and also the transparency and the uniformity of the index of refraction. The resputtered film may flake from the process chamber shields or be drawn to the film surface by the large electrostatic field present in an ion beam process. In any case, the particle defect density for particles greater than the film thickness also determines pin hole density or other defects caused by discontinuous deposition of the film because line of sight films can not coat over a particle that is larger than the thickness of the film, let alone a particle many times greater in size than the thickness of the film.

[009] In the case of ion-bias or self-bias energies exceeding several electron volts, the translational energy of the ion participating in the bias process can exceed the chemical binding energy of the film. The impacting ion, then, can either forward scatter atoms of the existing film or back sputter atoms of the existing film. Likewise, the participating ion can be adsorbed into the growing film or it can also scatter or absorb from the film surface. Sputtering of the existing film and scattering from the existing film are both favored at incoming angles of about 45° from the horizontal. In most ion coating processes, the ion beam is directed at a normal incidence to the

surface to be coated. However, as noted, at ion energies exceeding the chemical threshold, and particularly at energies exceeding 20 Volts or so, damage to the film or the substrate resulting from the ion energy in excess of the chemical binding energy is significant, and results in surface roughness, increased optical absorption characteristics, and creation of defects.

[010] In the case of the FCVA process, roughness is an increasing function of the film thickness, increasing from about 0.2 nanometers roughness for a 50 nanometer film to about 3 nanometers for a 400 nanometer Cu film indicating substantial roughening of the polycrystalline copper surface due to differential sputtering by the self biased incoming copper ions. Such a film will scatter light, particularly at the interface between two layers of different refractive index. To date, barrier or dielectric properties of FCVA produced films have not been found.

[011] Charging of the deposited film is also a particular problem with ion beam deposited dielectrics. To date, no low temperature dielectric and also no ion beam dielectric is known that has ever been shown to provide the electrical quality required for a transistor gate layer, for example. The ion beams embed charged ions in the film, leading to large negative flat band voltages and fields that can not be passivated at temperatures below about 450 °C. The surface charge of the dielectric layer results in slow accumulation of capacitance, preventing the sharp onset of conduction in a transistor application. Consequently, no as-deposited low temperature dielectric, biased or unbiased, has been proposed for low temperature transistor applications or is known at this time.

[012] Therefore, there is a need for high quality, dense dielectric layers for utilization as barrier layers in optical, electrical, tribological, and biomedical applications.

SUMMARY

[013] In accordance with the present invention, one or more dielectric layers formed from layers of metal-oxide materials deposited by a pulsed, biased, wide area physical vapor deposition process are presented. A dielectric barrier layer according to the present invention can be formed from at least one highly densified metal oxide layer. Dielectric barriers according to the present invention can be highly densified, highly uniform, ultra smooth amorphous layers with ultra low concentrations of defects, providing for superior performance as protective layers against physical wear and atmospheric contamination of underlying structures as well as overlying structures that may be deposited to form an electrical, optical, or medical device. Barrier layers according to the present invention can also be self-protecting optical layers, electrical layers, or tribological layers that can be utilized actively in optical or electrical devices.

[014] Therefore, barrier layers according to the present invention includes a densified amorphous dielectric layer deposited on a substrate by pulsed-DC, substrate biased physical vapor deposition, wherein the densified amorphous dielectric layer is a barrier layer. Further the deposition can be performed with a wide area target. A method of forming a barrier layer according to the present inventions includes providing a substrate and depositing a highly densified, amorphous, dielectric material over the substrate in a pulsed-dc, biased, wide target physical vapor deposition

process. Further, the process can include performing a soft-metal breath treatment on the substrate.

[015] Dielectric barrier stacks can include any number of individual layers including one or more barrier layers according to the present invention. In some embodiments, the individual barrier layers can be optical layers. Typically, alternating layers of low and high index of refractory metal oxide materials can be arranged to form anti-reflective or reflective coatings in optical devices, for example. As such, dielectric barriers according to the present invention provide a protective function as well as being a functional part of an optical device. In some embodiments of the invention, for example, dielectric barriers according to the present invention can be utilized in cavity enhanced LED applications, or in formation and protection of transistor structures. Additionally, the beneficial dielectric properties of some embodiments of barrier layers according to the present invention can be utilized as electrical layers to form resistors or capacitive dielectrics.

[016] In some embodiments, a soft metal (e.g., indium) breath treatment can be utilized before deposition of a barrier layer. Such a breath treatment is shown to significantly improve surface roughness and enhance WVTR characteristics for embodiments of barrier layers according to the present invention.

[017] These and other embodiments of the invention are further discussed and explained below with reference to the following Figures. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed. Further, specific explanations or theories regarding the deposition or performance of

barrier layers or soft-metal breath treatments according to the present invention are presented for explanation only and are not to be considered limiting with respect to the scope of the present disclosure or the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[018] Figures 1A and 1B illustrate a deposition apparatus for depositing barrier layer films according to the present invention.

[019] Figure 1C illustrates a barrier layer deposited on a substrate according to embodiments of the present invention.

[020] Figures 2A, 2B, 2C, 2D, 2E and 2F illustrate examples of devices with dielectric stacks of barrier layers according to embodiments of the present invention.

[021] Figure 3 shows a microcavity enhanced LED structure utilizing dielectric stacks of barrier layers according to embodiments of the present invention.

[022] Figure 4 shows a bottom gate transistor device with a dielectric stack of barrier layers according to embodiments of the present invention.

[023] Figure 5 shows a top gate transistor device with a dielectric stack of barrier layers according to embodiments of the present invention.

[024] Figure 6 shows an example of a microcavity enhanced LED structure similar to that shown in Figure 3 further protected by a dielectric stack of barrier layers according to embodiments of the present invention.

[025] Figure 7 shows another example of a microcavity enhanced LED structure similar to that shown in Figure 3 further protected by a dielectric stack of barrier layers according to embodiments of the present invention.

[026] Figure 8 shows an example TiO_2 barrier layer according to embodiments of the present invention deposited on a reactive aluminum layer after exposure to a high humidity, high temperature environment for an extended period of time.

[027] Figure 9 shows an example silica/alumina barrier layer according to embodiments of the present invention deposited on a reactive aluminum layer after exposure to a high humidity, high temperature environment for an extended period of time.

[028] Figure 10 shows an SEM photograph of a cross section of an embodiment of a dielectric stack of barrier layers according to embodiments of the present invention.

[029] Figure 11 shows transmission versus wavelength curves for various examples of dielectric stacks of barrier layers according to embodiments of the present invention.

[030] Figures 12A and 12B illustrate a single barrier layer structure deposited with and without a soft-metal breath treatment according to embodiments of the present invention.

[031] Figure 13 shows a Flexus Stress Measurement apparatus that can be utilized to test barrier layers.

[032] Figure 14 illustrates a measurement of the wafer bow using the Flexus Stress Measurement apparatus illustrated in Figure 13.

[033] Figure 15 illustrates the stress in various deposited barrier layers according to embodiments of the present invention as a function of temperature through a single temperature cycle after deposition.

[034] Figures 16A, 16B, 16C, and 16D show atomic force microscopy measurements of surface roughness for some barrier layer films according to embodiments of the present invention.

[035] Figure 17 illustrates a water vapor transmission test that can be utilized to characterize barrier layers deposited according to embodiments of the present invention.

[036] Figures 18A through 18D illustrate the effects of different In/Sn breath treatment parameters on the surface roughness of the deposited barrier layer according to the present invention.

[037] Figures 19A and 19B illustrate the effects of the substrate on surface roughness.

[038] Figure 20 illustrates a barrier layer according to the present invention that further operates as a thin film gate oxide.

[039] Figures 21A and 21B illustrate the effect of substrate composition on the surface roughness of a deposited barrier layer according to the present invention.

[040] Figures 22A and 22B illustrate that the character of the barrier layer deposition according to embodiments of the present invention effect surface roughness.

[041] In the figures, elements having the same designation have the same or similar functions.

DETAILED DESCRIPTION

[042] Barrier layers according to some embodiments of the present invention are deposited in a pulsed-dc, substrate biased, wide target physical vapor deposition process that is described further below with respect to some particular examples of such barrier layers. Some embodiments of barrier layers according to embodiments of the present invention can be characterized as highly densified, highly uniform, highly amorphous layers with particularly low defect concentrations and high surface smoothness. Further, barrier layers according to embodiments of the present invention can have beneficial optical and electrical characteristics that allow such barrier layers to be self-protecting optical or electrical layers in optical or electrical devices formed with these layers.

[043] For example, some embodiments of barrier layers according to the present invention can have excellent optical transparency characteristics. Further, the index of refraction of individual barrier layers is dependent on the material of deposition and therefore stacking of multiple barrier layers according to the present invention can result in highly controllable, and self protecting, reflecting or anti-reflecting coatings for optical devices. Additionally, barrier layers according to some embodiments of the present invention can be doped with optically active impurities to form optically active layers, which are also self-protecting. For example, depositions of rare-earth ions such as Erbium or Ytterbium can result in optical amplifiers or frequency converters.

[044] Additionally, embodiments of barrier layers according to the present invention can have highly beneficial dielectric properties and can therefore be utilized as self-protecting electrical layers. Some barrier lavers according to embodiments of

the present invention, for example, can be utilized as resistance layers. Other embodiments can be utilized as high-dielectric constant layers in capacitor devices. Embodiments of dielectrical barrier layers that are useful for such devices are further discussed below.

[045] RF sputtering of oxide films is discussed in Application Serial No. 09/903,050 (the '050 application), filed on July 10, 2001, by Demaray et al., entitled "Planar Optical Devices and Methods for Their Manufacture," assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Further, targets that can be utilized in a reactor according to the present invention are discussed in U.S. Application serial no. 10/101,341, filed on March 16, 2002, assigned to the same assignee as is the present invention, herein incorporated by reference in its entirety. Methods of depositing oxides in a pulsed-dc, substrate biased, wide-target physical vapor deposition (PVD) process are further discussed in U.S. Application serial no. 10/101863, filed on March 16, 2002, (hereinafter referred to as "the pulsed, biased process") assigned to the same assignee as is the present application, herein incorporated by reference in its entirety.

[046] Figures 1A and 1B illustrate a reactor apparatus 10 for sputtering of material from a target 12 according to embodiments of the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three or four deposition chambers connected by a vacuum transport chamber. These AKT PVD reactors can be modified such that

pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[047] Apparatus 10 includes a target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53 below target 12. Magnet 20 is scanned across the top of target 12. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18.

[048] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the period of positive potential, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency of pulsed DC power supply 14 can exceed a critical frequency that can depend, at least partly, on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering in apparatus 10.

[049] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this example supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. The reverse voltage is 10% of the negative target voltage. Utilization

of other power supplies will lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted to between 0 and 5 μs.

[050] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 is a 2 MHz RF power supply and, for example, can be a Nova-25 power supply made by ENI, Colorado Springs, Co. Therefore, filter 15 is a 2 MHz band rejection filter. In some embodiments, the band-width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[051] However, both RF and pulsed DC deposited films are not fully dense and most likely have columnar structures. These columnar structures are detrimental for optical applications and to formation of barrier layers due to the scattering loss and pinholes caused by the structure. By applying a RF bias on wafer 16 during deposition, the deposited film can be densified by energetic ion bombardment and the columnar structure can be substantially eliminated.

[052] In the production of some embodiments of a barrier layer according to the present invention using, for example, the AKT-1600 based system, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that can have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between about 50C and 500C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas (for example, but not limited to, mixtures of Ar and O_2) can be inserted into the chamber

of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about 0.7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimension about 150 mm by 600 mm.

[053] Figure 1C shows a dielectric barrier layer 110 deposited on a substrate 120 according to the present invention. Substrate 120 can be any substrate, for example plastic, glass, Si-Wafers or other material. Substrate 120 may further include devices or structures that can be protected by barrier layer 110, such as organic light-emitting diode (OLED) structures, semiconductor structures, or other barrier layer structures. Barrier layer 110 can be a metallic oxide where the metal can be Al, Si, Ti, In, Sn or other metallic oxides, nitrides, halides, or other dielectrics. For example, a high index of refraction barrier layer can be formed by deposition of TiO_2 from a titanium target with example deposition parameters designated as 7KW/200W/200KHz/60Ar/90O2/950s (7 KW of pulsed-dc target power, 200 W of substrate bias power, 200 KHz is the pulsing frequency of the pulsed-dc target power, 60 sccm Ar gas flow, 90 sccm O_2 gas flow, 950s total deposition time). Another example lower index of refraction barrier layer can be formed from a target that is 92% Al and 8% Si (i.e. 92-8 or 92/8 layers) in a process designated as 3KW/200W/200KHZ/85Ar/90O2/1025 (3KW of pulsed-dc target power, 200 W of substrate bias power, 200 KHz pulsing frequency of the pulsed-dc target power, 85 sccm Ar flow, 90 sccm O_2 flow for 1025 sec of deposition time). As is further

discussed below, a wide range of process parameters can be utilized to deposit barrier layers according to the present invention.

[054] Barrier layers according to the present invention can be formed from any oxide materials. For example, MgO, Ta_2O_5, TiO_2, Ti_4O_7, Al_2O_3, SiO_2, silicon-rich SiO_2, and Y_2O_3. Oxide compounds of Nb, Ba, Sr, and Hf can also be utilized to form barrier layers according to the present invention. Further, barrier layers can be doped with rare-earth ions to produce optically active layers. Parameters provided herein for deposition of particular layers (e.g., the TiO_2 layers and the 92-8 layers discussed above) are exemplary only and are not intended to be limiting. Further, individual process parameters are approximations only. A wide range of individual parameters (e.g., power levels, frequencies, gas flows, and deposition times) around those stated can be used to form barrier layers according to the present invention.

[055] Dielectric barrier layer 110 can be characterized as a highly dense, uniform, defect free amorphous dielectric layer that may also have high optical transparency. Such films can be deposited in a pulsed-dc, substrate biased PVD process from a metallic target in an Ar/O_2 gas flow. As is further discussed below, some embodiments of dielectric barrier layer 110 have excellent surface roughness characteristics as well. Typically, as is discussed further below and with the examples and data provided, water vapor transmission rates for dielectric films according to embodiments of the present invention are tested in a MOCON test apparatus (MOCON referes to MOCON testing service of Minneapolis, MN) to be less than $1 X 10^{-2}$ gm/m^2/day and are often less than $5 X 10^{-3}$ gm/m^2/day.

[056] Dielectric barrier stacks can be formed by depositing further barrier layers over barrier layer 110. Any number of stacked barrier layers can be utilized in order that the resulting structure not only function as a barrier layer, but may have other purposes in the resulting device as well. Further, a soft metallic breath treatment may be applied prior to deposition of a barrier layer according to embodiments of the present invention. A soft-metallic breath treatment refers to exposure of the substrate to a soft metallic vapor, as is further explained below.

[057] Figure 2A shows an embodiment of a dielectric stack 120 that can be utilized as a barrier structure as well as providing further optical functions. Dielectric stack 120 includes multiple barrier layers 101, 102, 103, 104, and 105 according to embodiments of the present invention. Each of barrier layers 101, 102, 103, 104, and 105 can be deposited utilizing deposition methods as described with more detail in U.S. Application Serial No. 10/101,863. The deposition is described generally above with respect to apparatus 10. In general, dielectric stack 120 can include any number of layers. In particular, dielectric stack 120 can include only a single barrier layer. The particular example of a barrier stack 120 shown in Figure 2A includes five layers, layers 101, 102, 103, 104 and 105. In the example of dielectric stack 120 shown in Figure 2A, dielectric layers 101, 103 and 105 are formed of a high index material such as titania (TiO_2). Layers 102 and 104 can be formed of a low index material such as silica (SiO_2), possibly doped with alumina (e.g., 92% silica and 8% alumina by cation percents, the 92-8 layer). Barrier stack 120 can be deposited directly on a substrate 100 as shown in Figure 2A or deposited on a layer 107 as shown in Figure 2D. Layer 107 is a layer to be protected from atmospheric contaminants or physical

damage and may include an optical or electrical device or another layer. Substrate 100 is a substrate on which layer 107 or dielectric stack 120 is formed. In some embodiments, substrate 100 can also provide a barrier to atmospheric contamination of layer 107. In some devices, further structures may be deposited over barrier layer structure 120.

[058] Table 1 illustrates deposition parameters for some example dielectric stack structures 120 according to the present invention. As described above, each of stacks 120 illustrated in Table 1 are formed utilizing an AKT 4300 PVD system using a Biased Pulsed DC Reactive Scanning Magnetron PVD Process as further described in U.S. Patent Application Serial No. 10/101,863, which has been previously incorporated by reference. Further, apparatus 10 as described above with respect to Figures 1A and 1B, can be clustered in the AKT 4300 PVD system with a loadlock chamber, an outgassing chamber, and may be equipped with plasma shields and a shield heater. As shown in Figure 2A, dielectric stack 120 for these examples includes 5 layers -- 3 alternating layers of TiO_2 and 2 layers of 92-8 SiO_2/Al_2O_3 (92%/8% by cation concentration).

[059] Dielectric stack 120 for each of the stacks shown in Table 1 was deposited directly on substrate 100. Substrate 100 for each of the stacks formed was first loaded into the loadlock of apparatus 10. The loadlock of apparatus 10 was pumped to a base pressure of less than about 10^{-5} Torr. The sheets of substrate 100, which may be of glass or plastic, was then transferred to a heat chamber of apparatus 10 and held at a temperature of about 300 °C for about 20 mins in order to outgas any moisture already accumulated by substrate 100. For polymer based substrates, for

example, the pre-heat step can be eliminated or performed at a lower temperature depending on the plastic substrate used. In some cases, the substrate and shield heaters of apparatus 10 can be disabled. The substrate column of Table 1 shows the composition of substrate 100 utilized in the deposition process.

[060] In each of stacks 1 through 6 illustrated in Table 1, the composition of the dielectric barrier layers in dielectric stack 120 is TiO_2/92-8/TiO_2/92-8/TiO_2, indicating that layers 101, 103 and 105 as shown in Figure 2A are TiO_2 layers and layers 102 and 104 as shown in Figure 2A are SiO_2/Al_2O_3 (92%/8% by cation concentration). The TiO_2 layers are deposited with the parameters shown in the TiO_2 Deposition Process column. The process details are given in the format: target power/bias power/pulsing frequency/Ar flow/O_2 flow/deposition time. Target power refers to the power supplied to target 12 of apparatus 10. Bias power refers to the power supplied by bias generator 18 to electrode 17 on which substrate 100 is mounted in place of substrate 16 as shown in Figure 1A and capacitively coupled to electrode 17. The Ar and O_2 flow rates across substrate 100 are then described in units of standard cubic centimeter/min (sccm). Finally, the deposition time is given. For example, the TiO_2 layers for stack number 1 illustrate in Table 1 were deposited with a target RF power of about 7 kW, with about 200 W of bias power, pulse frequency of about 200 KHz, an Ar flow rate of about 60 sccms, an O_2 flow rate of about 90 sccms, and a deposition time of about 950s. The measured thickness of a typical TiO_2 layer deposited according to the process described in the TiO_2 Deposition Process column is shown in the measured thickness TiO_2 column of Table 1.

[061] Similarly, the deposition parameters for deposition of silica/alumina layers for each dielectric stack 120 shown in Table 1 are shown in the silica/alumina (92/8) deposition process column. As indicated, each of the silica/alumina layers for stack numbers 1-6 shown in Table 1 are about 92% Silica and about 8% alumina by cation concentration. For example, in stack number 1 illustrated in Table 1, the silica/alumina layers were deposited with the power to target 12 being about 3 kW, the bias power to electrode 17 was about 200 W, the frequency of pulsed DC power supply 14 was about 200 kHz, the Ar flow rate was about 85 sccm, the O_2 flow rate was about 90 sccm, and the deposition time was about 1,005 sec.

[062] In general, in this disclosure a dielectric barrier layer referred to as 92/8 layer refers to a barrier layer formed from continuous deposition of a dielectric barrier layer from the 92% Silica/8% Alumina target. A dielectric barrier layer referred to as a 92-8 layer refers to a barrier layer formed in steps from the 92% Silica/8% Alumina target. A 92-8 layer can be formed, for example, on plastic substrates whereas 92/8 layers can be formed on Si-wafers or glass substrates that are not so sensitive to heat.

[063] In each of the stacks illustrated in Table 1, the reverse time for pulsed-DC power supply 14 was fixed at about 2.3 microseconds. The spacing between target 12 and substrate 100 was ~60mm, and the spacing between magnet 20 and target 12 was ~4-5 mm. The temperature of substrate 100 was about 200 °C and the shield heater of apparatus 10 was set to about 250 °C. The home offset of magnet 20 was set to be about 20 mm and the scan length was about 980 mm. The total pressure inside the chamber of apparatus 10, in plasma 53, during deposition of the

TiO_2 layers was about 5-6 mT. The total pressure inside the chamber, in plasma 53, during deposition of the silica/alumina layers was about 8-9 mT.

[064] In some barrier stacks according to the present invention, barrier layers are deposited by a reactively sputtered thin film layer or layers, formed by a process as previously described in the pulsed, biased deposition process, U.S. Application Serial No. 10/101,863. The pulsed, biased deposition process combines optical quality vacuum films having uniquely dense morphologies free of the columnar defects that are typical of non-biased vacuum thin films with parts per million uniformity and control of the optical index and birefringence. Very high resolution ellipsometry also demonstrates that a wide range of film index can be deposited with extinction coefficients which are zero across the visible and in the near IR region, and uniform on the order of parts per million providing substantially perfect transparency. As a result of the high level of densification and the low defect concentration, it is demonstrated that these very transparent films also provide superior diffusion barrier protection for moisture ingress as measured by steam permeation. Lastly, the same films demonstrate much higher dielectric breakdown under high voltage stress, also a result of the low levels of defects.

[065] Figure 8 shows a sample after exposure to a high-humidity, high temperature environment for an extended period of time. In the sample shown in Figure 8, about 200 nm of TiO_2 was deposited on a reactive aluminum layer that had been deposited on a 4" silicon wafer. The sample was kept in a chamber at about 85 °C with a relative humidity of about 100% for about 500 hours. As can be seen in

Figure 8, no defects are visible on the wafer indicating a high level of protection of the underlying reactive aluminum layer.

[066] Figure 9 shows a sample with a silica/alumina layer according to the present invention after exposure to a high-humidity, high-temperature environment for an extended period of time. In the sample shown in Figure 9, about 10 nm of aluminum is deposited on a 4" silicon wafer. About 100 nm of silica/alumina is deposited over the aluminum. The sample was then placed in a pressure cooker at about 250 °C with about 3.5 atm of saturated steam for about 160 hours. Again, no defects are visible on the wafer indicating a high level of protection of the underlying reactive aluminum layer. In another example, the thin reactive Al on a Si wafer was tested under the same conditions without a barrier layer and became transparent within minutes of the testing.

[067] Selected metal oxide films deposited with the previously disclosed process, from tens of nanometers to more than 15 microns, are not only impervious to moisture and chemical penetration as a film, but can also provide protection to an underlying layer or device from the effect of gas or moisture ingress while serving as an optical, electrical and/or tribological layer or device, rendering substantial manufacturing and environmental margins to the respective layers and devices. The subject process has been demonstrated on wide area substrates of glass and metal as well as low temperature material such as plastics.

[068] Table 4 shows Vickers Hardness (MPa) values obtained by testing an Al_2O_3 barrier layer and an Er-doped alumina/silicate (40% alumina/60% silica) films on a Si-Wafer. The Al_2O_3 barrier layer was deposited in a

3kW/100W/200KHz/30Ar/44O2/t process with a 2.2 μs reverse time. The Er, Yb doped Al_2O_3 was deposited with the process 6kW/100W/120KHz/60Ar/28O2/t process with a 1.2 μs reverse time. As can be seen in Table 4, the hardness as indicated generally by the Vickers number is large compared to conventionally deposited alumina films.

[069] Returning to Figure 2A, a dielectric stack 120 is deposited on substrate 100. Each of barrier layers 101, 102, 103, 104, and 105 can be optical layers (i.e., layers that are optically useful). Substrate 100 may be any glass, plastic, metallic, or semiconductor substrate. The thickness of layers 101, 102, 103, 104, and 105 of dielectric stack 120 can be varied to form either an anti-reflective coating or a reflective coating. Figure 2B shows a transparent conducting layer 106 deposited over dielectric stack 120. Transparent conducting layer 106 can be, for example, an indium tin-oxide layer. Figure 2C illustrates a substrate 100 with dielectric stacks 120 deposited on both a top surface and a bottom surface of substrate 100. The particular example shown in Figure 2C includes an embodiment of dielectric stack 120 with layers 101, 102, 103, 104, and 105 deposited on a top surface of substrate 100 and another embodiment of dielectric stack 120, shown having layers 108, 109, 110, 111, and 112 in Figure 2C, deposited on the bottom surface of substrate 100. Again, layers 108, 110, and 112 may be high index layers according to the present invention (e.g., TiO_2 layers) and layers 109 and 111 may be lower index layers such as silica/alumina layers. Examples of deposition parameters for dielectric stack 120 can be found in Table 1. As another example of a stack of barrier layers according to the present invention that provides good transmission characteristics is a four-layer stack

$TiO_2/SiO_2/TiO_2/SiO_2$ layering of thicknesses 12.43 nm, 36.35 nm, 116.87 nm, and 90.87 nm, respectively, deposited on glass provides a high transparency in the wavelength range of about 450 nm and 650 nm.

[070] In Figure 2D dielectric stack 120 is shown protecting a layer 107. Layer 107 is any layer of material that should be protected by a transparent barrier layer. For example, layer 107 may be a reactive metal such as aluminum, calcium or barium, layer 107 may be a fragile layer such as a conductive transparent oxide, or layer 107 may include an active optical or electrical device. As discussed above, the individual layers of dielectric stack 120 can provide protection both from incursion of atmospheric contaminants and protection against physical damage of layer 107. In some embodiments, the layer thickness of dielectric layers (e.g., layers 101, 102, 103, 104, and 105 shown in Figure 2D) of dielectric stack 120 are arranged to form either a transparent or reflective film at particular wavelengths. One skilled in the art can determine the thickness of individual films in dielectric stack 120 to form a reflective or anti-reflective film of dielectric stack 120. In some embodiments, where layer 107 is a metal such as aluminum, barium, or calcium, the device shown in Figure 2D forms a highly stable mirror. Figure 2E shows a dielectric stack 120 protecting a layer 107 where layer 107 has been deposited on substrate 100. Further, a transparent conducting layer 106 has further been deposited over dielectric stack 120. Figure 2F shows a structure where a second barrier stack 120 has been deposited on the bottom surface of substrate 100.

[071] Figure 10 shows a cross sectional SEM view of an example dielectric stack according to the present invention. Again, a five-layer TiO2/92-8 stack is

shown with thickness 550 nm for the TiO_2 layers and 970 nm fc=the 92-8 silica/alumina. The example shown in Figure 10 is a dielectric mirror stack such as that used to form a microcavity LED.

[072] Although Figures 2A through 2F show various configurations and utilizations of a barrier stack 120 having five layers, in general, a barrier stack 120 according to the present invention may be formed of any number of barrier layers. Further, the examples of barrier layers 101, 102, 103, 104, and 105 illustrated in Figures 2A through 2F illustrate examples of optical layers according to the present invention where those optical layers also function as self-protecting barrier layers in that they protect themselves as well as the particular surface or device on or below which they are deposited. Additionally, one or more of barrier layers 101, 102, 103, 104, and 105 may include optically active dopant ions such as rare-earth ions in order to provide more optically active functionality. Further, in accordance with the present invention, one or more of layers 101, 102, 103, 104, and 105 may be layers other than barrier layers according to the present invention. Each of the barrier layers described with respect to Figures 2A through 2F can be deposited utilizing a pulsed, biased deposition process as has been described in U.S. Application Serial No. 10/101,863 to form a highly densified layer of material with very low defect concentrations.

[073] Figure 3 shows another structure 321 utilizing dielectric stacks of barrier layers according to the present invention. As shown in Figure 3, structure 321 includes a dielectric stack 315 deposited on a substrate 316. Substrate 316 may be formed, for example, of glass or plastic materials. A transparent conductive layer 314, such as for example indium tin oxide, is deposited on dielectric stack 315. Layer

313 can be an electroluminescence layer such as, for example, a phosphor-doped oxide or fluoride material, rare earth doped silicon rich oxide light emitting device, or an organic light emitting polymer, OLED (organic light emitting diode) or polymer stack. A metal layer 312, which may be aluminum and may be doped with calcium or barium, is deposited on the side near layer 313. A second dielectric stack 317 can be formed on the bottom of substrate 316.

[074] Structure 321 illustrated in Figure 3 is an example of a microcavity enhanced LED, protected from water and reactive gas which may diffuse through substrate 316 by dielectric stacks 315 and 317. When layer 312 is a metal layer, a microcavity is formed between layer 312 and dielectric stack 315. Dielectric stack 315 can out-couple light emitted from electroluminescence layer 313. Layer 313 emits light when it is electrically biased as a result of a voltage applied between transparent conducting layer 314 operating as an anode and conducting layer 312 operating as a cathode. The layers of dielectric stack 315 and dielectric stack 317 may be arranged to contain the light emitted by layer 313 between layer 317 and metallic layer 312, forming an etalon arrangement to guide light along substrate 316. Additionally, dielectric layer 317 may be arranged to transmit light produced by layer 313, thereby forming a monitor arrangement with light being emitted substantially normal to substrate 316.

[075] Figure 11 illustrates the transmission data collected from examples of dielectric stacks according to the present invention. The metrology equipment utilized in taking the data resulting in Figure 11 was a Perkin Elmer Lambda-6 Spectrophotometer. Four samples were measured and each were 5 layer stacks of

TiO_2/92-8 as described above. Two samples have the same thickness layers (55 nm TiO_2 and 100 nm 92-8). As illustrated in Figure 11, the two different runs have almost the same transmission spectrum demonstrating the repeatability of the deposition process. The third example had a different thickness arranged so as to shift the transmission spectrum towards the blue. The fourth example was generated after the third example was maintained under 85/85 (85 C 85 % humidity) test conditions for 120 hours. It can be observed that the humidity and heat did not have a significant impact on the transmission characteristics of the mirror stack, again demonstrating the functionality of such dielectric stacks as protection layers as well as optical layers (i.e., no measurable wet-shift). A similar result was obtained after 500 hours of test with the 85/85 conditions with no measurable wet-shift.

[076] Figure 6 shows an example of another structure 633 with a microcavity enhanced LED structure 321 as described with Figure 3 covered and protected by a structure 622 such as those shown in Figures 2A through 2F. In structure 321, as shown in Figure 6, layers 314, 313, and 312 have been patterned. A structure 622 with dielectric stacks 618 and 620 deposited on opposite sides of a substrate 619 can be formed separately. Dielectric stacks 618 and 619 are formed as described with dielectric stacks 120 of Figures 2A through 2F. Structure 622 can then be epoxied over structure 321 in order to seal and protect structure 321. Epoxy layer 621, for example, can be an EVA epoxy.

[077] Figure 7 shows another structure 700 with an example of a microcavity enhanced LED structure 321 as described with Figure 3 covered and protected by a structure 623 such as those shown in Figures 2A through 2F. Covering

structure 623 includes substrate 619, with dielectric stack 620 deposited on substrate 619, epoxied to device 321.

[078] Figure 4 illustrates another example of barrier layers according to the present invention that also function as electrical layers (i.e., layers with electrical function such as providing resistance or function as the dielectric in a capacitor structure). The structure shown in Figure 4 illustrates an example of a bottom gate transistor structure 422 according to the present invention. Transistor structure 422 is formed on a substrate 416, which may be a plastic or glass material. In the embodiment illustrated in Figure 4, a dielectric stack 415 according to the present invention is deposited on a top surface of substrate 116 and a second dielectric stack 417 according to the present invention is deposited on a bottom surface of substrate 116. Dielectric stacks 417 and 415 each can include layers of high index and low index dielectric materials, as discussed above. The high index and low index dielectric materials, for example TiO_2 and silica/alumina layers as described above, each have low-voltage flat bands and low surface defects and therefore are suitable for use as thin film transistor structures. A semiconductor layer 423 is deposited on barrier stack 415 and patterned. Semiconductor layer 423 can be a semiconductor such as silicon, germanium, or may be of zinc oxide or a polymer material. Layers 424 and 425 form source and drain layers in contact with semiconductor layer 423. Layer 426 can be formed of a material with a high dielectric constant, such as any of the dielectric layers forming dielectric stacks 415 and 417, for example the high-dielectric strength TiO_2 material deposited by the processes described here. Layer 427 is an inter layer and layer 428 is the gate metal.

[079] Figure 5 shows an example of a top gate transistor device 529. Transistor device 529 is formed on a substrate 516 that is protected from atmospheric contamination (for example water or gasses) and physical wear and abrasion by dielectric stacks 515 and 517. Dielectric stacks 515 and 517 are formed from one or more layers of optical material as discussed above with dielectric stack 120. Gate layer 530 is deposited on dielectric stack 515. Layer 530 may be a metallic layer such as aluminum or chrome. A gate oxide layer 531 is deposited over layer 530. A semiconductor layer 532 is deposited on gate oxide layer 531 over layer 530. Semiconducting layer 532 can be similar to layer 423 of Figure 4. Layers 533 and 534 are source and drain layers, respectively, and are similar to layers 424 and 428 of device 422 of Figure 4 and may be formed from a conducting metal, conducting oxide, or a conducting polymer, for example.

[080] Dielectric stacks with barrier layers according to the present invention can have atomically smooth film surfaces, independent of the film thickness. Additionally, dielectric stacks with barrier layers according to the present invention can have film transparencies that are unmeasurably different from zero. These dielectric stacks represent a new capability for biased barrier film defect levels and barrier protection. Few products requiring dielectric barrier protection from water and oxygen, such as OLED displays, can tolerate a defect every square centimeter. Some embodiments of barrier layers as 2.5 nanometers and as thick as 15 microns have been deposited that exhibit an average surface roughness of about 0.2 nm, indicating a damage free process. Such layers exhibit an optical quality surface for all film thicknesses deposited, representative of the high amorphous film uniformity

attainable with these processes that produce embodiments of the barrier layer according to the present invention.

[081] Dielectric barrier layers according to the present invention have been shown to protect ultra thin reactive metal films of aluminum from steam heat oxidation from 125 to 250 °C at pressures of 3.5 ATM of pure steam for hundreds of hours with no visible defect on 100mm silicon wafers. Consequently, it is clear that both titanium oxide and alumina/silicate barrier layers, as described herein, can provide long term protection of reactive films which are pin hole free up to the area of one or both wafers. One pin hole in the protective dielectric barrier on a 100 mm wafer, with an area of approximately 75 square centimeters, would translate into a pin hole density of about 0.0133 per square centimeter. As shown in Figures 8 and 9, there were two wafers, one with aluminosilicate and one with titania barrier dielectric coatings, that were failure free. The total area between the two wafers was 150 square centimeters. If there were 1 defect on these two wafers the defect density would be 0.00666 per square centimeter. However, since the wafers were free of defects, the actual defect density could not be measured from the results of only two wafers. As indicated, then, the actual defect density was less than 0.0133 per square centimeter and likely less than 0.007 per square centimeter.

[082] In some embodiments of the invention, a soft metal, such as indium or indium-tin, breath treatment can be performed before deposition of one or more barrier layers such as those discussed above. It is likely that the soft metal breath treatment can be utilized to release stress between the dielectric barrier layer and the

substrate. Further, the soft metal breath treatment can act to nucleate for further growth of pin-hole free or defect-free barrier layer films on the substrate.

[083] Figures 12A and 12B show a single barrier layer structure 1200 with deposited on a substrate 1201 with and without a soft-metal breath treatment according to the present invention. In Figure 12A, a barrier layer 1203 such as is described above is deposited directly on substrate 1201. Substrate 1201 can be any suitable substrate material, including glass, plastic, or Si Wafers, for example. Substrate 1201 can, for example, include an OLED structure or other optically active structure which requires high optical throughput or an electrical structure that may utilize the barrier layers as electrical layers. Barrier layer 1203 can be any one or more barrier layers as is described above. As illustrated in Figure 12A, barrier layer 1203 can develop stress-related surface roughness during deposition and use.

[084] Figure 12B illustrates the results of depositing barrier layer 1203 following a soft-metal breath treatment according to some embodiments of the present invention. As is shown in Figure 12B, the stress is apparently relieved resulting in a barrier layer with much better surface smoothness.

[085] A soft-metal breath treatment according to some embodiments of the present invention includes an exposure of the substrate for a short time to a soft metal vapor followed by a heat treatment. An indium-tin breath treatment, for example, involves exposure of the substrate to indium-tin from an indium-tin target in a pulsed-dc process and a subsequent heat treatment. Direct exposure to indium-tin-oxide vapor does not yield the particular beneficial results illustrated below. Without being bound by a particular theory that may be presented in this disclosure, an In/Sn breath

treatment can relieve stress in the deposited barrier layer, improving surface smoothness and MOCON WVTR performance.

[086] In a particular example of formation of barrier layer structure 1200, an embodiment of a soft-metal breath treatment was performed on a plastic substrate 1201. A breath treatment of Indium/Tin, for example, can be performed from an Indium Tin (90%/10%) Target. The process for performing the indium/tin breath treatment can be designated as 750W/0W/200 KHz/20Ar/0O2/10sec. In other words, the pulsed-dc, biased, wide target PVD process is operated with a 90% Indium/10% Tin target, an Ar flow of 20 sccms running at a constant power of 750 W in a pulsed PVD system 10 (Figure 1A) (Pulsing Frequency 200 KHz, Reverse time 2.2 μsec) for 10 secs in the AKT 1600 PVD system using the Pinnacle Plus PDC power supply. Then, the breath treatment continued and substrate 1201 was transferred into a load lock of an AKT 4300 Tool and the Tool was pumped to a base pressure of less than about $1X10^{-5}$ Torr. The substrate was then transferred to a Heat Chamber at 130 °C at $1X10^{-8}$ Torr where it is thermally treated at 130 °C for about 25 min.

[087] Substrate 1201 (with the indium/tin breath treatment described above) was then moved to a second chamber where barrier layer 1203 is deposited. Barrier layer 1203 can be formed, as indicated above, from a 92-8 Alumino-Silicate (92% Si/8% Al) target with the deposition performed at room temperature.

[088] The process parameters for the deposition of the embodiment of 92-8 barrier layer 1203 can be 3KW/200W/200KHz/85Ar/90O2/x. Therefore, the process is performed with about 3 KW PDC power, about 200 KHz Pulsing Frequency, and about 2.2 microseconds reverse time. Bias power can be held at about 200 W. A Gas

flow of about 85 sccms of Ar and about 90 sccms of O_2 was utilized. In deposition of this particular embodiment, the deposition process was power cycled where the on cycle was about 180 secs long and the off cycle was about 600 secs long for 9 cycles. The thickness of the resulting barrier layer 1203 was then about 1600 Å. In a particular test, the process described above was utilized for deposition of a barrier structure 1200 with substrate 1201 being three plastic sheets of size 6 inch by 6 inch (Dupont Teijin PEN films 200 μm thick, referred to as a PEN substrate). In general, any barrier layer (e.g., the 92-8 or TiO_2 layers discussed above) can be deposited following a soft-metal breath treatment. As discussed before, examples of processes for embodiments of barrier layers according to the present invention are presented here but wide ranges of process parameters can result in barrier layers according to the present invention.

[089] Barrier layer structure 1200 on substrate 1201 can then be tested using a variety of techniques, some of which are described below. In particular, the stress in layer 1203 can be measured using a Flexus Stress Measurement technique. Surface roughness can be measured utilizing an atomic force microscope (AFM), and water vapor transmission rates (WVTR) can be measured in a high pressure, high humidity pressure cooker device.

[090] Figure 13 illustrates a Flexus Scanning Assembly 1300 that can be utilized to test barrier layer structure 1200. In Flexus Scanning Assembly 1300, a light beam for laser 1310 is directed onto the upper surface of barrier layer 1203 by a mirror 1312. The reflected light beam from barrier layer 1203 is detected by detector 1314. Detector 1314 measures the deflection of the light beam from the beam

reflected by mirror 1312. The optical section 1316, which can include laser 1310, mirror 1312, and detector 1314, can be scanned across substrate 1201 and the angle of deflection θ, which is related to the radius of curvature of substrate 1201 as shown in relation 1318.

[091] The thin film stress in barrier 1203 can be calculated utilizing the changes in substrate deformation measured by Flexus apparatus 1300 as optical portion 1316 is scanned. As is shown in relationship 1318, the angle of the reflected beam can be monitored during the scan and the inverse of the radius of curvature R of substrate 1201 can be calculated from the derivative of the angle as a function of position in the scan.

[092] In some cases, Flexus apparatus 1300 can utilize a dual wavelength technology to increase the range of film types that the tool is capable of measuring. Each Flexus apparatus 1300, then, can have more than one laser 1310 available for scanning the wafer since different film types will reflect different wavelengths of light. Further, the reflected laser intensity provides a good indication of the quality of the measurement. In general, low light intensity at detector 1314 indicates a poor measurement condition.

[093] In Flexus apparatus 1300, stress can be determined using Stoney's equation. In particular, stress in layer 1203 can be determined by measurements of the radius of curvature before deposition of layer 1203 and the radius of curvature after deposition of layer 1203. In particular, according to Stoney's equation, the stress can be given by

$$\sigma = \frac{E_s}{(1-\nu_s)} \frac{t_s^2}{6t_f} \left(\frac{1}{R_s} - \frac{1}{R_f} \right),$$

where $E_s/(1-\nu_s)$ is the biaxial modulus of substrate 1201, σ is the stress of substrate 1201, t_s is the substrate thickness, t_f is the film thickness, R_s is the pre-deposition radius of curvature, and R_f is the post deposition radius of curvature. To obtain the best results, both measurements of the radius of curvature should be performed on the same tool to minimize systematic error in the measured radius. In addition, because the shape of a wafer is unique and because stress is calculated based on the change in deformation of the substrate, each wafer should have a baseline radius measurement. A positive radius indicates tensile stress and a negative radius indicates compressive stress. Wafer bow can be calculated, as shown in Figure 14, by measuring the maximum point of deflection from the chord connecting the end-points of a scan of Flux apparatus 1300.

[094] Measurements of stress performed on several embodiments of barrier films 1203 where barrier film 1203 is a 92-8 film as discussed above with and without a nucleation layer 1202 formed by a soft-metal breath treatment is tabulated in Table 2. As shown in Table 2, sample 1 was a 1.5 KÅ 92-8 film of actual thickness 1760 Å deposited on a Si-Wafer substrate. The resulting stress at about room temperature was -446.2 MPa. Sample 2 was a 1.5 KÅ 92-8 film of actual thickness 1670 Å over an Al-breath deposition resulted in a stress of about -460.2 MPa. In sample 3, a 1.5 KÅ 92-8 film of thickness 1860 Å was deposited subsequent to a In-breath deposition and resulted in a stress of -330.2 MPa, nearly 100 MPa lower than either of the other two depositions depicted.

1, sample 2, and sample 3 as shown in Table 1 over a temperature cycle. The temperature cycle included heating from room temperature to about 160 °C and cooling back to room temperature. In a Si-Wafer substrate, the radius of the wafer is assumed not to change with temperature. Stress data in each case was taken at the temperature indicated. As can be seen from Figure 15, 92-8 films deposited over an In-breath treatment exhibited much less stress than did either a 92-8 film deposited over an Al-breath treatment or a 92-8 film deposited over the substrate without a soft-metal breath treatment.

[096] Atomic-force microscopy (AFM) can be utilized to measure surface roughness of a film. In AFM, a miniature probe is physically scanned over the surface of a film such that the probe is in contact, and follows the surface, of the film. The probe has a small tip and therefore is capable of accurately monitoring the surface roughness for features on the order of a few nanometers.

[097] Figure 16A shows the surface roughness of a PEN substrate (Dupont Teijin PEN films 200 μm thickness), before deposition of a barrier layer according to the present invention. As is shown in Figure 16A, a PEN substrate typically has a surface roughness of average 2.2 nm, root-mean-square average RMS of 3.6 nm, and a typical maximum roughness of about 41.0 nm. As shown in Figure 16B, deposition of a 1.5 KÅ 92-8 after an indium-tin breath treatment on a PEN substrate results in an average surface roughness of 1.0 nm with RMS roughness of 1.7 nm and maximum roughness of 23.6 nm. As is shown in Figure 16C, an indium-tin-oxide (ITO) breath treatment was performed before the 1.5 K Å 92-8 barrier layer film deposition

resulted in an average roughness of 2.1 nm with RMS roughness of 3.4 nm and maximum roughness of 55.4 nm. The deposition shown in Figure 16C is performed with a 125 μm PEN substrate rather than a 200 μm PEN substrate. Therefore, a direct ITO treatment does not perform as well as treatment with an indium-tin breath. As shown in Figure 16D, deposition of a barrier layer of 1.5 K Å directly on a 125 μm PEN substrate resulted in a barrier layer with average surface roughness of about 5.2 nm with RMS roughness of 8.5 nm and maximum roughness of 76.0 nm. Therefore, although the ITO breath treatment was better than no soft-metal treatment at all with respect to surface roughness, an indium-tin breath treatment resulted in the best surface roughness yielding an average surface roughness of about 1.0 nm.

[098] Figure 17 illustrates a water vapor transmission (WVTR) testing apparatus 1700 that can be utilized to characterize barrier layer films according to embodiments of the present invention. A sample 1701 can be mounted into apparatus 1700 in such a way that the surface of substrate 1201 (Figure 12) is isolated from the surface of barrier layer 1203 (Figure 12). A moisture-free gas is input to port 1702, contacts one surface of sample 1701, and is directed to sensor 1703 where the water vapor coming from sample 1701 is monitored. A humid gas is directed to the opposite side of sample 1701 through port 1705. An RH probe 1704 can be utilized to monitor the water content of the gas input to port 1705. Sensor 1703, then, monitors the water vapor that is transmitted through sample 1701.

[099] Such tests are performed by Mocon Testing Service, 7500 Boone Avenue North, Minneapolis, MN 55428. In addition, the Mocon testing is pereformed in accordance with ASTM F1249 standards. Typically, instruments

utilized for WVTR testing by Mocon can detect transmission in the range 0.00006gm/100in^2/day to 4gm/100in^2/day. The Mocon 3/31 instrument, for example, has a lower detection limit of about 0.0003gm/100in^2/day.

[0100] A barrier layer deposition formed with an Al-breath treatment followed by a 1.5 K Å 92-8 barrier layer deposition on a 200 μm PEN substrate resulted in a Mocon test WVTR of 0.0631 gm/100in^2/day. A barrier layer deposition formed with an In-breath treatment followed by a 1.5 K Å 92-8 on 200 μm PEN substrate resulting in no measurable WVTR in the Mocon 3/31 instrument (i.e., the transmission rate was less than 0.0003 gm/100in^2/day).

[0101] As was further discussed above, Figures 16A through D illustrates the role that a soft-metal breath treatment (in particular an indium breath treatment) can play in determining the surface roughness of a deposited barrier layer according to the present invention. The surface roughness of a barrier layer can also affect the WVTR characteristics of a barrier layer. Smoother barrier layer result in better WVTR performance. As such, Figure 16A shows a bare 200 μm PEN substrate with no barrier. Figure 16B shows a 200 μm PEN substrate with a 1500 Å thickness 92-8 barrier layer deposited after a In/Sn breath treatment according to the present invention. Figure 16C illustrates a 200 μm PEN substrate with a 1500 Å 92-8 barrier layer deposited after treatment with ITO breath. Figure 16D is a 200 μm PEN substrate with a 1500 Å 92-8 barrier layer directly deposited on the substrate. As can be seen, the structure of Figure 16B shows the best surface smoothness characteristics.

[0102] Table 3 illustrates several examples of barrier layers, with surface smoothness characteristics and MOCON WVTR testing results. In Table 3, the samples described in rows 1-4 are 92-8 layers (as described above) of thickness about 2000 Å deposited on one or both sides of a 700 μm thick polycarbonate (LEXAN produced by General Electric, corp.). The data shows that the double-side coated barrier layer structure (rows 1 and 2) perform about an order of magnitude better in MOCON WVTR test than does the one sided structures (rows 3 and 4).

[0103] Rows 5 through 8 illustrate various deposition on a PEN substrate (with rows 5-6 describing deposition on a 200 μm PEN substrate and rows 7 and 8 describing depositions on a 125 μm PEN substrate). The In breath treatment parameters refer to In/Sn breath treatments as discussed above. The AFM parameters are shown in Figures 16B through 16D as described earlier. As discussed before, the best surface smoothness and the best WVTR characteristics are shown in row 6, with In breath treatment followed by deposition of a 92-8 layer. The data in row 9 indicates an In breath treatment (In/Sn) with higher power on a thinner (125 μm) PEN substrate. Presumably, the thermal stress behavior on a 125 μm PEN substrate is worse than that for a 200 μm PEN substrate. Further indication of this effect is shown in the data of rows 30 through 33 along with Figures 19A and 19B. The data in rows 30 and 31 include a indium/tin breath treatment (at 750W) on a 200 μm PEN substrate followed by about 1.5 kÅ 92-8 layer deposition, which yields a very smooth surface (e.g., about 1.1nm average) as shown in Figure 19A and an undetectable MOCON WVTR characteristic on the MOCON 3/31 test equipment. The data in rows 32 and 33, with In/Sn breath treatment followed by 1.5 kÅ 92-8 layer deposition

on 125 μm PEN substrate, shows worse smoothness (about 2.0 nm average roughness) and a WVTR test in the MOCON apparatus of about 1.7 X 10^{-2} $gm/m^2/day$. The 92-8 depositions illustrated in rows 30 through 33 were concurrently performed in a single operation.

[0104] The data in rows 12 and 13 of Table 3 indicate an In-breath treatment plus 1.5 kÅ TiO_2 deposition on a 125 μm PEN substrate. Data in rows 10 and 11 indicate an In/Sn-breath treatment plus 1.5 kÅ 92-8 deposition on a 125 μm PEN substrate. As can be seen in Table 3, the WVTR characteristics of 92-8 layers is more than an order of magnitude better than the WVTR characteristics of TiO_2 layers. Representative smoothness for rows 12 and 13 are presented in Figure 22A and representative smoothness for rows 10 and 11 are presented in Figure 22B. As is shown in Table 3, the average smoothness for 92-8 layers is approximately an order of magnitude better than the average smoothness for TiO_2.

[0105] The data in rows 14 and 15 of Table 3 illustrate an In/Sn breath treatment on a 125 μm LEXAN substrate followed by a 92-8 layer deposition. The data in rows 14 and 15 can be compared with the data in rows 32 and 33, which are In/Sn breath treatment on a 125 μm PEN substrate followed by a 1.5 KÅ 92-8 layer deposition. The smoothness is comparable between the LEXAN and PEN substrate, although as can be seen in a comparison of Figures 21A and 21B, the morphology is different, i.e. barrier layers according to the present invention deposited on the LEXAN substrate show more granularity than barrier layers deposited on the PEN substrate.

[0106] The data in rows 16 through 18 of Table 3 illustrate different process parameters for an In/Sn breath treatment followed by 1.5 KÅ 92-8 deposition on a 200 μm PEN substrate. The data in row 16 illustrates a setting where the current is set rather than power. The data in row 16 is taken with a current of 6.15 amps. In the barrier layer illustrated in row 17, the In/Sn breath treatment is performed at 1.5 kW of operating power. In the barrier layer illustrated in row 18, the In/Sn breath treatment is performed at 750 W of operating power. In each case, the MOCON WVTR characteristic of the resulting barrier layer is below detectability on the MOCON 3/31 instrument.

[0107] The data in rows 19-29 of Table 3 illustrate different In/Sn breath treatments and their effects on the surface smoothness of the resulting barrier layers and on the MOCON WVTR characteristics. The data in rows 19-22 are all examples of where the In/Sn breath treatment is replaced with a evaporated In layer followed by a 130 C preheat treatment. The surface roughness characteristics are illustrated in Figure 18A and shows an average roughness of about 1.1 nm. However, the morphology is very granular as is shown in Figure 18A, with presumably a lot of porosity, resulting in MOCON WVTR test on the order of .8 gm/m^2/day. The data shown in row 23 of Table 3 illustrates the case where no In/Sn breath treatment is utilized and the 200 μm PEN substrate is preheated before deposition of a 1.5 kÅ 92-8 deposition, which as shown in Figure 18C has a surface roughness of about 5.2 nm average and a MOCON WVTR of about 0.8 gm/m^2/day, or the same as is shown with the indium evaporation vapor data shown in rows 19-22. Therefore, the same characteristics result whether an indium evaporation vapor treatment is applied or not.

[0108] Rows 24-29 of Table 3 illustrate data where an In/Sn breath treatment was performed at 280 °C rather than at room temperature. The surface roughness, as is illustrated in Figure 18B, was about 1.1 nm average. However, the MOCON WVTR data was about 3 X 10^{-2} gm/m^2/day. This value is much higher than that shown in the similar depositions of rows 30 and 31, which were below 5 X 10^{-3} gm/m^2/day detectability limits of the MOCON 3/31 instrument.

[0109] The data in rows 34 and 35 illustrates deposition of a 1.5 kÅ 35-65 layer (i.e., a deposition with a target having 35% Si and 65 % Al) following a In/Sn deposition on a 200 μm PEN substrate. As is illustrated, the MOCON WVTR are 1.4 X 10^{-1} gm/m^2/day, which shows the possible necessity of a biased process for producing barrier layers according to the present invention.

[0110] Figure 20 illustrates a barrier layer 2002 that can also operate as a thin film gate oxide deposited on a substrate 2001. A thin film gate oxide 2002 can be deposited as a barrier layer according to the present invention. Such a layer as the benefit of protecting moisture and oxygen sensitive transistor layer compounds of germanium, tin oxide, zinc oxide, or pentacene, for example, while functioning as the thin oxide electrical layer. Substrate 2001 can include any electrical device that can be formed on, for example, a silicon wafer, plastic sheet, glass plate, or other material. Barrier layer 2002 can be a thin layer, for example from 25 to 500 Å.

[0111] Titanium oxide is well known as the preferred material for biological implantation due to the lack of immunological response to titanium oxide. In addition, it is preferred that a thin film of TiO_2, which is an immunologically indifferent barrier layer, can simultaneously protect a device such as a voltage or

charge sensor or an optical device such as a waveguide while performing the role of coupling the device capacitively or optically due to its' high dielectric constant or its' high optical index.

[0112] An array of capacitors can be coupled by the high capacitive density due to the proximity of the sensor provided by a very thin high-k dielectric such as TiO_2. In practice, a micron or sub micron array can be used to monitor the electrical activity, amplitude, and direction of very low electrical signals such as those that accompany the propagation of electrical signals in single axion of single neural ganglia. Conversely, it can also be used to electrically couple stimulus to adjacent cells or tissue. High resolution, high-capacitance coupling to the optic nerve, the auditory nerve, or neural tissue on the order of 5 to 50 femto-farads/μm^2 is made uniquely feasible by such a capacitive barrier film without immunological reaction.

[0113] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. This disclosure is not limited by any theories or hypothesis of operation that are utilized to explain any results presented. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims. As such, this application is limited only by the following claims.

TABLE 1

Stack #	Substrates	Stack layer composition	TiO2 Deposition Process	Measured Thickness TiO2 (Å)	Silica/alumina (92-8) Deposition Process	Measured Thickness Silica/Alumina (92-8) (Å)
1	6 Microscope slides + 1 6inch wfr	TiO2/92-8/ TiO2/92-8/ TiO2	7KW/200W/200KHz/60Ar /90O2/950s	580	3KW/200W/200KHz/85Ar /90O2/1005	980
2	6 Microscope slides + 1 6inch wfr	TiO2/92-8/ TiO2/92-8/ TiO2	7KW/200W/200KHz/60Ar /90O2/835s	510	3KW/200W/200KHz/85Ar /90O2/1006	910
3	2 Sodalime Glass + 4 Microscope Slides	TiO2/92-8/ TiO2/92-8/ TiO2	7KW/200W/200KHz/60Ar /90O2/901s	550	3KW/200W/200KHz/85Ar /90O2/1025	1000
4	2 Sodalime Glass + 4 Microscope Slides	TiO2/92-8/ TiO2/92-8/ TiO2	7KW/200W/200KHz/60Ar /90O2/901s	550	3KW/200W/200KHz/85Ar /90O2/1025	1000
5	4 Microscope Slides	TiO2/92-8/ TiO2/92-8	7KW/200W/200KHz/60Ar /90O2/901s	550	3KW/200W/200KHz/85Ar /90O2/1025	1000
6	3 Sodalime Glass + 4 Microscope Slides	TiO2/92-8/ TiO2/92-8/ TiO2	7KW/200W/200KHz/60Ar /90O2/901s	550	3KW/200W/200KHz/85Ar /90O2/1025	1000

TABLE 2

Id	Comment	Temp °C	Radius (m)	Stress Mpa	Film Thickness (Å)	Bow (µm)
Sample 1	pre-deposition	21	-4.76E+03	N/A	N/A	1.58
	1.5 KÅ 92-8 film deposition/ no In-breath treatment	27	-145.978	-446.2	1760	11.74
Sample 2	pre-deposition	29	-4.10E+03	N/A	N/A	1.38
	Al breath deposition then 1.5 KÅ 92-8 film treatment	36	-169.482	-460.2	1670	10.18
Sample 3	pre-deposition	25	-230.249	N/A	N/A	4.36
	In breath treatment then 1.5 KÅ 92-8 film deposition	25	-67.169	-330.2	1860	10.25

TABLE 3

Sample ID	Sample Description	Substrate Material	Thickness µm	MOCON WVTR (g/100inch2/day)	MOCON WVTR (g/m2/day)	AFM Results
1 (Film (coated on both sides) - A)	2 KÅ 92-8 on Polycarbonate, deposited on both sides-A	LEXAN	700	7.2000E-04	1.1160E-02	
2 (Film (coated on both sides) - B)	2 KÅ 92-8 on Polycarbonate, deposited on both sides-B	LEXAN	700	5.8000E-04	8.9900E-03	
3 (Film (coated on one side) - A)	2 KÅ 92-8 on Polycarbonate - A	LEXAN	700	8.3000E-03	1.2865E-01	
4 (Film (coated on one side) - B)	2 KÅ 928 on Polycarbonate - B	LEXAN	700	1.7200E-02	2.6660E-01	
5 (Al+1.5K928)	Al -breath (500W 10sec+ 130c heat treatment) + 1.5 KÅ 92-8 on PEN	PEN Q65	200	6.3100E-02	9.7805E-01	

6 (InB + 1.5K928)	In Breath (750W 5sec+ 130c heat treatment) + 1.5 KÅ 92-8 on PEN	PEN Q65	200	3.0000E-04	4.6500E-03	Ra=1.3nm RMS=1.5nm Rmax=9.8nm *See* Figure 16B
7 (102- MOCON ID: 1619-003)	NO In Breath + 130c Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65	125	4.0200E-02	6.2310E-01	Ra=5.2nm RMS=8.5nm Rmax=76.0nm *See* Figure 16D
8 (103- MOCON ID: 1619-002)	ITO breath + 130c Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65	125	2.4900E-02	3.8595E-01	Ra=2.1nm RMS=3.4nm Rmax=55.5nm *See* Figure 16C
9 (104- MOCON ID: 1619-001)	In Breath (1.5KW + 130c Preheat) + 1.5 KÅ 92-8 on PEN	PEN Q65	125	2.5900E-02	4.0145E-01	
10 (PEN-A)	In Breath+92-8 on PEN	PEN Q65	125	1.8323E-03	2.8400E-02	Ra=3.4nm, RMS=4.2nm Rmax=29.4nm *See* Figure 22B
11 (PEN-B)	In Breath+92-8 on PEN	PEN Q65	125	2.3871E-03	3.7000E-02	Ra=3.4nm RMS=4.2nm Rmax=29.4nm *See* Figure 22B

12 (PEN2-A)	In Breath+TiO2 on PEN	PEN Q65	125	1.0065E-01	1.56	Ra=7.7nm RMS=9.7nm Rmax=72.4nm *See* Figure 22A
13 (PEN2-B)	In Breath+TiO2 on PEN	PEN Q65	125	8.9032E-02	1.38	Ra=7.7nm RMS=9.7nm Rmax=72.4nm *See* Figure 22A
14 (LEXAN-A)	InB+92-8 on LEXAN	LEXAN	125	1.4194E-02	2.2000E-01	Ra=0.9nm RMS=1.1nm Rmax=9.5nm *See* Figure 21A
15 (LEXAN-B)	In Breath+92-8 on LEXAN	LEXAN	125	2.8387E-03	4.4000E-02	Ra=0.9nm RMS=1.1nm Rmax=9.5nm *See* Figure 21A
16 (6.15A)	In Breath (6.15A 5sec+ 130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	Below Detection	Below Detection	
17 (1.5KW)	In Breath (1.5KW 5sec+ 130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	Below Detection	Below Detection	

18 (750W)	In Breath (750W 5sec+ 130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	Below Detection	Below Detection	
19 (.037-A)	In Breath from Evap 0.037 + 130 °C Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	5.1097E-02	7.9200E-01	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18A
20 (.037-B)	In Breath from Evap 0.037 + 130 °C Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	3.9935E-02	6.1900E-01	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18A
21 (.113-A)	In Breath from Evap 0.113 + 130 °C Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	5.6323E-02	8.7300E-01	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18A
22 (.113-B)	In Breath from Evap 0.113 + 130 °C Preheat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	4.1097E-02	6.3700E-01	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18A
23 (MON-A)	NO In Breath + 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	4.9806E-02	7.7200E-01	Ra=5.2nm RMS=8.5nm Rmax=76.0nm *See* Figure 18C

24 (12-17-03-01-A)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	7.8710E-04	1.2200E-02	Ra=1.1nm, RMS=1.4nm Rmax=9.4nm *See* Figure 18B
25 (12-17-03-01-B)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	1.1484E-03	1.7800E-02	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18B
26 (12-17-03-03-A)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	1.9548E-03	3.0300E-02	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18B
27 (12-17-03-03-B)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	1.1935E-03	1.8500E-02	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18B
28 (12-17-03-02_A)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#1	200	2.2065E-03	3.4200E-02	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18B
29 (12-17-03-02_B)	In Breath @280c+ 130 °C heat + 1.5 KÅ 92-8 on Pen	PEN Q65 Lot#1	200	2.7677E-03	4.2900E-02	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figure 18B

30 (165-A)	InB 750W 5sec+4300 130c Preheat + 1.5KA 92-8 on PEN	PEN Q65 Lot#2	200	Below Detection	Below Detection	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figures19A and 18D
31 (165-B)	In Breath (750W 5sec+130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#2	200	Below Detection	Below Detection	Ra=1.1nm RMS=1.4nm Rmax=9.4nm *See* Figures 19A and 18D
32 (167-A)	In Breath (750W 5sec+ 130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#2	125	9.0323E-04	1.4000E-02	Ra=2.0nm RMS=2.6nm Rmax=18.0nm *See* Figures 19B and 21B
33 (167-B)	In Breath (750W 5sec+ 130 °C heat) + 1.5 KÅ 92-8 on PEN	PEN Q65 Lot#2	125	1.4194E-03	2.2000E-02	Ra=2.0nm RMS=2.6nm Rmax=18.0nm *See* Figures 19B and 21B
34 (170-A)	In Breath (750W 5sec+130 °C heat) + 1.5 KÅ 35-65 (no bias) on PEN	PEN Q65 Lot#2	125	8.7742E-03	1.3600E-01	
35 (170-B)	In Breath (750W 5sec+130 °C heat) + 1.5 KÅ 35-65 (no Bias) on PEN	PEN Q65 Lot#2	125	2.6258E-02	4.0700E-01	

TABLE 4

	Hv [Vickers]	H [MPa]	E [GPa]	□ d [□m]
MN-Al2O3 5mN	1 836	19 814	211.49	0.129
MN-Al2O3 2.5mN	2 087	22 520	230.51	0.084
Y10822-1 5 mN	753	8 123	104.03	0.194
808-0Y10822-1 2.5 mN	834	8 996	104.29	0.130

WHAT IS CLAIMED IS:

1. A dielectric layer, comprising:

a densified amorphous dielectric layer deposited on a substrate by pulsed-DC, substrate biased physical vapor deposition,

wherein the densified amorphous dielectric layer is a barrier layer.

2. The layer of claim 1, wherein the deposition is performed with a wide area target.

3. The layer of claim 1, wherein the barrier layer is also an optical layer.

4. The layer of claim 3, wherein the barrier layer includes a TiO_2 layer.

5. The layer of claim 3, wherein the barrier layer includes an Alumina/Silica layer.

6. The layer of claim 3, further including a soft-metal breath treatment.

7. The layer of claim 6, wherein the soft-metal breath treatment is an indium-tin vapor treatment.

8. The layer of claim 1, wherein the barrier layer is also an electrical layer.

9. The layer of claim 8, wherein the barrier layer includes a capacitive layer.

10. The layer of claim 9, wherein the capacitive layer is a TiO_2 layer.

11. The layer of claim 9, wherein the capacitive layer is an Alumina/silica layer.

12. The layer of claim 8, wherein the barrier layer includes a resistive layer.

13. The layer of claim 12, wherein the resistive layer is indium-tin metal or oxide.

14 The layer of claim 8, further including a soft-metal breath treatment.

15. The layer of claim 14, wherein the soft-metal breath treatment is an indium-tin vapor treatment.

16. The layer of claim 1, wherein the barrier layer includes a tribological layer.

17. The layer of claim 16, wherein the tribological layer is a TiO_2 layer.

18. The layer of claim 16, wherein the tribological layer is Alumina/silica.

19. The layer of claim 16, further including a soft-metal breath treatment.

20. The layer of claim 19, wherein the soft-metal breath treatment is an indium-tin vapor treatment.

21. The layer of claim 1, wherein the barrier layer is a biologically immune compatible layer.

22. The layer of claim 1, wherein the biologically immune compatible layer is TiO_2.

23. The layer of claim 21, further including a soft-metal breath treatment.

24. The layer of claim 23 wherein the soft-metal breath treatment is an indium-tin vapor treatment.

25. The layer of claim 1, wherein the dielectric film is TiO_2.

26. The layer of claim 1, wherein a target utilized to form the dielectric film has a concentration of 92% Al and 8% Si.

27. The layer of claim 1, wherein the target utilized to form the dielectric film is formed from metallic magnesium.

28 The layer of claim 1, wherein the target material comprises materials chosen from a group consisting of Mg, Ta, Ti, Al, Y, Zr, Si, Hf, Ba, Sr, Nb, and combinations thereof.

29 The layer of claim 28, wherein the target material includes a concentration of rare earth metal.

30 The layer of claim 1, wherein the target material comprises a sub-oxide of a group consisting of Mg, Ta, Ti, Al, Y, Zr, Si, Hf, Ba, Sr, Nb, and combinations thereof.

31. The layer of claim 1, further including a soft-metal breath treatment.

32. The layer of claim 31, wherein the soft-metal breath treatment is an indium-tin vapor treatment.

33. The layer of claim 1, wherein the dielectric film has a permeable defect concentration of less than about 1 per square centimeter.

34. The layer of claim 1, wherein the water vapor transmission rate is less than about $1 X 10^{-2}$ $gm/m^2/day$.

35. The layer of claim 1, wherein the optical attenuation is less than about 0.1 dB/cm in a continuous film.

36. The layer of claim 1, wherein the barrier layer has a thickness less than about 500 nm.

37. The layer of claim 36, wherein the water vapor transmission rate is less than about $1 X 10^{-2}$ $gm/m^2/day$.

38. The layer of claim 1, wherein the barrier layer thickness is less than about 1 micron and the water vapor transmission rate is less than about $1 X 10^{-2}$ $gm/m^2/day$.

39. The layer of claim 1, wherein the barrier layer operates as a gate oxide for a thin film transistor.

40. A method of forming a barrier layer, comprising:

providing a substrate;

depositing a highly densified, amorphous, dielectric material over the substrate in a pulsed-DC, biased, wide target physical vapor deposition process.

41. The method of claim 40, further including

performing a soft-metal breath treatment on the substrate.

42. The method of claim 40, wherein the dielectric material is formed from a target comprising 92% Al and 8% Si.

43. The method of claim 40, wherein the dielectric material is formed from a target comprising of Titanium.

44. The method of claim 40, wherein the dielectric material is formed from a target material comprising materials chosen from a group consisting of Mg, Ta, Ti, Al, Y, Zr, Si, Hf, Ba, Sr, Nb, and combinations thereof.

45. The method of claim 41, wherein the soft-metal breath treatment is an indium/tin breath treatment.

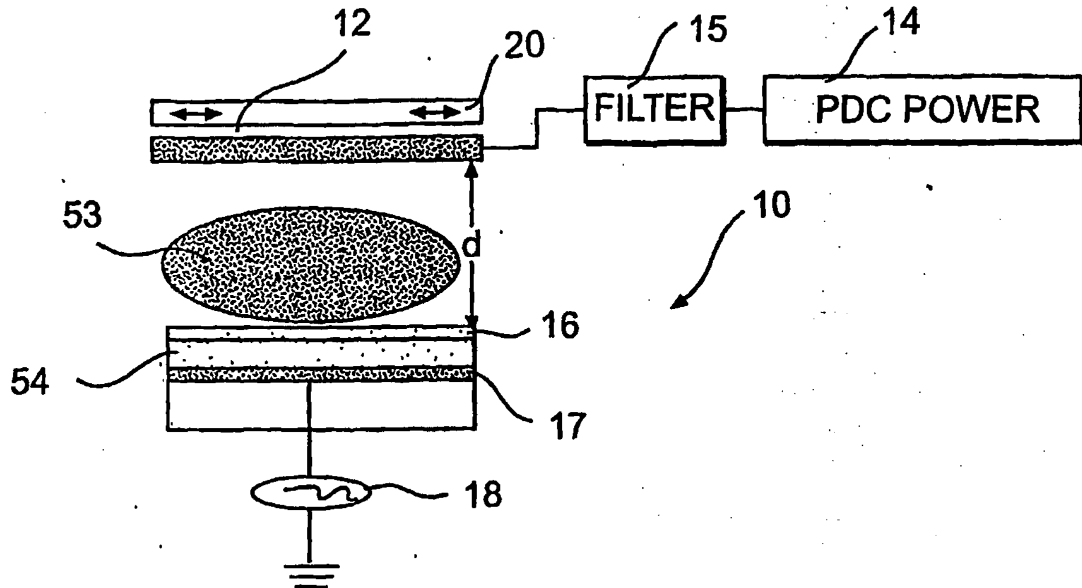


FIG. 1A

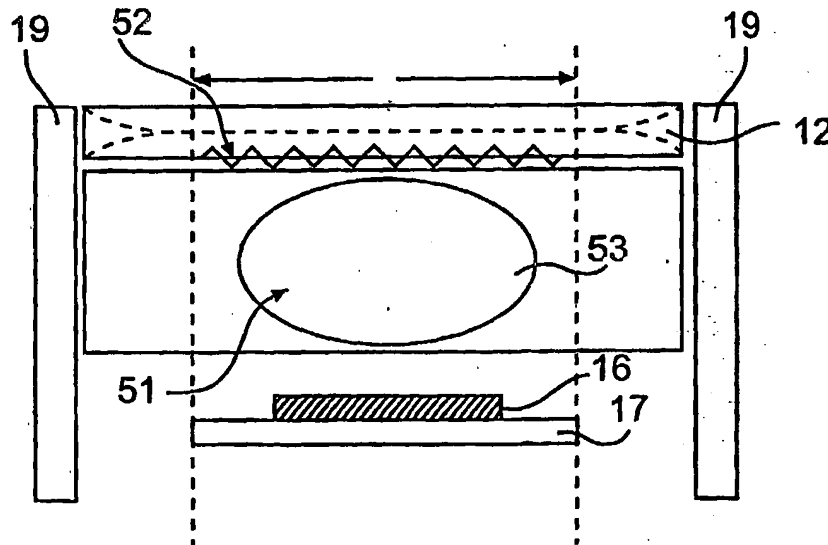


FIG. 1B

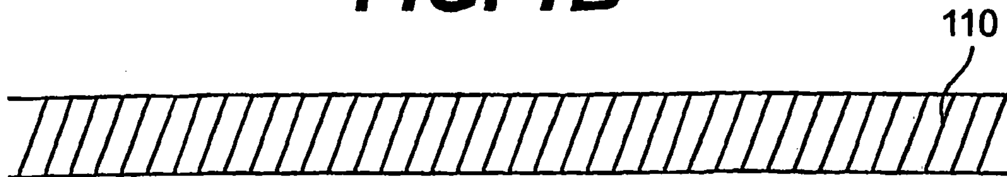


FIG. 1C

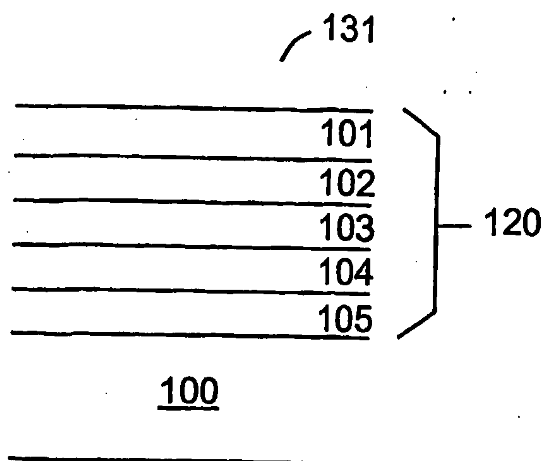


FIG. 2A

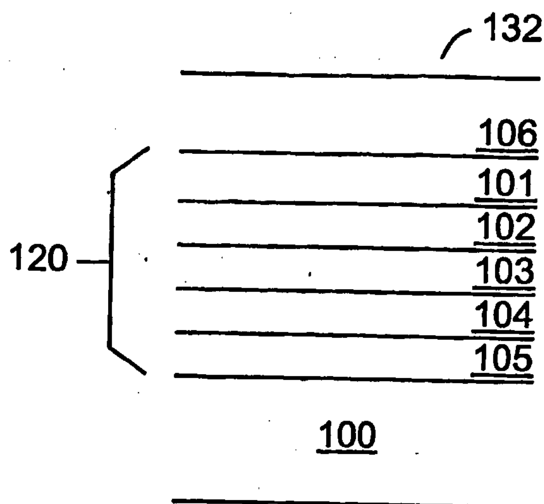


FIG. 2B

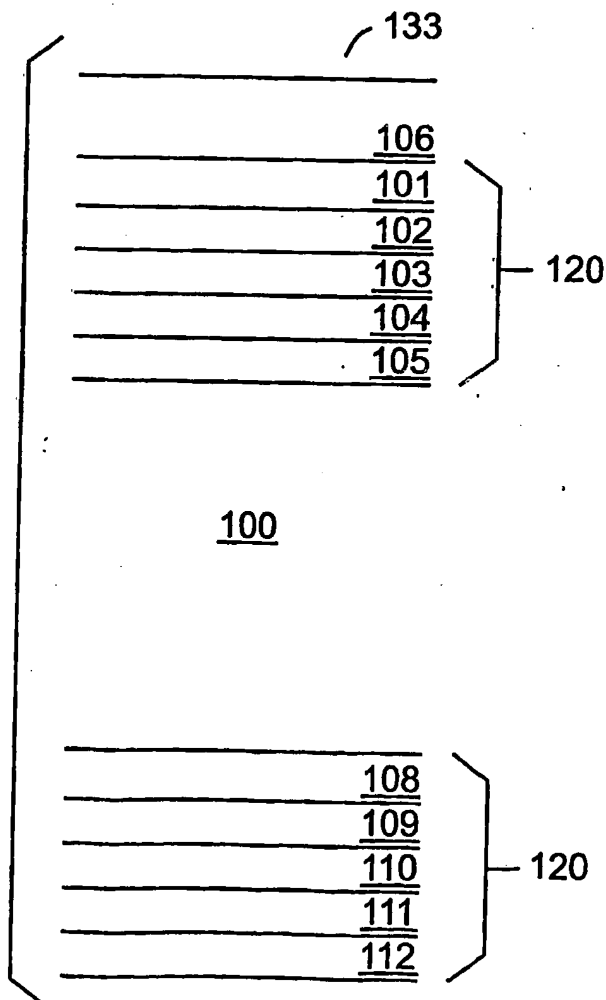


FIG. 2C

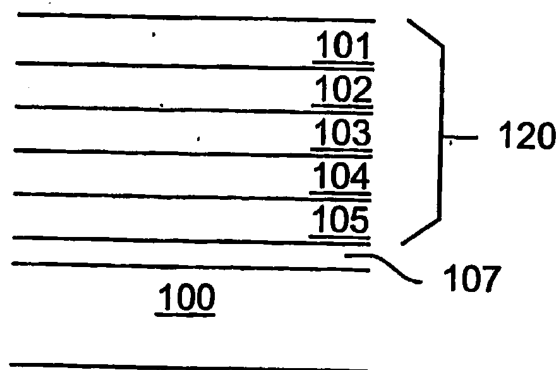


FIG. 2D

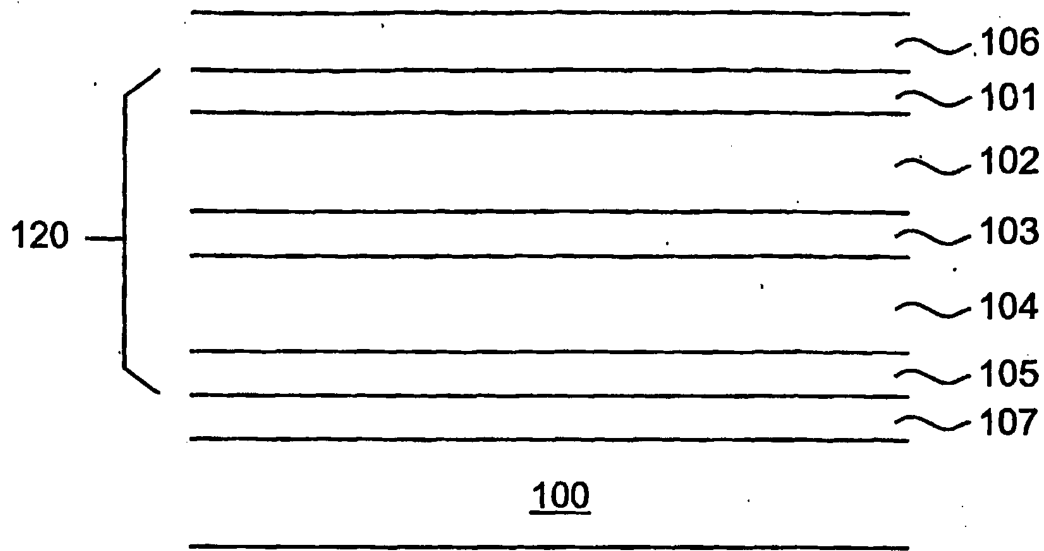


FIG. 2E

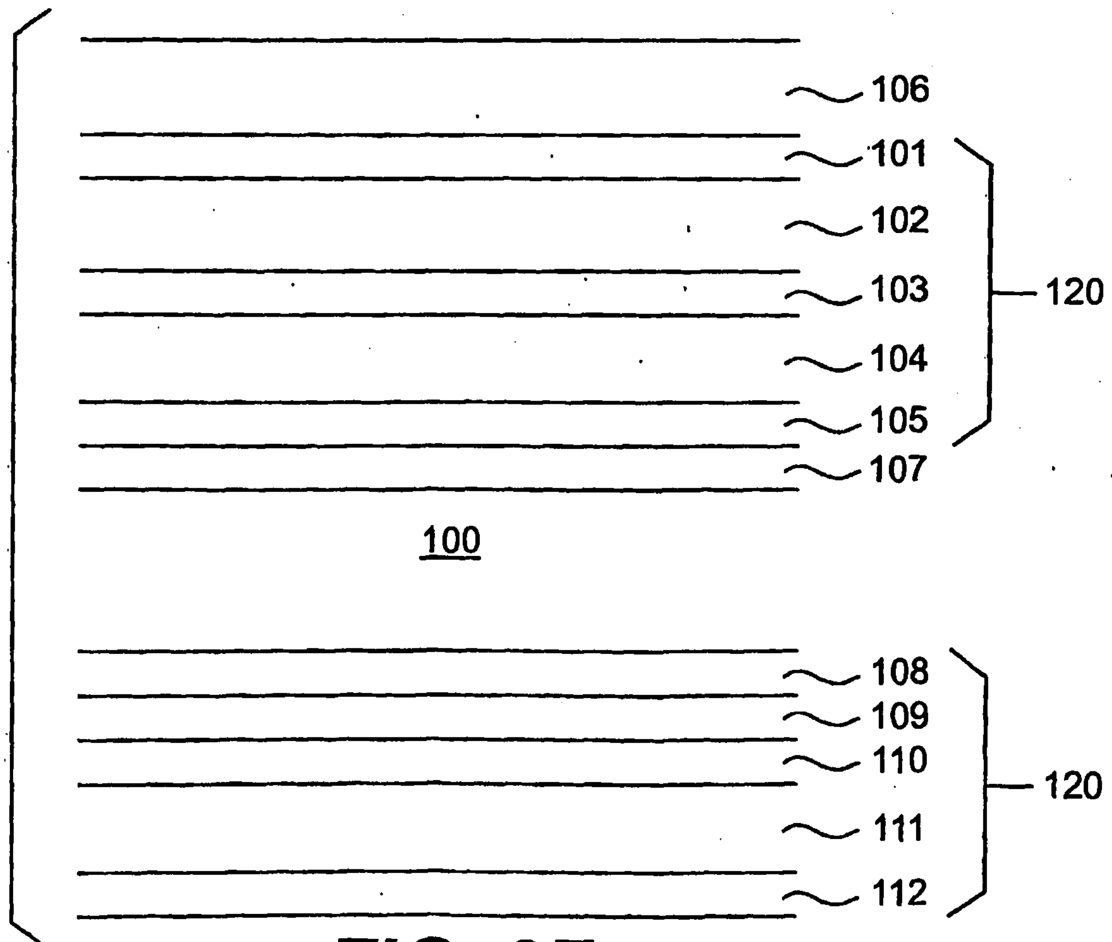


FIG. 2F

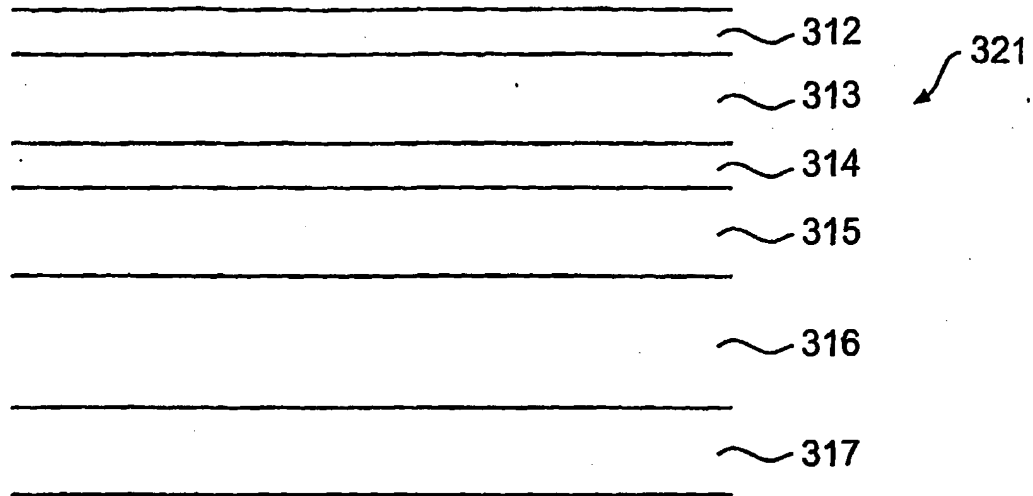


FIG. 3

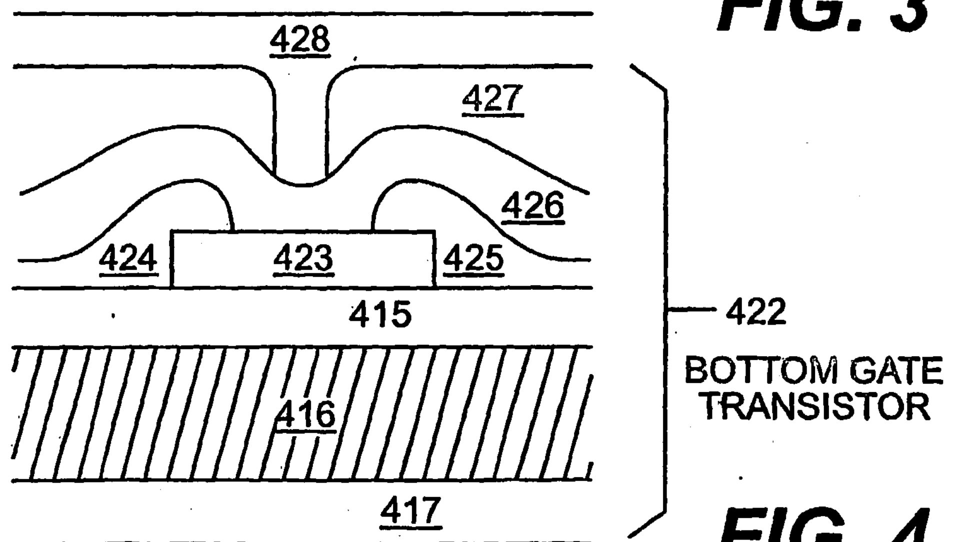


FIG. 4

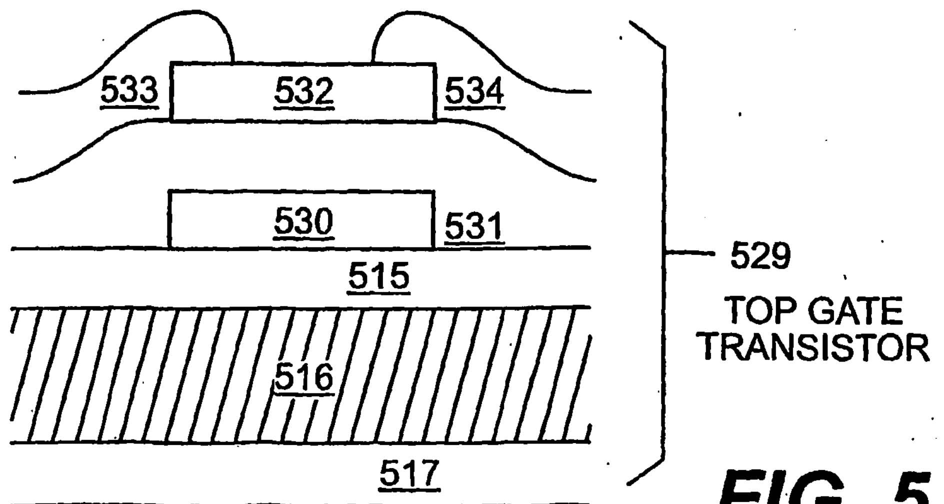


FIG. 5

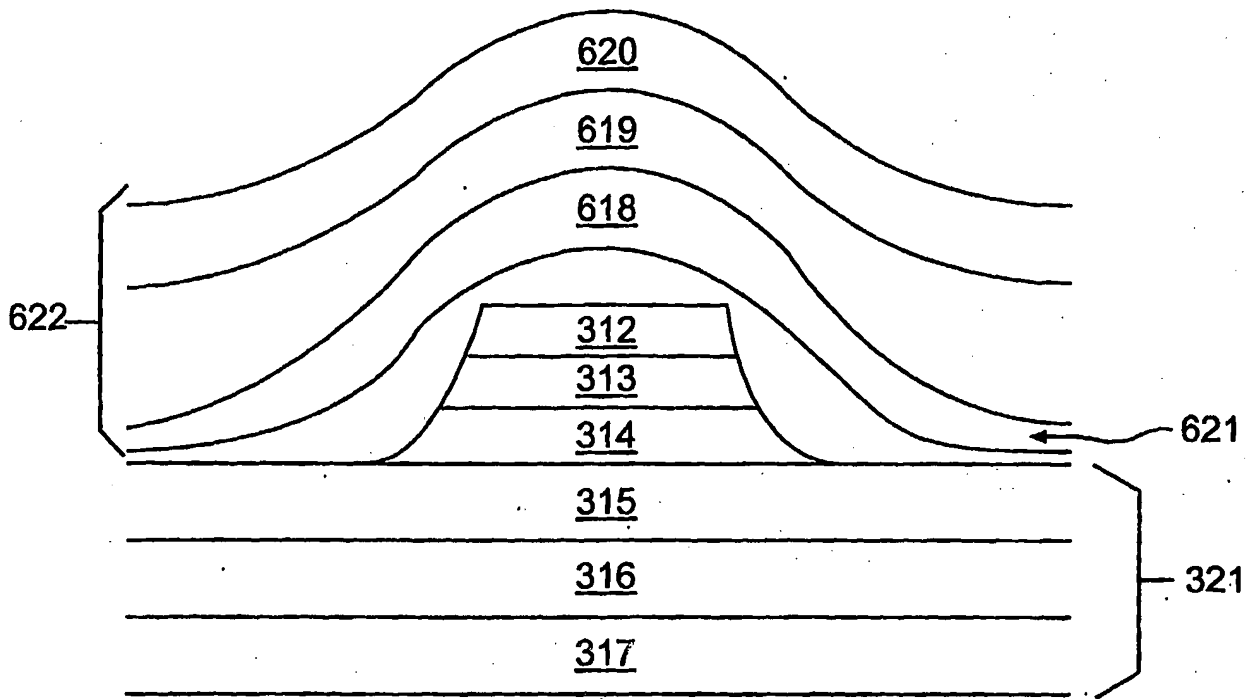


FIG. 6

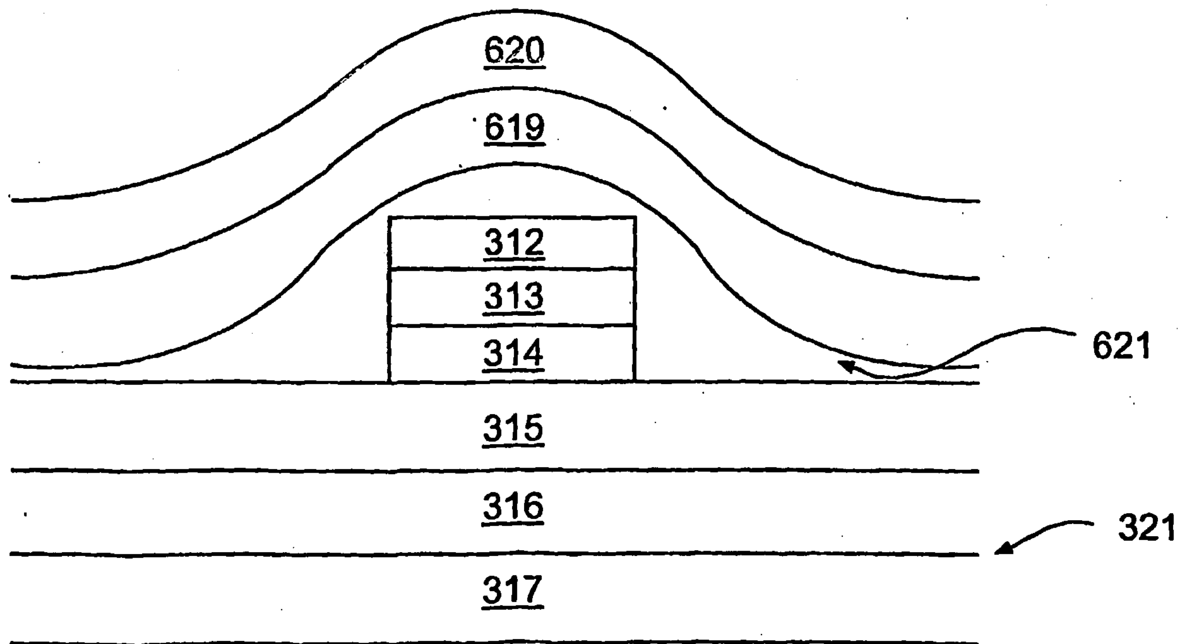


FIG. 7

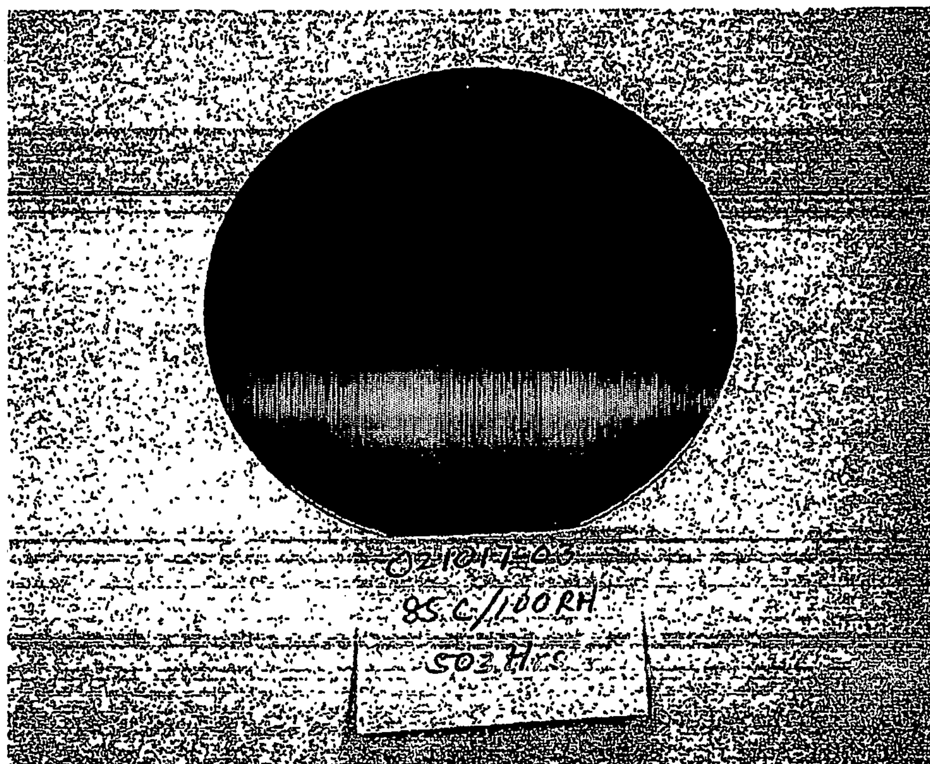


FIG. 8

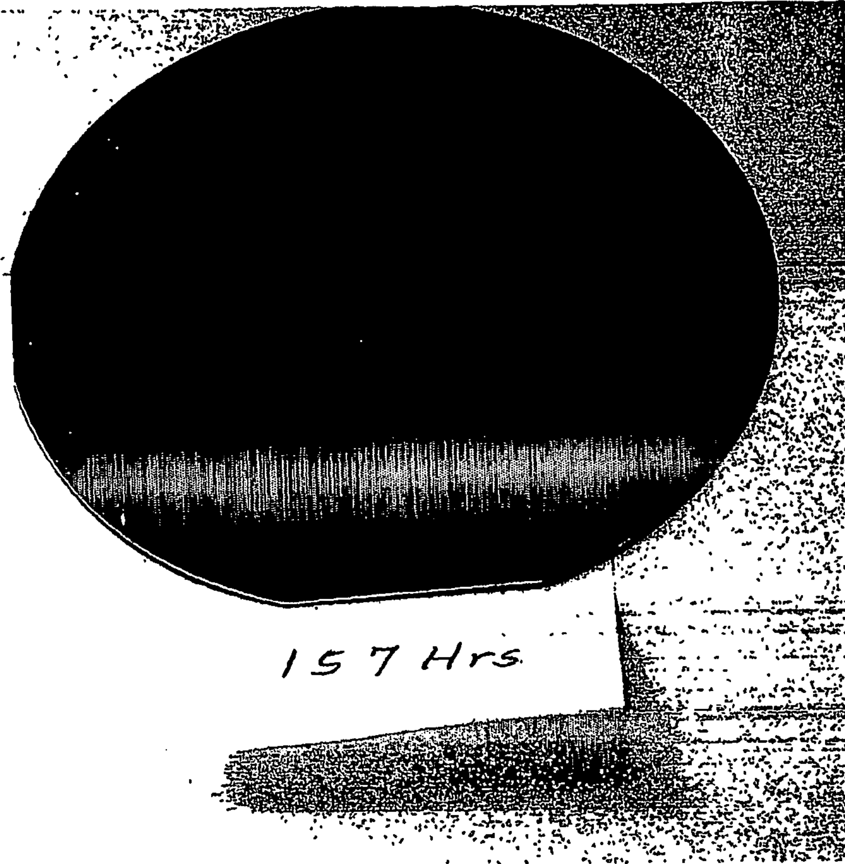


FIG. 9

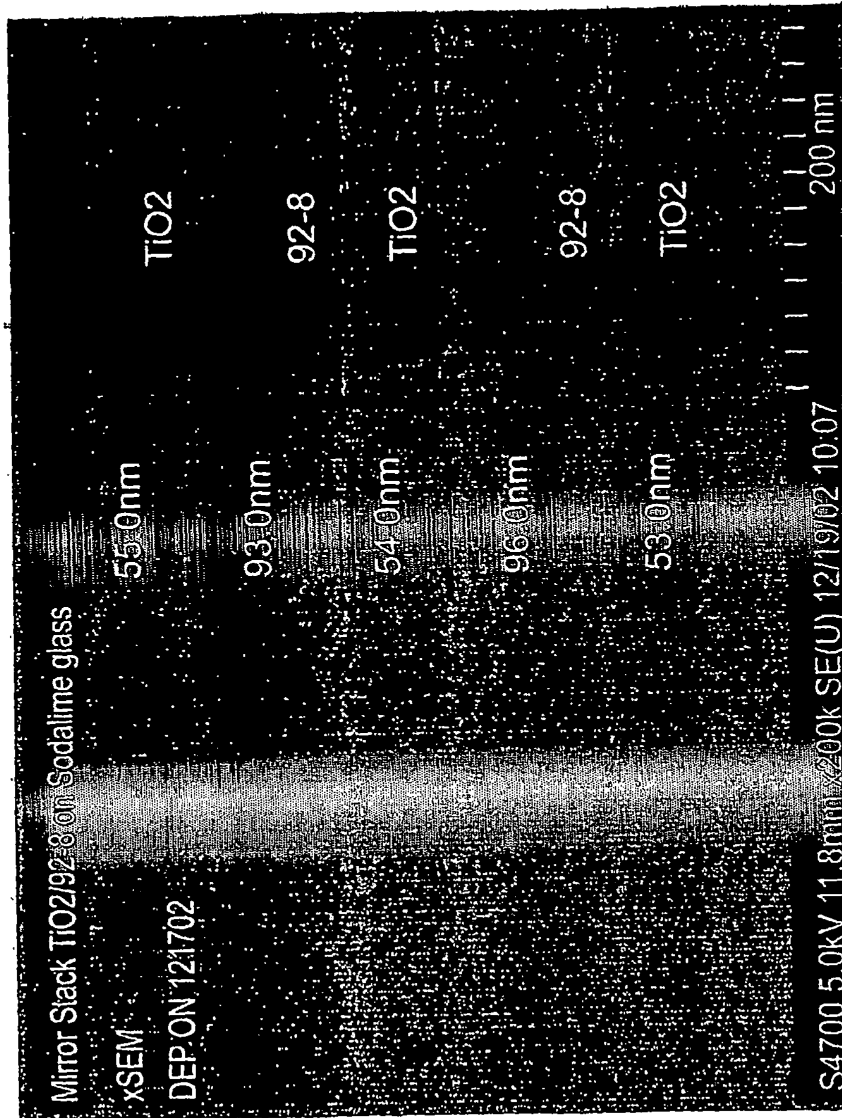


FIG. 10

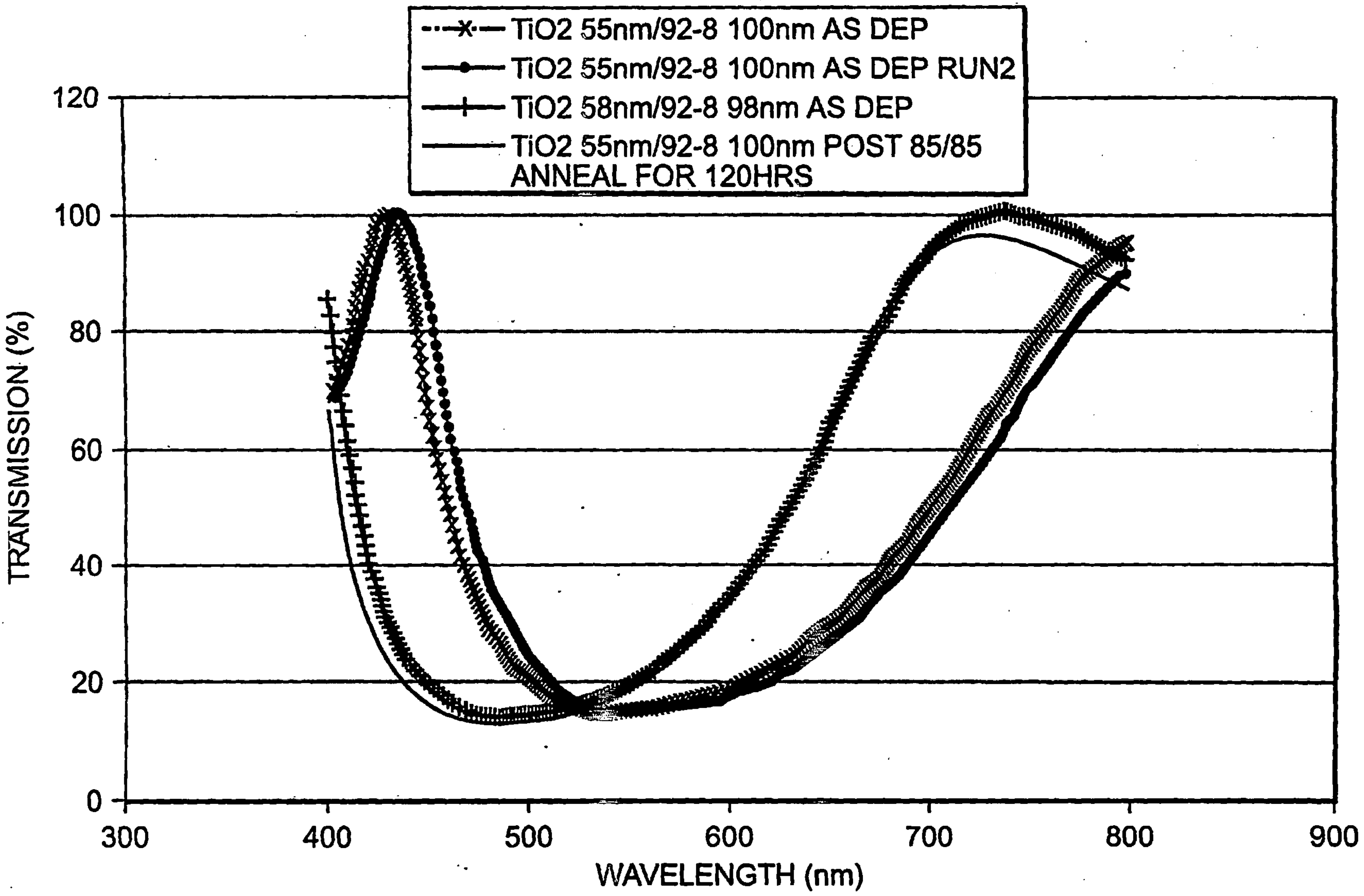


FIG. 11

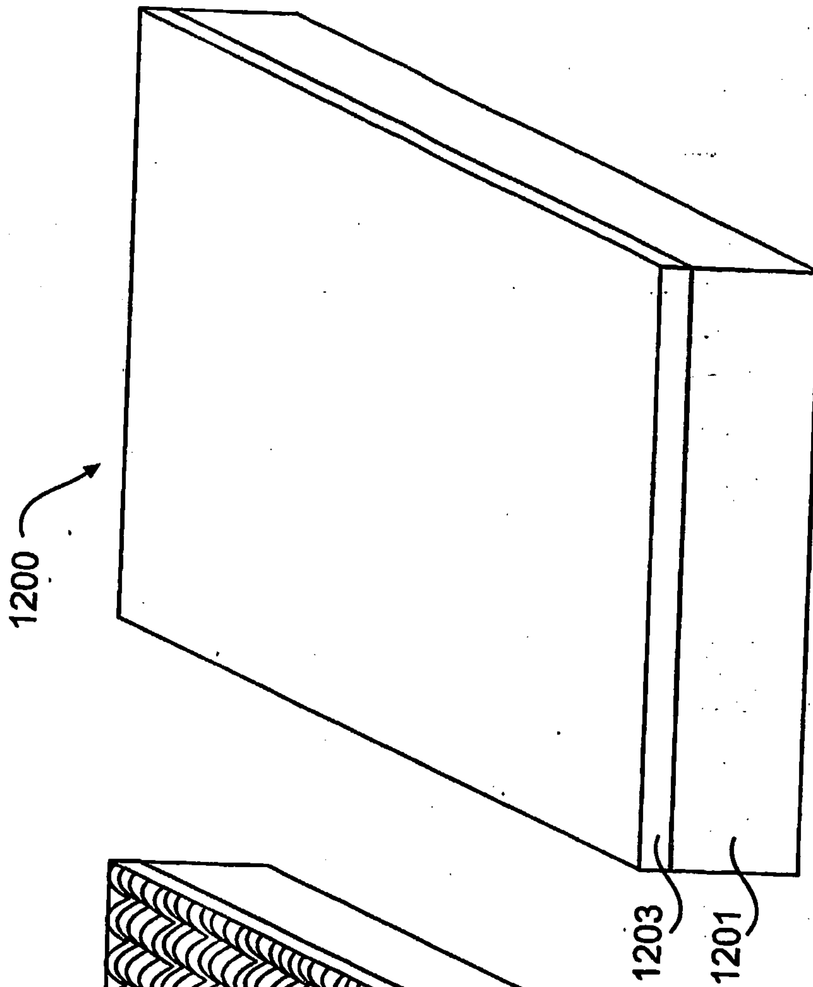


FIG. 12B

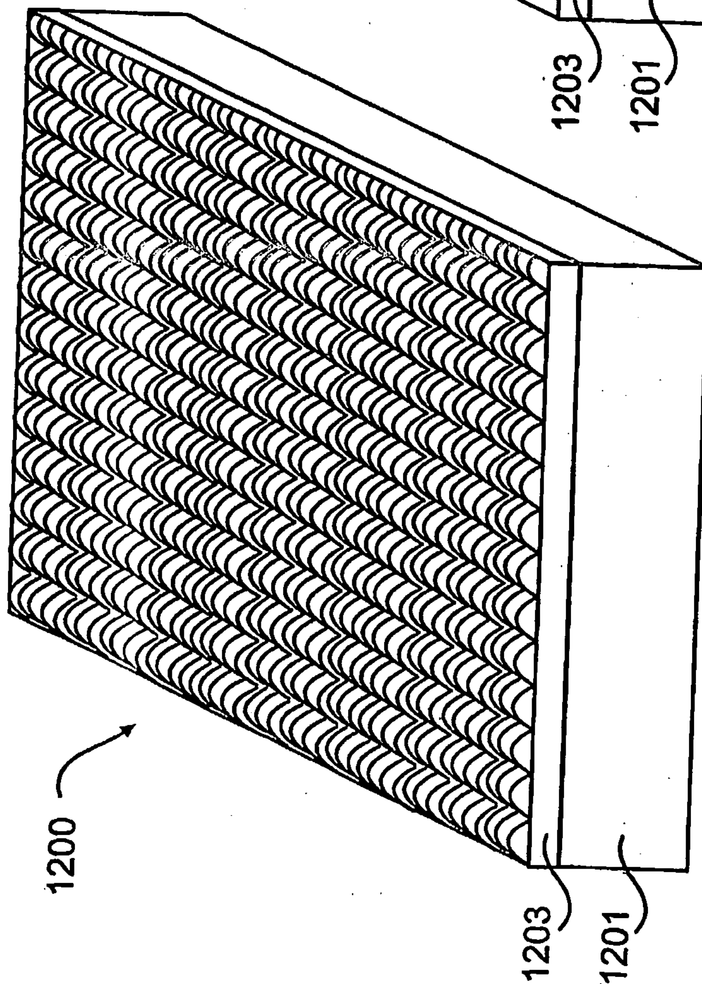


FIG. 12A

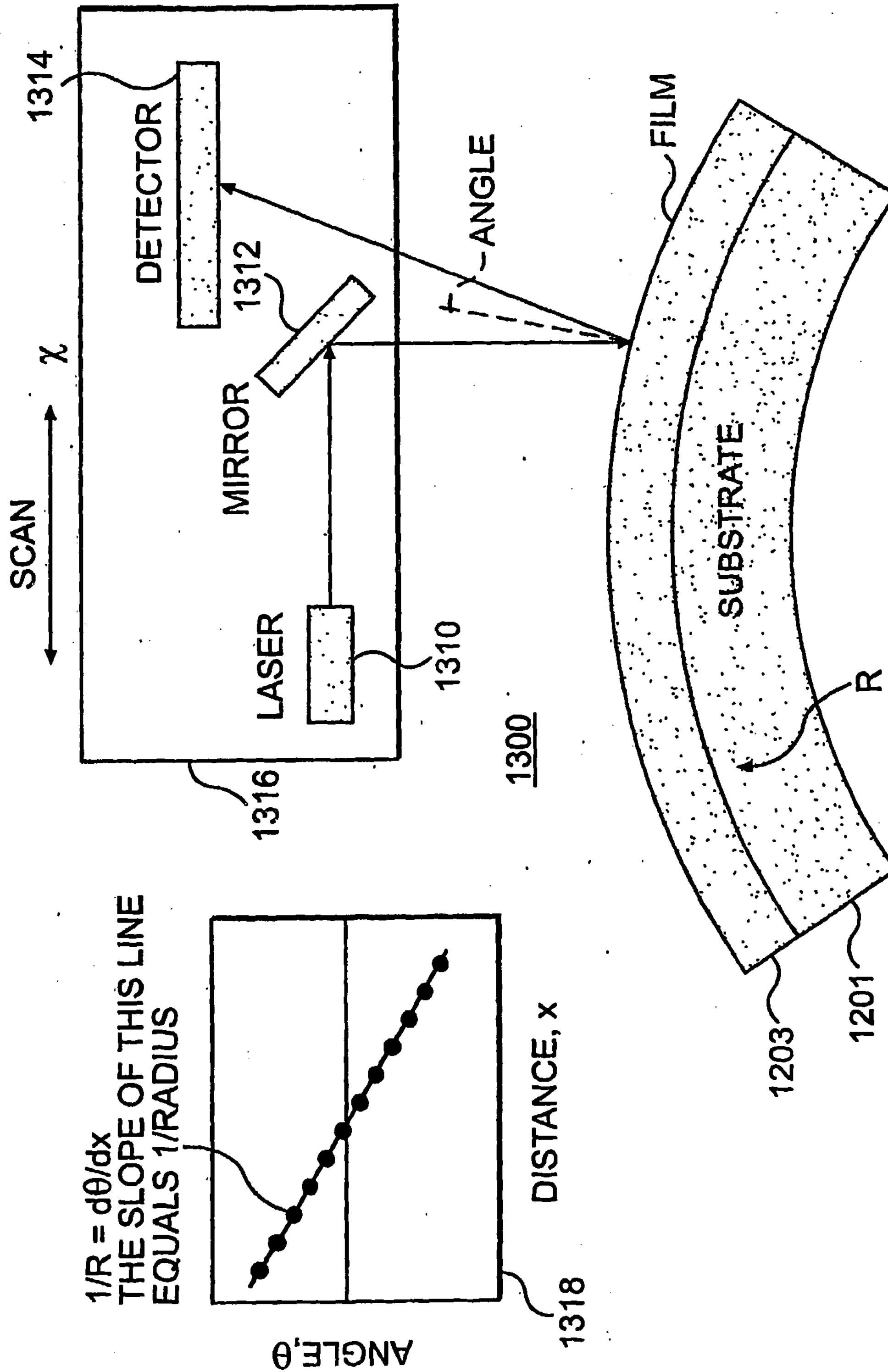


FIG. 13

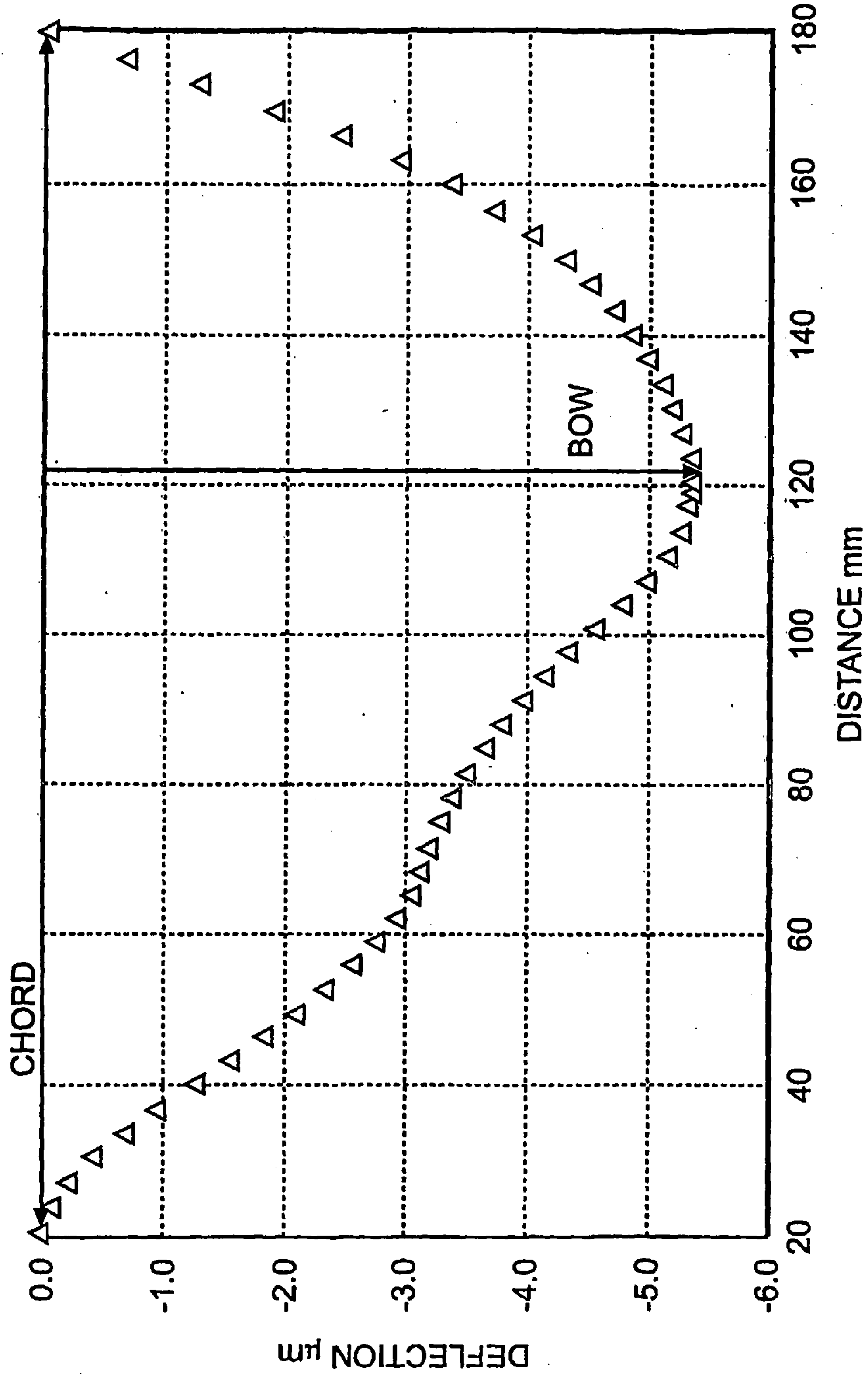


FIG. 14

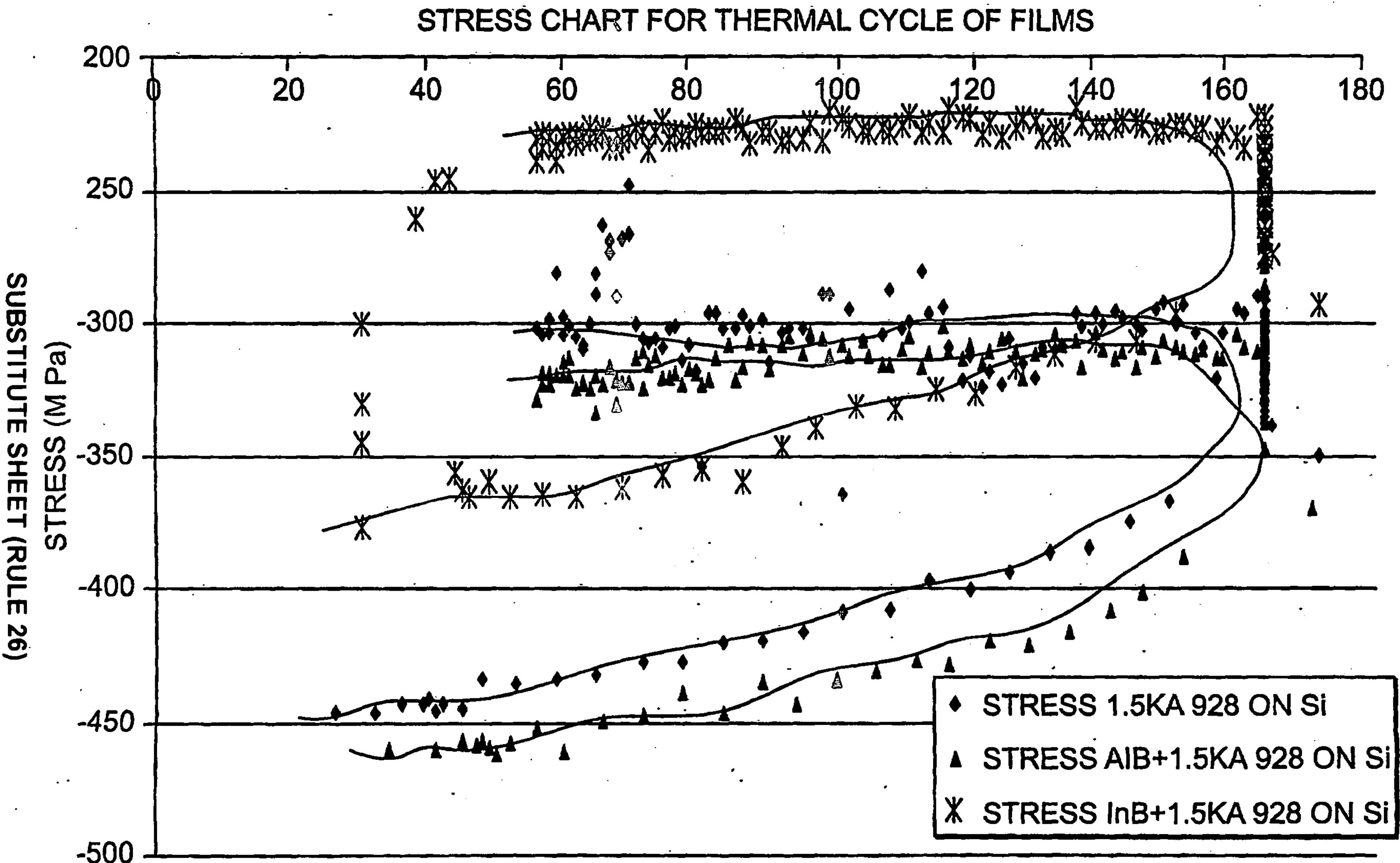


FIG. 15

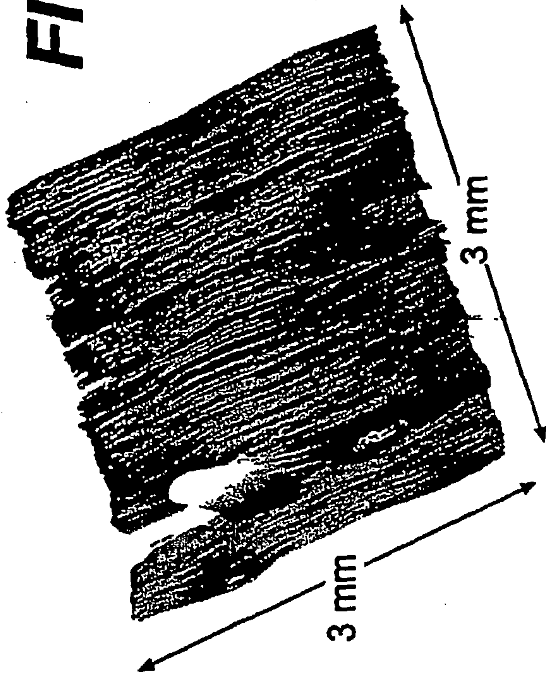


FIG. 16B

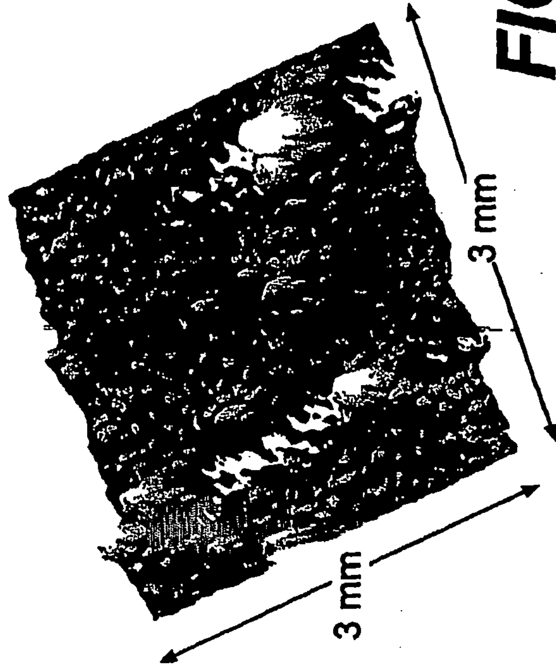


FIG. 16D

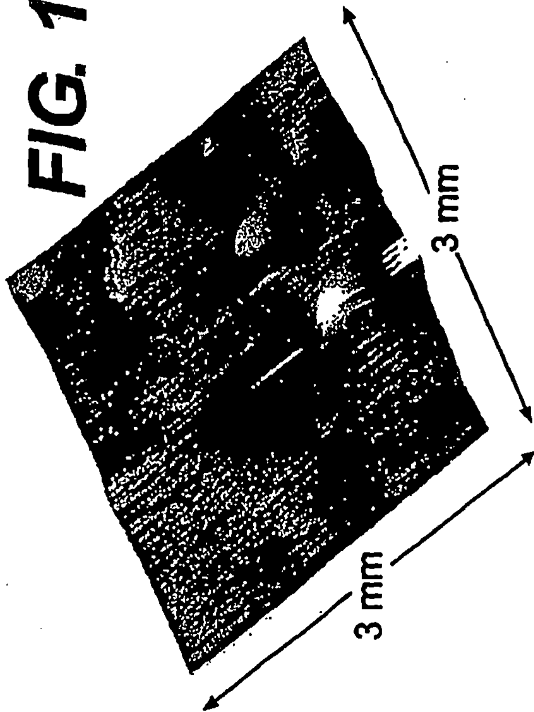


FIG. 16A

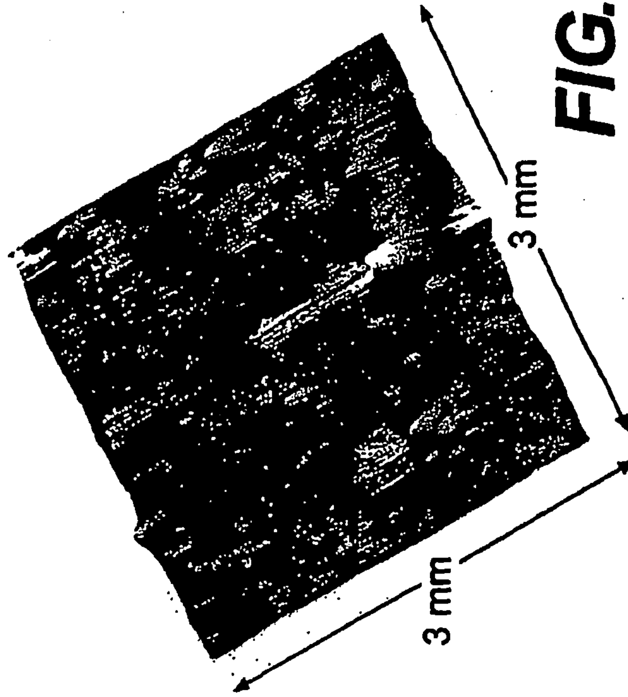


FIG. 16C

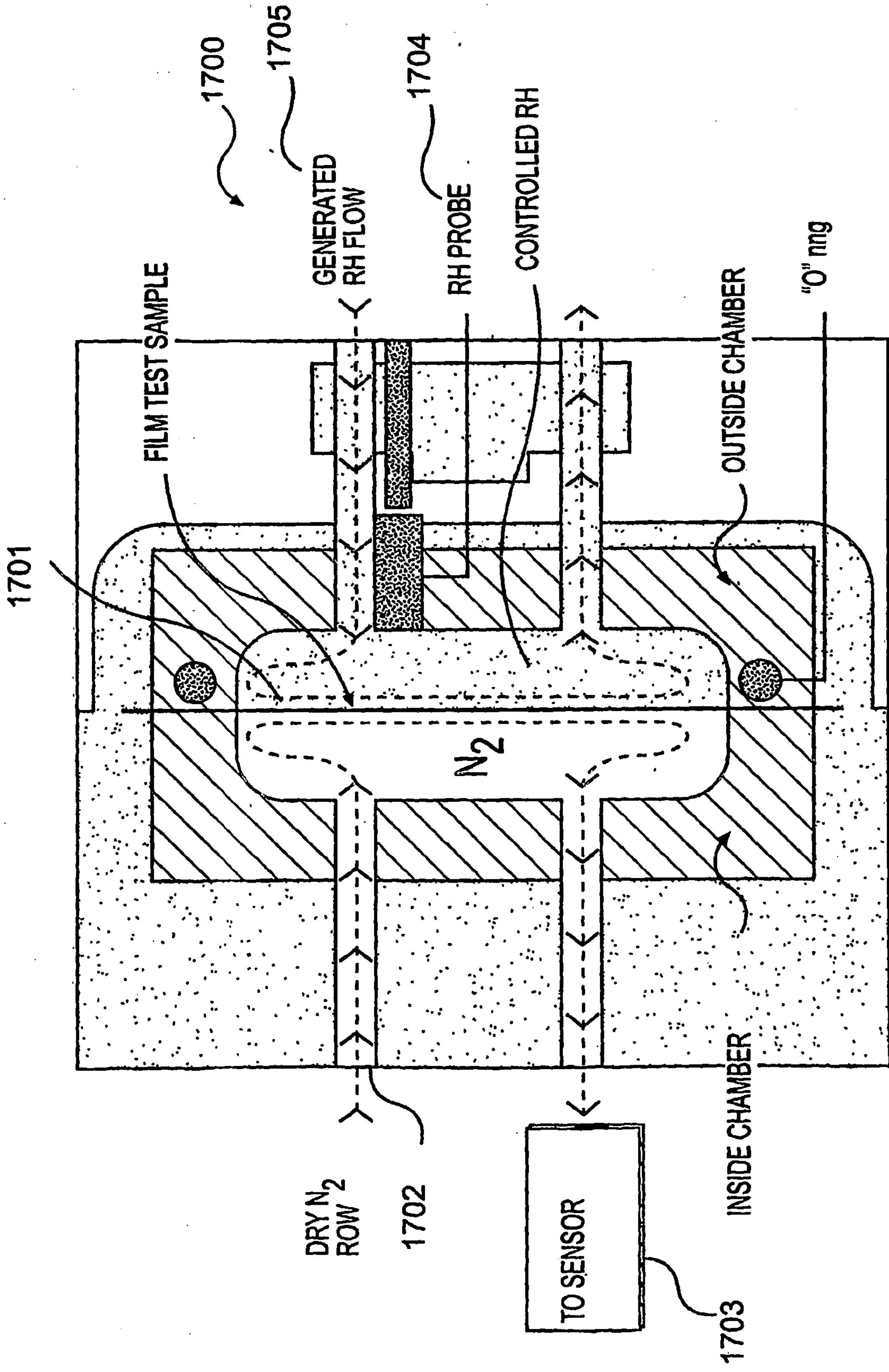


FIG. 17

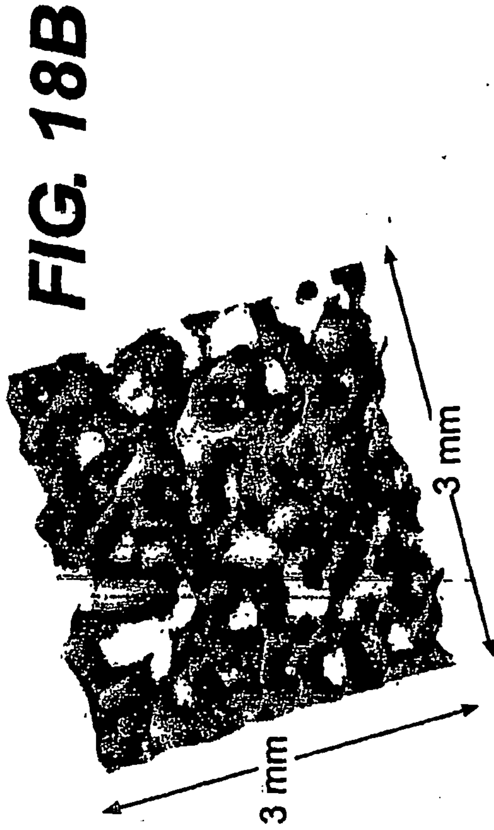


FIG. 18B

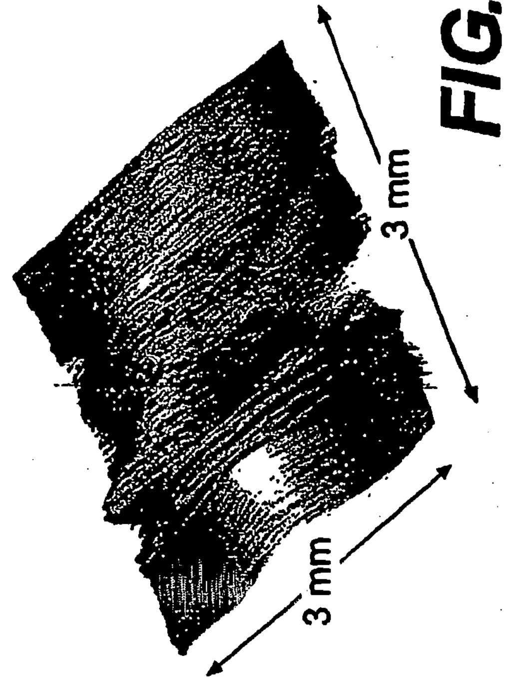


FIG. 18D

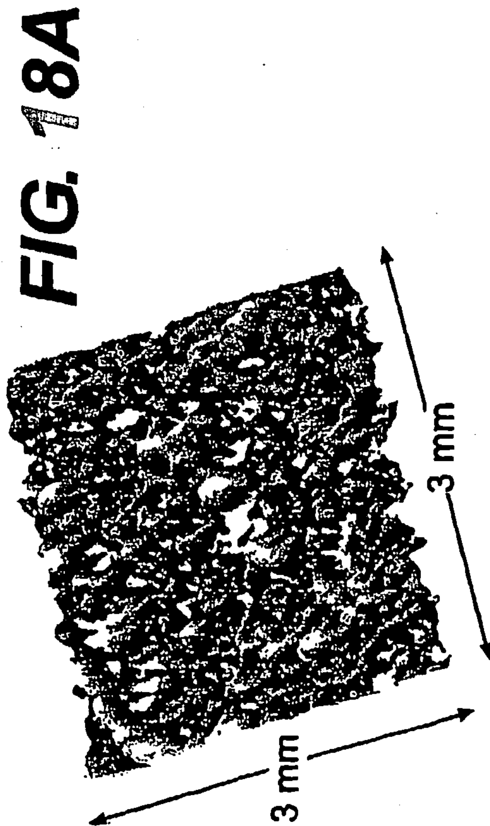


FIG. 18A

FIG. 18C

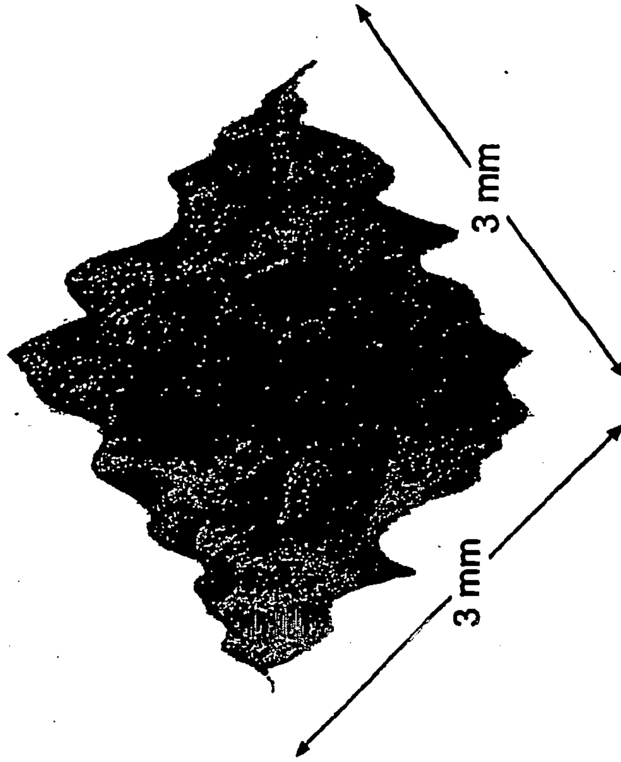


FIG. 19B

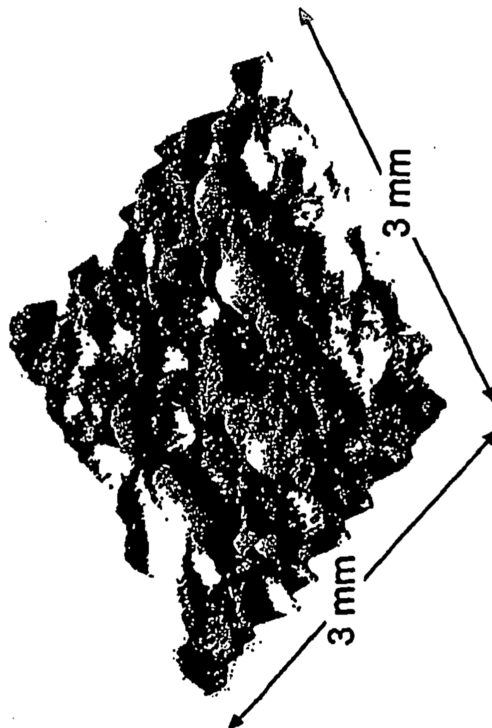


FIG. 19A

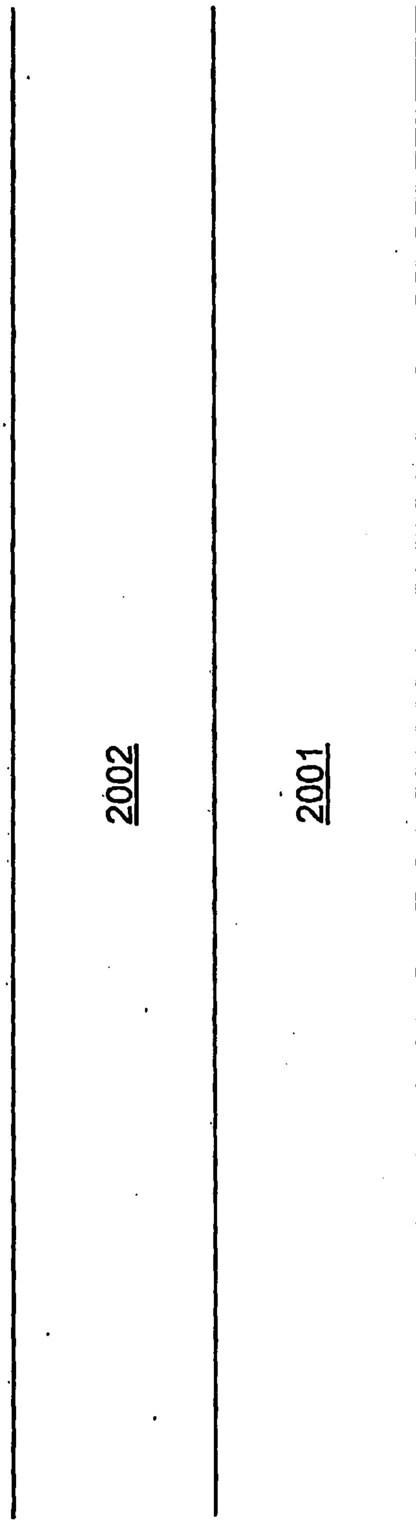


FIG. 20

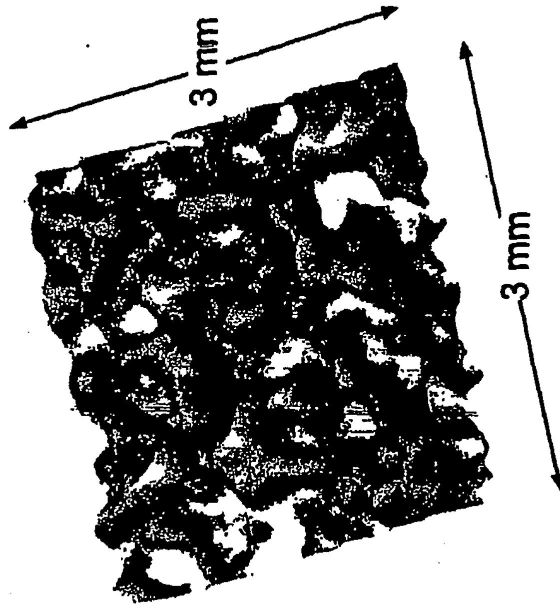


FIG. 21B

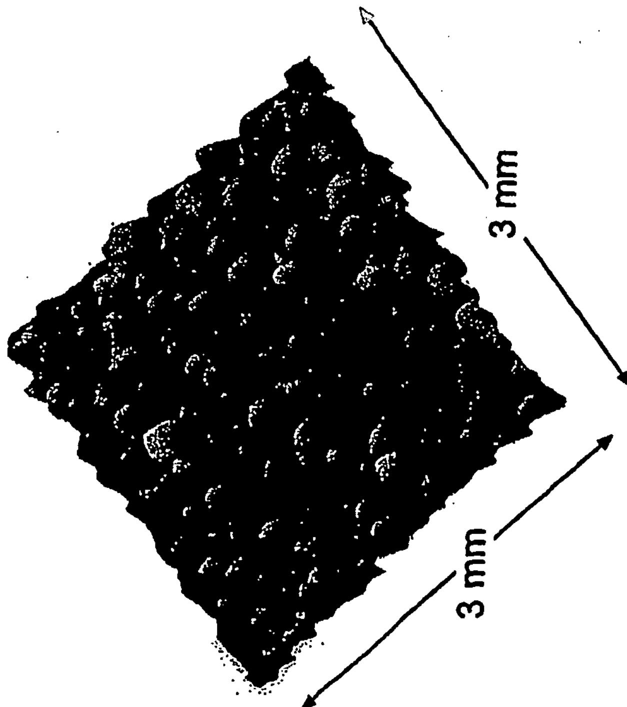


FIG. 21A

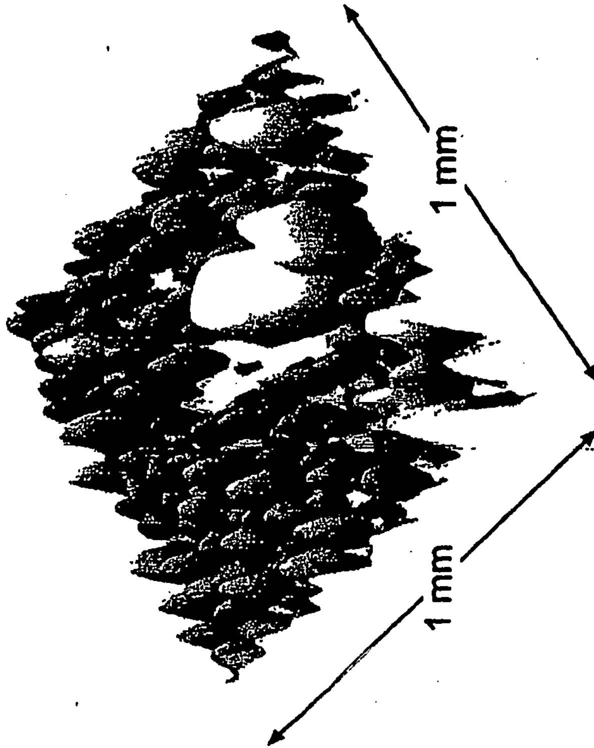


FIG. 22B

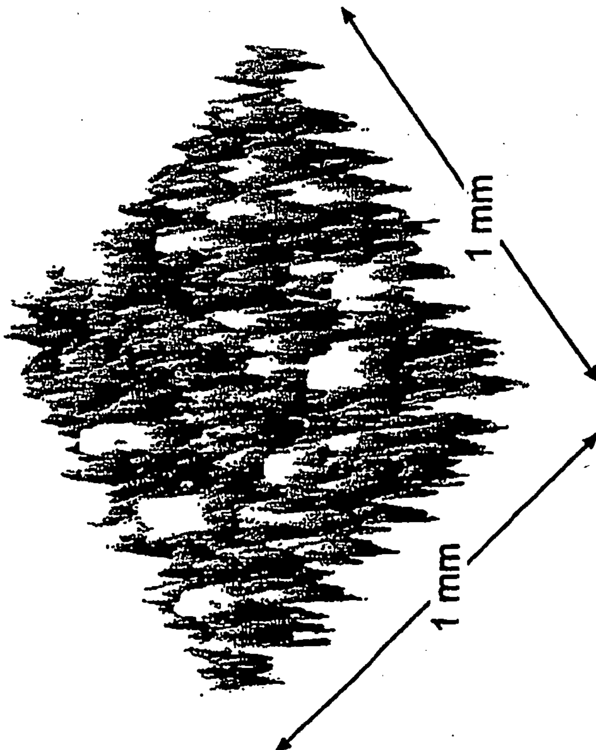


FIG. 22A

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371 (c) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938

OC000000014956746

FINNEGAN, HENDERSON, FARABOW
GARRETT & DUNNER, L.L.P.
1300 I STREET N.W.
WASHINGTON, DC 20005-3315

Date Mailed: 01/13/2005

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2003.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

JANICE L ROBERTSON
2800 (571) 272-1613

OFFICE COPY

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371 (c) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938

OC000000014956630

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

Date Mailed: 01/13/2005

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2003.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

JANICE L ROBERTSON
2800 (571) 272-1613

OFFICE COPY

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

7590 01/13/2005

FINNEGAN, HENDERSON, FARABOW
GARRETT & DUNNER, L.L.P.
1300 I STREET N.W.
WASHINGTON, DC 20005-3315

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

DATE MAILED: 01/13/2005

Remail
Corr address

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No. 10/101,863	Applicant(s) ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	

-- *The MAILING DATE of this communication appears on the cover sheet with the correspondence address* --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *23 July 2004*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-14 and 20-24* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-13 and 20* is/are rejected.

7)☒ Claim(s) *7,14 and 21-24* is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *7/23/04,9/2/04*.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

DETAILED ACTION

Claim Objections

Claim 14 is objected to because of the following informalities: in line 2, it appears that "12" should be deleted. Appropriate correction is required.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-13 and 20 are rejected under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938).

With respect to claim 1, Le et al. disclose providing pulsed DC power (22) to a target (14) (Page 4, Paragraph [0070]); providing bias power to a substrate (16) positioned opposite the target (Page 5, lines 13-14); providing process gas between the target and the substrate (Page 4, Paragraph [0067]).

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

With respect to claim 8, Le et al. disclose wherein the process gas includes a mixture of oxygen and argon (Page 4, Paragraph [0067]).

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

With respect to claim 10, Le et al. disclose wherein the process gas further includes nitrogen (Page 5, Paragraph [0074]).

With respect to claim 11, Le et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 3).

With respect to claim 12, Le et al. disclose further including uniformly sweeping the target with a magnetic field (Page 5, Paragraph [0073]).

With respect to claim 13, Le et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Page 5, Paragraph [0073]).

With respect to claim 20, Le et al. disclose conditioning a target (Page 4, Paragraph [0070]); preparing the substrate (Page 3, Paragraph [0065]); adjusting the bias power to the substrate (Page 4, Paragraph [0041]); setting the process gas flow (Page 4, Paragraph [0067]); and applying pulsed DC power to the target to deposit the film (Page 4, Paragraph [0071]).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range

of values disclosed. Furthermore, Le et al. disclose that sets of process parameters depend on the specific process chamber (Page 6, Paragraph [0081]).

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Le et al. do not disclose providing a DC power through a filter.

With respect to claims 1 and 5, Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form the DC power supply (Col. 6, lines 32-37).

Allowable Subject Matter

Claims 7, 14 and 21-24 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Response to Arguments

Applicant's arguments filed 7/23/04 have been fully considered but they are not persuasive. Applicant argues that Le et al. do not disclose a bias applied to the substrate. However, Applicant is directed to Page 5, lines 13-14, wherein Le et al. disclose applying a RF energy (bias) to the gas supplied to the substrate.

Applicant argues that Fukui does not teach a pulsed DC power supply. However, Fukui was not relied on upon for that purpose. Fukui teaches supplying power from a DC supply through a filter to the target. Fukui was relied on for the use of a filter to supply a power to the target.

In response to applicant's argument that the examiner's conclusion of obviousness is based upon improper hindsight reasoning, it must be recognized that any judgment on obviousness is in a sense necessarily a reconstruction based upon hindsight reasoning. But so long as it takes into account only knowledge which was within the level of ordinary skill at the time the claimed invention was made, and does not include knowledge gleaned only from the applicant's disclosure, such a reconstruction is proper. See *In re McLaughlin*, 443 F.2d 1392, 170 USPQ 209 (CCPA 1971).

Applicant argues that utilizing a filter provided for a DC power supply is not obvious and may not be necessary in the system taught by Le because of the lack of a bias. However, Le discloses applying a bias to energize the gas being applied to the substrate, as explained above. Therefore, a filter may be used to provide the pulsed DC power through the filter since a bias is being applied.

Applicant argues that there is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply with a pulsed DC power supply. However, the Examiner is not substituting the pulsed DC power supply for the

RF power supply coupled to the target. The rejection is based on utilizing the filter of Fukui to be used in the pulsed DC power supply of Le.

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

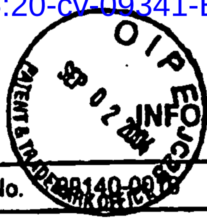
Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri can be reached on 571-272-1855. The fax phone numbers for the organization where this application or proceeding is assigned are 703-308-7722 for regular communications and 703-308-7724 for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

MEstrada
October 4, 2004

Olik Chaudhuri
Supervisory Patent Examiner
Technology Center 2800



OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0018	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
MHE		3,616,403	Oct. 26, 1971	Collins et al.	204	192	
MHE		3,850,604	Nov. 26, 1974	Klein	65	32	
MHE		4,111,523	Sep. 5, 1978	Kaminow et al.	350	96.14	
MHE		4,619,680	Oct. 28, 1986	Nourshargh et al.	65	3.12	
MHE		5,196,041	Mar. 23, 1993	Tumminelli et al.	65	30.1	
MHE		5,287,427	Feb. 15, 1994	Atkins et al.	385	124	
MHE		6,511,615 B1	Jan. 28, 2003	Dawes et al.	264	1.21	
MHE		6,563,998 B1	May 13, 2003	Farah et al.	385	131	
MHE		6,605,228 B1	Aug. 12, 2003	Kawaguchi et al.	216	24	
MHE		6,615,614 B1	Sep. 9, 2003	Makikawa et al.	65	386	

FOREIGN PATENT DOCUMENTS

		Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

Examiner *Michelle Estrada* Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS							
Examiner Initial*	Document Number	Issue Date	Name	Class	Sub Class	Filing Date, If Appropriate
ME	2002/0106297		Ueno et al.	419	12	Aug. 08, 2002
ME	2003/0019326		Han et al.	45	245	Jan. 30, 2003
ME	2003/0063883		Demaray et al.	385	129	Apr. 3, 2003
ME	2003/0175142		Milonopoulou et al.	419	49	Sep. 18, 2003
ME	4,437,966	Mar. 7, 1961	Hope et al	204	298	
ME	4,915,810	Apr. 10, 1990	Kestigian et al.	204	298.04	
ME	4,978,437	Dec. 18, 1990	Wirz	204	192.	
ME	5,174,876	Dec. 29, 1992	Buchal et al.	427	526	
ME	5,200,029	Apr. 6, 1993	Bruce et al.	156	657	
ME	5,206,925	Apr. 27, 1993	Nakazawa et al.	385	142	
ME	5,225,288	Jul. 6, 1993	Beeson et al.	428	475.5	
ME	5,237,439	Aug. 17, 1993	Misono et al.	359	74	
ME	5,252,194	Oct. 12, 1993	Demaray et al.	204	298	
ME	5,303,319	Apr. 12, 1994	Ford et al.	385	131	
ME	5,381,262	Jan. 10, 1995	Arima et al.	359	341	
ME	5,427,669	Jun. 27, 1995	Drummond	204	298.2	
ME	5,475,528	Dec. 12, 1995	LaBorde	359	341	
ME	5,483,613	Jan. 9, 1996	Bruce et al.	385	129	
ME	5,555,127	Sep. 10, 1996	Abdelkader et al.	359	341	
ME	5,565,071	Oct. 15, 1996	Demaray et al.	204	192	
ME	5,603,816	Feb. 18, 1997	Demaray et al.	204	298	

Examiner Michelle Estrada	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 — Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
[initials]		5,613,995	Mar. 25, 1997	Bhandarkar et al.	65	384	
[initials]		5,654,054	Aug. 5, 1997	Tropsha et al.	428	36.6	
[initials]		5,693,956	Dec. 2, 1997	Shi et al.	257	40	
[initials]		5,718,813	Feb. 17, 1998	Drummond	204	192.2	
[initials]		5,719,976	Feb. 17, 1998	Henry et al.	385	50	
[initials]		5,792,550	Aug. 11, 1998	Phillips et al.	428	336	
[initials]		5,841,931	Nov. 24, 1998	Foresi et al.	385	131	
[initials]		5,847,865	Dec. 8, 1998	Gopinath et al.	359	343	
[initials]		5,855,744	Jan. 5, 1999	Halsey et al.	204	192	
[initials]		5,948,215	Sep. 7, 1999	Lantsman	204	192.12	
[initials]		5,961,682	Oct. 5, 1999	Lee et al.	65	384	
[initials]		5,977,582	Nov. 2, 1999	Fleming et al.	257	310	
[initials]		6,001,224	Dec. 14, 1999	Drummond	204	192.12	
[initials]		6,024,844	Feb. 15, 2000	Drummond et al.	204	192.12	
[initials]		6,051,114	Apr. 18, 2000	Yao et al.	204	192.3	
[initials]		6,093,944	Jul. 25, 2000	VanDover	257	310	
[initials]		6,162,709	Dec. 19, 2000	Raux et al.	438	513	
[initials]		6,176,986	Jan. 23, 2001	Watanabe et al.	204	298.13	
[initials]		6,248,291	Jun. 19, 2001	Nakagama et al.	419	46	
[initials]		6,280,585 B1	Aug. 28, 2001	Obinata et al.	204	298.19	
[initials]		6,287,986	Sep. 11, 2001	Mihara	438	763	

Examiner [signature]	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 — Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 16, 2002	Group:	2823

U.S. PATENT DOCUMENTS

Examiner Initial*	Document Number	Issue Date	Name	Class	Sub Class	Filing Date If Appropriate
ME	6,290,822	Sep. 18, 2001	Fleming et al.	204	192.22	
ME	6,344,419	Feb. 5, 2002	Forster et al.	438	758	
ME	6,350,353	Feb. 26, 2002	Gopalraja et al.	204	192.3	
ME	6,358,810	Mar. 19, 2002	Dornfest et al.	438	398	
ME	6,409,965	Jun. 25, 2002	Nagate et al.	419	26	
ME	6,413,382	Jul. 2, 2002	Wang et al.	204	192.12	
ME	6,537,428	Mar. 25, 2003	Xiong et al.	204	192.13	
ME	6,602,338	Aug. 5, 2003	Chen et al.	252	301.4	

FOREIGN PATENT DOCUMENTS

	Document Number	Publication Date	Country	Class	Sub Class	Translation Yes or No
ME	EP 0 820 088	01/21/98	Europe	H 01 J	37/34	
ME	EP 0 867 985 A1	09/01/98	Europe	H 01 S	3/06	
ME	JP 6-010127	01/18/94	Japan	C 23 C	14/35	Abstract
ME	JP 6-100333	12/04/94	Japan	C 03 C	21/00	Abstract
ME	WO 00/22742	04/01/00	PCT	H 04 B		
ME	WO 00/36665	06/22/00	PCT	H 01 L	51/20	
ME	WO 02/12932	02/14/02	PCT	H 01 S	3/16	
ME	WO 96/23085	08/01/96	PCT	C 23 C	14/34	
ME	WO 97/35044	09/25/97	PCT	C 23 C	14/40	

Examiner Michelle Estrada	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No. 09140-0016	Appln. No. 10/101,863
Applicant ZHANG et al.	
Filing Date March 16, 2002	Group: 2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
MF	BARBIER, Denis, "Performances and potentioal applications of erbium doped planar waveguide amplifiers and lasers," GeeO, pp. 58-63.
MF	BELKIND et al., "Using pulsed direct current power for reactive sputtering of Al_2O_3," *J. Vac. Sci. Technol.* A 17(4), pp. 1934-40 (Jul. 1999).
MF	BYER et al., "Nonlinear Optics and Solid-state Lasers," *IEEE Journal on Selected Topics in Quantum Electronics*, Vol. 6, No. 6, pp. 921-929 (Nov. 2000).
MF	FUJII et al, "1.54 mm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals for Er^{3+}", *Appl. Phys. Lett.*, 71 (9), pp. 1198-1200 (September, 1997).
MF	KELLY et al., "Reactive pulsed magnetron sputtering process for alumina films," *J. Vac. Sci. Technol.* A 18(6), pp. 2890-96 (Nov. 2000).
MF	KELLY et al., "Control of the structure and properties of aluminum oxide coatings deposited by pulsed magnetron sputtering," *J. Vac. Sci. Technol.* A 17(3), pp. 945-953 (May 1999).
MF	PAN et al., "Planar Er3+-doped aluminosilicate waveguide amplifier with more than 10 dB gain across C-band," Optical Society of America, 3 pages (2000).
MF	ROBERTS et al., "The Photoluminescence of Erbium-doped Silicon Monoxide," Department of Electronics and Computer Science, 7 pages (June 1996).
MF	SCHILLER et al. "PVD Coating of Plastic Webs and Sheets with High Rates on Large Areas," European Materials Research Society 1999 Spring Meeting, Strasbourg, France (June 1-4, 1999).
MF	SHAW et al. "Use of Vapor Deposited Acrlate Coatings to Improve the Barrier Properties of MetallizedFilm," Society of Vacuum Coaters 505/856-7168, 37th Annual Technical Conference Proceedings, pp. 240-244 (1994).
MF	SHIN et al. "Dielectric and Electrical Properties of Sputter Grown (Ba,Sr)TiO_3 Thin Films," *J. Appl. Phys.*, Vol. 86, No. 1, pp. 506-513, (July 1, 1999).
MF	SHMULOVICH et al., "Recent progress in Erbium-doped waveguide amplifiers," Bell Laboratories, 3 pages (1999).
MF	TING et al., "Study of planarized sputter-deposited SiO2," *J. Vac. Sci. Technol.*, 15(3) pp. 1105-1112 (May/Jun. 1978).

Examiner [signature]	Date Considered 9/28/04
*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.	
Form PTO 1449	Patent and Trademark Office - U.S. Department of Commerce

OMB No. 0651-0011

INFORMATION DISCLOSURE CITATION

Atty. Docket No.	09140-0016	Appln. No.	10/101,863
Applicant	ZHANG et al.		
Filing Date	March 18, 2002	Group:	2823

	OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)
[initials]	VAN DOVER, R.B. "Amorphous Lanthanide-Doped TiO_x Dielectric Films," *Appl. Phys. Lett.*, Vol. 74, No. 20, pp. 3041-3 (May 17 1999).
[initials]	WESTLINDER et al. "Simulation and Dielectric Characterization of Reactive dc Magnetron Cosputtered $(Ta_2O_5)_{1-x}(TiO_2)_x$ Thin Films," *J. Vac. Sci. Technol.* B, Vol 20, No. 3, pp. 855-861 (May/Jun 2002).
[initials]	YOSHIKAWA, K. et al., "Spray formed aluminium alloys for sputtering targets," *Power Metallurgy*, Vol. 43, No. 3, pp. 198-99 (2000)
[initials]	ZHANG, Hongmei et al. "High Dielectric Strength, High k TiO_2 Films by Pulsed DC, Reactive Sputter Deposition," (2002).

Examiner [signature]	Date Considered 9/28/04

*Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Form PTO 1449 — Patent and Trademark Office - U.S. Department of Commerce

2823

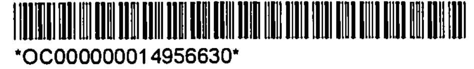
IFW

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371 (c) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938



OC000000014956630

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

Date Mailed: 01/13/2005

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2003.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

Janice Robertson

JANICE L ROBERTSON
2800 (571) 272-1613

FORMER ATTORNEY/AGENT COPY

RECEIVED
MAR 17 2005
OIPE/JCWS

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	PATENT NUMBER	GROUP ART UNIT	FILE WRAPPER LOCATION
10/101,863		2823	06B0

Correspondence Address / Fee Address Change

The following fields have been set to Customer Number 22852 on 04/08/2005

- Correspondence Address

The address of record for Customer Number 22852 is:
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON,DC 20001-4413

2823 IFW

IFW

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371 (c) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US

CONFIRMATION NO. 6938

OC000000014956630

Skjerven Morrill Macpherson LLP
Suite 700
250 Metro Drive
San Jose, CA 95110

Date Mailed: 01/13/2005

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2003.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

Janice Robertson

JANICE L ROBERTSON
2800 (571) 272-1613

FORMER ATTORNEY/AGENT COPY

RECEIVED
MAR 17 2005
OIPE/JCWS

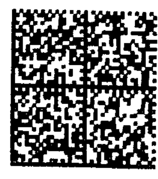
RECEIVED
APR 18 2005
OIPE/JCWS

Organization ______ Bldg./Room ______
UNITED STATES PATENT AND TRADEMARK OFFICE
P.O. Box 1450
Alexandria, VA. 22313-1450
If Undeliverable Return In Ten Days

Official Business
Penalty For Private Use, $300

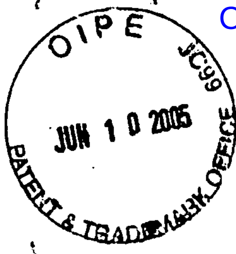
RECEIVED
APR 0 8 2005
USPTO MAIL CENTER

AN EQUAL OPPORTUNITY EMPLOYER
FORWARDING ORDER
EXPIRED



Best Available Copy

35110+1363 04
22313/1450



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed January 13, 2005, the period for response having been extended to June 13, 2005 by a request for extension of 2 months with the Commissioner being authorized to charge the requisite fee to our Deposit Account No. 06-0916, please amend the above-identified application as follows:

Amendments to the Claims are reflected in the listing of claims in this paper.

Remarks/Arguments follow the amendment sections of this paper.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Currently amended) A method of depositing a film on a substrate, comprising:

   providing pulsed DC power through a filter to a target;

   providing RF bias power to a substrate positioned opposite the target; and

   providing process gas between the target and the substrate,

   wherein the filter protects a pulsed DC power supply from the bias power, and

   wherein a plasma is created between the target and the substrate.

2. (Original): The method of Claim 1, further including holding the temperature of the substrate substantially constant.

3. (Original): The method of Claim 1, wherein providing pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Original): The method of Claim 1, wherein providing bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Original): The method of Claim 4, wherein the filter is a band reject filter at the frequency of the bias power.

6. (Original): The method of claim 4, wherein the bias power is zero.

7. (Original): The method of Claim 1, wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

8. (Original): The method of Claim 1, wherein the process gas includes a mixture of Oxygen and Argon.

9. (Original): The method of Claim 9, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

10. (Original): The method of Claim 8, wherein the process gas further includes nitrogen.

11. (Original): The method of Claim 1, wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate.

12. (Original): The method of Claim 1, further including uniformly sweeping the target with a magnetic field.

13. (Original): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Currently amended): The method of Claim 1, further including depositing a film on the backside of the target [[12]].

15.-19. (Canceled).

20. (Currently Amended): A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting a RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target through a filter to create a plasma and deposit the film.

21. (Original): The method of Claim 20, wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. (Original): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Original): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Original): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

REMARKS

Claims 15-19 and 25-39 were previously withdrawn from consideration in this application and canceled. Claims 1-13 and 20-24 are being considered in the present application. The Examiner has rejected claims 1-13 and 20 and has objected to claims 7, 14 and 21-24. Claims 1, 14, and 20 have been amended in this Amendment.

Claim Objections

The Examiner has objected to claim 14 because "in line 2, it appears that '12' should be deleted." Applicants have amended claim 14 accordingly.

Claim Rejections under 35 USC § 103

The Examiner has rejected claims 1-13 and 20 under 35 U.S.C. 103(a) as being unpatentable over the combination of Le et al. (2003/0077914) and Fukui et al. (5,755,938). The Examiner has rejected Applicant's reasoning and has reiterated this rejection. Applicants herein traverse the Examiner's further comments.

1. Claims 1-13 and 20 are allowable over Le and Fukui because the combination of Le and Fukui does not teach all of the elements of these claims

Claim 1 recites "providing pulsed DC power through a filter to a target," "providing RF bias power to a substrate," and "wherein a plasma is created between the target and the substrate" Claim 20 recites "adjusting a RF bias power to the substrate" and "applying pulsed DC power to the target through a filter to create a plasma and deposit the film." As explained more fully in the Response filed on July 23, 2004, the combination of Le and Fukui does not

teach providing pulsed DC power to the target to create a plasma and a RF bias power to the substrate.

The teachings of Le

Le teaches a processing chamber that supplies power, for example pulsed DC power, to a target (*See, e.g.,* Le, par. 0070, Figure 3). As described in Le, the PVD chamber "may also have a shield 20 to protect a wall 12 of the chamber 36a from sputtered material, and typically, to also serve as an anode grounding plane." *Id.* The shield is either electrically floating or grounded. *Id.* The target is coupled to the power source. *Id.*

Therefore, as described in Le, a pulsed DC power supply is connected to the target. No bias is applied to the substrate as is suggested by the Examiner. (*See,* OA, pgs. 2). At most, Le teaches that "shield 20 is electrically floating or grounded," (Le, par. 0070), which is not a bias as claimed in claims 1 and 20 of the present application, and certainly not an RF bias.

The Examiner's comments regarding Le

The Examiner, in the response to Applicant's previous submission, states that

> Applicant argues that Le et al. do not disclose a bias applied to the substrate. However, Applicant is directed to Page 5, lines 13-14, wherein Le et al. disclose applying a RF energy (bias) to the gas supplied to the substrate.

(Office Action, page 5). Le, however, does not teach or imply energizing the gas with RF energy AND utilization of a pulsed DC power supply. Le teaches either energizing the gas with RF energy or energizing the gas with pulsed DC power. Further, Le teaches creating a plasma by application of RF power and not biasing the substrate by application of RF power, as is suggested by the Examiner.

As taught in Le, "[t]he multi-chamber platform 100 has at least one PVD chamber 36a, as for example illustrated in FIG. 3, to sputter deposit a titanium oxide (TiO_x) layer 210, on the substrate 16." (Le, par. 0066). In the description of the chamber for depositing the titanium oxide, Le teaches that "[t]he PVD chamber 36a further comprises a sputtering target 14 comprising titanium, facing the substrate 16." (Le, par. 0070). Further, "[t]he target 14 is electrically isolated from the chamber 36a and is connected to a voltage source, such as a pulsed DC power source 22, but which may also be other types of voltage sources." *Id.* Further, Le explains that "[t]he electric field generated in the chamber 36a from the voltage applied to the sputtering target 14 energizes the sputtering gas to form a plasma that sputters off the target material." *Id.* Therefore, in the teachings of Le, pulsed DC power may be supplied to the target in the deposition of titanium oxide. Also, as discussed in Le, energizing the sputter gas creates the plasma, it does not bias the substrate as suggested by the Examiner's comments above.

Le further states that "[a]n advantage of the present process is that a number of steps for forming a stacked layer comprising the anti-reflective coating 205 may be carried out in a single PVD sputtering chamber 36a." (Le, par. 0074) Le further states that

> [f]or example, the substrate 16 need not be transferred to different chambers when forming an anti-reflective coating 205 comprising multiple layers of, for example, titanium 230, titanium nitride 220, and titanium oxide 210. In one example, prior to forming the titanium oxide layer 210, the same chamber 36a is used to deposit an elemental titanium layer 230 on the substrate 16 using a sputtering gas comprising substantially only argon, and by maintaining the target at suitable voltage levels which may include DC or RF bias levels.

(Le, par. 0074). Therefore, Le teaches utilizing multiple chambers to form a stacked layer system and teaches utilizing different techniques in the same chamber for deposition of different layers.

Additionally, Le teaches another example of "a stacked layer 200 fabricated according to the present invention . . . having a diffusion barrier layer 255, a conductor layer 240, and an overlying anti-reflective coating 205 comprising a titanium layer 230 and a titanium oxide layer 210, or only a titanium oxide layer 210 . . . ." (Le, par. 0075) In forming this structure, Le teaches that "[t]he diffusion barrier layer 255 comprising layers of titanium 260 and titanium nitride 250 may be formed on the substrate 16 in the PVD chamber 36a or in one of the other chambers 36, by for example, using a sputtering target comprising titanium, introducing a sputtering gas comprising argon to form the titanium layer 260, or argon and nitrogen to form the titanium nitride layer 250, and energizing the gas by capacitively coupling RF energy to the gas." *Id.* Therefore, the layer is RF sputtered onto the substrate. The RF power is not supplied to the gas to create a bias on the substrate, but rather to create the plasma in the gas. Further, Le teaches that "[t]hereafter, the substrate 16 is transferred to the chamber 36a to form an anti-reflective coating 205 comprising various layers that include a titanium oxide layer 210, on the conductor layer 240." *Id.*

Therefore, the RF power is utilized in sputtering one film, and Pulsed DC power is utilized to deposit another film, the titanium oxide layer 210. Le does not teach utilizing both RF and pulsed DC powers in the same system. Le does not teach the combination of providing pulsed DC power to the target and a bias power to the substrate as was suggested by the Examiner.

The Teachings of Fukui et al.

As is more fully explained in the Response to Office Action filed on July 23, 2004, Fukui et al. does not cure the defects in the teachings of Le. Fukui teaches an RF sputtering chamber and not a pulsed-DC PVD chamber.

Fukui teaches a deposition chamber where an RF power supply is coupled to the target through a matching circuit and a second RF power supply is coupled to the substrate through a second matching circuit. (*See, e.g.,* Fukui, col. 6, lines 19-41). The matching circuits are configured so that reflected waves back to the power supplies are eliminated. *Id.* Further, a DC power supply (NOT a pulsed DC power supply) is coupled to the target through a low-pass filter. *Id.* As taught in Fukui, "[t]he band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a DC power from the DC power supply 28." (Fukui, col. 6, lines 34-37). Utilizing this arrangement, Fukui claims that "[t]he film manufacturing apparatus shown in FIG. 1 can deposit three thin films (e.g., a gate insulating film, a semiconductor film and an ohmic contact layer) successively in the single deposition chamber 10." (Fukui, col. 6, lines 62-65).

As a result, Fukui only teaches RF plasma deposition processes and not a pulsed DC plasma deposition process. Further, Fukui only teaches a low pass filter coupled between a target bias DC power supply and the target. The DC power supply is simply a low power bias supply and is not a pulsed DC power supply that applies sufficient power to the target to create the plasma and sputter material from the target. The filter taught by Fukui is provided to protect a simple low power DC supply utilized for biasing the target and would not be applicable to such a pulsed DC power supply utilized for creating a plasma and sputtering material from the target.

Further, Utilization of a low pass filter with a pulsed DC power supply would also block the output power of the pulsed DC power supply.

The Examiner's comments regarding Fukui

The Examiner, in the response to Applicant's previous submission, states that

> Applicant argues that Fukui does not teach a pulsed DC power supply. However, Fukui was not relied on upon for that purpose. Fukui teaches supplying power from a DC supply through a filter to the target. Fukui was relied on for the use of a filter to supply a power to the target.

(Office Action, page 6). As explained further above, the DC power supply and filter taught in Fukui is a low power bias supply and is not a pulsed DC power supply sufficient to create a plasma and sputter material from the target.

The combination of Le and Fukui

The combination of Le and Fukui does not teach "providing pulsed DC power through a filter to a target," "providing RF bias power to a substrate," and "wherein a plasma is created between the target and the substrate," as is recited in Claim 1, or "adjusting a bias power to the substrate" and "applying pulsed DC power to the target through a filter to create a plasma and deposit the film," as is recited in Claim 20. In particular, as is discussed above, even the combined teachings of Le and Fukui do not teach the combination of providing pulsed DC power to the target to create a plasma and an RF bias power to the substrate.

2. Claims 1-13 and 20 are allowable over Le and Fukui because there is no motivation to combine Le and Fukui as is suggested by the Examiner

As more fully discussed in the Response to Office Action filed on July 23, 2004, there is no motivation to combine Le and Fukui as is suggested by the Examiner. Le teaches a pulsed DC PVD system and Fukui teaches an RF based PVD system. The differences between those technologies is great. The use of a DC bias power supply to bias the target in an RF PVD system does not, in any way, imply a pulsed DC PVD system, as is claimed in claims 1 and 20.

The Examiner simply states that "[i]t would have been within the scope of one of ordinary skill in the art to combine the teachings of Le et al. and Fukui et al. to enable the use of a DC power supply through a filter to be used in the process of Le et al. to adjust the impedance to have an infinite value so that no RF waves are superposed on a DC power form [sic] the DC power supply (Col. 6, lines 32-37)." (Office Action of July 23, 2004, page 5). However, Le utilizes a DC power supply for biasing the target and not for generating a plasma for deposition of a material. Therefore, it would not be obvious to one skilled in the art to apply a filter provided for a DC power supply utilized for biasing a target to protect a much higher powered pulsed DC power supply that is utilized in the plasma generation.

Fukui teaches an RF power supply for creating the plasma and sputtering material from the target. There is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply of Fukui with a pulsed DC power supply. Further, there is no suggestion in Le to substitute a pulsed DC supply for an RF power supply. Placing the low pass filter taught by Fukui between the pulsed DC power supply and the target of Le would be inoperative

because, assuming the filter survived the power requirements, the filter would not pass the pulsed DC power to the target.

As discussed above, therefore, there is no motivation for one skilled in the art to combine the references Le and Fukui in the fashion suggested by the Examiner.

The Examiner's further comments regarding obviousness

The Examiner, in the response to Applicant's previous submissions, states that

> Applicant argues that utilizing a filter provided for a DC power supply is not obvious and may not be necessary in the system taught by Le because of the lack of a bias. However, Le discloses applying a bias to energize the gas being applied to the substrate, as explained above. Therefore, a filter may be used to provide the pulsed DC power through the filter since a bias is being applied.

(Office Action, page 6). However, as discussed above, Le does not teach applying both a pulsed DC power and RF power to the gas. Le teaches utilizing pulsed DC power for one process and RF power for a separate process, but not the two together. Further, application of RF power to the gas is not a bias, but rather a separate method of generating the plasma (exciting the gas) and sputtering material from the target. Therefore, there is no need to provide a filter between the pulsed DC power supply and the target as suggested by the Examiner. Furthermore, the low pass filter taught by Fukui would not be a suitable filter for that purpose as it would also block the pulsed DC power generated by the pulsed DC power supply from reaching the target.

The Examiner further states that

> Applicant argues that there is no suggestion in Fukui that a pulsed DC power supply can be substituted for the RF power supply coupled to the target, nor would one skilled in the art be inclined to replace that RF power supply with a pulsed DC power supply. However, the Examiner is not substituting the pulsed DC power supply for the RF power supply coupled to the target. The

> rejection is based on utilizing the filter of Fukui to be used in the pulsed DC power supply of Le.

(Office Action, pgs. 6-7). As discussed above, the low pass filter taught by Fukui is inapplicable for use with a pulsed DC power supply. The filter itself would block the power generated by the pulsed DC power supply. Furthermore, the DC power supply taught by Fukui is only for the purpose of biasing the target and does not generate a plasma or sputter material from the target, as does the pulsed DC power supply taught by Le. Those are two very different functions. One skilled in the art would not be inclined to utilize the filter taught by Fukui as is suggested by the Examiner.

Therefore, claims 1 and 20 are not obvious from the references Le and Fukui. Claims 2-13 depend from claim 1 and are therefore allowable for at least the same reasons as is claim 1. The Examiner's comments with regard to claims 2-13 are rendered mute by this discussion and therefore Applicant's neither comments on nor agrees with those comments.

Allowable Subject Matter

The Examiner has objected to claims 7, 14 and 21-24 "as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims." (OA, page 5).

Request for Interview

In the event that the Examiner persists in rejecting any of claims 1-13 and 20, Applicant requests an interview with the Examiner to discuss those claims and the prior art. The Examiner can contact the undersigned at 650-849-6622 in order to arrange a suitable time for such an interview.

Conclusion

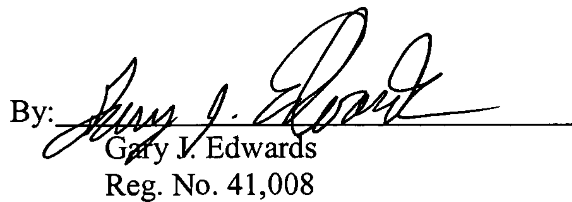
In view of the foregoing amendments and remarks, Applicant respectfully requests reconsideration and reexamination of this application and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

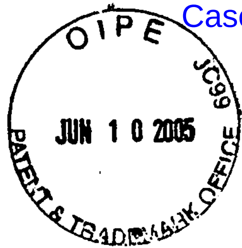
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 10, 2005

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 724128283 US



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

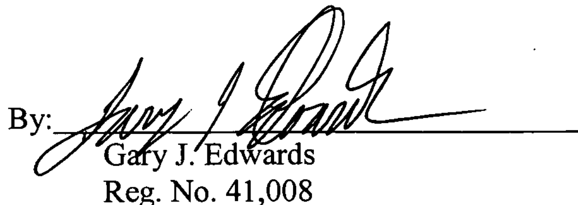
Applicants petition for a two month extension of time to reply to the Office action of January 13, 2005. The Commissioner is hereby authorized to charge the fee of $450.00 to our Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 10, 2005

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 724128283 US

06/15/2005 WABDELR1 00000123 060916 10101863
01 FC:1252 450.00 DA

PTO/SB/06 (08-03)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 10/101863

CLAIMS AS FILED – PART I

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	SMALL ENTITY RATE	SMALL ENTITY FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY FEE
BASIC FEE (37 CFR 1.16(a))				$	OR		$
TOTAL CLAIMS (37 CFR 1.16(c))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(b))	minus 3 =	*	X $ =		OR	X $ =	
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(d))			+ $ =		OR	+ $ =	
			TOTAL		OR	TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

CLAIMS AS AMENDED – PART II

4/18/05

AMENDMENT A — N.E.

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE	ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	ADDITIONAL FEE
Total (37 CFR 1.16(c))	* 19	Minus	** 20	= ↓	x $25 =	↓	OR	x $50 =	↓
Independent (37 CFR 1.16(b))	* 2	Minus	*** 3	= ↓	x $100 =		OR	x $200 =	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(d))					+ $180 =		OR	+ $360 =	
					TOTAL ADD'L FEE	↓	OR	TOTAL ADD'L FEE	↓

AMENDMENT B

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
Total (37 CFR 1.16(c))	*	Minus	**	=	x $25 =		OR	x $50 =	
Independent (37 CFR 1.16(b))	*	Minus	***	=	x $100 =		OR	x $200 =	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(d))					+ $180 =		OR	+ $360. =	
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT C

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
Total (37 CFR 1.16(c))	*	Minus	**	=	x $25 =		OR	x $50 =	
Independent (37 CFR 1.16(b))	*	Minus	***	=	x $100 =		OR	x $200 =	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(d))					+ $180 =		OR	+ $360 =	
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

22852 7590 07/01/2005

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

DATE MAILED: 07/01/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

Advisory Action Before the Filing of an Appeal Brief	Application No.	Applicant(s)	
	10/101,863	ZHANG ET AL.	
	Examiner	Art Unit	
	Michelle Estrada	2823	

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

THE REPLY FILED 10 June 2005 FAILS TO PLACE THIS APPLICATION IN CONDITION FOR ALLOWANCE.

1. ☒ The reply was filed after a final rejection, but prior to or on the same day as filing a Notice of Appeal. To avoid abandonment of this application, applicant must timely file one of the following replies: (1) an amendment, affidavit, or other evidence, which places the application in condition for allowance; (2) a Notice of Appeal (with appeal fee) in compliance with 37 CFR 41.31; or (3) a Request for Continued Examination (RCE) in compliance with 37 CFR 1.114. The reply must be filed within one of the following time periods:
   a) ☐ The period for reply expires _______months from the mailing date of the final rejection.
   b) ☒ The period for reply expires on: (1) the mailing date of this Advisory Action, or (2) the date set forth in the final rejection, whichever is later. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of the final rejection.
   Examiner Note: If box 1 is checked, check either box (a) or (b). ONLY CHECK BOX (b) WHEN THE FIRST REPLY WAS FILED WITHIN TWO MONTHS OF THE FINAL REJECTION. See MPEP 706.07(f).

Extensions of time may be obtained under 37 CFR 1.136(a). The date on which the petition under 37 CFR 1.136(a) and the appropriate extension fee have been filed is the date for purposes of determining the period of extension and the corresponding amount of the fee. The appropriate extension fee under 37 CFR 1.17(a) is calculated from: (1) the expiration date of the shortened statutory period for reply originally set in the final Office action; or (2) as set forth in (b) above, if checked. Any reply received by the Office later than three months after the mailing date of the final rejection, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

NOTICE OF APPEAL

2. ☐ The Notice of Appeal was filed on _____. A brief in compliance with 37 CFR 41.37 must be filed within two months of the date of filing the Notice of Appeal (37 CFR 41.37(a)), or any extension thereof (37 CFR 41.37(e)), to avoid dismissal of the appeal. Since a Notice of Appeal has been filed, any reply must be filed within the time period set forth in 37 CFR 41.37(a).

AMENDMENTS

3. ☒ The proposed amendment(s) filed after a final rejection, but prior to the date of filing a brief, will not be entered because
   (a)☒ They raise new issues that would require further consideration and/or search (see NOTE below);
   (b)☒ They raise the issue of new matter (see NOTE below);
   (c)☒ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal; and/or
   (d)☐ They present additional claims without canceling a corresponding number of finally rejected claims.
   NOTE: *Upon cursory review, the proposed amendment to claims 1 and 20 and the arguments filed 6/10/05 do not clearly place the case in condition for allowance. Applicant's arguments rely on the proposed amendment which has not been entered. The proposed amendment would change the scope of claims 1 and 20 raising new issues requiring further consideration and/or search*. (See 37 CFR 1.116 and 41.33(a)).
4. ☐ The amendments are not in compliance with 37 CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☐ Applicant's reply has overcome the following rejection(s): _____.
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☒ For purposes of appeal, the proposed amendment(s): a) ☒ will not be entered, or b) ☐ will be entered and an explanation of how the new or amended claims would be rejected is provided below or appended.
   The status of the claim(s) is (or will be) as follows:
   Claim(s) allowed: *none*.
   Claim(s) objected to: *7,14 and 21-24*.
   Claim(s) rejected: *1-13 and 20*.
   Claim(s) withdrawn from consideration: *none*.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ The affidavit or other evidence filed after a final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
9. ☐ The affidavit or other evidence filed after the date of filing a Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing a good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
10. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

11. ☐ The request for reconsideration has been considered but does NOT place the application in condition for allowance because: _____.
12. ☐ Note the attached Information Disclosure Statement(s). (PTO/SB/08 or PTO-1449) Paper No(s). _____
13. ☐ Other: _____.

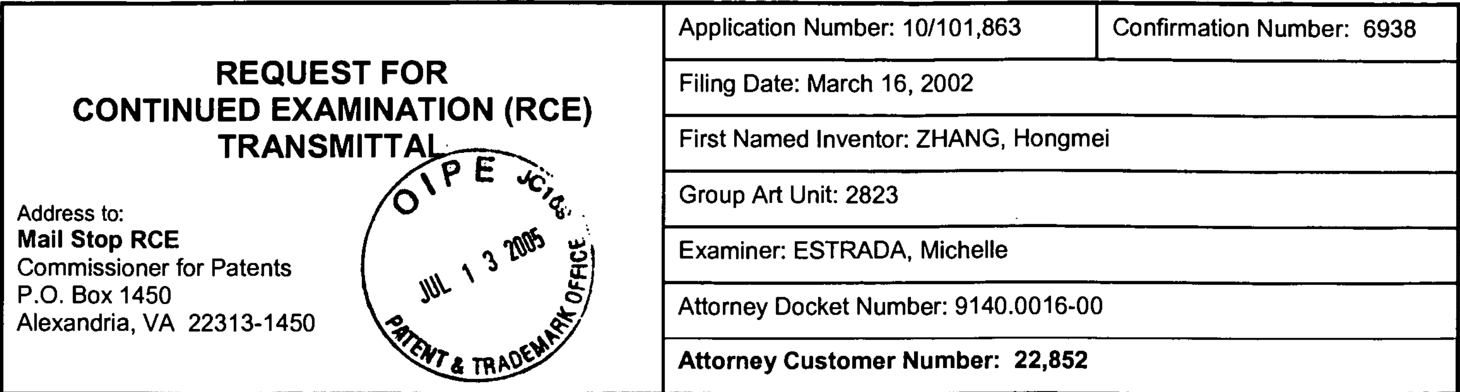
Michelle Estrada
Patent Examiner
AU 2823

Continuation Sheet (PTOL-303)
U.S. Patent and Trademark Office
PTOL-303 (Rev. 4-05)

Application No.

Advisory Action Before the Filing of an Appeal Brief

Part of Paper No. 20050628



REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL	Application Number: 10/101,863	Confirmation Number: 6938
	Filing Date: March 16, 2002	
	First Named Inventor: ZHANG, Hongmei	
Address to: **Mail Stop RCE** Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450	Group Art Unit: 2823	
	Examiner: ESTRADA, Michelle	
	Attorney Docket Number: 9140.0016-00	
	Attorney Customer Number: 22,852	

OIPE JC148 JUL 13 2005 PATENT & TRADEMARK OFFICE

This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of the above-identified application.

Request for Continued Examination (RCE) practice under 37 C.F.R. § 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application.

1. **Submission required under 37 C.F.R. § 1.114: Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, application must request non-entry of such amendment.**
   a. ☒ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.
      i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on__________.
      ii. ☒ Other Amendment and Response to Office Action dated June 10, 2005.
   b. ☐ **DO NOT ENTER** the amendment(s) previously filed on__________. An alternate submission is attached.
   c. ☒ Enclosed submission: .
      i. ☐ Amendment/Reply
      ii. ☐ Affidavit(s)/Declaration(s)
      iii. ☒ Information Disclosure Statement
      iv. ☐ Other __________

2. Miscellaneous
   a. ☐ Suspension of action on the above-mentioned application is requested under 37 C.F.R. § 1.103(c) for a period of months. (Period of suspension shall not exceed 3 months; fee under 37 C.F.R. § 1.17(i) required.)
   b. ☐ Other __________

3. Fees
   a. ☒ The filing fee is calculated as follows:
      i. ☒ $790.00 RCE fee required under 37 C.F.R. § 1.17(e)
      ii. ☒ Petition for extension of time for (3 Months) $1,020.00 - $450.00 = $570.00
      iii. ☐ Other
   b. ☒ The Commissioner is hereby authorized to charge the total fee of $1,360.00 to Deposit Account No. 06-0916.
   c. ☒ The Commissioner is authorized to charge any deficiencies in the filing fees, or credit any overpayments to Deposit Account No. 06-0916.

Signature of Applicant, Attorney, or Agent Required

Name: Gary J. Edwards	Reg. No.: 41,008
Signature: [signature]	Date: July 13, 2005

EXPRESS MAIL LABEL NO.
EV 727732935 US

07/18/2005 WABDELR1 00000085 060916 10101863
02 FC:1801 790.00 DA

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
	)
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938
	)

Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

Based on reasonable inquiry, no document listed in this Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Information Disclosure Statement was known to any individual

designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Information Disclosure Statement.]

A copy of the listed non-patent literature document is attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and applicants determine that the cited documents do not constitute "prior art" under United States law, applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

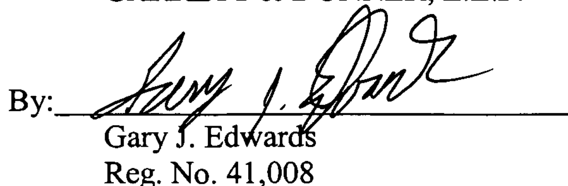
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

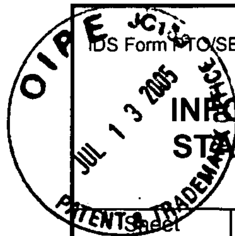
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 13, 2005

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 727732935 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-2004/0077161	04-22-2004	Chen et al.	
		US-2003/0175142	09-18-2003	Milonopoulou et al.	
		US-2003/0077914	04-24-2003	Le et al.	
		US-6,361,662	03-26-2002	Chiba et al.	
		US-6,281,142	08-28-2001	Basceri et al.	
		US-6,117,279	09-12-2000	Smolanoff et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Office Action dated March 25, 2005, received in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01000).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 727732935 US**

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

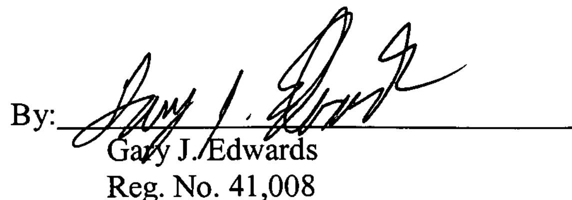
Applicants petition for a three month extension of time to reply to the Advisory Action of July 1, 2005. Applicants filed a Petition for Extension of Time on June 10, 2005, paying a fee of $450.00. The fee of $450.00 is subtracted from the fee of $1,020.00 for a three month extension of time. Therefore, the Commissioner is hereby authorized to charge the remaining fee of $570.00 to our Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 13, 2005

By: 
Gary J. Edwards
Reg. No. 41,008

07/18/2005 WABDELR1 00000085 060916 10101863
01 FC:1253 570.00 DA

EXPRESS MAIL LABEL NO.
EV 727732935 US

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	
ZHANG, Hongmei et al.	Group Art Unit: 2823
Application No.: 10/101,863	Examiner: ESTRADA, Michelle
Filed: March 16, 2002	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	Confirmation No.: 6938

Entered per RCE
PM 7/13/05

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

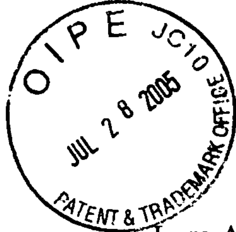
AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed January 13, 2005, the period for response having been extended to June 13, 2005 by a request for extension of 2 months with the Commissioner being authorized to charge the requisite fee to our Deposit Account No. 06-0916, please amend the above-identified application as follows:

Amendments to the Claims are reflected in the listing of claims in this paper.

Remarks/Arguments follow the amendment sections of this paper.

2823



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
	)
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938
	)

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

Based on reasonable inquiry, no document listed in this Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Information Disclosure Statement was known to any individual

designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Information Disclosure Statement.

Copies of the listed foreign patents and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and applicants determine that the cited documents do not constitute "prior art" under United States law, applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: July 28, 2005

By: Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO. EV 727733065 US

O I P E JUL 2 8 2005 PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 2005/0006768 A1	01-13-2005	Narasimhan et al.	
		US 2005/0000794 A1	01-06-2005	Demaray et al.	
		US 2004/0259305 A1	12-23-2004	Demaray et al.	
		US 2004/0105644 A1	06-03-2004	Dawes	
		US 2003/0174391 A1	09-18-2003	Pan et al.	
		US 2003/0141186 A1	07-31-2003	Wang et al.	
		US 2003/0127319 A1	06-10-2003	Demaray et al.	
		US 2003/0097858 A1	05-29-2003	Strohhofer et al.	
		US 2002/0170821 A1	11-21-2002	Sandlin et al.	
		US 2001/041460 A1	11-15-2001	Wiggins	
		US 2001/0027159 A1	10-04-2001	Kaneyoshi	
		US 6,750,156 B2	06-15-2004	Le et al.	
		US 6,576,546 B2	06-10,-2003	Gilbert et al.	
		US 6,444,750 B1	09-03-2002	Touhsaent	
		US 6,433,380 B2	08-13-2002	Shin	
		US 6,423,776 B1	07-23-2002	Akkapeddi et al.	
		US 6,416,598 B1	07-09-2002	Sircar	
		US 6,413,645 B1	07-02-2002	Graff et al.	
		US 6,365,319 B1	04-02-2002	Heath et al.	
		US 6,302,939 B1	10-16-2001	Rabin et al.	
		US 6,300,215 B1	10-09-2001	Shin	
		US 6,261,917 B1	07-17-2001	Quek et al.	
		US 6,248,640 B1	06-19-2001	Nam	
		US 6,232,242	05-15-2001	Hata et al.	
		US 6,214,660 B1	04-10-2001	Uemoto et al.	
		US 6,210,544 B1	04-03-2001	Sasaki	
		US 6,204,111 B1	03-20-2001	Uemoto et al.	
		US 6,198,217 B1	03-06-2001	Suzuki et al.	
		US 6,197,167 B1	03-06-2001	Tanaka	
		US 6,165,566	12-26-2000	Tropsha	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	2	of	9	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS					
		US 6,157,765	12-05-2000	Bruce et al.	
		US 6,146,225	11-14-2000	Sheats et al.	
		US 6,106,933	08-22-2000	Nagai et al.	
		US 6,080,643	06-27-2000	Noguchi et al.	
		US 6,077,642	06-20-2000	Ogata et al.	
		US 6,071,323	06-06-2000	Kawaguchi	
		US 6,058,233	05-02-2000	Dragone	
		US 6,052,397	04-18-2000	Jeon et al.	
		US 6,051,296	04-18-2000	McCaulley et al.	
		US 6,046,081	04-04-2000	Kuo	
		US 6,004,660	12-21-1999	Topolski et al.	
		US 5,966,491	10-12-1999	DiGiovanni	
		US 5,952,778	09-14-1999	Haskal et al.	
		US 5,930,584	07-27-1999	Sun et al.	
		US 5,900,057	05-04-1999	Buchal et al.	
		US 5,882,946	03-16-1999	Otani	
		US 5,870,273	02-09-1999	Sogabe et al.	
		US 5,853,830	12-29-1998	McCaulley et al.	
		US 5,831,262	11-03-1998	Greywall et al.	
		US 5,811,177	09-22-1998	Shi et al.	
		US 5,771,562	06-30-1998	Harvey, III et al.	
		US 5,762,768	06-09-1998	Goy et al.	
		US 5,757,126	05-26-1998	Harvey, III et al.	
		US 5,738,731	04-14-1998	Shindo et al.	
		US 5,731,661	03-24-1998	So et al.	
		US 5,689,522	11-18-1997	Beach	
		US 5,686,360	11-11-1997	Harvey, III et al.	
		US 5,654,984	08-05-1997	Hershbarger et al.	
		US 5,607,789	03-04-1997	Treger et al.	
		US 5,591,520	01-07-1997	Migliorini et al.	
		US 5,563,979	10-08-1996	Bruce et al.	
		US 5,538,796	07-23-1996	Schaffer et al.	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	3	of	9	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS					
		US 5,499,207	03-12-1996	Miki et al.	
		US 5,457,569	10-10-1995	Liou et al.	
		US 5,355,089	10-11-1994	Treger	
		US 5,309,302	05-03-1994	Vollmann	
		US 5,306,569	04-26-1994	Hiraki	
		US 5,303,319	04-12-1994	Ford et al.	
		US 5,296,089	03-22-1994	Chen et al.	
		US 5,173,271	12-22-1992	Chen et al.	
		US 5,119,460	06-02-1992	Bruce et al.	
		US 5,107,538	04-21-1992	Benton et al.	
		US 5,085,904	02-04-1992	Deak et al.	
		US 4,587,225	05-06-1986	Tsukuma et al.	
		RE 32,449	06-30-1987	Claussen	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		EP 1 189 080 A2	03-20-2002	Agere Systems Optoelectronics Guardian Corporation		
		EP 1 092 689 A1	04-18-2001	BPS Alzenau GmbH		
		EP 1068899 A1	01-17-2001	Nippon Sheet Glass Co., Ltd.		
		EP 0 639 655 A1	02-22-1995	Asahi Glass Co, Ltd.		
		EP 0 652 308 A2	10-13-1994	Mega Chips Corp.		
		EP 0 510 883 A2	10-28-1992	AT&T		
		JP 7-233469	09-05-1995	Asahi Glass Co, Ltd.		
		JP 2-054764 A2	02-23-1990	Leybold AG		
		WO 00/21898 A1	04-20-2000	Samsung Electronics Co.		

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	4	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		AFFINITO et al., "PML/oxide/PML Barrier Layer Performance Differences Arising from Use of UV or Electron Beam Polymerization of the PML Layers," *Thin Solid Films* Vol. 308-309, pp. 19-25 (1997)	
		AFFINITO et al., "Polymer-Oxide Transparent Barrier Layers," Society of Vacuum Coaters, 39th Ann. Technical Conference Proceedings, May 5-10, 1996, Philadelphia, PA, pp. 392-397 (1996).	
		ALDER, T. et al., "High-Efficiency Fiber-to-Chip Coupling Using Low-Loss Tapered Single-Mode Fiber," IEEE Photonics Technology Letters, 12(8):1016-1018 (2000).	
		ALMEIDA, Vilson R. et al., "Nanotaper for compact mode conversion," *Optics Letters*, 28(15):1302-1304 (2003).	
		ASGHARI et al., "ASOC--A Manufacturing Integrated Optics Technology," Part of the SPIE Conference on Integrated Optics Devices III, vol. 3620, pp. 252-262 (Jan. 1999).	
		BARBIER et al, "Amplifying Four-Wavelength Combiner, Based on Erbium/Etterbium-Doped Waveguide Amplifiers and Integrated Splitters", *IEEE PHOTONICS TECHNOLOGY LETTTERS*, Vol.9, pp 315-317, 1997, 4 pages	
		BEACH R.J., "Theory and optimization of lens ducts," *Applied Optics,* 35:12:2005-15 (1996)	
		BESTWICK, T., "ASOC silicon integrated optics technology," Part of the SPIE Conferences on Photonics Packaging and Integration, SPIE vol. 3631, pp. 182-190 (Jan. 1999).	
		BORSELLA et al., "Structural incorporation of silver insoda-lime glass by the ion-exchange process: a photoluminescence spectroscopy study", *Applied Physics* A 71, pp. 125-132 (2000)	
		CAMPBELL et al., "Titanium dioxide (TiO_2)-based gate insulators," *IBM J. Res. Develop.* 43(3), 383-391, (May 1999).	
		CHANG, C.Y. (edited by), "ULSI Technology," The McGraw-Hill Companies, Inc., New York, 1996, Chapter 4, pp. 169-170, 226-231 (1996)..	
		CHEN et al. "Development of Supported Bifunctional Electrocatalysts for Unitized Regenerative Fuel Cells," *Journal of the Electrochemical Society*, 149(8), A1092-99, (2002).	
		CHOI et al., "Er-Al-codoped silicate planar light waveguide-type amplifier fabricated by radio-frequency sputtering," *Optics Letters*, vol. 25, No. 4, pp. 263-265 (Feb. 15, 2000).	
		COOKSEY et al. "Predicting Permeability & Transmission Rate for Multilayer Materials," *Foodtechnology*, Vol. 53, No. 9, pp. 60-63 (September 1999).	
		Crowder, et al., "Low-Temperature Single-Crystal Si TFT's Fabricated on Si Films Processed via Sequential Lateral Solidification," IEEE, vol. 19, no. 8 (August 1998), pages 306-308.	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** *(Use as many sheets as necessary)*				***Complete if Known***	
				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
				Examiner Name	ESTRADA, Michelle
Sheet	5	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		DELAVAUX et al., "Integrated optics erbium ytterbium amplifier system in 10 Gb/s fiber transmission experiment", 22nd European Conference on Optical Communication - ECOC' 96, Oslo, 4 pages (1996).	
		Distiributed Energy Resources: Fuel Cells, Projects, http://www.eere.energy.gov/der/fuel_cells/projects.html (2003).	
		DuPont Teijin Films, Mylar 200 SBL 300, Product Information (2000).	
		Electrometals Technologies Limited, Financial Report for the year 2002, Corporate Directory, Chairman's Review, Review of Operations (2002).	
		E-Tek website: FAQ, Inside E-Tek, E-Tek News, Products; http://www.etek-inc.com/ (2003).	
		FLYTZANIS et al, "nonlinear Optics in Composite Materials," E. Wolf, Progress in Optics XXIX (c) Elsevier Scince Publishers B.V., pp. 323-425 (1991).	
		FRAZAO et al., "EDFA Gain Flattening Using Long-Period Fibre Gratings Based on the Electric Arc Technique," (date unknown).	
		GARCIA, C. "Size Dependence of Lifetime and Absorption Cross Section of Si Nanocrystals Embedded in SiO_2," Appl. Phys. Lett., Vol. 82, No. 10, pp. 1595-7 (March 2003).	
		GOOSSENS et al., "Sensitization of TiO_2 with p-type semiconductor polymers," Delft Interfaculty Research Center, Delft University of Technology Laboratory of Inorganic Chemistry, The Netherlands (1998).	
		Greene et al., "Morphological and electrical properties of rf sputtered Y203-doped Zr02 thin films," J. Vac. Sci. Tecnol., vol. 13, no. 1 (Jan/Feb 1976), pages 72-75.	
		HAN, Hak-Seung et al. "Optical Gain at 1.54 □m in Erbium-Doped Silicon Nanocluster Sensitized Waveguide," *Appl. Phys. Lett.*, Vol. 79, No. 27, pp. 4568-70 (December 2001).	
		HAYAKAWA et al., "Enhanced fluorescence from Eu^{3+} owing to surface plasma oscillation of silver particles in glass", *Journal of Non-Crystalline Solids*, Vol. 259, pp. 16-22 (1999).	
		HAYAKAWA et al, "Field enhancement effect of small Ag particles on the fluorescence from Eu^{3+}-doped SiO_2 glass", *Appl. Phys. Lett.*, Vol. 74, No 11, pp. 1513-1515 (March 1999).	
		HAYFIELD, P.C.S., "Development of a New Material-Monolithic Ti4O7 Ebonix Ceramic," Royal Society Chemistry," (2002).	
		HEHLEN et al. "Spectroscopic Properties of Er^{3+} - and Yb^{3+}-doped Soda-Lime Silicate and Aluminosilicate Glasses," *Physical Review B*, Vol. 56, No. 15, pp. 9302-9318 (October 1997).	
		HEHLEN et al. "Uniform Upconversion in High-Concentration Er^{3+}-doped Soda Lime Silicate and Aluminosilicate Glasses," *Optics Letters*, Vol. 22, No. 11, pp. 772-774 (June 1997).	
		HORST et al., "Compact, Tunable Optical Devices in Silicon-Oxynitride Wave Guide Technology," IBM Research Division, 3 pages (1999).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				**Complete if Known**	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	6	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		HUBNER, J. and Guldberg-Kjaer, S., "Planar Er-and Yb-Doped Amplifiers and Lasers," COM Technical University of Denmark, 10.sup.th European Conf. On Integrated Optics, Session WeB2, pp. 71-74 (2001).	
		Hwang, Man-Soo et al., "The effect of pulsed magnetron sputtering on the properties of indium tin oxide thin films," Elsevier Science B.V., P. 29-33, (2003).	
		Im, et al. "Controlled Super-lateral Growth of Si Films for Microstructural Manipulation and Optimization," Materials Science Program (1998), pages. 603-617.	
		Im, et al., "Crystalline Si Films for Integrated Active-Matrix LiquidCrystal Displays," MrS Bulletin (March 1996), pages. 39-48.	
		Im, et al., "Single-crystal Si films for thin-film transistor devices," American Institute of Physics (1997), pages. 3434-3436.	
		ITOH, M. et al., "Large reduction of singlemode-fibre coupling loss in 1.5% delta planar lightwave circuits using spot-size converters," Electronics Letters, 38(2):72-74 (2002).	
		JACKSON et al. "An Accurate Compact EDFA Model," Dept. of Electrical and Computer Engineering, University of BC (date unknown).	
		JANSSEN et al. "Photoinduced electron transfer from conjugated polymers onto nanocrystalline TiO_2," Eindhoven University of Technology, The Netherlands (date unknown).	
		JOHNSON, J.E. et al., "Monolithically Integrated Semiconductor Optical Amplifier and Electroabsorption Modulator with Dual-Waveguide Spot-Size Converter Input," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):19-25, (2000).	
		JONSSON L.B. et al. "Frequency response in pulsed DC reactive sputtering processes," *Thin Solid Films,* Vol. 365, pp. 43-48 (2000).	
		KATO et al., "Recent progress on PLC hybrid integration," Part of the SPIE Conference on Optoelectric Integrated Circuits III, SPIE. vol. 3631, pp. 28-36 (Jan. 1999).	
		KATO, Kuniharu et al., "PLC Hybrid Integration Technology and Its Application to Photonic Components," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):4-13 (2000).	
		KIK, P.G. et al. "Gain Limiting Processes in Er-doped Si Nanocrystal Waveguides in SiO_2," *J. Appl. Phys.*, Vol. 91, No. 1, pp. 534-536 (January 1, 2002).	
		KIM et al. "Frequency-dependent pulsed direct current magnetron sputtering of titanium oxide films," *J. Vac. Sci. Technol.* A 19(2); 429-434 (March 2001).	
		KIM et al. "Mixture Behaviour and Microwave Dielectric Properties in the Low-fired TiO_2-CuO System," *Jpn. J. Appl. Phys.*, 39, 2696-2700, (2000).	
		LADOUCEUR, F. et al., " 8.8 Evaluation of Results", Silica-based Buried Channel Waveguides and Devices,, Chapman & Hall, London, pp. 98-99 (1996).	
		LADOUCEUR, F. et al., "Effect of side wall roughness in buried channel waveguides," *IEEE Proc.*, vol. 141, pp. 242-248 (Aug. 1994).	
		LAMB, William B., "Designing Nonfoil Containing Skins for VIP Applications," DuPont VIA Symposium Presenation, (1999).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	7	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		LAMB, William et al. "Designing Non-Foil Containing Skins for Vacuum InsulationPanel (VIP) Applications," *Vuoto*, Vol. XXVIII, No. 1-2 - Gennaio-Giugno 1999, pp. 55-58 (1999).	
		LANGE et al, "High Gain Ultra-Short Length Phosphate glass Erbium-Doped Fiber Amplifier Material", OSA Optical Fiber Communications (OFC), 3 pages (2002).	
		LAPORTA et al, "Diode-pumped cw bulk Er: Yb: glass laser", 1952 Optics Letters/Vol. 16, No. 24/Dec. 15, 6 pages (1991).	
		LAURENT-LUND, C. et al., "PECVD Grown Multiple Core Planar Waveguides with Extremely Low Interface Reflections and Losses," *IEEE Photonics Technology Letters*, Vol. 10, No. 10, pp. 1431-1433 (Oct. 1998).	
		LEE et al., "Effect of size and roughness on light transmission in a S/SiO.sub.2 waveguide: Experiments and model," Department of Materials Science and Engineering, Massachusetts Institute of Technology, (Jul. 12, 2000).	
		LEE et al. "Effects of interfacial layer growth on the electrical characteristics of thin titanium oxide films on silicon," *Applied Physics Letters*, 74(21), 3143-3145, (May 1999).	
		LOVE, J.D. et al., "Quantifying Loss Minimisation in Single-Mode Fibre Tapers," Electronics Letters, 22(17):912-914, (1986).	
		MARDARE et al. "On the structure of Titanium Oxide Thin Films," *Analele Stiintifice Ale Universitatii AL. I. Cuza IASI*, Vol. XLV-XLVI, 201-208 (1999).	
		MARQUES, P.V.S. et al., "Planar Silica-on-Silicon Waveguide Lasers Based in Two Layer Core Devices," 10.sup.th European Conference on Integrated Optics, Session WeB2, pp. 79-82 (2001).	
		MEIJERINK et al, LUMINESCENCE OF AG^{+} IN CRYSTALLINE AND GLASSY SrB_40_7, Journal of Physics and Chemistry of Solids, Vol. 54, No. 8, pp. 901-906, (1993).	
		MESNAOUI et al, "Spectroscopic properties of AG^{+} ions in phospage glasses of $NaPO_3$.$AgPO_3$ system", EUROPEAN JOURNAL OF SOLID STATE AND INORGANIC CHEMISTRY, Vol. 29, pages 1001-1013, 14 pages (1992).	
		MITOMI, O. et al., "Design of a Single-Mode Tapered Waveguide for Low-Loss Chip-to-Fiber Coupling,: IEEE Journal of Quantum Electronics, 30(8):1787-1793, (1994).	
		MIZUNO et al. "Temperature dependence of oxide decomposition on titanium surfaces in UHV," submitted to Journal of Vacuum Science and Technology, (October 28, 2001).	
		OHKUBO et al., "Polarization-Insensitive Arrayed-Waveguide Grating Using Pure Si)2 Cladding," Fifth Optoelectronics and Communication Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	
		OHMI et al., "Rare earth metal oxides for high-K gate insulator," Tokyo Institute of Technology,(date unknown).	
		OHTSUKI et al., "Gain Characteristics of a high concentration Er^{3+}-doped phosphate glass waveguide", *J. Appl. Phys.* 78(6), pp. 3617-3621 (1995).	
		ONO et al., "Design of a Low-loss Y-branch Optical Waveguide," Fifth Optoelectronic and Communications Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	8	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		PADMINI et al. "Realization of High Tunability Barium Strontium Titanate Thin Films by RF Magnetron Sputtering," College of Engineering, University of California, Santa Barbara. (date unknown).	
		PETERS et al., "Formation mechanism of silver nanocrystals made by ion irradiation of Na^+--Ag^+ ion-exchanged sodalime silicate glass", Nuclear Instruments and Methods in Physics Research B 168, pp. 237-244 (2000).	
		RAJARAJAN, M. et al., “Numerical Study of Spot-Zise Expanders for an Efficient OEIC to SMF Coupling,” IEEE Photonics Technology Letters, 10(8):1082-1084, (1998).	
		RAMASWAMY et al., "Ion-Exchanged Glass Waveguides: A Review", *Journal of Lightwave Technology*, Vol. 6, No. 6, pp. 984-1001 (1988)	
		Sanyo Vacuum Industries Co., Ltd. Products Info, TiO_2, (2003). http://www.sanyovac.co.jp/Englishweb/products/ETiO2.htm	
		SCHERMER, R. et al., "Investigation of Mesa Dielectric Waveguides,", Proceedings of the OSA Integrated Photonics Research Topical Meeting and Exhibit, Paper No. IWB3 (Jun 2001).	
		Second International Symposium of Polymer Surface Modification: Relevance to Adhesion, Preliminary Program (1999).	
		Seventh International Conference on TiO_2 Photocatalysis: Fundamentals & Applications, Toronto, Ontario, Canada, Final Program (November 17-21, 2002)	
		SEWELL, P. et al., “Rib Waveguide Spot-Size Transformers: Modal Properties,” Journal of Lightwave Technology, 17(5):848-856, (1999).	
		SLOOFF et al, "Optical properties of Erbium-doped organic polydentate cage complexes", *J. Appl. Phys.* 83, pp. 497-503 (Jan. 1998).	
		SMITH, R.E., “Reduced Coupling Loss Using a Tapered-Rib Adiabatic-Following Fiber Coupler,” *IEEE Photonics Technology Letters,* 8(8):1052-1054 (1996).	
		STROHHOFER, et al. "Energy transfer to Er^{3+}in Ag ion-exchanged glass", FOM Institute for Atomic and Molecular Physics, 10 pages (date unknown).	
		SUGIYAMA et al., "Gas Permeation Through the Pinholes of Plastic Film Laminated with Aluminium Foil," Vuoto, Vol. XXVIII, N. 1-2 - Gennaio-Guigno (1999).	
		TERVONEN, A., "Challenges and opportunities for integrated optics in optical networks," Part of the SPIE Conference in Integrated Optics Devices III, SPIE vol. 3620, pp. 2-11 (Jan. 1999).	
		TREICHEL et al., “The influence of pulsed magnetron sputtering on topography and crystallinity of TiO2 films on glass,” *Space and Coatings Technology*, Vol. 123, pp. 268-272 (2000).	
		Tukamoto, H. et al., “Electronic Conductivity of $LiCoO_s$ and Its Enhancement by Magnesium Doping,” J. Electrochem. Soc., vol. 44, no. 9, pages 3164-3168 (September 1997).	
		VILJANEN et al, "Planar Optical Coupling Elements for Multimode Fibers with Two-Step Ion Migration Process", Applied Physics, 24, No. 1, pp. 61-63 (January 1981).	
		VILLEGAS et al, "Optical spectroscopy ofa soda lime glass exchanged with silver", Physics and Chemistry of Glasses 37(6), pp. 248-253 (1996).	

Examiner Signature		Date Considered	

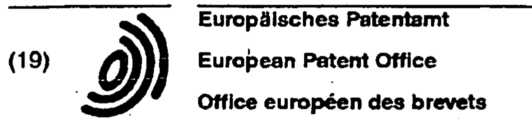
EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	9	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		VON ROTTKAY et al. "Influence of stoichiometry on electrochromic cerium-titanium oxide compounds," Lawrence Berkeley National Laboratory, UC Berkeley, CA, (date unknown).	
		WILKES, Kenneth T. "Gas Permeation Through Vacuum Barrier Films and its Effect on VIP Thermal Performance," Vacuum Insulation Panel Symp., Baltimore, Maryland, (May 3, 1999).	
		YANAGAWA, H. et al., "Index-and-Dimensional Taper and Its Application to Photonic Devices," Journal of Lightwave Technology, 10(5):587-591 (1992).	
		Response to Office Action filed on March 14, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Office Action issued on June 15, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Response to Office Action filed on September 3, 2002 in U.S. Patent No. 6,533,907 (Attorney Docket No. 09140-0004-00).	
		Response to Office Action filed on August 10, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on February 12, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Amendment/RCE filed on March 10, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on March 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed on June 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on July 8, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on May 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on August 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on March 3, 2004 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on February 23, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Response to Office Action filed on December 08, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on March 14, 2005 in U.S. Serial No. 10/789,953 (Attorney Docket No. 09140-0030-00).	
		Office Action issued March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

(19) 
Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 189 080 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.03.2002 Bulletin 2002/12

(51) Int Cl.7: G02B 6/12

(21) Application number: 01307867.0

(22) Date of filing: 14.09.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 15.09.2000 US 663013

(71) Applicant: Agere Systems Optoelectronics Guardian Corporation
Orlando, Florida 32819-8698 (US)

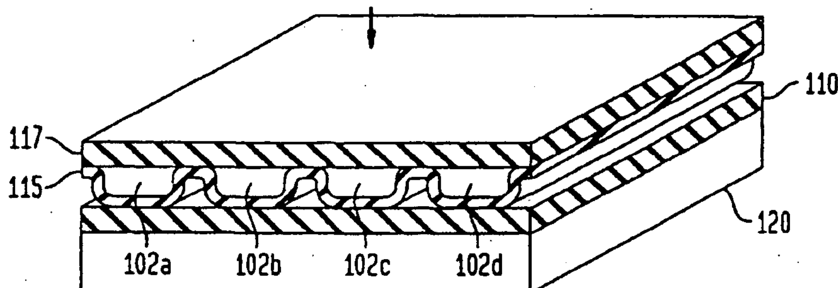
(72) Inventor: Shmulovich, Joseph
Murray Hill, NJ 07974 (US)

(74) Representative: Williams, Celli
Stevens Hewlett & Perkins
Halton House
20/23 Holborn
London EC1N 2JD (GB)

(54) Method for making a planar optical waveguide

(57) The present invention is a method for making planar waveguides. The method comprises the steps of providing a workpiece comprising a layer of material suitable for the waveguide strip; patterning the layer so that the workpiece comprises a base portion and the at least one protruding portion; forming a cladding layer on the protruding portion; and attaching the cladding layer to a substrate. Depending on the composition of the workpiece, the process may further require removing the base portion to expose the bottom surface of the protruding portion. With this method, a planar waveguide or a planar waveguide amplifier may be fabricated having thickness dimensions greater than 5 μm, or more preferably, in the range of 10-20 μm.

FIG. 2E



EP 1 189 080 A2

Description

[0001] The present invention relates to a method for making planar waveguides having relatively large thickness dimensions. The invention is useful in fabricating planar waveguide arrays and planar waveguide amplifiers for communications systems.

[0002] Optical communications systems can transmit optical signals over long distances at high speeds. An optical signal is transmitted from a light source to a waveguide and ultimately to a detector. Waveguide structures such as optical fibers transmit the light signals. Basically, a waveguide structure comprises an inner core region fabricated from a material having a certain index of refraction, and an outer cladding region contiguous the core comprised of a material having a lower index of refraction. A light beam propagated along the core will be guided along the length of the waveguide by total internal reflection.

[0003] Planar waveguides are flat waveguide structures that guide light in essentially the same way as optical fibers. A planar waveguide structure comprises a higher index core strip of material (the "waveguide strip") embedded in a lower index substrate.

[0004] Optical communication systems typically include a variety of devices (*e.g.*, light sources, photodetectors, switches, optical fibers, amplifiers, and filters). Amplifiers and filters may be used to facilitate the propagation light pulses along the waveguide.

[0005] The connections between the various system components inherently produce loss in optical communication systems. For example, in planar waveguide amplifiers it would be desirable to couple planar waveguides with a multimode signal collection fiber. However, applying conventional processing, planar waveguide amplifiers typically cannot be made with cores that are more than about 5 μm thick, and conventional sputtered films have a thickness of about 2-3 μm. On the other hand, a multimode signal collection fiber has a core that is typically more than 50 μm in diameter. This mismatch in vertical dimension makes it very difficult to efficiently couple light from a multimode signal collection fiber to a planar waveguide. Losses can amount to up to 17 dB or in some cases up to ~ 97 to 98 percent of the transmitted light.

[0006] Many other factors also contribute to losses in waveguide connections. Such factors include overlap of fiber cores, misalignment of the fiber axes, fiber spacing, reflection at fiber ends, and the numerical aperture (NA) mismatch. If a fiber receiving light has a smaller NA than a fiber delivering the light, some light will enter the receiving fiber in modes that are not confined to the core and will leak out of the fiber. The loss can be quantified by the formula: Loss (dB) = $10 \log_{10} (NA_2/NA_1)^2$. Thus, significant losses can occur if fibers are mismatched and signals are traveling from a large core into a smaller core.

[0007] With the increasing demand for efficient, large-scale manufacturing of hybrid integrated opto-electronic devices, there is a need to more efficiently couple various waveguide devices together while minimizing losses.

[0008] The present invention is a method for making planar waveguides. The method comprises the steps of providing a workpiece comprising a layer of material suitable for the waveguide strip; patterning the layer so that the workpiece comprises a base portion and the at least one protruding portion; forming a cladding layer on the protruding portion; and attaching the cladding layer to a substrate. Depending on the composition of the workpiece, the process may further require removing the base portion. With this method, a planar waveguide or a planar waveguide amplifier may be fabricated having thickness dimensions greater than 5 μm, or more preferably, in the range of 10-20 μm.

[0009] The advantages, nature and various additional features of the invention will appear more fully upon consideration of the illustrative embodiments now to be described in detail in connection with the accompanying drawings. In the drawings:

FIG. 1 is a block diagram showing steps of the inventive method;

FIGS. 2A-2E schematically illustrate a planar waveguide structure at various steps of the Fig. 1 process; and

FIG. 3 is a schematic illustration of part of an optical communications system using a planar waveguide structure fabricated by the process of Fig. 1.

[0010] It is to be understood that these drawings are for the purposes of illustrating the concepts of the invention and are not to scale.

[0011] Referring to the drawings, Fig. 1 is a schematic block diagram showing the steps in making a planar waveguide. As shown in Block A of Fig. 1, the first step is to provide a workpiece comprising a layer of material suitable for the waveguide strip. The workpiece can be a bulk disk of the strip material or a substrate-supported layer of the strip material. The layer, if desired, can exceed the thickness of the waveguide strip to be formed.

[0012] The next step, shown in Block B is to pattern the layer of strip material to form at least one protruding portion corresponding in dimension to a waveguide strip to be fabricated. The patterning can be conveniently effected by photolithography, masking one or more protruding strips and etching the unmasked material as by wet etching. Preferably a plurality of protruding portions are patterned to produce an array of waveguides.

[0013] Fig. 2A illustrates the result of this step on a workpiece comprising bulk disk 100 of core glass. The disk is patterned by wet-etching at selected portions so that it comprises a base portion 101 and a plurality of protruding portion, 102a, 102b, ..., 102d. This can be

achieved by etching various channels in the disk. The protruding portions have a thickness and width corresponding substantially in dimension to the waveguide strips sought to be fabricated. The disk advantageously comprises aluminosilicate glass, but other glasses, such as soda-lime glass may be used. If it is desired that the waveguide structure should be a waveguide amplifier, the waveguide strip material should be doped with a small percentage of rare earth dopants by techniques well known in the art. The preferred rare earth dopant is erbium.

[0014] Etchants for wet etching the channels may be selected from HF etchant (~ 1% HF), $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $Na_2S_2O_3$, and KOH in H_2O. Alternatively, other patterning techniques such as dry etching or microscale imprinting can be used to produce the protruding portions.

[0015] Ultimately, the protruding portions or 102a, 102b,..., 102d, etc., will form the waveguide strips of the planar waveguide. Thus, the etching of the channels will be controlled to produce protruding portions having the desired dimensions. Protruding portions having a height (thickness) and/or width dimension of greater than 5μm may be formed. Preferably the channels are etched such that the protruding portions have a height h in the range of 10-20 μm and a width *w* in the range of 50-100 μm.

[0016] A third step shown in Block C of Fig. 1 is to deposit a cladding layer on the surface of the protruding portion(s). The cladding layer can be silica deposited by conventional techniques well known in the art. It is preferably deposited by the BPTEOS process.

[0017] Referring to FIG. 2B, a cladding layer 115 is shown deposited over the etched bulk glass, filling the channels. The material for this cladding layer will be selected depending on the waveguide strip material. The cladding material should have a lower index of refraction than the strip material. Silica cladding material can be used with aluminosilicate strip material. A plastic cladding may be used with a soda-lime strip material.

[0018] The patterned workpiece with the cladding layer thereon is then attached to a substrate for the planar waveguide (FIG. 1, block D). The cladding layer is attached to the waveguide substrate.

[0019] Fig. 2C shows the workpiece 100 inverted and the cladding layer is attached to the waveguide substrate 120. The substrate can be any of a wide variety of materials including glasses, ceramics and semiconductors. Preferably it is silicon. A dielectric or insulating layer 110, such as a layer of silica (SiO_2), may be disposed on the surface of between the substrate 120. The workpiece cladding can be attached to the substrate, by molecular bonding, such as with aluminosilicate or silicon, or by other appropriate bonding agents such as ceramic bakeable pastes. At this stage, the core (protruding portions 102a, 102b,...,102d) may be isolated with cladding on three sides and bound to the disk 100 at the fourth side. There is much flexibility in selecting the type of bonding agent because the core is protected from contacting the adhesive. Interstices 111a, 111b,...,111d, between the silica layer 110 and substrate 120 may be filled, if desired, with cladding material.

[0020] If the workpiece comprises a thin layer of strip material on a cladding material support, the waveguide is substantially complete. If the layer of strip material is thick or workpiece is a bulk disk of strip material, then the next step (Block E of Fig. 1) is to remove the base portion of the workpiece selectively leaving the protruding portions.

[0021] Referring to FIG. 2D, the base of the bulk glass disk 101 may be etched away, leaving the protruding portions 102a, 102b... partially surrounded by cladding layer 115 to comprise planar waveguide strips.

[0022] As a further optional final step, a top cladding layer 117 may be deposited over the exposed protruding portions 102a, 102b (FIG. 2E). If desired, the resulting structure may be diced into smaller pieces.

[0023] The method of the invention may be used to fabricate a waveguide structure or waveguide amplifier having waveguide core strips with relatively large dimensions. For example, a waveguide or waveguide amplifier may be made having cross-sectional dimensions of tens of microns, i.e., the height of the waveguide strips may be greater than 5 μm and more preferably in the range of about 10 μm - 20 μm or greater. The width of the strips also may be greater than 5 μm and more preferably in the range of about 30 μm - 50 μm or greater. Thus, the method allows for the making of planar waveguide structures having larger dimensions than possible with conventional methods. Such a structure is advantageous as it helps to reduce the vertical dimension mismatch between planar waveguides and optical fibers and thereby to reduce the losses that occur when such components are coupled together. The method is also advantageous as it can use wet etching which is faster than the dry etching and deposition techniques conventionally used for producing planar waveguides.

[0024] FIG. 3 shows a communications system comprising a transmitter 100, an amplifier 60 fabricated by the inventive method, and a detector 200. The amplifier 60 has larger dimensions than planar waveguides made using conventional processing. These dimensions enable more efficient coupling with optical fibers 110a, 110b. Couplers 55, 75 are used to connect the planar waveguide 60 to input 110a and output 110b fibers. Advantageously, these couplers have the configuration described in applicant's co-pending US patent application Serial No 09/663,014, entitled "Article Comprising a Multimode Optical Fiber Coupler".

[0025] More particularly, the couplers 55, 75 each comprise a plurality of fibers with claddings that are tapered from zero thickness at the first ends of the fibers to a final thickness at the second ends (or "cladded ends") of the fibers. At the first ends of the fibers (also referred to herein as the "core exposed ends"), the core is exposed *i.e.* there is no surrounding cladding. The ta-

pered fibers are arranged so that their core-exposed ends are bundled together. The bundle is preferably formed into a single rod such as by fusion to define bundles 51, 71, respectively, of couplers 55, 75. The bundled, fused ends are coupled to the cores of the optical fibers 110a, 110b, carrying the transmitted signal.

[0026] At the input end, a free space combiner 54 is used to combine signals from a pump input fiber 50 and signal input fiber 52 which are directed into the first fiber coupler 55, having bundle 51 at the input end. The plurality of fibers comprising the bundle 51 have claddings that are tapered outward, so that the fibers in the bundle are splayed into individual fibers 57a, 57b,...,57d, and coupled to an array of large dimension waveguide strips 61a, 61b, 61c, 61d of the planar waveguide amplifier 60. The second coupler 75 is connected at the output of the planar waveguide 60 with light from each of the waveguide films being directed into individual splayed fibers 77a, 77b,..., 77d, that are tapered down into fiber bundle 71. Light from bundle 71 could be directed into output fiber 72 toward receiver 200, and/or a splitter 74 may be disposed in the output path. The receiver bundle 71 can be optimized independent of the input constraints. According to another aspect of the invention, the receiver bundle 71 is continued as a "fiber bundle transmission line" (not shown) to a remote location and/or to the detector. This approach may be advantageous in that smaller cores will produce less dispersion than larger cores, as they support fewer modes.

[0027] The cores of the optical fibers 110a, 110b, may be relatively large, *e.g.*, greater than 50 μm, and multimode collection fibers may be used and coupled to the planar waveguide amplifier. Yet, there is little or no loss with this configuration. The number of fibers used in the bundles, the dimensions of the fiber cores and planar waveguides, the degree of taper, the composition of the components, and other design considerations may be adjusted depending on the application as one skilled in the field would appreciate. In matching the coupler with the planar waveguides and/or multimode fiber, a matching consideration is that the cross-sectional area of the core, times the square of the numerical aperture, optimally should be the same on both sides of a juncture. In other if "A" denotes the cross-sectional core area for signal input or output and NA is the numerical aperture, then $A \times (NA)^2$ should be substantially constant throughout the system.

[0028] The invention is advantageous in that planar waveguides may be more efficiently fabricated and also, they may made with larger dimensions to reduce the vertical dimension mismatches and allow for coupling of planar waveguides with multimode collection fibers and other large core fibers. Planar waveguide amplifiers may be more highly doped than optical fiber amplifiers. Additionally, in multimode applications, dispersion is an important factor as an increase in modes results in greater dispersion. With this invention, there is no modal noise penalty in the amplifier, beyond the modal dispersion in the individual waveguides, which is small, given the dimensions of the waveguides. Additionally, with the invention an increase in the input image size does not impact upon (*e.g.*, cause or increase) a modal noise penalty. By providing low-dispersion optical amplification, the invention increases the flexibility of the system with regard to use of photodetectors. Using conventional systems, avalanche diodes are too slow for 10 Gbit/sec detection (per channel), and while PIN diodes are fast enough, they are not sufficiently sensitive. Low-dispersion optical amplification addresses these problems with conventional systems by enabling use of avalanche diodes as photodetectors.

[0029] With this invention, the amplification of individual waveguides 61a ...61d may be manipulated to compensate for or create possible patterns in the image. Also, the planar waveguides may be structured to reduce dispersion. It is beneficial to utilize a narrower core in the planar waveguides (*i.e.*, in the height dimension parallel to the substrate surface and transverse to the propagation direction), to support fewer modes and hence, cause less dispersion. The waveguide amplifier structure 60 may be pumped in a cladding-pumping mode from the side by one or more extended cavity laser pumps schematically illustrated at boxed region 80 (FIG. 3). This edge-pumping scheme may be helpful in increasing pumping efficiency -- the pumping efficiency of planar waveguides is typically lower than that of optical fibers. The cladding of the planar waveguide may be so shaped and dimensioned as to confine the edge-pumped radiation, *e.g.*, it may be a ring-shaped or serpentine cladding arrangement.

[0030] It is understood that the embodiments described herein are merely exemplary and that a person skilled in the art may make variations and modifications without departing from the scope of the invention.

5 10 15 20 25 30 35 40 45 50 55

Claims

1. A method for making a planar waveguide comprising a waveguide strip on a waveguide substrate, the method comprising the steps of:

   providing a workpiece comprising a layer of material suitable for use as the planar waveguide strip;
   patterning the layer so that the workpiece comprises a base portion and at least one protruding portion, wherein the protruding portion corresponds substantially in dimension to the waveguide strip to be fabricated;
   forming a cladding layer on the workpiece overlying the protruding portion; and
   attaching the cladding layer to the substrate.

2. The method of claim 1 further comprising the step of removing the base portion of the workpiece after

attaching the cladding layer to the substrate.

3. The method of claim 1 or claim 2 wherein the substrate comprises a dielectric layer and the cladding layer is attached to the dielectric layer.

4. The method of claim 1, 2 or 3 wherein the layer of waveguide strip material comprises aluminosilicate.

5. The method of claim 3 wherein the dielectric layer comprises silica.

6. The method of any preceding claim wherein the patterning step comprises wet etching.

7. The method of any preceding claim wherein the patterning step comprises etching portions of the layer to define at least one protruding portion having a height dimension greater than 5µm.

8. The method of claim 7 wherein the patterning step comprises etching portions of the waveguide strip layer to define at least one protruding portion having both height and width dimensions of greater than 5µm.

9. The method of claim 8 wherein the patterning comprises etching portions of the waveguide strip layer to define at least one protruding portion having both height and width dimensions greater than 10µm.

10. The method of any one of claims 2 to 9, further comprising a step of depositing a second cladding layer over the protruding portion.

11. A method for making a planar waveguide structure comprising the steps of:

providing a bulk disk of a material suitable for use as the waveguide strip;
etching selected portions of the disk so that the disk comprises a base portion and at least one protruding portion, wherein the protruding portion corresponds substantially in dimension to the waveguide strip:

forming a first cladding layer on the top surface of the protruding portion;
attaching the first cladding layer to a substrate; and
removing the base portion of the bulk disk.

12. The method of claim 11 wherein the bulk disk comprises glass doped with a rare earth dopant.

13. The method of claim 11 or 12, further comprising a step of depositing a second cladding layer over the protruding portion.

14. An optical communications system including a planar waveguide fabricated according to any preceding claim.

5 10 15 20 25 30 35 40 45 50 55

FIG. 1

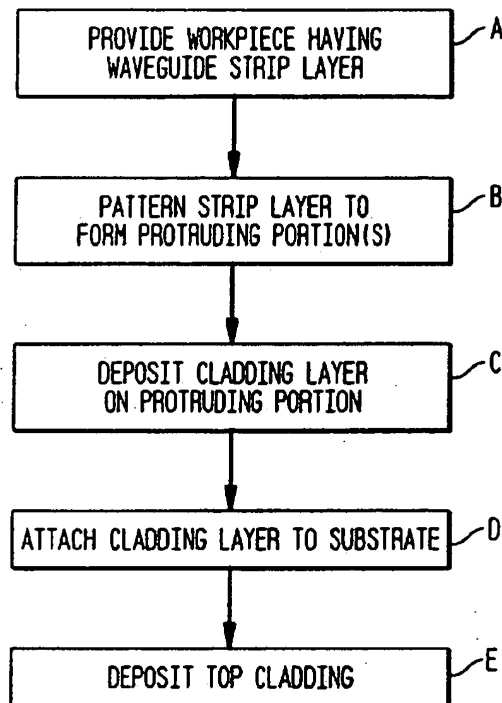


FIG. 2A

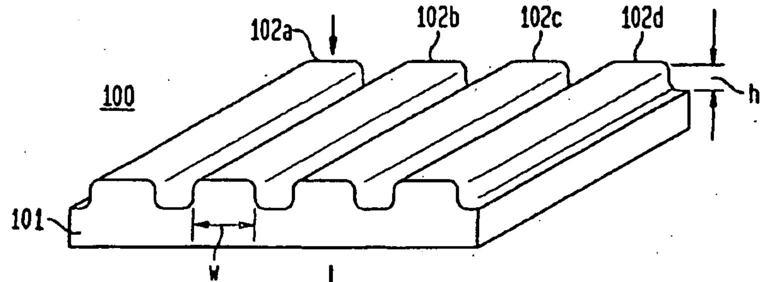


FIG. 2B

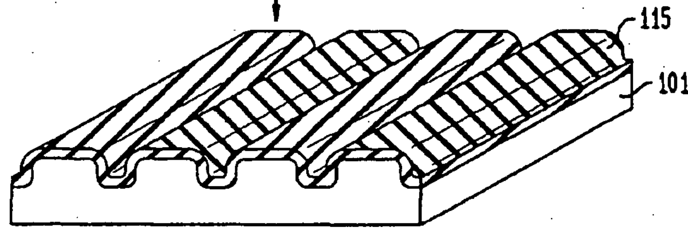


FIG. 2C

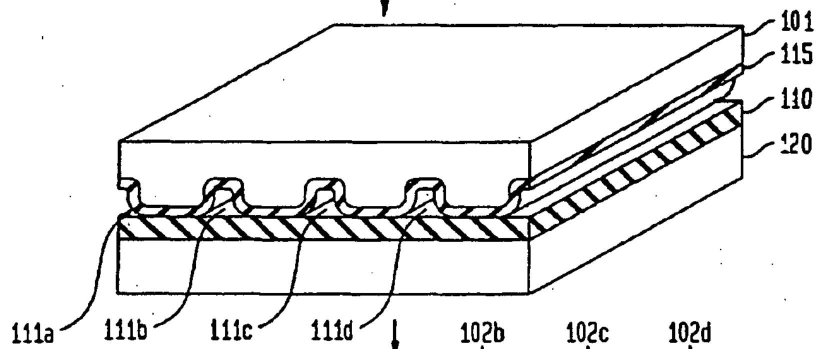


FIG. 2D

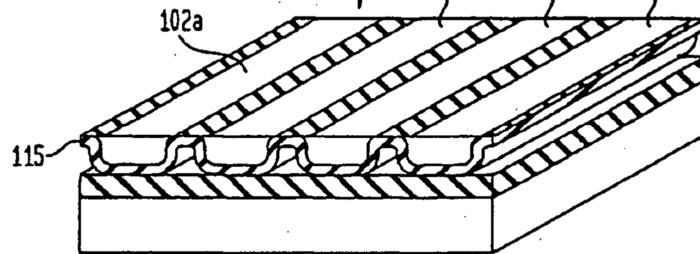
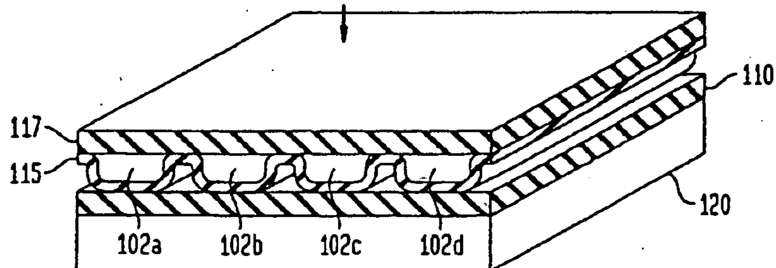


FIG. 2E



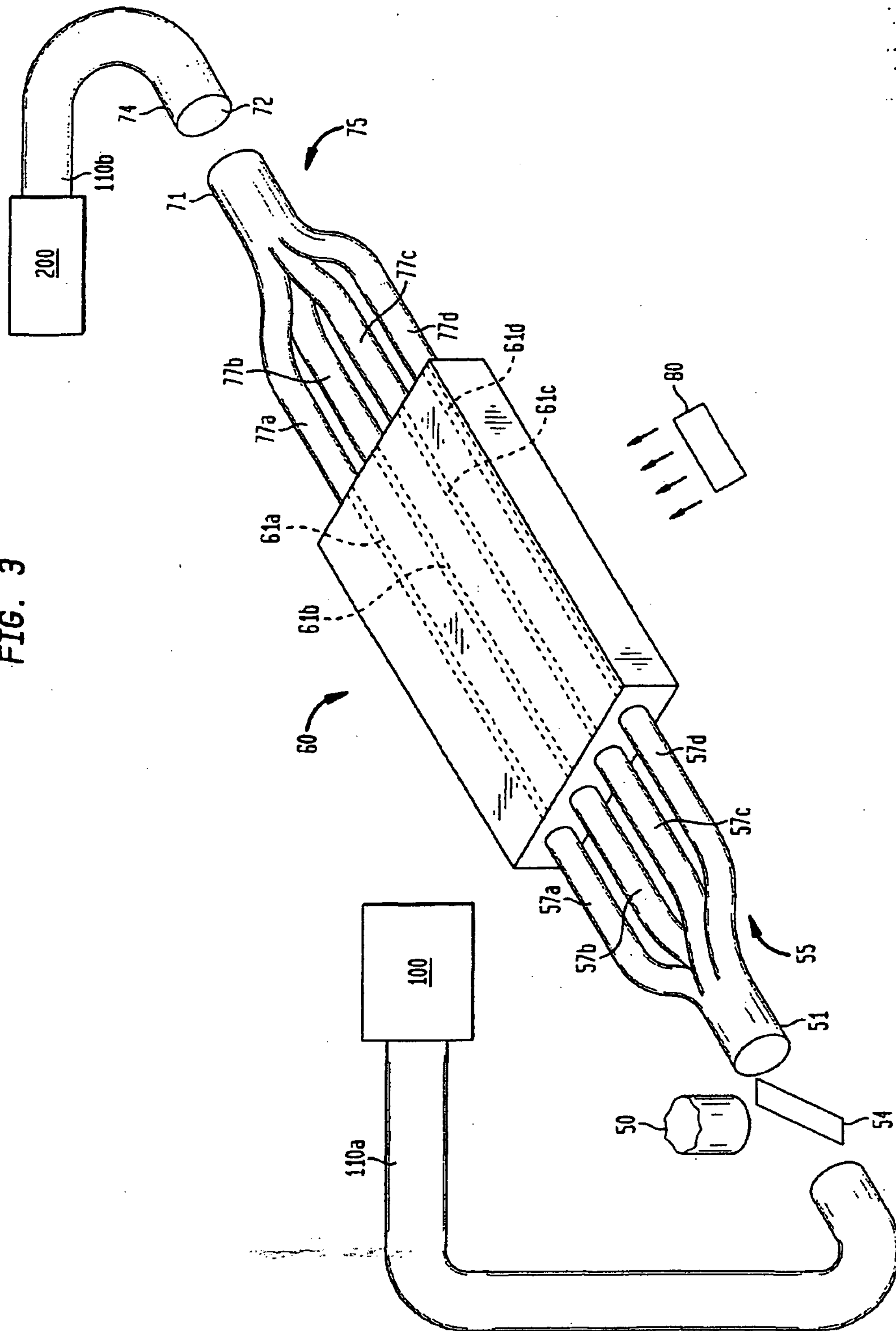


FIG. 3
200
110b
74
72
75
71
77c
77d
61d
77b
77a
61c
80
61a
61b
60
57d
57c
57a
57b
55
100
51
50
54
110a

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 652 308 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **94116188.7**

(51) Int. Cl.6: **C30B 23/02**

(22) Date of filing: **13.10.94**

(30) Priority: **14.10.93 JP 281748/93**
20.10.93 JP 285674/93
10.12.93 JP 341281/93
29.03.94 JP 58887/94

(43) Date of publication of application:
10.05.95 Bulletin 95/19

(84) Designated Contracting States:
DE FR GB NL

(71) Applicant: **NEURALSYSTEMS CORPORATION**
Minamisawa Bldg.,
21-8, Ichigayasanai-cho,
Shinjuku-ku
Tokyo-to (JP)
Applicant: **MEGA CHIPS CORPORATION**
1-12-38, Esaka-cho
Suita-shi,
Osaka-fu (JP)

(72) Inventor: **Asakawa, Toshifumi**
6-9-25, Tsukimino
Yamato-shi,
Kanagawa-ken (JP)
Inventor: **Shindo, Masahiro, c/o Mega Chips Corporation**
1-12-38, Esaka-cho
Suita-shi,
Osaka-fu (JP)
Inventor: **Yoshimizu, Toshikazu, c/o Mega Chips Corporation**
1-12-38, Esaka-cho
Suita-shi,
Osaka-fu (JP)
Inventor: **Ueyama, Sumiyoshi, c/o Mega Chips Corporation**
1-12-38, Esaka-cho
Suita-shi,
Osaka-fu (JP)

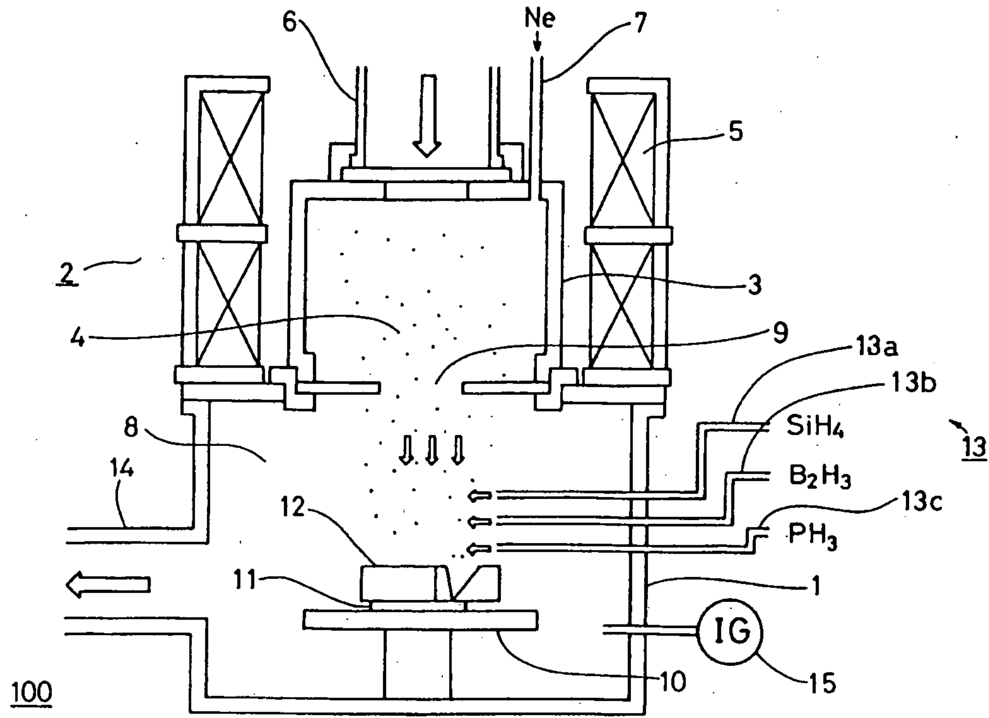
(74) Representative: **KUHNEN, WACKER & PARTNER**
Alois-Steinecker-Strasse 22
D-85354 Freising (DE)

(54) **Method of and apparatus for forming single-crystalline thin film.**

(57) In order to form a single-crystalline thin film on a polycrystalline substrate using plasma CVD, a downwardly directed mainly neutral Ne atom current is formed by an ECR ion generator (2). A reaction gas such as silane gas which is supplied from a reaction gas inlet pipe (13) is sprayed onto an SiO_2 substrate (11) by an action of the Ne atom current, so that an amorphous Si thin film is grown on the substrate (11) by a plasma CVD reaction. At the same time, a part of the Ne atom current having high directivity is directly incident upon the substrate (11), while another part thereof is incident upon the substrate (11) after its course is bent by a reflector (12). The reflector (12) is so set that all directions of the parts of the Ne atom current which are incident upon the substrate (11) are perpendicular to densest planes of single-crystalline Si. Therefore, the as-grown amorphous Si is sequentially converted to a single-crystalline Si thin film having crystal axes which are so regulated that the densest planes are oriented perpendicularly to the respective directions of incidence, by an action of the law of Bravais. Thus, a single-crystalline thin film is formed on a polycrystalline substrate.

EP 0 652 308 A2

FIG. 13



BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of and an apparatus for forming a single-crystalline thin film on a substrate, i.e., an arbitrary medium, and it relates to a method of and an apparatus for forming a single-crystalline thin film, which implement selective and efficient formation of a single-crystalline thin film, and it also relates to a beam irradiator, a beam irradiating method, and a beam reflecting device for enabling efficient formation of a single-crystalline thin film or an axially oriented polycrystalline thin film on a substrate.

Background of the Invention

Plasma chemical vapor deposition (plasma CVD) is a sort of chemical vapor deposition process (CVD), which is adapted to bring a reaction gas into a plasma state for forming active radicals and ions and to cause a chemical reaction under active environment, thereby forming a thin film of a prescribed material on a substrate under a relatively low temperature. The plasma CVD, which can form various types of films under low temperatures, has such advantages that it is possible to form an amorphous film while preventing crystallization, to employ a non-heat-resistant substrate such as a plastic substrate, and to prevent the as-formed film from a reaction with the substrate. Therefore, the application range of the plasma CVD is increasingly widened particularly in relation to semiconductor industry.

It is possible to epitaxially form a single-crystalline thin film of a prescribed material on a single-crystalline substrate by carrying out the plasma CVD under a temperature facilitating crystallization.

Generally, in order to form a single-crystalline thin film of a prescribed material on a single-crystalline substrate of the same material having the same crystal orientation, it is possible to employ an epitaxial growth process. In the epitaxial growth process, however, it is impossible to form a single-crystalline thin film on a polycrystalline substrate or an amorphous substrate. Therefore, in order to form a single-crystalline thin film on a substrate having a different crystal structure such as an amorphous substrate or a polycrystalline substrate, or a substrate of a different material, an amorphous thin film or a polycrystalline thin film is temporarily formed on the substrate so that the same is thereafter converted to a single-crystalline thin film.

In general, a polycrystalline or amorphous semiconductor thin film is single-crystallized by fusion recrystallization or lateral solid phase epitaxy.

However, such a process has the following problems: In the fusion recrystallization, the substrate is extremely thermally distorted when the thin film is prepared from a material having a high melting point, to damage physical and electrical properties of the thin film as employed. Further, an electron beam or a laser beam is employed for fusing the thin film. Therefore, it is necessary to scan spots of the electron beam or the laser beam along the overall surface of the substrate, and hence a long time and a high cost are required for recrystallization.

On the other hand, the lateral solid phase epitaxy is easily influenced by a method of crystallizing the material forming the substrate, while the growth rate is disadvantageously slow in this process. In order to grow a single-crystalline thin film over a distance of about 10 µm, for example, this process requires at least 10 hours. Further, it is difficult to obtain a large crystal grain since a lattice defect is caused to stop growth of the single crystal upon progress of the growth to some extent.

In each process, further, it is necessary to bring a seed crystal into contact with the polycrystalline or amorphous thin film. In addition, the single crystal is grown in a direction along the major surface of the thin film, i.e., in a lateral direction, whereby the distance of growth to the crystal is so increased that various hindrances take place during the growth of the single crystal. When the substrate is made of an amorphous material such as glass, for example, the substrate has no regularity in lattice position and this irregularity influences on growth of the single crystal to disadvantageously result in growth of a polycrystalline film having large crystal grain sizes. In addition, it is difficult to selectively form a single-crystalline thin film having a prescribed crystal orientation on an arbitrary region of the substrate, due to the lateral growth.

In order to solve the aforementioned problems of the prior art, there has been made an attempt for reducing the growth distance by utilizing vertical growth of the thin film, thereby reducing the growth time. In other words, there has been tried a method of bringing a seed crystal into contact with the overall surface of a polycrystalline or amorphous thin film for making solid phase epitaxial growth in a direction perpendicular to the major surface of the thin film, i.e., in the vertical direction. As the result, however, the seed crystal was merely partially in contact with the amorphous thin film or the like and it was impossible to

form a single-crystalline thin film by the as-expected vertical solid phase epitaxial growth, since only lateral epitaxial growth was caused from the contact portion. According to this method, further, the seed crystal adhered to the as-grown single-crystalline film and it was extremely difficult to separate the former from the latter, such that the as-grown thin film was disadvantageously separated from the substrate following the seed crystal. Further, it is impossible in practice to selectively form a single-crystalline thin film having a prescribed crystal orientation on an arbitrary region of the substrate, since it is necessary to accurately arrange a seed crystal of a prescribed shape on a prescribed position.

When the substrate itself has a single-crystalline structure, it is impossible to form a single-crystalline thin film having a crystal orientation which is different from that of the substrate on the substrate by any conventional means. This also applies to a polycrystalline thin film having single crystal axes which are regulated along the same direction between crystal grains, i.e., an axially oriented polycrystalline thin film. In other words, it is difficult to form an axially oriented polycrystalline thin film which is oriented in a desired direction on an arbitrary substrate by the prior art.

SUMMARY OF THE INVENTION

The inventor has found that, when a physical seed crystal is employed in vertical growth of solid phase epitaxy, it is difficult to separate a single-crystalline thin film as grown from the seed crystal due to adhesion therebetween, and that this problem can be solved when a virtual seed crystal of a large area is employed in place of the physical seed crystal to obtain a virtual seed crystal for attaining the same effect as a seed crystal adhering to the overall surface of a single crystal in an excellent state with no physical adhesion on the surface of the single crystal in termination of the crystal growth. The present invention is based on this basic idea.

According to the present invention, a method of forming a single-crystalline thin film is adapted to form a single-crystalline thin film of a prescribed material on a substrate by previously forming an amorphous thin film or a polycrystalline thin film of the prescribed material on the substrate and irradiating the amorphous thin film or the polycrystalline thin film with beams of neutral atoms or neutral molecules of low energy levels causing no sputtering of the prescribed material under a high temperature of not more than a crystallization temperature of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes, having different directions, in the single-crystalline thin film to be formed.

The thin film is at a high temperature below a crystallization temperature, whereby the single crystal which is formed in the vicinity of the surface serves as a seed crystal, so that a single crystal is grown toward a deep portion by vertical solid phase epitaxial growth to single-crystallize the overall region of the thin film along its thickness. When the thin film is at a temperature exceeding the crystallization temperature, the as-formed single crystal is converted to a polycrystalline structure which is in a thermal equilibrium state. On the other hand, no crystallization toward a deep portion progresses at a temperature which is extremely lower than the crystallization temperature. Therefore, the temperature of the thin film is adjusted to be at a high level below the crystallization temperature, such as a level immediately under the crystallization temperature.

The seed crystal, which is formed by conversion from the amorphous thin film or the polycrystalline thin film, is integral with an amorphous thin film or the polycrystalline layer remaining in the deep portion. Namely, this layer is completely in contact with the seed crystal. Therefore, vertical solid phase epitaxial growth progresses in an excellent state. Further, the seed crystal and the single crystal formed by solid epitaxial growth are made of the same material having the same crystal orientation, whereby it is not necessary to remove the seed crystal after formation of the single-crystalline thin film. Further, the single-crystalline thin film, which is formed by vertical solid phase epitaxial growth, can be efficiently obtained in a desired state in a short time.

In the method according to the present invention, it is possible to form a single-crystalline thin film on a substrate including a polycrystalline substrate or an amorphous substrate, while it is not necessary to increase the temperature of the substrate to an extremely high level. Therefore, it is possible to easily obtain a single-crystalline thin film such as a wide-use semiconductor thin film which is applied to a thin film transistor of liquid crystal display or a single-crystalline thin film which is applied to a three-dimensional LSI. While a well-known metal evaporation film is inferior in quality due to a number of vacancies such that a migration phenomenon takes place to easily cause disconnection when the same is applied to interconnection of an electronic circuit, it is possible to prevent such a problem according to the present invention.

Preferably, the atomic weights of atoms forming the beams are lower than the maximum one of the atomic weights of elements forming the prescribed material.

The atomic weights of atoms forming the beams which are applied to the thin film or atoms forming molecules are lower than the maximum one of the atomic weights of elements forming the thin film, whereby most parts of the atoms forming the as-applied beams are rearwardly scattered on the surface of the thin film or in the vicinity thereof, to hardly remain in the thin film. Thus, electronic/physical properties of 5 the thin film are hardly changed by residual of such atoms in the single-crystalline thin film.

Preferably, the beams are obtained by a single electron cyclotron resonance type ion generation source and a reflector which is arranged in a path between the ion generation source and the amorphous thin film or the polycrystalline thin film.

The beams which are applied to the thin film are obtained by a single beam source and a reflector 10 which is arranged in a path, whereby it is possible to irradiated the substrate with the beams from a plurality of prescribed directions which are different from each other with no requirement for a plurality of beam sources. Namely, only a single beam source having a complicated structure is sufficient in the method according to the present invention, whereby a single-crystalline thin film can be formed with a simple apparatus structure. Since only one beam source is sufficient, it is possible to form the thin film under a 15 high vacuum. Further, the beam source is formed by an electron cyclotron resonance type ion generation source, whereby the ion beams have high directivity and it is possible to obtain strong neutral beams having excellent directivity at positions beyond prescribed distances from the ion source with no means for neutralizing ions.

In the method according to the present invention, an amorphous thin film or a polycrystalline thin film 20 which is previously formed on a substrate surface is irradiated with beams of atoms or molecules from a plurality of directions. The beams are at energy levels causing no sputtering on the material as irradiated, whereby the law of Bravais acts such that a layer close to the surface of the amorphous thin film or the polycrystalline thin film is converted to a crystal having such a crystal orientation that planes perpendicular to the directions irradiated with the beams define densest crystal planes. The plurality of beams are applied 25 from directions perpendicular to a plurality of densest crystal planes having different directions, whereby the orientation of the as-formed crystal is set in a single one. In other words, a single-crystalline thin film having a regulated crystal orientation is formed in the vicinity of a surface of the amorphous thin film or the polycrystalline thin film.

The inventor has also found that a single-crystalline thin film can be obtained by growing a thin film and 30 converting the same to a single-crystalline simultaneously instead of previously forming a thin film. This invention is also based on this idea.

According to the present invention, a method of forming a single-crystalline thin film forms a single-crystalline thin film of a prescribed material on a polycrystalline substrate or an amorphous substrate using plasma chemical vapor deposition by supplying a reaction gas onto the substrate under a low temperature 35 allowing no crystallization of the prescribed material with the plasma chemical vapor deposition alone while simultaneously irradiating the substrate with beams of a low energy gas causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed.

In the method according to the present invention, a thin film of a prescribed material is formed on a 40 substrate by plasma chemical vapor deposition, while the substrate is irradiated with beams of a gas from a plurality of directions. The gas beams are at energy levels causing no sputtering on the material as irradiated, whereby the law of Bravais acts such that the thin film of the prescribed material as being formed is sequentially converted to a crystal in such a crystal orientation that planes perpendicular to directions of the beams define densest crystal planes. The substrate is irradiated with a plurality of gas beams from 45 directions perpendicular to a plurality of densest crystal planes having different directions, whereby the as-formed crystal has only one orientation. In other words, a single-crystalline thin film having a regulated crystal orientation is formed.

Under a temperature facilitating crystallization of a prescribed material by plasma chemical vapor deposition alone with no beam irradiation, crystal orientations are arbitrarily directed regardless of directions 50 of beam irradiation and cannot be regulated, while a polycrystalline film is formed. Therefore, temperature control is performed to a low level for facilitating no crystallization with plasma chemical vapor deposition alone.

In the method according to the present invention, further, conversion to a single crystal simultaneously sequentially progresses in the process of growth of the thin film by plasma chemical vapor deposition. 55 Thus, it is possible to form a single-crystalline thin film having a large thickness under a low temperature.

Preferably, the gas is an inert gas.

The substrate is irradiated with an inert gas, whereby atoms or ions which may remain in the as-formed thin film after irradiation exert no bad influence on electronic/physical properties of the single-crystalline thin

film as impurities.

Preferably, the atomic weight of an element forming the inert gas is lower than the maximum one of the atomic weights of elements forming the prescribed material.

The atomic weight of an element forming the inert gas is lower than the maximum atomic weight of elements forming the prescribed material which is grown as a thin film, whereby most parts of atoms or ions of the as-applied inert gas rearwardly recoil on the surface of the thin film or in the vicinity thereof, to hardly remain in the thin film.

Preferably, the prescribed material contains an element forming a gas material which is in a gas state under ordinary temperatures, and the beams of the gas are those of the gas material.

The gas as applied contains elements forming the material which is grown as the thin film. Even if atoms or ions of the elements remain after irradiation, therefore, the same exert no bad influence on the as-formed single-crystalline thin film as impurities. Further, it is also possible to supply the element to the thin film only by application of the gas beams without introducing the same into the reaction gas.

Preferably, the reaction gas contains a reaction gas material which is formed by an impurity element to be added to the prescribed material.

The reaction gas contains an impurity element to be added to the material which is grown as the thin film, whereby it is possible to form a p-type or n-type semiconductor single-crystalline thin film in formation of a semiconductor single-crystalline thin film, for example. In other words, it is possible to form a single-crystalline thin film containing a desired impurity.

Preferably, a plurality of types of impurity elements are so employed that a plurality of types of reaction gas materials which are formed by respective ones of the plurality of types of impurity elements are alternately supplied onto the substrate.

A plurality of types of reaction gas materials formed by respective ones of a plurality of types of impurity elements are alternately supplied onto the substrate, whereby it is possible to form a single-crystalline thin film having a plurality of types of single-crystalline layers containing the respective ones of the plurality of types of impurities such that an n-type semiconductor single-crystalline layer is formed on a p-type semiconductor single-crystalline layer in formation of a semiconductor single-crystalline thin film, for example.

Preferably, the beams of the gas are obtained by a single beam source and a reflector which is arranged in a path between the beam source and the substrate.

The beams of the gas which are applied to the substrate are obtained by a single beam source and a reflector which is arranged on a path, whereby it is possible to irradiate the substrate with the gas beams from directions which are perpendicular to a plurality of densest crystal planes having different directions with no requirement for a plurality of beam sources. In other words, only a single beam source having a complicated structure may be so prepared that it is possible to form the single-crystalline thin film with a simple structure in the method according to the present invention. Since a single beam source may be sufficient, further, it is possible to form the thin film under a high vacuum.

Preferably, the beam source is an ion generation source generating an ion beam of the gas, and the reflector is a metal reflector which is substantially made of a metal.

The beam source has an ion generation source which generates an ion beam of the gas, and the reflector is prepared from a metal reflector which is substantially made of a metal. Therefore, the ion beam of the gas generated from the ion source is converted to a neutral beam when the same is reflected by the metal reflector. Therefore, the substrate is irradiated with parallel beams which are regulated in direction. Further, it is possible to prepare the substrate from an electrical insulating substrate.

Preferably, the beam source is an electron cyclotron resonance type ion generation source.

The beam source is formed by an electron cyclotron resonance type ion generation source. Therefore, the ion beam has high directivity, while it is possible to obtain a strong neutral beam in a portion which is separated beyond a prescribed distance from the ion source with no employment of means for neutralizing ions. It is possible to irradiate the substrate with parallel beams from a plurality of prescribed directions by reflecting the neutral beam by the reflector and applying the same to the substrate. Further, it is also possible to prepare the substrate from an electrical insulating substrate.

According to the present invention, a method of forming a single-crystalline thin film of a prescribed material comprises (a) a step of forming an amorphous or polycrystalline thin film of the prescribed material on a substrate, (b) a step of forming a masking material on the thin film, (c) a step of selectively removing the masking material, and (d) a step of irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed while utilizing the selectively removed masking material as a screen under a high temperature below the

crystallization temperature of the prescribed material.

Preferably, the steps (b) to (d) are carried out plural times while varying directions for applying the beams in the step (d), thereby selectively converting the thin film to a single crystal having a plurality of types of crystal orientations.

5 In the method according to the present invention, the amorphous or polycrystalline thin film which is previously formed on the substrate is irradiated with gas beams from a plurality of directions. These beams are at energy levels causing no sputtering on the material as irradiated, whereby the law of Bravais acts so that a layer which is in the vicinity of the surface of the as-irradiated thin film is converted to a crystal having such a crystal orientation that planes perpendicular to the directions of the beams define densest 10 crystal planes. The plurality of gas beams are applied from directions which are perpendicular to a plurality of densest crystal planes having different directions, whereby the as-formed crystal is set in a single orientation. Namely, a single-crystalline layer having a regulated crystal orientation is formed in the vicinity of the surface of the polycrystalline thin film. Further, a masking material is formed on the thin film to be irradiated in advance of irradiation, and this masking material is selectively removed. Thus, irradiation 15 progresses with limitation on a specific region of the substrate corresponding to the selectively removed portion of the masking material, whereby the single-crystalline layer is formed only in the vicinity of the surface portion of the thin film corresponding to the specific region.

Further, the thin film is at a high temperature below the crystallization temperature and hence the single crystal which is formed in the vicinity of its surface serves as a seed crystal to be grown toward a deep 20 portion by vertical solid phase epitaxial growth, whereby the overall region of the as-irradiated thin film is single-crystallized along the thickness. If the thin film is at a temperature exceeding the crystallization temperature, the as-formed single crystal is converted to a polycrystalline structure which is in a thermal equilibrium state. On the other hand, no crystallization toward a deep portion progresses at a temperature which is extremely lower than the crystallization temperature. Therefore, the temperature of the thin film is 25 adjusted to be at a high level below the crystallization temperature, such as a level immediately under the crystallization temperature, for example.

According to the inventive method, as hereinabove described, it is possible to selectively form a single-crystalline thin film having a regulated crystal orientation on an arbitrary specific region of a substrate.

In the method according to the present invention, the steps from formation of the masking material to 30 irradiation with the gas beams are repeated while varying directions of irradiation. Therefore, it is possible to selectively form single-crystalline thin films having different crystal orientations on a plurality of arbitrary specific regions of the substrate.

According to the present invention, a method of forming a single-crystalline thin film of a prescribed material comprises (a) a step of forming an amorphous or polycrystalline thin film of the prescribed material 35 on a substrate, (b) a step of forming a masking material on the thin film, (c) a step of selectively removing the masking material, (d) a step of etching the thin film while utilizing the selectively removed masking material as a screen, thereby selectively removing the thin film while leaving a specific region on the substrate, and (e) a step of irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal 40 planes having different directions in the single-crystalline thin film to be formed under a high temperature below the crystallization temperature of the prescribed material.

In the method according to the present invention, the amorphous or polycrystalline thin film is selectively removed while leaving a specific region on the substrate and thereafter the thin film is irradiated with gas beams under a prescribed temperature to facilitate action of the law of Bravais and vertical solid 45 phase epitaxial growth, thereby converting the thin film to a single-crystalline thin film. Thus, it is possible to selectively form a single-crystalline thin film having a regulated crystal orientation on an arbitrary specific region of the substrate.

According to the present invention, a method of forming a single-crystalline thin film of a prescribed material comprises (a) a step of forming an amorphous or polycrystalline thin film of the prescribed material 50 on a substrate, (b) a step of irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed under a high temperature below the crystallization temperature of the prescribed material, (c) a step of forming a masking material on the thin film after the step (b), (d) a step of selectively removing the masking material, and (e) a step of 55 etching the thin film while utilizing the selectively removed masking material as a screen, thereby selectively removing the thin film.

In the method according to the present invention, the amorphous or polycrystalline thin film formed on the substrate is irradiated with gas beams under a prescribed temperature to facilitate action of the law of

Bravais and vertical solid phase epitaxial growth, thereby converting the thin film to a single-crystalline thin film. Thereafter the single-crystalline thin film is selectively removed while leaving a specific region on the substrate. Therefore, it is possible to selectively form a single-crystalline thin film having a regulated crystal orientation on an arbitrary specific region on the substrate.

5 According to the present invention, a method of forming a single-crystalline thin film of a prescribed material comprises (a) a step of forming an amorphous or polycrystalline thin film of the prescribed material on a substrate, (b) a step of irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed under a low temperature 10 causing no crystallization of the prescribed material by the step (a) alone while carrying out the step (a), (c) a step of forming a masking material on the thin film after the steps (a) and (b), (d) a step of selectively removing the masking material, and (e) a step of etching the thin film while utilizing the selectively removed masking material as a screen, thereby selectively removing the thin film.

In the method according to the present invention, an amorphous or polycrystalline thin film is formed on 15 the substrate with application of gas beams under a prescribed temperature for facilitating action of the law of Bravais, thereby converting the thin film as being formed sequentially to a single-crystalline thin film. Thereafter the single-crystalline thin film is selectively removed while leaving a specific region on the substrate. Thus, it is possible to selectively form a single-crystalline thin film having a regulated crystal orientation on an arbitrary specific region of the substrate.

20 According to the present invention, a method of forming a single-crystalline thin film of a prescribed material comprises (a) a step of forming an amorphous or polycrystalline thin film of the prescribed material on a substrate, (b) a step of irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed under a high temperature 25 below the crystallization temperature of the prescribed material, (c) a step of forming a masking material on the thin film after the step (b), (d) a step of selectively removing the masking material, and (e) a step of irradiating the substrate with the gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to the plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed and different from those in the step (b), while 30 utilizing the selectively removed masking material as a screen.

In the method according to the present invention, the amorphous or polycrystalline thin film formed on the substrate is irradiated with gas beams under a prescribed temperature to facilitate action of the law of Bravais and vertical solid phase epitaxial growth, thereby converting the thin film to a single-crystalline thin film. Thereafter a masking material is selectively formed on this single-crystalline thin film, which in turn is 35 again irradiated with gas beams from new directions. At this time, the masking material serves as a screen for the gas beams, whereby the single-crystalline thin film is converted to a second single-crystalline thin film having a new crystal orientation on a region where the masking material is selectively removed. Namely, it is possible to selectively form single-crystalline thin films having different crystal orientations on a plurality of arbitrary specific regions of the substrate.

40 The atomic weight of an element forming the gas is preferably lower than the maximum one of the atomic weights of elements forming the prescribed material.

The atomic weight of the element forming the gas beams which are applied onto the substrate is lower than the maximum one of the atomic weights of the elements forming the thin film as irradiated, whereby most parts of the atoms forming the applied gas are rearwardly scattered on the surface of the thin film as 45 irradiated or in the vicinity thereof, to hardly remain in the thin film. Thus, it is possible to obtain a single-crystalline thin film having a small amount of impurities.

The atomic weight of an element forming the gas is preferably lower than the maximum one of the atomic weights of elements forming the masking material.

The atomic weight of the element forming the gas beams which are applied onto the substrate is lower 50 than the maximum one of the atomic weights of the elements forming the masking material, whereby most parts of the atoms forming the gas as applied are rearwardly scattered on the surface of the masking material or in the vicinity thereof, to hardly penetrate into the masking material and the thin film as irradiated. Thus, it is possible to obtain a single-crystalline thin film having a small amount of impurities.

The present invention is also directed to an apparatus for forming a single-crystalline thin film. 55 According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises irradiation means for irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed,

and substrate moving means for making the substrate scanned with respect to the irradiation means.

Preferably, the apparatus for forming a single-crystalline thin film further comprises beam focusing means for bringing sections of the gas beams into strip shapes on the substrate.

In the apparatus according to the present invention, the substrate can be scanned by the substrate moving means, whereby it is possible to form a single-crystalline thin film having high homogeneity on a long substrate.

Further, the apparatus according to the present invention comprises beam focusing means for bringing sections of the gas beams into strip shapes on the substrate, whereby it is possible to efficiently form a single-crystalline thin film with higher homogeneity by scanning the substrate.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises a single beam source for supplying a beam of a gas, a reflector for reflecting at least a part of the beam which is supplied by the beam source, thereby implementing irradiation of the substrate with the gas in a plurality of prescribed directions of incidence, and reflector driving means for varying the angle of inclination of the reflector.

In the apparatus according to the present invention, the gas beams to be applied to the thin film are obtained by a single beam source and a reflector which is arranged in a path, whereby it is possible to irradiate the thin film with the gas beams from a plurality of prescribed directions which are different to each other with no requirement for a plurality of beam sources. Further, this apparatus comprises reflector driving means, whereby it is possible to change and re-set directions of incidence of the beams upon the substrate. Thus, it is possible to form a plurality of types of single-crystalline thin films having different crystal structures or different crystal orientations by a single apparatus.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises a single beam source for supplying a beam of a gas, a plurality of reflectors, each of which reflects at least a part of the beam supplied by the beam source, thereby implementing irradiation of the substrate with the gas in a plurality of prescribed directions of incidence related to the angle of inclination of the reflector, and reflector exchange means for selecting a prescribed one from the plurality of reflectors and utilizing the same for reflecting the beam.

In the apparatus according to the present invention, the gas beams to be applied to the thin film are obtained by a single beam source and a reflector which is arranged in a path, whereby it is possible to irradiate the thin film with the gas beams from a plurality of prescribed directions which are different from each other with no requirement for a plurality of beam sources. Further, this apparatus comprises reflector exchange means, whereby it is possible to arbitrarily select directions of incidence of the beams upon the substrate from a plurality of reflectors to re-set the same. Thus, it is possible to form a plurality of types of single-crystalline thin films having different crystal structures or crystal orientations by a single apparatus.

The apparatus for forming a single-crystalline thin film preferably further comprises film forming means for forming an amorphous or polycrystalline thin film of the same material as the single-crystalline thin film on the substrate.

The apparatus of the present invention comprises film forming means such as chemical vapor deposition means, for example, whereby it is possible to sequentially convert the thin film as being formed to a single-crystalline thin film by forming the thin film while irradiating the same with gas beams. Thus, there is no need to facilitate vertical epitaxial growth of the thin film, whereby the single-crystalline thin film can be formed under a low temperature.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises etching means for etching a surface of the substrate, film forming means for forming an amorphous or polycrystalline thin film of the prescribed material on the surface of the substrate, and irradiation means for irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed. Treatment chambers provided in the aforementioned means for storing the substrate communicate with each other. The apparatus further comprises substrate carrying means for introducing and discharging the substrate into and from the respective treatment chambers.

The apparatus according to the present invention comprises etching means, film forming means and irradiation means having treatment chambers communicating with each other, whereby it is possible to start film formation by carrying out etching treatment for removing an oxide film and preventing new progress of oxidation before forming the thin film on the substrate by employing this apparatus. Further, this apparatus comprises substrate carrying means, whereby the substrate can be efficiently carried into the respective treatment chambers.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate having a single-crystalline structure comprises irradiation means for irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed, and attitude control means for controlling the attitude of the substrate for setting prescribed relations between directions of crystal axes of the substrate and directions of incidence of the beams.

The apparatus according to the tenth aspect of the present invention comprises attitude control means, whereby it is possible to set prescribed relations between the crystal axes of the single-crystalline substrate and the directions of incidence of the gas beams by employing this apparatus. Thus, it is possible to epitaxially form a new single-crystalline thin film on a single-crystalline substrate at a temperature below the crystallization temperature.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises film forming means for forming an amorphous or polycrystalline thin film of the prescribed material on the substrate by supplying a reaction gas, irradiation means for irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed, and substrate rotating means for rotating the substrate.

The apparatus according to the present invention comprises substrate rotating means, whereby it is possible to facilitate formation of an amorphous or polycrystalline thin film by intermittently applying the beams while regularly supplying the reaction gas and rotating the substrate during application pauses. Thus, it is possible to form an amorphous or polycrystalline thin film having high homogeneity, whereby high homogeneity is also attained in a single-crystalline thin film which is obtained by converting the same.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises film forming means for forming an amorphous or polycrystalline thin film of the prescribed material on the substrate by supplying a reaction gas, and irradiation means for irradiating the substrate with gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed. The film forming means has supply system rotating means for rotating an end portion of a supply path for supplying the substrate with the reaction gas with respect to the substrate.

The apparatus according to the present invention comprises supply system rotating means, whereby it is possible to obtain a single-crystalline thin film having high homogeneity while regularly supplying the reaction gas and applying the beams with no intermittent application of the beams. Namely, it is possible to efficiently form a single-crystalline thin film having high homogeneity.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises a plurality of irradiation means for irradiating the substrate with a plurality of gas beams of low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed respectively, and control means for independently controlling operating conditions in the plurality of irradiation means respectively.

In the apparatus according to the present invention, control means independently controls operating conditions in irradiation means such as output beam densities, for example, whereby states of a plurality of beams which are applied to the substrate are optimumly controlled. Thus, it is possible to efficiently form a high-quality single-crystalline thin film.

The irradiation means preferably comprises an electron cyclotron resonance type ion source, and the gas beams are supplied by the ion source.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises irradiation means for irradiating the substrate with beams of a gas supplied by an ion source at low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed, and bias means for applying a bias voltage across the ion source and the substrate in a direction for accelerating ions.

In the apparatus according to the present invention, bias means applies a bias voltage across the ion source and the substrate, whereby the gas beams are improved in directivity. Thus, it is possible to form a high-quality single-crystalline thin film having high homogeneity of the crystal orientation.

According to the present invention, an apparatus for forming a single-crystalline thin film of a prescribed material on a substrate comprises irradiation means for irradiating the substrate with beams of a gas

supplied by an ion source at low energy levels causing no sputtering of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes having different directions in the single-crystalline thin film to be formed, with a grid which is provided in the vicinity of an ion outlet of the ion source, and grid voltage applying means for applying a voltage to the grid for controlling conditions for extracting ions from the ion source.

In the apparatus according to the present invention, grid voltage applying means optimumly controls conditions for extracting ions from the ion source, whereby it is possible to efficiently form a high-quality single-crystalline thin film.

In the apparatus according to the present invention, the beam source is preferably an electron cyclotron resonance type ion source.

In the apparatus according to the present invention, the gas beams are supplied by an electron cyclotron resonance type ion source, whereby the ion beams are excellent in directivity while it is possible to obtain strong neutral beams having excellent directivity at positions beyond a prescribed distance from the ion source without employing means for neutralizing ions.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a container for storing the sample, and a beam source for irradiating the target surface of the sample which is set in a prescribed position of the container with the gas beam, and at least a surface of a portion irradiated with the beam is made of a material having threshold energy which is higher than energy of the beam in sputtering by irradiation with the beam among an inner wall of the container and a member which is stored in the container.

At least the surface of the portion irradiated with the beam is made of a material having threshold energy which is higher than energy of the beam in sputtering by the irradiation with the beam among the inner wall of the container and the member stored in the container, whereby no sputtering is caused even if the beam reaches the member. Therefore, consumption of the member by sputtering is suppressed, while contamination of the target sample with the material element forming the member is prevented.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a container for storing the sample, and a beam source for irradiating the target surface of the sample which is set in a prescribed position of the container with the gas beam, and at least a surface of a portion irradiated with the beam is made of a material having threshold energy with respect to sputtering which is higher than that in the target surface of the sample among an inner wall of the container and a member which is stored in the container.

At least the surface of the portion irradiated with the beam is made of a material having threshold energy with respect to sputtering which is higher than that in the target surface of the sample among the inner wall of the container and the member stored in the container, whereby no sputtering is caused in this member when the target surface of the sample is irradiated with the beam causing no sputtering. Therefore, consumption of the member by sputtering is suppressed under such usage, while contamination of the target sample with the material element forming the member is prevented.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a container for storing the sample, and a beam source for irradiating the target surface of the sample which is set in a prescribed position of the container with the gas beam, and at least a surface of a portion irradiated with the beam is made of a material containing an element which is larger in atomic weight than that forming the gas among an inner wall of the container and a member which is stored in the container.

At least the surface of the portion irradiated with the beam is made of a material containing an element which is larger in atomic weight than that forming the beam gas among the inner wall of the container and the member stored in the container, whereby permeation of a different element in the member is suppressed. Therefore, deterioration of the member caused by invasion of the different element is suppressed.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a container for storing the sample, and a beam source for irradiating the target surface of the sample which is set in a prescribed position of the container with the gas beam, and at least a surface of a portion irradiated with the beam is made of the same material as that forming the target surface of the sample among an inner wall of the container and a member which is stored in the container.

At least the surface of the portion irradiated with the beam is made of the same material as that forming the target surface of the sample among the inner wall of the container and the member stored in the container, whereby the target sample is not contaminated with the material element forming the member even if sputtering is caused in this member.

The member stored in the container preferably includes reflecting means which is interposed in a path of the beam for separating the beam into a plurality of components and irradiating the target surface of the sample with the plurality of components from directions which are different from each other.

The reflecting means is stored in the container and at least the surface of the portion irradiated with the beam is made of a material causing no sputtering, the same material as that of the target surface of the sample, or a material containing an element which is larger in atomic weight than that forming the beam gas, whereby contamination of the sample by sputtering of the reflecting means is prevented or deterioration of the reflecting means is suppressed.

The present invention is also directed to a beam irradiating method. According to the present invention, a beam irradiating method of irradiating a target surface of a sample with a gas beam comprises a step of setting the sample in a prescribed position of a container, and a step of irradiating the target surface of the sample which is set in the container with the gas beam, and the target surface is irradiated with the beam at energy which is lower than threshold energy of sputtering in a surface of a portion which is irradiated with the beam among an inner wall of the container and a member stored in the container.

The target surface is irradiated with the beam at energy which is lower than threshold energy of sputtering on the surface of the portion irradiated with the beam among the inner wall of the container and the member stored in the container, whereby no sputtering is caused even if the beam reaches the member. Therefore, consumption of the member by sputtering is suppressed, while contamination of the target sample with the material element forming the member is prevented.

The present invention is also directed to a method of forming single-crystalline thin film. According to the present invention, a method of forming a single-crystalline thin film of a prescribed material on a substrate comprises a step of depositing the prescribed material on the substrate under a low temperature causing no crystallization of the prescribed material and irradiating the prescribed material as deposited with a gas beam of low energy causing no sputtering of the prescribed material from one direction, thereby forming an axially oriented polycrystalline thin film of the material, and a step of irradiating the axially oriented polycrystalline thin film with gas beams of low energy causing no sputtering of the prescribed material under a high temperature below a crystallization temperature of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes of different directions in the single-crystalline thin film, thereby converting the axially oriented polycrystalline thin film to a single-crystalline thin film.

The axially oriented polycrystalline thin film is previously formed on the substrate and thereafter irradiated with the beams from a plurality of directions so that the thin film is converted to a single-crystalline thin film. Therefore, even if the substrate is not uniformly irradiated with the beams from the plurality of directions due to a screen formed on the substrate, for example, at least either a single-crystalline thin film or an axially oriented polycrystalline thin film is formed on any portion on the substrate, whereby no remarkable deterioration of characteristics is caused.

According to the present invention, a method of forming a single-crystalline thin film of a prescribed material on a substrate comprises a step of depositing the prescribed material on the substrate thereby forming a thin film of the material, a step of irradiating the thin film with a gas beam of low energy causing no sputtering of the prescribed material under a high temperature below a crystallization temperature of the prescribed material from one direction after the step, thereby converting the thin film to an axially oriented polycrystalline thin film, and a step of irradiating the axially oriented polycrystalline thin film with gas beams of low energy causing no sputtering of the prescribed material under a high temperature below the crystallization temperature of the prescribed material from directions which are perpendicular to a plurality of densest crystal planes of different directions in the single-crystalline thin film, thereby converting the axially oriented polycrystalline thin film to a single-crystalline thin film.

The axially oriented polycrystalline thin film is previously formed on the substrate and thereafter irradiated with the beams from a plurality of directions, so that the thin film is converted to a single-crystalline thin film. Therefore, even if the substrate is not uniformly irradiated with the beams from the plurality of directions due to a screen formed on the substrate, for example, at least either a single-crystalline thin film or an axially oriented polycrystalline thin film is formed on any portion on the substrate, whereby no remarkable deterioration of characteristics is caused.

The direction of the gas beam in formation of the axially oriented polycrystalline thin film is preferably identical to one of the plurality of directions of the gas beams in the conversion of the axially oriented polycrystalline thin film to the single-crystalline thin film.

The direction of application of the gas beam in formation of the axially oriented polycrystalline thin film is identical to one of the plurality of directions of gas beams for converting the axially oriented polycrystalline thin film to a single-crystalline thin film, whereby conversion to the single-crystalline thin film is

smoothly carried out.

The gas is preferably an inert gas.

The beam of an inert gas is so applied that no particularly remarkable influence is exerted on the electrophysical properties of the thin film even if the gas remains in the single-crystalline thin film as formed, while it is possible to easily remove the as-invaded gas from the thin film.

The atomic weight of an element forming the inert gas is preferably lower than the maximum atomic weight among those of elements forming the prescribed material.

The atomic weight of the element forming the inert gas is lower than the maximum atomic weight of elements forming the prescribed material which is grown as the thin film, whereby most part of atoms or ions of the applied inert gas are rearwardly scattered on the surface of the thin film or in the vicinity thereof, to hardly remain in the thin film.

The prescribed material preferably contains an element forming a gas material which is a gas under a normal temperature, and the gas beam is preferably a beam of the gas material.

The gas as applied contains an element forming the material grown as a thin film. Even if atoms or ions of the element remain in the thin film after irradiation, therefore, these will not exert a bad influence on the single-crystalline thin film as impurities.

The gas beam is preferably formed by an electron cyclotron resonance ion source.

The beam generation source is an electron cyclotron resonance ion generation source. Therefore, the ion beam has high directivity, while a strong neutral beam can be obtained at a distance exceeding a prescribed length from the ion generation source without employing means for neutralizing ions. Further, it is possible to employ an electrically insulating substrate without employing means for neutralizing the ions.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a single beam source for supplying the beam, and reflecting means for reflecting the beam which is supplied by the beam source, thereby enabling irradiation of the target surface with the gas in a plurality of prescribed directions of incidence, and the reflecting means comprises a reflector having a plurality of reflecting surfaces for reflecting the beam in a plurality of directions, and a screen which is interposed in a path of the beam between the beam source and the reflecting surfaces for selectively passing the beam thereby preventing multiple reflection by the plurality of reflecting surfaces.

Multiple reflection of the beam by the plurality of reflecting surfaces is prevented by the screen, whereby no beam is applied from a direction other than a prescribed direction of incidence.

The screen preferably further selectively passes the beam to uniformly irradiate the target surface with the beam.

The target surface is uniformly irradiated with the beam by action of the screen. Therefore, a high quality single-crystalline thin film is formed when the apparatus is applied to formation of a single-crystalline thin film, for example.

The present invention is also directed to a beam reflecting device. According to the present invention, a beam reflecting device for reflecting a gas beam which is supplied from a single beam source thereby enabling irradiation of a target surface of a sample with the gas in a plurality of prescribed directions of incidence comprises a reflector having a plurality of reflecting surfaces for reflecting the beam in a plurality of directions, and a screen which is interposed in a path of the beam between the beam source and the reflecting surfaces for selectively passing the beam thereby preventing multiple reflection by the plurality of reflecting surfaces.

Multiple reflection of the beam by the plurality of reflecting surfaces is prevented by the screen, whereby no beam is applied from a direction other than a prescribed direction of incidence.

The screen preferably further selectively passes the beam to uniformly irradiate the target surface with the beam.

The target surface is uniformly irradiated with the beam by action of the screen. Therefore, a high-quality single-crystalline thin film is formed when the apparatus is applied to formation of a single-crystalline thin film, for example.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with a gas beam comprises a single beam source for supplying the beam, and reflecting means for reflecting the beam which is supplied by the beam source, thereby enabling irradiation of the target surface with the gas in a plurality of prescribed directions of incidence, and the reflecting means comprises a first reflector which is arranged in a path of the beam supplied from the beam source for reflecting the beam in a plurality of directions thereby generating a plurality of divergent beams having beam sections which are two-dimensionally enlarged with progress of the beams, and a second reflector having a concave reflecting surface for further reflecting the plurality of divergent beams to be incident upon the target surface substantially as parallel beams from a plurality of directions.

The gas beams applied to the target surface of the sample are obtained by the single beam source and the reflecting means provided in the path, whereby it is possible to irradiate the target surface with gas beams from a plurality of different prescribed directions with no requirement for a plurality of beam sources. Further, the beam is reflected by the first reflector to be two-dimensionally diverged in a plurality of directions and then converted to substantially parallel beams by the second reflector, whereby the beam can be uniformly applied to the target surface which is wider than the section of the beam supplied from the beam source. Therefore, it is possible to widely and efficiently form a single-crystalline thin film of a prescribed material on a wide substrate provided with a thin film of the prescribed material on its surface or a wide substrate having a thin film of the prescribed material being grown on its surface without scanning the substrate, by irradiating the substrate with a gas beam by this apparatus.

The reflecting means preferably further comprises rectifying means which is provided in a path of the beams between the first reflector and the substrate for regularizing directions of the beams.

The rectifying means is arranged in the path of the beam between the first reflector and the sample, whereby the beam can be regulated along a prescribed direction. Therefore, no strict accuracy is required for the shapes and arrangement of the respective reflectors, whereby the apparatus can be easily structured.

The reflecting means preferably further comprises beam distribution adjusting means which is interposed in a path of the beam between the beam source and the first reflector for adjusting distribution of the beam on a section which is perpendicular to the path, thereby adjusting the amounts of respective beam components reflected by the first reflector in the plurality of directions.

The beam distribution adjusting means adjusts the amounts of a plurality of beam components reflected by the first reflector, whereby the amounts of a plurality of beam components which are incident upon the target surface from a plurality of directions can be adjusted. Therefore, the amounts of the respective beam components incident upon the substrate can be optimumly set to be identical to each other, for example, whereby it is possible to efficiently form a high-quality single-crystalline thin film.

According to the present invention, a beam reflecting device for reflecting a gas beam which is supplied from a single beam source thereby enabling irradiation of a target surface of a sample with the gas in a plurality of prescribed directions of incidence comprises a first reflector for reflecting the beam in a plurality of directions thereby generating a plurality of divergent beams having beam sections which are two-dimensionally enlarged with progress of the beams, and a second reflector having a concave reflecting surface for further reflecting the plurality of divergent beams to be incident upon the target surface substantially as parallel beams from a plurality of directions.

The gas beam which is supplied from the single beam source is reflected by the first reflector to be two-dimensionally diverged in a plurality of directions and then converted to substantially parallel beams by the second reflector, whereby it is possible to irradiate the target surface which is wider than the section of the beam supplied from the beam source from a plurality of directions with no requirement for a plurality of beam sources. Therefore, it is possible to widely and efficiently form a single-crystalline thin film of a prescribed material on a wide substrate provided with a thin film of the prescribed material on its surface or a wide substrate having a thin film of the prescribed material being grown on its surface without scanning the substrate, by irradiating the substrate with a gas beam by this apparatus.

According to the present invention, a beam irradiator for irradiating a target surface of a sample with gas beams comprises a plurality of beam sources for supplying the gas beams, and a plurality of reflecting means for reflecting the beams which are supplied by the plurality of beam sources thereby enabling irradiation of a common region of the target surface with the gas in a plurality of prescribed directions of incidence, and each reflecting means comprises a first reflector which is arranged in a path of each beam supplied from each beam source for reflecting the beam thereby generating a beam having a beam section which is two-dimensionally enlarged with progress of the beam, and a second reflector having a concave reflecting surface for further reflecting the divergent beam to be incident upon a linear or strip-shaped common region of the target surface substantially as a parallel beam, while the beam irradiator further comprises moving means for scanning the sample in a direction intersecting with the linear or strip-shaped common region.

The beams are reflected by the first reflector to be substantially one-dimensionally diverged and thereafter converted to substantially parallel beams by the second reflector, whereby it is possible to irradiate a linear or strip-shaped region which is wider than the beams supplied from the beam sources with parallel beams from prescribed directions of incidence. Further, the sample is scanned in a direction intersecting with the linear or strip-shaped region, whereby the beams can be uniformly applied to a wide target surface. In addition, a plurality of beam sources and a plurality of reflecting means are so provided that a wide target surface can be uniformly irradiated with beams from a plurality of directions of incidence.

Each reflecting means preferably further comprises rectifying means which is provided in a path of each beam between the first reflector and the substrate for regulating the direction of the beam.

The rectifying means is arranged in the beam path between the first reflector and the substrate, whereby the beams can be regulated in a prescribed direction. Therefore, no strict accuracy is required for the shapes and arrangement of the respective reflectors, whereby the apparatus can be easily structured.

According to the present invention, a beam reflecting device for reflecting a gas beam which is supplied from a beam source thereby enabling irradiation of a target surface of a sample with the gas in a prescribed direction of incidence comprises a first reflector for reflecting the beam thereby generating a divergent beam having a beam section which is two-dimensionally enlarged with progress of the beam, and a second reflector having a concave reflecting surface for further reflecting the divergent beam to be incident upon a linear or strip-shaped region of the target surface substantially as a parallel beam.

The beams are reflected by the first reflector to be substantially one-dimensionally diverged and thereafter converted to substantially parallel beams by the second reflector, whereby it is possible to irradiate a linear or strip-shaped region which is wider than the beams supplied from the beam sources with the beams.

Accordingly, an object of the present invention is to provide a technique which can form an axially oriented polycrystalline thin film oriented in a desired direction and a single-crystalline thin film having a desired crystal orientation on an arbitrary substrate including a single-crystalline substrate.

Another object of the present invention is to provide a beam irradiator and a beam reflecting device for enabling efficient formation of a single-crystalline thin film.

Throughout the specification, the term "substrate" is not restricted to a substance simply serving as a base to be provided thereon with a thin film, but generally indicates a medium to be provided thereon with a thin film, including a device having a prescribed function, for example.

Throughout the specification, the term "gas beam" is a concept including all of a beam-type ion current, an atom current and a molecular flow.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a model diagram showing an apparatus which is suitable for carrying out a method according to a first preferred embodiment of the present invention;

Figs. 2A to 2C are perspective views showing a structure of a collimator;

Figs. 3A and 3B are sectional views showing a sample;

Fig. 4 is a front sectional view showing an apparatus which is suitable for carrying out a method according to a second preferred embodiment of the present invention;

Fig. 5 is a perspective view showing a reflector which is employed in the method according to the second preferred embodiment of the present invention;

Figs. 6A, 6B and 6C are a plan view, a side elevational view and a front elevational view showing an example of the reflector which is employed in the method according to the second preferred embodiment of the present invention;

Fig. 7 is a graph showing characteristics of an ECR ion generator which is employed in the method according to the second preferred embodiment of the present invention;

Fig. 8 illustrates experimental data verifying the method according to the second preferred embodiment of the present invention;

Fig. 9 is a perspective view showing another example of the reflector employed in the method according to the second preferred embodiment of the present invention;

Figs. 10A, 10B and 10C illustrate three surfaces of still another example of the reflector employed in the method according to the second preferred embodiment of the present invention;

Figs. 11A and 11B are structural diagrams showing a further example of the reflector employed in the method according to the second preferred embodiment of the present invention;

Figs. 12A and 12B are structural diagrams showing a further example of the reflector employed in the method according to the second preferred embodiment of the present invention; and

Fig. 13 is a front sectional view showing an apparatus which is suitable for carrying out a method according to a preferred embodiment of the present invention.

Fig. 14 is a front sectional view showing an apparatus according to a fourth preferred embodiment of the present invention;

Fig. 15 illustrates a result of a verification test in the apparatus according to the fourth preferred embodiment of the present invention;
Fig. 16 is a front sectional view showing an apparatus according to a fifth preferred embodiment of the present invention;
5 Fig. 17 is a perspective view showing a reflector in the fifth preferred embodiment;
Fig. 18 is a plan view of the reflector shown in Fig. 17;
Fig. 19 is an exploded perspective view of the reflector shown in Fig. 17;
Fig. 20 is an exploded perspective view of the reflector shown in Fig. 17;
Fig. 21 is a plan view of the reflector shown in Fig. 17;
10 Fig. 22 is a sectional view taken along the line A - A in Fig. 21;
Fig. 23 is a perspective view showing an apparatus according to a sixth preferred embodiment of the present invention;
Fig. 24 is a perspective view showing an apparatus according to a seventh preferred embodiment of the present invention;
15 Fig. 25 is a process diagram for illustrating a method according to an eighth preferred embodiment of the present invention;
Fig. 26 is a process diagram for illustrating the method according to the eighth preferred embodiment of the present invention;
Fig. 27 is a process diagram for illustrating the method according to the eighth preferred embodiment of
20 the present invention;
Fig. 28 is a front sectional view of an apparatus according to a ninth preferred embodiment of the present invention;
Fig. 29 is a front sectional view showing a reflecting unit in the ninth preferred embodiment of the present invention;
25 Fig. 30 is a plan view showing a reflecting unit in the ninth preferred embodiment;
Fig. 31 is a front sectional view showing an apparatus according to a tenth preferred embodiment of the present invention;
Fig. 32 is a perspective view showing an apparatus according to an eleventh preferred embodiment of the present invention;
30 Fig. 33 is a plan view showing the apparatus according to the eleventh preferred embodiment of the present invention;
Fig. 34 is a front elevational view of the apparatus according to the eleventh preferred embodiment of the present invention;
Fig. 35 is a plan view of the apparatus according to the eleventh preferred embodiment of the present
35 invention; and
Fig. 36 is a perspective view showing an apparatus according to a twelfth preferred embodiment of the present invention.
Fig. 37 is a process diagram showing a method according to a thirteenth preferred embodiment of the present invention;
40 Fig. 38 is a process diagram showing the method according to the thirteenth preferred embodiment of the present invention;
Fig. 39 is a process diagram showing the method according to the thirteenth preferred embodiment of the present invention;
Fig. 40 is a process diagram showing the method according to the thirteenth preferred embodiment of
45 the present invention;
Fig. 41 is a process diagram showing the method according to the thirteenth preferred embodiment of the present invention;
Fig. 42 is a process diagram showing the method according to the thirteenth preferred embodiment of the present invention;
50 Fig. 43 is a process diagram showing a method according to a fourteenth preferred embodiment of the present invention;
Fig. 44 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;
Fig. 45 is a process diagram showing the method according to the fourteenth preferred embodiment of
55 the present invention;
Fig. 46 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;

Fig. 47 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;
Fig. 48 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;
5 Fig. 49 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;
Fig. 50 is a process diagram showing the method according to the fourteenth preferred embodiment of the present invention;
Fig. 51 is a process diagram showing the method according to the fourteenth preferred embodiment of
10 the present invention;
Fig. 52 is a process diagram showing a method according to a seventeenth preferred embodiment of the present invention;
Fig. 53 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
15 Fig. 54 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
Fig. 55 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
Fig. 56 is a process diagram showing the method according to the seventeenth preferred embodiment of
20 the present invention;
Fig. 57 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
Fig. 58 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
25 Fig. 59 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
Fig. 60 is a process diagram showing the method according to the seventeenth preferred embodiment of the present invention;
Fig. 61 is a process diagram showing a method according to an eighteenth preferred embodiment of the
30 present invention;
Fig. 62 is a front elevational view showing an apparatus according to a nineteenth preferred embodiment of the present invention;
Fig. 63 is a plan view showing the apparatus according to the nineteenth preferred embodiment of the present invention;
35 Fig. 64 is a front sectional view showing the apparatus according to the nineteenth preferred embodiment of the present invention;
Fig. 65 is a perspective view showing the apparatus according to the nineteenth preferred embodiment of the present invention;
Fig. 66 is a front elevational view showing an apparatus according to a twentieth preferred embodiment
40 of the present invention;
Fig. 67 is a plan view showing an apparatus according to a twenty-first preferred embodiment of the present invention;
Fig. 68 is a plan view showing an apparatus according to a twenty-third preferred embodiment of the present invention;
45 Fig. 69 is a front sectional view showing an apparatus according to a twenty-fourth preferred embodiment of the present invention;
Fig. 70 is a front sectional view showing another apparatus according to the twenty-fourth preferred embodiment of the present invention;
Fig. 71 is a partially fragmented sectional view showing an apparatus according to a twenty-fifth
50 preferred embodiment of the present invention;
Fig. 72 is a plan view showing another apparatus according to the twenty-fifth preferred embodiment of the present invention;
Fig. 73 is a front sectional view showing an apparatus according to a twenty-sixth preferred embodiment of the present invention;
55 Fig. 74 is a front sectional view showing an apparatus according to a twenty-seventh preferred embodiment of the present invention;
Fig. 75 is a front sectional view showing an apparatus according to a twenty-eighth preferred embodiment of the present invention; and

Fig. 76 is a front sectional view showing an apparatus according to a twenty-ninth preferred embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5

⟨A. Formation of Single-Crystalline Thin Film or Axially Oriented Polycrystalline Thin Film⟩

Preferred embodiments for efficiently forming a single-crystalline thin film or axially oriented polycrystalline thin film on a substrate are now described.

10

⟨A-1. First Preferred Embodiment⟩

A first preferred embodiment of the present invention is now described.

15 ⟨A-1-1. Structure of Apparatus⟩

Fig. 1 is a model diagram showing the structure of an apparatus 80 for effectively implementing a method according to the first preferred embodiment of the present invention. This apparatus 80 is adapted to convert a polycrystalline thin film 82, which is formed on a substrate 81, to a single-crystalline thin film.
20 Therefore, the apparatus 80 is supplied with a sample prepared by the polycrystalline thin film 82 of a prescribed material which is already formed on the substrate 81 by a well-known method.

For example, the substrate 81 is prepared from polycrystalline SiO_2 (quartz), and a polycrystalline Si (silicon) thin film 82 is formed on this quartz substrate 81, to be converted to a single-crystalline Si thin film. The apparatus 80 comprises cage-type ion sources 83. Inert gases are introduced into the ion sources 83
25 from conduits 84 and ionized therein by electron beams, thereby forming plasmas of the inert gases. Further, only ions are extracted from the ion sources 83 by action of electric fields which are formed by lead electrodes provided in the ion sources 83, whereby the ion sources 83 emit ion beams. For example, it is possible to accelerate Ne (neon) ions to 200 to 600 eV by the ion sources 83 of 10 cm in diameter, for example, with current densities of 1 to 9 mA/cm^2.
30 The ion beams which are emitted from the ion sources 83 are guided to reflection deaccelerators 85 and collimators 86, and thereafter applied to the surface of the polycrystalline thin film 82 at prescribed angles. Each reflection deaccelerator 85 is provided with two silicon single-crystalline plates having major surfaces of (100) planes. These silicon single-crystalline plates are in the form of discs having diameters of 15 cm, for example. These silicon single-crystalline plates successively reflect the ion beams which are
35 incident on the major surfaces thereof at angles of incidence of 45° to reduce energy levels and neutralize electric charges thereof, thereby converting the ion beams to low-energy neutral atomic beams.

Figs. 2A to 2C are perspective views showing the structure of each collimator 86. Fig. 2A is an overall perspective view, Fig. 2B is an enlarged perspective view and Fig. 2C is a further enlarged perspective view. The collimator 86 regulates directions of the atomic beams, thereby supplying the polycrystalline thin
40 film 82 with atomic beams having high directivity. The collimator 86 is formed by alternately stacking corrugated members, which are prepared by evaporating silicon films 86b on both sides of aluminum plates 86a as shown in Fig. 2C, and flat plate members having similar structures as shown in Fig. 2B. This collimator 86 has 30 layers, for example. Both surfaces of the aluminum plates 86a are covered with the silicon films 86b, so that aluminum atoms which are different atoms will not reach the polycrystalline Si thin
45 film 82 even if the corrugated members and the flat plate members are struck by an neutral atom current to cause sputtering. The atomic beams are regularized in direction within a range of ±0.5° while passing through thin channels defined between the corrugated and flat plate members, to be converted to atomic beams having high directivity.

The quartz substrate 81 is mounted on a heater 87, which is adapted to maintain the quartz substrate
50 81 at a prescribed high temperature.

⟨A-1-2. Operation of Apparatus⟩

The operation of the apparatus 80 is now described. The sample which is supplied to the apparatus 80
55 can be prepared by forming the polycrystalline Si thin film 82 on the quartz substrate 81 by well-known chemical vapor deposition (CVD), for example. The quartz substrate 81 is 1.5 mm in thickness, for example, and the polycrystalline Si thin film 82 is about 2000 Å in thickness, for example. First, the sample as prepared is mounted on the heater 87. This heater 87 maintains the sample, i.e., the quartz substrate 81

and the polycrystalline Si thin film 82, at a temperature of 550°C. This temperature is lower than the crystallization temperature of silicon, whereby no single-crystalline Si is converted to polycrystalline Si under this temperature. However, this temperature is so high that polycrystalline Si can be grown to single-crystalline Si if a seed crystal is present.

5 Then, Ne (neon) gases are introduced into the ion sources 83 from the conduits 84, to form Ne ion beams. The as-formed Ne ion beams pass through the reflection deaccelerators 85 and the collimators 86, to reach the surface of the polycrystalline Si thin film 82 as low energy neutral Ne atomic beams.

The two Ne atomic beams which are started from the two ion sources 83 are incident upon the surface of the polycrystalline Si thin film 82 at angles of incidence of 35° so that the directions of incidence are 10 two-fold symmetrical with each other about a normal line on the surface of the polycrystalline Si thin film 82. The directions of incidence of these two beams, which are at an angle of 70° to each other, correspond to normal line directions of independent two densest planes, i.e., (111) planes of single-crystalline Si having a diamond crystal structure.

The energy levels of the plasmas formed by the ion sources 83 are so set that the Ne atoms reaching 15 the polycrystalline Si thin film 82 are at levels causing no sputtering of the polycrystalline Si thin film 82, i.e., at levels lower than a value (= 27 eV) known as a threshold energy level in sputtering of Si caused by irradiation with Ne atoms. Therefore, the so-called law of Bravais acts on the polycrystalline Si thin film 82. Namely, Si atoms provided in the vicinity of the surface of the polycrystalline Si thin film 82 are so rearranged that planes perpendicular to the directions of incidence of the Ne atomic beams which are 20 applied to the polycrystalline Si thin film 82 define densest crystal planes.

Since the Ne atomic beams are incident from two directions corresponding to those perpendicular to the independent densest planes of the single-crystalline Si, whereby the Si atoms are so rearranged that planes perpendicular to the directions of incidence define the densest planes. Namely, two independent (111) planes are controlled by the two Ne atoms beams having independent directions of incidence to be 25 rearranged in constant directions, whereby the crystal orientation is univocally decided. Thus, a layer which is close to the surface of the polycrystalline Si thin film 82 is converted to a single-crystalline Si layer having a regulated crystal orientation.

The above description corresponds to a first stage of single-crystallization of the polycrystalline Si thin film 82. Figs. 3A and 3B are model diagrams showing internal structures of the sample in the first stage and 30 a following second stage of single-crystallization. In the first stage, a single-crystalline Si layer 88 is formed only in the vicinity of the surface of the polycrystalline Si thin film 82, as shown in Fig. 3A.

As hereinabove described, the temperature of the polycrystalline Si thin film 82 is adjusted to a level which is suitable for growing a seed crystal. Therefore, the single-crystalline Si layer 88 which is formed on the surface of the polycrystalline Si thin film 82 serves as a seed crystal, to be grown toward a deep portion 35 of the polycrystalline Si thin film 82. Finally the overall region of the polycrystalline Si thin film 82 is converted to the single-crystalline Si layer 88, as shown in Fig. 3B. Thus, a single-crystalline Si thin film having a regulated crystal orientation is formed on the quartz substrate 81. Since the polycrystalline Si thin film 82 is maintained at a temperature which is lower than the crystallization temperature of Si as hereinabove described, the single-crystalline Si layer 88 will not return to the polycrystalline structure, which 40 is a thermal equilibrium state.

The single-crystalline Si layer 88, which is formed on the polycrystalline Si thin film 82 by irradiation to serve as a seed crystal, is integrated with a polycrystalline Si layer remaining in its deep portion since this layer 88 is converted from the polycrystalline Si thin film 82. Namely, the polycrystalline Si layer 82 is completely in contact with the seed crystal. Therefore, vertical solid phase epitaxial growth progresses in an 45 excellent state. Further, the seed crystal and the single-crystalline Si which is formed by the solid phase epitaxial growth are single crystals of the same material having the same crystal orientation, whereby it is not necessary to remove the seed crystal after formation of the single-crystalline Si thin film 88. Further, the single-crystalline Si thin film 88 is formed by the vertical solid phase epitaxial growth, whereby it is possible to efficiently obtain a desired single-crystalline Si thin film in a short time as compared with the prior art 50 utilizing transverse growth.

An element forming the atomic beams which are applied to the polycrystalline Si thin film 82 is preferably prepared from Ne, as hereinabove described. Since Ne atoms are lighter than Si atoms, there is a high possibility that the relatively heavy Si atoms rearwardly scatter the relatively light Ne atoms when the atomic beams are applied to the Si thin film, whereby the Ne atoms hardly penetrate into the Si thin film to 55 remain therein. Further, the inert element such as Ne is selected as an element forming the as-applied atomic beams since the inert element forms no compound with any element forming the thin film such as Si even if the same remains in the Si thin film, whereby the electronic/physical properties of the Si thin film are hardly influenced by this element and this element can be easily removed by increasing the temperature of

the as-finished single-crystalline Si thin film to some extent.

The sample is irradiated with the neutralized atomic beams in place of direct Ne ion beams, for the following reasons: First, charged particle beams such as ion beams are spread to lose directivity by repulsion between the particles caused by static electricity. Second, charges are stored in the thin film when charged particle beams are employed for the thin film which is made of a material having high resistivity or the like, such that the beams cannot reach the thin film beyond a certain amount due to repulsion of the stored charges. When neutral atomic beams are employed, on the other hand, no charges are stored in the thin film while parallel beams having excellent directivity reach the thin film to facilitate smooth crystallization.

⟨A-1-3. Other Exemplary Sample⟩

While the above description has been made on the case of converting the polycrystalline Si thin film 82 to a single-crystalline Si thin film, the inventive method is applicable not only to a polycrystalline thin film but to an amorphous thin film, to attain a similar effect. Experimental data verifying this point is now described.

In the experiment, a sample was prepared by previously forming an amorphous Si thin film on a quartz substrate by plasma CVD. Inert gases to be applied to the sample were prepared from Ne gases. The quartz substrate was 1.5 mm in thickness, and the amorphous Si thin film was about 2000 Å in thickness. This sample was mounted on the heater 87, and maintained at a temperature of 550 °C. In this state, the sample was irradiated with beams for about 20 seconds under conditions of acceleration voltages of ion sources of 2000 V and current densities of 2 mA/cm^2. As the result, a brown color specific to amorphous Si disappeared from the as-irradiated central portion of the sample, and this portion was changed to a slightly yellowish transparent state. In this portion, a part of about 1 cm^2 was examined with X rays and by directive etching, whereby it was provide that single-crystalline Si was formed with (110) axes along a normal line direction of the substrate.

The crystal orientation was decided by covering the crystal planes with SiO_2 (silicon dioxide) films, forming small holes in these oxide films, etching the same with KOH (potassium hydroxide) and confirming etching bits. As the result, it was possible to confirm that the etching bits were hexagonal, thereby confirming that single-crystalline Si having (110) axes in the normal line direction was completed.

⟨A-2. Second Preferred Embodiment⟩

A second preferred embodiment of the present invention is now described.

⟨A-2-1. Overall Structure of Apparatus⟩

Fig. 4 is a front sectional view showing an apparatus 101 for effectively implementing a method according to the second preferred embodiment of the present invention. This apparatus 101 is also adapted to convert a polycrystalline thin film, which is previously formed on a substrate 11, to a single-crystalline thin film, similarly to the aforementioned apparatus 80.

This apparatus 101 comprises a reaction vessel 1, and an electron cyclotron resonance (ECR) ion generator 2 which is built in an upper portion of the reaction vessel 1. The ECR ion generator 2 comprises a plasma container 3 which defines a plasma chamber 4 in its interior. A magnetic coil 5 is provided around the plasma container 3, to apply a dc high magnetic field to the plasma chamber 4. Further, a waveguide 6 and an inlet pipe 7 are provided on an upper surface of the plasma container 3 for introducing a microwave and an inert gas such as Ne gas into the plasma chamber 4 respectively.

The reaction vessel 1 defines an reaction chamber 8 in its interior. The bottom portion of the plasma container 3 defines an outlet 9 for passing a plasma in its center. The reaction chamber 8 and the plasma chamber 4 communicate with each other through the outlet 9. In the interior of the reaction chamber 8, a sample holder 10 is arranged on a position immediately under the outlet 9. The substrate 11 is placed on the sample holder 10, while a reflector 12 is placed to be located above the substrate 11. The sample holder 10 comprises a heater (not shown), to heat the substrate 11 and hold the same at a proper high temperature level.

The reflector 12 is preferably made of a metal. The sample holder 10 is coupled to a rotation driving mechanism (not shown), to be rotatable in a horizontal plane. Further, the sample holder 10 can horizontally move the substrate 11 while fixing the reflector 12.

The reaction chamber 8 communicates with an evacuation pipe 14. An end of the evacuation pipe 14 is coupled with a vacuum unit (not shown) to evacuate the reaction chamber 8 through the evacuation pipe 14, thereby maintaining the reaction chamber 8 at a prescribed degree of vacuum. A vacuum gauge 15 for displaying the degree of vacuum in the reaction chamber 8 is provided in communication with the reaction chamber 8.

⟨A-2-2. Structure of Reflector⟩

Fig. 5 is a perspective view showing an exemplary reflector 12a. This reflector 12a is adapted to form a single crystal having a diamond structure, such as single-crystalline Si. The reflector 12a defines an opening on a central portion of a flat plate type base 21. Three blocks 22 in the form of rectangular parallelopipeds are fixedly provided around the opening, and reflecting blocks 23 are fixed to inner sides of the blocks 22 respectively. Consequently, an equilateral triangular opening 24 which is trimmed with the reflecting blocks 23 is defined at the central portion of the base 21. In the reflecting blocks 23, slopes 25 facing the opening 24 serve as reflecting surfaces for reflecting a gas beam. Therefore, the angles of inclination of the slopes 25 are set at proper levels in correspondence to the directions of crystal axes of the single crystal to be formed.

Figs. 6A, 6B and 6C are a plan view, a side elevational view and a front elevational view of the reflector 12a which is formed by the blocks 22 and the reflecting blocks 23 respectively. As shown in Fig. 6B, the angle of inclination of each slope 25 is set at 55°. The reflector 12a is in a structure not fixing the substrate 11, whereby the substrate 11 can be relatively horizontally moved with respect to the reflector 12a. Therefore, it is possible to form a single-crystalline thin film on the substrate 11 having a large area by horizontally moving the substrate 11 while fixing the reflector 12a on the sample holder 10.

⟨A-2-3. Operation of ECR Ion Generator⟩

Referring again to Fig. 4, the operation of the ECR ion generator 2 is now described. An inert gas such as Ne gas or Ar gas is introduced from the inert gas inlet pipe 7 into the plasma chamber 4, while a microwave is simultaneously introduced from the waveguide 6 into the plasma chamber 4. Further, a dc current is also simultaneously supplied to the magnetic coil 5, to form a dc magnetic field in the plasma chamber 4 and its periphery. The gas as supplied is maintained in a plasma state by actions of the microwave and the dc magnetic field. This plasma is formed by high-energy electrons which are in screw motion in the principle of cyclotron by the microwave and the dc magnetic field.

These electrons, which have diamagnetic properties, are moved to a weaker magnetic field side, to form an electron stream along a line of magnetic force. Consequently, positive ions also form an ion current along the line of magnetic force following the electron stream, in order to maintain electrical neutrality. In other words, the electron stream and the ion current are downwardly directed from the outlet 9 into the reaction chamber 8. The ion current and the electron stream thus flowing in parallel with each other are recombined with each other after a lapse of a deionization time, to form a neutral atom current. Therefore, substantially only a neutral atom current is formed in a position downwardly separated from the outlet 9 beyond a prescribed distance.

Fig. 7 is a graph showing the result of relation between ion current density and the distance from the outlet 9 actually measured when Ar^+ ions of 10 eV were discharged from the outlet 9 by the ECR ion generator 2. It is understood from this graph that the ion current density is abruptly reduced at a distance of about 4 to 5 cm from the outlet 9, and attenuated to a level of 1/10 to 1/12 at a position of 14 cm. The neutral atom current is increased by such attenuation of the ion current, whereby substantially only a neutral atom current downwardly flows in a position downwardly separated from the outlet 9 by at least 14 cm.

Thus, the ECR ion generator 2 for generating ions forms an ion current in parallel with the electron stream, whereby it is possible to easily obtain a neutral atom current having high density by employing the ECR ion generator 2, with no employment of other means for neutralizing the ion current. Since the ion current is formed in parallel with the electron stream, further, it is possible to obtain an ion current which is close to a parallel current having a regulated direction of progress substantially with no divergence. Since the parallel ion current is converted to the neutral atom current, the atom current is also close to a parallel current having a regulated direction of progress.

⟨A-2-4. Operation of Apparatus 101⟩

Referring again to Fig. 4, the operation of the apparatus 101 is now described. It is assumed that the reflector 12 is implemented by the reflector 12a shown in Figs. 5 and 6A to 6C and the substrate 11 is prepared from polycrystalline SiO_2 (quartz), so that a single-crystalline Si thin film is formed on the quartz substrate 11. A polycrystalline Si thin film is previously formed on the quartz substrate 11 by a well-known method such as CVD.

First, the sample is mounted between the sample holder 10 and the reflector 12a (12). The heater provided in the sample holder 10 holds the sample, i.e., the quartz substrate 11 and the polycrystalline Si thin film, at a temperature similar to that in the first preferred embodiment, i.e., a temperature of 550°C.

An inert gas which is introduced from the inert gas inlet pipe 7 is preferably prepared from Ne gas having a smaller atomic weight than Si atoms. Due to the action of the ECR ion generator 2, an Ne^+ ion current and an electron stream are formed downwardly from the outlet 9. The distance between the outlet 9 and the reflector 12a (12) is preferably set at a sufficient level for substantially converting the Ne^+ ion current to a neutral Ne atom current. The reflector 12a (12) is set in a position receiving the downwardly directed Ne atom current.

A part of the downwardly directed Ne atom current is reflected by the three slopes 25 which are formed in the reflector 12a, to be applied to the polycrystalline Si thin film provided on the SiO_2 substrate 11 through the opening 24. Another part of the Ne atom current is not incident upon the slopes 25 but directly incident upon the polycrystalline Si thin film through the opening 24. In other words, the polycrystalline Si thin film is irradiated with four Ne atom current components, i.e., a component straightly received from the outlet 9 and three components reflected by the three slopes 25. Since the angles of inclination of the slopes 25 are set at 55°, directions of incidence of the four Ne atom current components correspond to four directions which are perpendicular to four independent densest crystal planes of the Si single crystal to be formed, i.e., (111) planes.

The energy of the plasma which is formed by the ECR ion generator 2 is so set that the Ne atoms reaching the SiO_2 substrate 11 are at energy levels which are lower than threshold energy (= 27 eV) in sputtering of Si by irradiation with Ne atoms. Therefore, the law of Bravais acts on the polycrystalline Si thin film. As the result, the Si atoms in the polycrystalline Si thin film are so rearranged that planes which are perpendicular to the direction of incidence of the Ne atomic current as applied define densest crystal planes. Since the Ne atom current as applied has four components which are incident in directions corresponding to those perpendicular to four independent densest planes of the single-crystalline Si, the Si atoms are so rearranged that all planes perpendicular to the directions of incidence define the densest planes. Namely, the directions of rearrangement of the four independent (111) planes are controlled by four Ne atomic beams having directions of incidence which are independent of each other, whereby the crystal orientation is univocally decided. Thus, a layer in the vicinity of the surface of the polycrystalline Si thin film is converted to a single-crystalline Si layer having a regulated crystal orientation.

The temperature of the polycrystalline Si thin film 82 is adjusted to 550°C, i.e., a level within a range suitable for growing a seed crystal. Therefore, the single-crystalline Si layer which is formed on the surface of the polycrystalline Si thin film 82 serves as a seed crystal, to be grown toward a deep portion of the polycrystalline Si thin film 82. Then, the overall region of the polycrystalline Si thin film 82 is converted to a single-crystalline Si layer. Thus, a single-crystalline Si layer having a regulated crystal orientation is formed on the quartz substrate 11. The aforementioned Figs. 3A and 3B typically express the aforementioned formation of the single-crystalline Si layer and the process of its growth.

As hereinabove described, the reflector 12 is preferably made of a metal, since Ne^+ ions are converted to neutral atoms when an Ne^+ ion current which is slightly mixed in the neutral Ne atom current is reflected by the conductive reflector 12, so that the substrate 11 is irradiated with the as-converted neutral Ne atom current. The neutral atom current is advantageously incident upon the substrate 11 as a flow having a regulated direction since its direction of progress hardly diverges dissimilarly to an ion current.

In the process of irradiating the sample with the Ne atomic current, the rotation driving mechanism (not shown) may be driven to rotate the sample holder 10. Thus, it is possible to improve homogeneity in distribution of an amount of irradiation on the polycrystalline Si thin film.

⟨A-2-5. Valid Data⟩

Description is now made on a test verifying formation of a single-crystalline thin film by the method according to the second preferred embodiment. Fig. 8 illustrate experimental data showing electron beam diffraction images of samples comprising polycrystalline SiO_2 substrates and single-crystalline Si thin films

formed thereon on the basis of the aforementioned method. The sample was obtained by irradiating a substrate with four Ne atom current components using a reflector.

In this sample, three-fold rotation-symmetrical diffraction spots were obtained as shown in Fig. 8. This verifies that the as-obtained sample was formed as single-crystalline Si having regulated crystal axes. Since it was possible to convert a polycrystalline Si thin film having a polycrystalline structure of higher regularity in atomic arrangement than an amorphous structure to a single-crystalline Si thin film, it is conceivably decided possible to convert a thin film having an amorphous structure such as amorphous Si to a single-crystalline thin film, as a matter of course.

〈A-2-6. Methods of Forming Single-Crystalline Thin Films other than Si Thin Film〉

While the structure and the operation of the apparatus 101 have been described with reference to formation of a single-crystalline Si thin film, it is also possible to form single-crystalline thin films other than an Si thin film through the apparatus 101.

Table 1

Gas Material for Crystal Forming Step	
for GaAs	
Ion Beam	Ar, Ne
Element	$Ga(CH_3)_3$ AsH_3
Impurity	$Zn(CH_3)_3$, $Zn(C_2H_5)_3$ (p-type) SiH_4 (n-type)
for GaN	
Ion Beam	Ar, Ne, NH_3
Element	$Ga(CH_3)_3$ NH_3
Impurity	$Zn(CH_3)_3$, $Zn(C_2H_5)_3$ (p-type) SiH_4 (n-type)
for Si	
Ion Beam	Ne
Element	SiH_4 Si_2H_6
Impurity	B_2H_3 (p-type) AsH_3 (n-type) PH_3 (n-type)

Table 1 shows values of sputtering threshold energy in various combinations of types of atoms or ions as applied and elements forming target thin films. In each combination, it is necessary to apply an ion current or an atom current which is at a lower energy level than the as-listed threshold energy. As to thin films formed by compounds, refer to threshold energy levels related to elements having the maximum atomic weights among the elements. The values shown in Table 1 have been obtained on the basis of simulation, unless otherwise stated.

When the thin film as irradiated is formed not by a simple substance such as Si but a compound such as GaAs, for example, it is advisable to apply atoms which are lighter than an element having the maximum atomic weight. Further, beams of a compound such as those of N_2 may be applied in place of beams of simple atoms, for example. In this case, an element (for example, N atoms) forming the compound is preferably lighter than the element having the maximum atomic weight forming the thin film as irradiated.

⟨A-2-7. Other Examples of Reflector⟩

Description is now made on other exemplary structures of the reflector. Figs. 9 and 10A to 10C illustrate a reflector 12b for forming a single-crystalline thin film having a diamond crystal structure whose (111) planes define densest planes, similarly to the reflector 12a shown in Fig. 5. Fig. 9 is a perspective view of the reflector 12b, and Figs. 10A to 10C illustrate three surfaces thereof. This reflector 12b is provided with a groove 31a for sliding the substrate 11 on an upper surface of a base 31 which is mounted on the sample holder 10, so that the substrate 11 is built in the base 31. Therefore, the substrate 11 is fixed to the groove 31a when the same is irradiated, dissimilarly to the reflector 12a. Bottom surfaces of reflecting blocks 33 are placed on the upper surface of the base 31, so that the reflecting blocks 33 are located on the substrate 11. As shown in Fig. 10B, the angles of inclination of slopes 35 provided in the reflecting blocks 33 are set at 55°, similarly to those of the reflector 12a.

It is also possible to form a single-crystalline thin film having a crystal structure other than a diamond structure. In this case, still another reflector may be prepared to have a crystal structure which is suitable for the target crystal structure. Further, it is also possible to form a single-crystalline thin film having various crystal orientations in the same crystal structure. In this case, a reflector which is suitable for respective crystal orientations is prepared, as hereinafter described.

Figs. 11A and 11B illustrate an exemplary reflector 12c corresponding to a single crystal of a diamond structure, whose (100) planes are parallel to a substrate surface. Fig. 11A is a front sectional view taken along the line A - A in Fig. 11B, which is a plan view showing the reflector 12c. A groove 42 is formed on an upper surface of a flat plate type base 41. The substrate 11 is inserted in this groove 42. Namely, the reflector 12c is adapted to receive the substrate 11, which cannot be relatively horizontally moved with respect to the reflector 12c when the same is irradiated. This base 41 is placed on the sample holder 10.

Four reflecting blocks 43 are arranged on the base 41 around the substrate 11, to be perpendicularly adjacent to each other. A shielding plate 46 having openings 47 only above slopes 45 of the reflecting blocks 43 is set on upper surfaces of the reflecting blocks 43. An atom current or an ion current which is incident upon the shielding plate 46 downwardly from above passes through the openings 47 alone, to be entirely reflected by the slopes 45. Namely, only four components of the atom current or the ion current as reflected are incident upon the substrate 11, with no presence of a component which is directly incident from the above. The angles of inclination of the slopes 45 are set at 62.63°. Therefore, the directions of incidence of the four components match with directions perpendicular to four (111) planes, which are independent of each other, in the crystal of the diamond structure.

Figs. 12A and 12B illustrate a reflector 12d corresponding to a single crystal of a diamond structure whose (110) planes are parallel to a substrate surface. Fig. 12A is a front sectional view taken along the line B - B in Fig. 12B, which is a plan view showing the reflector 12d. A groove 52 is formed on an upper surface of a base 51 having an angle of inclination of 35°. The substrate 11 is inserted in this groove 52. Namely, this reflector 12d is adapted to receive the substrate 11, which cannot be relatively horizontally moved with respect to the reflector 12d when the same is irradiated. This base 51 is placed on the sample holder 10.

A single reflecting block 53 is arranged on the base 51. A slope 55 of the reflecting block 53 is set at an angle of inclination of 90° with respect to the upper surface of the base 51. Therefore, an atom current or an ion current which is incident from above is divided into two components including that which is directly incident upon the substrate 11 at an angle of incidence of 35° and that which is reflected by the slope 55 and incident from an opposite side similarly at an angle of incidence of 35°. Directions of incidence of these components match with directions which are perpendicular to two independent planes among four independent (111) planes in the crystal of a diamond structure. Namely, these two components define directions of two densest planes which are independent of each other, whereby it is possible to form a single-crystalline thin film of a diamond structure having a regulated crystal orientation so that the (110) planes are parallel to the substrate surface by employing the reflector 12d.

⟨A-3. Third Preferred Embodiment⟩

A third preferred embodiment of the present invention is now described.

⟨A-3-1. Overall Structure of Apparatus⟩

Fig. 13 is a front sectional view showing a structure of a single-crystalline thin film forming apparatus 100 for effectively implementing a method of forming a single-crystalline thin film according to a preferred

embodiment of the present invention. In Fig. 13, the identical numerals are employed with Fig. 4 to represent the identical components, and therefore, the detailed description of the numerals in Fig. 13 is omitted. Similarly to the apparatus 101, the apparatus 100 comprises a reaction vessel 1, and an electron cyclotron resonance (ECR) ion generator 2 which is built in an upper portion of the reaction vessel 1. In the
5 interior of the reaction chamber 8, a sample holder 10 is arranged on a position immediately under the outlet 9. In this apparatus 101, the sample holder 10 is not required to comprise a heater. A substrate 11 is placed on the sample holder 10, while a reflector 12 is placed to be located above the substrate 11. The substrate 11, which is a flat plate of a material having a polycrystalline structure or an amorphous structure, is one of elements forming a sample. A desired single-crystalline thin film is formed on this substrate 11.
10 The reflector 12a (Fig. 5, Figs. 6A to 6C), 12b (Fig. 9, Figs. 10A and 10B), 12c (Figs. 11A and 11B) or 12b (Figs. 12A and 12B) can be adopted as the reflector 12.

The reaction chamber 8 communicates with reaction gas supply pipes 13. Reaction gases are supplied through the reaction gas supply pipes 13, for forming a thin film of a prescribed material on the substrate 11 by plasma CVD. The preferred embodiment shown in Fig. 1 is provided with three reaction gas supply
15 pipes 13a, 13b and 13c. Similarly to the apparatus 101, an end of the evacuation pipe 14 is coupled with a vacuum unit (not shown) to evacuate the reaction chamber 8 through the evacuation pipe 14, thereby maintaining the reaction chamber 8 at a prescribed degree of vacuum.

⟨A-3-2. Operation of Apparatus 100⟩

20

The operation of the apparatus 100 is now described. It is assumed that the reflector 12 is implemented by the reflector 12a shown in Figs. 5 and 6A to 6C and the substrate 11 is prepared from polycrystalline SiO_2 (quartz), so that a thin film of single-crystalline Si is formed on the quartz substrate 11. The reaction gas supply tubes 13a, 13b and 13c supply SiH_4 (silane) gas for supplying Si, which is a main material for
25 the single-crystalline Si, and B_2H_3 (diborane) gas and PH_3 (phosphine) gas for doping the substrate 11 with p-type and n-type impurities respectively. An inert gas which is introduced from the inert gas inlet pipe 7 is preferably prepared from Ne gas having a smaller atomic weight than Si atoms.

Due to the action of the ECR ion generator 2, an Ne^+ ion current and an electron stream are formed downwardly from the outlet 9. The distance between the outlet 9 and the reflector 12a (12) is preferably set
30 at a sufficient level for substantially converting the Ne^+ ion current to a neutral Ne atom current. The reflector 12a (12) is set in a position receiving the downwardly directed Ne atom current. The silane gas which is supplied from the reaction gas supply tube 13a is dashed against the SiO_2 substrate 11 by the Ne^+ ion current or the Ne atom current. Consequently, a plasma CVD reaction progresses on the upper surface of the SiO_2 substrate 11, to grow a thin film formed by Si which is supplied by the silane gas, i.e.,
35 an Si thin film. On the other hand, the diborane gas or the phosphine gas is supplied with a properly adjusted flow rate, whereby a plasma CVD reaction caused by this gas also progresses to form the Si thin film containing B (boron) or P (phosphorus) in desired density.

The SiO_2 substrate 11 is not heated and hence maintained substantially at an ordinary temperature, whereby the Si thin film is grown substantially under the ordinary temperature. In other words, the Si thin
40 film is formed at a temperature not more than a level facilitating crystallization by plasma CVD. Thus, the Si thin film is first formed as an amorphous Si film by plasma CVD.

A part of the downwardly directed Ne atom current is reflected by the three slopes 25 which are formed in the reflector 12a, to be incident upon the upper surface of the SiO_2 substrate 11 through the opening 24. Another part of the Ne atom current is not incident upon the slopes 25 but directly incident upon the upper
45 surface of the SiO_2 substrate 11 through the opening 24. In other words, the Si thin film being formed on the upper surface of the SiO_2 substrate 11 is irradiated with four Ne atom current components, i.e., a component straightly received from the outlet 9 and three components reflected by the three slopes 25. Since the angles of inclination of the slopes 25 are set at 55°, directions of incidence of the four Ne atom current components correspond to four directions which are perpendicular to four independent densest
50 crystal planes of the Si single crystal to be formed, i.e., (111) planes.

The energy of the plasma which is formed by the ECR ion generator 2 is so set that the Ne atoms reaching the SiO_2 substrate 11 are at energy levels causing no sputtering in the as-formed Si thin film, i.e., levels lower than the threshold energy level in sputtering of Si by irradiation with Ne atoms (= 27 eV). Therefore, the law of Bravais acts on the as-grown amorphous Si thin film. Namely, the Si atoms in the
55 amorphous Si are rearranged so that planes which are perpendicular to the Ne atom current components applied to the amorphous Si define densest crystal planes. Since the Ne atom current as applied has four components which are incident in directions corresponding to those perpendicular to the densest planes of the single-crystalline Si having a single crystal orientation, the Si atoms are so rearranged that all planes

perpendicular to the directions of incidence of the respective components define the densest planes. The directions of the (111) planes are controlled by the plurality of components of the Ne atom current having directions of incidence which are independent of each other, whereby single-crystalline Si having a single crystal orientation is formed by such rearrangement of the Si atoms. In other words, the amorphous Si thin film being grown by plasma CVD is sequentially converted to a single-crystalline Si thin film having a regulated crystal orientation.

The diborane gas or the phosphine gas is supplied by the reaction gas supply pipe 13b or 13c simultaneously with the silane gas, thereby forming a p-type or n-type single-crystalline Si thin film containing B or P. It is also possible to form an equiaxed n-type single-crystalline Si layer on a p-type single-crystalline Si layer, for example, by alternating these reaction gases containing impurity elements.

As hereinabove described, the SiO_2 substrate 11 is not heated and the Si thin film is formed under a temperature which is lower than that facilitating crystallization by plasma CVD. This is because the crystal orientation is arbitrarily directed regardless of the directions of the Ne atom current components and cannot be controlled while a polycrystal is inevitably formed under a high temperature facilitating crystallization of Si by plasma CVD alone with no application of the Ne atom current components.

As described in the first preferred embodiment, Ne which is lighter than Si atoms is preferably selected as an element forming the atom current which is applied to the Si thin film. As described in the second preferred embodiment, the reflector 12 is preferably made of a metal.

In the apparatus 100, conversion to a single crystal sequentially progresses at the same time in the process of growth of the Si thin film by plasma CVD. Thus, it is possible to form a single-crystalline Si thin film having a large thickness under a low temperature. Since a single-crystalline thin film can be formed under a low temperature, it is possible to further form a new single-crystalline thin film on a substrate which is already provided with a prescribed device without changing properties of the device, for example.

Thus, it is possible to form a single-crystalline thin film not only on a substrate which serves only as a support member for a thin film but on a substrate of a device having a prescribed structure and functions in this apparatus 100.

An experimental test was performed in order to verify the formation of a single-crystalline thin film by the aforementioned method. A similar electron beam diffraction image to that shown in Fig. 8 was observed for a sample comprising polycrystalline SiO_2 substrates and single-crystalline Si thin films formed thereon.

This verifies that the sample obtained by use of the reflector 12 was formed as single-crystalline Si having regulated crystal axes. Since it was possible to form a single-crystalline Si thin film on an SiO_2 substrate of a polycrystalline structure having higher regularity than an amorphous structure in atomic arrangement, it is conceivably decided possible to form a single-crystalline thin film on a substrate having an amorphous structure, such as an amorphous Si substrate, as a matter of course.

⟨A-3-3. Preferred Methods of Forming Single-Crystalline Thin Films other than Si Thin Film⟩

While the structure and the operation of the apparatus 100 have been described with reference to formation of a single-crystalline thin film, it is also possible to form single-crystalline thin films other than an Si thin film through the apparatus 100. Tables 2 to 5 show conditions for forming semiconductor single-crystalline thin films having relatively high demands, including the Si thin film as already described, for example. Table 2 shows types of inert gases and reaction gases as supplied.

Tables 3 to 5 show reaction gas flow rates, inert gas flow rates and other process control conditions in formation of respective semiconductor single-crystalline thin films.

Table 2

Target	Threshold Energy						
	Incident Ion (* Actually Measured Value)						
	He	Ne	Ar	Kr	Xe	Hg	Hg (Actually Measured Value)
Al	127	59	59	77	100	136	120 ~ 140
Si	60	27	27 25*	35	45	61	60 ~ 70
GaAs			25*				
Ge	225	66	49	45	48	57	40 ~ 50
Ta	1620	385	233	233	159	147	120 ~ 140
W	1037	245	147	100	89	87	89 ~ 87
Pt	850	198	118	79	69	67	70 ~ 90

Table 3

Process Control Condition for Forming Si	
Gas Flow Rate	
SiH_4 or Si_2H_6	5sccm ($1 \times 10^{-5} \sim 4 \times 10^{-5}$ mol/min)
AsH_3 (Diluted to 10% with Ne)	5sccm (5×10^{-7} mol/min) for n-type Crystal
B_2H_6 (Diluted to 10% with Ne)	5sccm (5×10^{-7} mol/min) for p-type Crystal
Ne (for ECR Chamber)	25sccm (1×10^{-3} mol/min)
Substrate Temperature (SiO_2 Substrate)	Room Temperature
Degree of Vacuum	
Back Pressure	$\sim 10^{-7}$ Torr
Operating Pressure	$1 \times 10^{-4} \sim 4 \times 10^{-4}$ Torr
Microwave Power (2.34 GHz)	300 W
Growth Rate	2 μ/hr

Table 4

Process Control Condition for Forming GaN	
Gas Flow rate	
TMG (Trimethyl Gallium) Carrier Gas N_2 NH_3 DMZ (Dimethyl Zinc) Carrier Gas N_2 SiH_4 (Diluted to 10% with Ne) Ne (For ECR Chamber)	Bubbler employed. Held at -12 °C ~ 10 °C 5sccm (1×10^{-5} ~ 4×10^{-5} mol/min) 10sccm (4×10^{-4} mol/min) for Forming p-type Crystal 5sccm (1×10^{-5} ~ 2.4×10^{-5} mol/min) for Forming n-type Crystal 5sccm (1×10^{-5} ~ 2.4×10^{-5} mol/min) 15ccm (7×10^{-4} mol/min)
Substrate Temperature (Si Substrate)	370 °C
Degree of Vacuum	
Back Pressure Operating Pressure	~ 10^{-7} Torr 1×10^{-4} ~ 4×10^{-4} Torr
Microwave Power (2.34 GHz)	300 W
Growth Rate	0.1 ~ 0.3 µ/hr

Table 5

Process Control Condition for Forming GaAs	
Gas Flow rate	
TMG (Trimethyl Gallium) Carrier Gas Ar AsH_3 (Diluted to 10% with Ar) DMZ (Dimethyl Zinc) Carrier Gas Ar H_2Te (Diluted to 10% with Ar) Ar (For ECR Chamber)	Bubbler employed. Held at -12 °C ~ 10 °C 5sccm (1×10^{-5} ~ 4×10^{-5} mol/min) 10sccm (4×10^{-4} mol/min) for Forming p-type Crystal 5sccm (1×10^{-5} ~ 2.4×10^{-5} mol/min) for Forming n-type Crystal 5sccm (1×10^{-5} ~ 2.4×10^{-5} mol/min) 15ccm (7×10^{-4} mol/min)
Substrate Temperature (Si Substrate)	500 °C
Degree of Vacuum	
Back Pressure Operating Pressure	~ 10^{-7} Torr 1×10^{-4} ~ 4×10^{-4} Torr
Microwave Power (2.34 GHz)	300 W
Growth Rate	0.1 ~ 0.3 µ/hr

Thus, in each of the apparatuses 100 and 101, it is possible to form not only the aforementioned Si single-crystalline thin film but various types of single-crystalline thin films on substrates such as compound single-crystalline thin films of GaAs, GaN and the like and a single-crystalline thin film of an insulator such as SiO_2, for example.

⟨A-4. Modifications of First to Third Preferred Embodiments⟩

(1) In the first or second preferred embodiment, in order to form single-crystalline thin film of GaN, for example, a polycrystalline GaN film may be first grown on an Si substrate by general CVD. Thereafter, by use of the apparatus 101, for example, N_2 (nitrogen) gas or NH_3 (ammonia) gas containing N atoms

may be introduced into the inert gas inlet pipe 7, to irradiate the GaN thin film with a molecular flow of the gas or a dissociated N atom current. N atoms which may remain in the interior of GaN are assembled into the single crystal as an element forming GaN, and hence there is no possibility of exerting a bad influence on properties of GaN.

5 (2) In the first or second preferred embodiment, in order to form a GaAs single-crystalline thin film, a GaAs polycrystalline thin film may be first grown on an Si substrate by general molecular beam epitaxy, so that conditions identical to those for forming an Si single-crystalline thin film are employed except that the substrate temperature is maintained at 500 °C, the gas as applied is prepared from low-priced Ar gas and the reflector is prepared from a Ta plate. It was possible to obtain a GaAs single-crystalline thin film

10 by this method.

(3) In the third preferred embodiment, in order to form single-crystalline thin film of GaN, for example, N_2 (nitrogen) gas or NH_3 (ammonia) gas containing N atoms may be introduced into the inert gas inlet pipe 7 of the apparatus 100, to irradiate the GaN thin film with a molecular flow of the gas or a dissociated N atom current. Nitrogen which may remain in the interior of GaN is assembled into the single crystal as an

15 element forming GaN, and hence there is no possibility of exerting a bad influence on properties of GaN.

(4) In place of the reflector 12, ECR ion generators 2 may be provided in a number corresponding to that of components of an atom current which is applied to the thin film, to directly apply the atom current from the ECR ion generators 2 to the thin film. As compared with this method, however, the method shown in Fig. 4 or Fig. 13 employing a single ECR ion generator 2 and a single reflector 12 is superior

20 since the apparatus can be simplified in structure and it is possible to maintain a high degree of vacuum in the reaction chamber 8.

In the apparatus 100, further, the ECR ion generator 2 also serves as an energy source which is required for providing energy to the reaction gas for carrying out plasma CVD. Namely, the method shown in Fig. 13 employing a single ECR ion generator 2 and a single reflector 12 has a specific

25 advantage such that the same can be carried out by simply adding the reflector 12 to a structure which is originally necessary for carrying out plasma CVD.

(5) The ECR ion generator 2 may be replaced by another ion source such as a Cage type or Kaufmann type one. In this case, however, flow of the as-formed ion current is inclined to be diffused by repulsion caused by static electricity between ions, leading to reduction of directivity. Therefore, it is desirable to

30 provide means for neutralizing ions and converting the same to an atom current or means for improving the directivity such as a collimator in a path of the ion current. When an electrical insulating substrate is employed as the substrate 11, in particular, it is desirable to provide the means for neutralizing ions in order to prevent the progress of irradiation from being disabled due to storage of charges in the substrate 11. Alternatively, the reflector 12 may be made of a conductive material such as a metal, to

35 simultaneously carry out reflection of the ion current and conversion to a neutral atom current.

In the aforementioned method employing the ECR ion generator 2, on the other hand, a neutral atom current can be easily obtained in a form close to a parallel current with no employment of means for neutralizing the ion current. Therefore, the thin film can be easily irradiated with an atom current having high incidence angle accuracy. Since a neutral atom current is mainly incident upon the thin film, further, the

40 substrate 11 can be prepared from an insulating substrate such as an SiO_2 substrate.

⟨A-5. Fourth Preferred embodiment⟩

Next, an apparatus according to a fourth preferred embodiment of the present invention is described.

45 Fig. 14 is a front sectional view showing the overall structure of an axially oriented polycrystalline thin film forming apparatus 122 according to the fourth preferred embodiment. This apparatus 122 is adapted to grow a thin film of a prescribed material on a substrate and to simultaneously convert the thin film to a uniaxially oriented polycrystalline thin film, thereby forming an axially oriented polycrystalline thin film on the substrate. This apparatus 122 is characteristically different from the apparatus 100 shown in Fig. 13 in

50 that a reflector 12 is not provided therein.

Referring to Fig. 14, the operation of the apparatus 122 is now described. It is assumed that the substrate 11 is prepared from polycrystalline SiO_2 (quartz), so that a thin film of single-crystalline Si is formed on the quartz substrate 11. The reaction gas supply tubes 13a, 13b and 13c supply SiH_4 (silane) gas for supplying Si, which is a main material for the single-crystalline Si, and B_2H_3 (diborane) gas and PH_3

55 (phosphine) gas for doping the substrate 11 with p-type and n-type impurities respectively. The inert gas introduced from the inert gas inlet pipe 7 is preferably prepared from Ne gas, which has smaller atomic weight than Si atoms and is inert gas.

Due to the action of the ECR ion generator 2, an Ne^+ ion current and an electron current are formed downwardly from the outlet 9. The distance between the outlet 9 and the substrate 11 is preferably set at a value which is sufficient for converting most part of the Ne^+ ion current to a neutral Ne atom current. The silane gas which is supplied from the reaction gas supply tube 13a is dashed against the substrate 11 by the Ne^+ ion current or the Ne atom current. Consequently, a plasma CVD reaction progresses on the upper surface of the substrate 11, to grow a thin film formed by Si which is supplied by the silane gas, i.e., an Si thin film. On the other hand, the diborane gas or the phosphine gas is supplied with a properly adjusted flow rate, whereby a plasma CVD reaction caused by this gas also progresses to form the Si thin film containing B (boron) or P (phosphorus) in desired density.

The substrate 11 is not heated and hence maintained substantially at an ordinary temperature. Therefore, the Si thin film is grown substantially under the ordinary temperature. In other words, the Si thin film is formed at a temperature not more than a level facilitating crystallization by plasma CVD. Thus, the Si thin film is first formed as an amorphous Si film by plasma CVD.

The aforementioned downwardly directed Ne atom current is perpendicularly incident upon the upper surface of the substrate 11. Namely, the Si thin film being formed on the upper surface of the substrate 11 is irradiated with the Ne atom current which is linearly discharged from the outlet 9.

The energy of the plasma which is formed by the ECR ion source 2 is so set that the energy of Ne atoms reaching the substrate 11 is at a value causing no sputtering in the Si thin film, i.e., lower than the threshold energy (= 27 eV) in sputtering of Si by irradiation with Ne atoms. Therefore, the so-called law of Bravais acts on the amorphous Si thin film as being grown. Namely, the Si atoms in the amorphous Si are rearranged so that a plane which is perpendicular to the direction of incidence of the Ne atom current applied to the amorphous Si defines the densest crystal plane, i.e., the (111) plane.

In other words, the amorphous Si thin film being grown by plasma CVD is sequentially converted to a polycrystalline Si thin film in which directions of crystal axes perpendicular to a single densest plane are regulated in a direction perpendicular to the surface of the substrate 11, i.e., a uniaxially oriented polycrystalline crystalline Si thin film. Consequently, a polycrystalline Si thin film is formed on the substrate 11, so that a (111) plane is exposed on the surface of any crystal grain forming this polycrystalline structure.

The diborane gas or the phosphine gas is supplied by the reaction gas supply pipe 13b or 13c simultaneously with the silane gas, thereby forming a p-type or n-type uniaxially oriented polycrystalline Si thin film containing B or P.

In the apparatus 122, portions which may be irradiated with the Ne atom current or the Ne ion current before neutralization, such as the inner wall of the reaction vessel 1 and the upper surface of the sample holder 10, for example, are made of materials causing no sputtering by the irradiation. In other words, the same are made of materials having higher threshold energy values than the energy of the Ne ion current. Therefore, no sputtering is caused in these members by irradiation with the Ne atom current or the Ne ion current, whereby the thin film is prevented from contamination with material elements forming these members. Further, these members are prevented from damage caused by sputtering.

Since the energy of the Ne ion current is set to be lower than the threshold energy in the Si thin film to be formed, the reaction vessel 1, the sample holder 10 and the like may be made of materials, such as Ta, W, Pt and the like shown in Table 2, for example, having threshold energy values which are higher than that of the Si thin film in Ne irradiation. Alternatively, the surfaces of these members, such as the inner wall of the reaction vessel 1 and the surface of the sample holder 10, for example, may be coated with materials such as Ta having high threshold energy, to obtain a similar effect.

While the structure and the operation of the apparatus 122 have been described with reference to formation of an Si thin film, it is also possible to form an axially oriented polycrystalline thin film of a material other than Si. For example, it is also possible to form a GaAs thin film. In this case, reaction gases supplied from the reaction gas supply pipes 13a, 13b and 13c are prepared from reaction gases containing $Ga(CH_3)_3$ etc., which are suitable for formation of GaAs. While GaAs is a compound consisting of two elements, an element for forming the ion current or the atom current as applied may be prepared from an element such as Ne or Ar, for example, which is lighter than As having larger atomic weight in these two elements. The irradiation energy is similarly set to be lower than the threshold energy which is related to As having large atomic weight.

When the thin film to be formed is made of a plurality of elements, the element forming the ion current or the atom current as applied may be prepared from that which is lighter than that having the maximum atomic weight among the plurality of elements, in general. The irradiation energy is similarly set to be lower than threshold energy which is related to the element having the maximum atomic weight. In this case, the surface of the member such as the sample holder 10 which is irradiated with the ion current or the atom

current in the apparatus 122 may be made of a material having higher threshold energy than the material for the thin film.

Alternatively, the surface may be made of the same material as the thin film. When the apparatus 122 is structured as that for forming an axially oriented polycrystalline thin film of Si, for example, the surface of the sample holder 10 etc. may be coated with Si. In this case, no contamination of the Si thin film is caused by a different element even if sputtering is caused in the sample holder 10 or the like.

Further, the surface of the member such as the sample holder 10 which is irradiated with the ion current or the atom current may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied. In this case, the element forming the ion current or the atom current hardly penetrates into the member following application of the ion current or the atom current. Thus, deterioration of the member caused by penetration of a different element is suppressed.

In the apparatus 122, conversion to a uniaxially oriented polycrystalline film sequentially progresses simultaneously with growth of the Si thin film by plasma CVD. Thus, it is possible to form an axially oriented polycrystalline Si thin film having a large film thickness under a low temperature. Since the axially oriented polycrystalline thin film can be formed under a low temperature, it is possible to form a uniaxially oriented crystalline thin film on a substrate which is already integrated with a prescribed device, for example, without changing characteristics of this device.

In the above description, the substrate 11 is horizontally placed on the sample holder 10, whereby the atom current is perpendicularly incident upon the substrate 11. When an axially oriented polycrystalline thin film of Si, for example, is formed on the substrate 11, therefore, the surface of the thin film is defined by a (111) plane. However, it is also possible to form an axially oriented polycrystalline thin film of Si in which (111) planes are uniformly oriented in a desired direction which is inclined with respect to the surface of the thin film, by placing the substrate 11 on the sample holder 10 in an inclined manner.

The sample holder 10 may be coupled to a rotary mechanism or the like, to be capable of horizontally rotating the substrate 11. Alternatively, the sample holder 10 may be coupled to a horizontal moving mechanism or the like, to be capable of horizontally moving the substrate 11. Thus, it is possible to uniformly form a uniaxially oriented thin film on the substrate 11.

⟨A-1-4. Valid Data⟩

Description is now made on a test verifying formation of an axially oriented polycrystalline thin film by the aforementioned method. Fig. 15 illustrates experimental data showing an electron beam diffraction image of a sample comprising an axially oriented polycrystalline Si thin film formed on a polycrystalline quartz substrate 11 on the basis of the aforementioned method. In this verification test, the surface of the substrate 11 was perpendicularly irradiated with an Ne atom current.

As shown in Fig. 15, a diffraction spot appears on a single point, and is continuously distributed along a circumference around the same. Namely, the result of the experiment indicates that a single (111) plane of the Si thin film as formed is oriented to be perpendicular to the direction of incidence of the atom current, while orientation around the direction of incidence is arbitrary and not regulated in one direction. Namely, it is verified that this sample is formed as polycrystalline Si in which only a single crystal axis is regulated, i.e., as axially oriented polycrystalline Si.

Since it was possible to form an axially oriented polycrystalline Si thin film on the quartz substrate 11 having a polycrystalline structure which is higher in regularity in atom arrangement than an amorphous structure, it can be decided possible to form an axially oriented polycrystalline thin film on a substrate having an amorphous structure of amorphous Si or the like, as a matter of course. It can also be decided possible to form an axially oriented polycrystalline thin film on a substrate having a single-crystalline structure which is equivalent to a structure obtained by enlarging polycrystal grains, similarly to the above.

⟨A-6. Fifth Preferred embodiment⟩

A fifth preferred embodiment of the present invention is now described.

⟨A-6-1. Overall Structure of Apparatus⟩

Fig. 16 is a front sectional view showing the overall structure of an apparatus 120 according to the fifth preferred embodiment. This apparatus 120 is, similarly to the apparatus 100 shown in Fig. 13, an apparatus for forming single-crystalline thin film which is adapted to grow a thin film of a prescribed material on a substrate and to simultaneously convert the thin film to a single-crystalline thin film, thereby forming a

single-crystalline thin film on the substrate. This apparatus 120 is characteristically different from the apparatus 100 shown in Fig. 13 in structure of the reflector 12. Furthermore, each part of the apparatus 103 is composed of specific materials, as described later.

The reflector 12e is adapted to reflect an atom current which is supplied from an ECR ion source 2, thereby irradiating a substrate 11 with the atom current from a plurality of directions. Therefore, the reflector 12e is set to be located immediately under an outlet 9 above the substrate 11.

⟨A-6-2. Structure and Function of Reflector⟩

Fig. 17 is a perspective view showing a preferable example of the reflector 12e. Fig. 18 is a plan view of the reflector 12e shown in Fig. 17, and Figs. 19 and 20 are exploded views. With reference to these figures, the example of the reflector 12e is now described.

This reflector 12e is an exemplary reflector for forming a single crystal such as single-crystalline Si, having a diamond structure. The reflector 12e defines an equilateral hexagonal opening in a central portion of a flat plate type screen plate 151. Three reflecting blocks 153 are fixedly provided on a lower surface of the screen plate 151, to enclose the opening. These reflecting blocks 153 are fastened to the screen plate 151 by screws passing through holes 157 to be fitted with screw holes 158. Consequently, an equilateral triangular opening 154 which is trimmed with these reflecting blocks 153 is defined immediately under the opening of the screen plate 151.

The atom current which is applied from above is selectively screened by the screen plate 151, to pass only through the equilateral hexagonal opening. In the reflecting blocks 153, slopes 154 facing the opening 154 serve as reflecting surfaces for reflecting the gas beam. As shown in Fig. 18 in a plan view, the three slopes 155 are selectively exposed on the equilateral hexagonal opening of the screen plate 151 respectively. Therefore, the atom current which is applied from above is divided into four components in total including a first component passing through the opening 154 to be directly perpendicularly incident upon the substrate 11 and second to fourth components reflected by the three slopes 155 respectively to be incident upon the substrate 11 from oblique directions.

As shown in Fig. 18, each of three corners of the equilateral triangular opening 154 coincides with every other corner of the equilateral hexagonal opening, as viewed from above. In other words, the three slopes 155 are selectively exposed on three isosceles triangles having adjacent pairs of sides of the equilateral hexagonal opening as isosceles sides. This prevents multiple reflection by the plurality of slopes 155, while enabling uniform irradiation of the substrate 11 with the respective atom current components. This is now described with reference to Figs. 21 and 22.

Fig. 21 is a plan view of the reflector 12e, which is similar to Fig. 18. Fig. 22 is a sectional view taken along the line A - A in Fig. 21. As shown in Figs. 21 and 22, an atom current which is incident upon a position (B in the figures) on one slope 155 corresponding to the apex of the equilateral triangle is reflected and then incident upon an opposite apex (C in the figures) of the equilateral triangular opening 154. Assuming that D represents an intersection between one side of the opening 154 and the line A - A, an atom current which is applied across the points B and D on the slope 155 is uniformly distributed across the points D and C of the opening 154.

This also applies to an atom current which is applied onto an arbitrary line E - E deviating in parallel with the line A - A. Namely, the atom current which is discharged from the outlet 9 is selectively supplied onto the slopes 155 by the screen plate 151, whereby as-reflected atom currents of three components are uniformly incident upon a region of the substrate 11 which is located immediately under the opening 154.

Each atom current which is supplied to one slope 155 through the equilateral hexagonal opening is entirely incident upon the opening 154, and is not incident upon the adjacent slope 155. Thus, no components multiplexly reflected by the plurality of slopes 155 are incident upon the substrate 11.

The angle of inclination of each slope 155 is set at 55°, for example, as shown in Fig. 22. The atom current which is reflected by each slope 155 is incident upon the substrate 11 which is located immediately under the opening 154 at an angle of incidence of 70°. Namely, the first component is perpendicularly incident upon the substrate 11, while the second to fourth components are incident upon the same at angles of incidence of 70° in directions which are three-fold symmetrical about the direction of incidence of the first component. At this time, the directions of incidence of the first to fourth components correspond to four directions which are perpendicular to four (111) planes, being densest planes of the Si single crystal.

⟨A-6-3. Operation of Apparatus⟩

Referring again to Fig. 16, the operation of the apparatus 120 is now described. It is assumed that the reflector 12e is prepared from that shown in Figs. 17 to 20, and the substrate 11 is prepared from polycrystalline SiO_2 (quartz), so that a thin film of single-crystalline Si is formed on the quartz substrate 11. It is also assumed that the slopes 155 in the reflector 12e are set at 55°.

Reaction gas supply pipes 13a, 13b and 13c supply SiH_4 (silane) gas for supplying Si, which is a main material for the single-crystalline Si, and B_2H_3 (diborane) gas and PH_3 (phosphine) gas for doping the substrate 11 with p-type and n-type impurities respectively. Inert gas which is introduced from an inert gas inlet pipe 7 is preferably prepared from Ne gas, which has smaller atomic weight than Si atoms.

Due to the action of an ECR ion generator 2, an Ne^+ ion current and an electron current are formed downwardly from the outlet 9. The distance between the outlet 9 and the reflector 12e is preferably set at a value sufficient for converting most part of the Ne^+ ion current to a neutral Ne atom current.

Thus, a plasma CVD reaction progresses on the upper surface of the substrate 11 similarly to the apparatus 122 shown in Fig. 13, to grow an amorphous Si thin film. On the other hand, the diborane gas or the phosphine gas is supplied with a properly adjusted flow rate, whereby a plasma CVD reaction caused by this gas also progresses to form the Si thin film containing B (boron) or P (phosphorus) in desired density.

At the same time, the amorphous Si thin film which is being formed on the substrate 11 is irradiated with the four components of the Ne atom current, by the action of the reflector 12e. As hereinabove described, directions of incidence of these four components correspond to directions which are perpendicular to four (111) planes of an Si single crystal. Similarly to the apparatus 122, further, the energy of plasma which is formed by the ECR ion source 2 is so set that the energy of Ne atoms reaching the substrate 11 is at a value causing no sputtering in the Si thin film, i.e., lower than the threshold energy (= 27 eV) in sputtering of Si by irradiation with Ne atoms. Therefore, the amorphous Si thin film being grown by plasma CVD is sequentially converted to a single-crystalline Si thin film having a regulated crystal orientation, similarly to the apparatus 100. Consequently, a single-crystalline Si thin film having a regulated crystal orientation is finally formed on the substrate 11. This single-crystalline Si thin film has a (111) plane on its surface.

In the apparatus 120, due to employment of the reflector 12e, no multiple reflection of the atom current is caused by the plurality of slopes 155. Thus, the substrate 11 is irradiated with no atom current from a direction other than the prescribed four directions. Further, the reflector 12e implements uniform irradiation of the substrate 11 with the atom current, whereby the substrate 11 is uniformly irradiated with the atom current from the prescribed four directions. Thus, the single-crystalline Si thin film is uniformly formed on the substrate 11.

In the apparatus 120, portions which may be irradiated with the Ne atom current or an Ne ion current before neutralization, such as the reflector 12e, the inner wall of the reaction vessel 1 and the sample holder 10, for example, are made of materials causing no sputtering by the irradiation, i.e., materials having higher threshold energy values than the energy of the Ne ion current, such as Ta, W, Pt or the like shown in Table 2, for example. Therefore, no sputtering is caused in these members by irradiation with the Ne atom current or the Ne ion current, whereby the thin film is prevented from contamination with material elements forming these members.

Alternatively, surfaces of the members irradiated with the Ne atom current such as the upper surface of the screen plate 151 and the slopes 155 may be coated with materials such as Ta having high threshold energy, to attain a similar effect.

While the structure and the operation of the apparatus 120 have been described with reference to formation of an Si thin film, it is also possible to form an axially oriented polycrystalline thin film of a material other than Si. For example, it is also possible to form a GaAs thin film. It is possible to form a single-crystalline thin film of an arbitrary material having a desired crystal structure and a desired crystal orientation by properly changing the structure of the reflector 12e such as the angles of inclination and the number of the slopes 155. The surface of the reflector 12e etc. is made of a material having higher threshold energy than that of the thin film.

Alternatively, the surface of the reflector 12e etc. may be made of the same material as that for the thin film. When the apparatus 120 is structured as an apparatus for forming a single-crystalline thin film of Si, for example, the surface of the reflector 12e etc. may be coated with Si. In this case, no contamination of the Si thin film is caused by a different element even if sputtering is caused in the reflector 12e or the like.

Further, the surface of the reflector 12e etc. may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied. Thus, the element forming the ion

current or the atom current hardly penetrates into the members following irradiation with the ion current or the atom current. Thus, these members are inhibited from deterioration caused by penetration of the different element.

5 ⟨A-7. Sixth Preferred Embodiment⟩

An apparatus according to a sixth preferred embodiment of the present invention is now described. Figure 13 is a front sectional view showing the overall structure of the apparatus 121 according to this preferred embodiment. This apparatus 121 is, similarly to the apparatus 101 shown in Fig. 4, a single-
10 crystalline thin film forming apparatus, which is adapted to previously form a thin film of a prescribed material having an amorphous or polycrystalline structure on a substrate and to thereafter convert the thin film to a single-crystalline thin film, thereby forming a single-crystalline thin film on the substrate.

This apparatus 121 is characteristically different from the apparatus 101 in structure of the reflector 12e. Furthermore, each part of the apparatus 121 is composed specific materials, as described later. A sample
15 holder 10, which comprises a heater (not shown), can heat a substrate 11 to hold the same at a proper high temperature.

Referring to Fig. 23, the basic operation of the apparatus 121 is now described. It is assumed that a reflector 12e is implemented by that shown in Figs. 17 to 20 and the substrate 11 is prepared from a polycrystalline quartz substrate, so that a single-crystalline Si thin film is formed on the quartz substrate 11.
20 It is also assumed that a polycrystalline Si thin film is previously formed on the quartz substrate 11 by a well-known method such as CVD (chemical vapor deposition).

First, the substrate 11 is mounted between the sample holder 10 and the reflector 12e. The heater provided in the sample holder 10 holds the substrate 11 at a temperature of 550 °C. Since this temperature is lower than the crystallization temperature of silicon, single-crystalline Si once formed will not return to
25 polycrystalline Si under this temperature. At the same time, this temperature is so high that polycrystalline Si can be grown into single-crystalline Si from a nuclear of a seed crystal.

For the same reason as that described in relation to the fourth preferred embodiment, an Ne atom current is selected as an atom current to be applied to the substrate 11, and energy of Ne plasma which is formed by an ECR ion source 2 is so set that energy of Ne atoms reaching the substrate 11 is lower than
30 threshold energy in sputtering of Si. Further, the polycrystalline Si thin film which is formed on the substrate 11 is irradiated with four components of the Ne atom current by the action of the reflector 12e. Directions of incidence of these four components correspond to those perpendicular to four (111) planes of the Si single crystal.

Therefore, the overall region of the polycrystalline Si thin film is converted to a single-crystalline Si
35 layer similarly to the apparatus 101. Thus, a single-crystalline Si layer having a regulated crystal orientation is formed on the quartz substrate 11.

In the apparatus 121, due to employment of the reflector 12e, no multiple reflection of the atom current is caused by the plurality of slopes 155. Thus, the substrate 11 is irradiated with no atom current from a direction other than the prescribed four directions. Further, the reflector 12e implements uniform irradiation
40 of the substrate 11 with the atom current, whereby the substrate 11 is uniformly irradiated with the atom current from the prescribed four directions. Thus, the single-crystalline Si thin film is uniformly formed on the substrate 11.

Similarly to the apparatus 120, portions which may be irradiated with the Ne atom current or an Ne ion current before neutralization, such as the reflector 12e, the inner wall of a reaction vessel 1 and the sample
45 holder 10, for example, are made of materials causing no sputtering by the irradiation such as Ta, W, Pt or the like shown in Table 2, for example, also in the apparatus 121. Therefore, no sputtering is caused in these members by irradiation with the Ne atom current or the Ne ion current, whereby the thin film is prevented from contamination with material elements forming these members.

While the structure and the operation of the apparatus 121 have been described with reference to
50 formation of an Si thin film, it is also possible to form an axially oriented polycrystalline thin film of a material other than Si with the apparatus 121. For example, it is also possible to form a GaAs thin film. Also in this case, the surface of the reflector 12e etc. is made of a material having higher threshold energy than that forming the thin film. Alternatively, the surface of the reflector 12e etc. may be made of the same material as that for the thin film, similarly to the apparatus 120. Further, the surface of the reflector 12e etc.
55 may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied.

⟨A-8. Seventh Preferred Embodiment⟩

An apparatus according to a seventh preferred embodiment of the present invention is now described. Fig. 24 is a front sectional view showing the overall structure of the apparatus 123 according to this preferred embodiment. This apparatus 123 is an axially oriented polycrystalline thin film forming apparatus which is adapted to previously form a thin film of a prescribed material having an amorphous or polycrystalline structure on a substrate and to thereafter convert the thin film to an axially oriented polycrystalline thin film, thereby forming an axially oriented polycrystalline thin film on the substrate.

As shown in Fig. 24, this apparatus 123 has such a structure that the reflector 12e is removed from the apparatus 121 (Fig. 23). Similarly to the apparatus 121, a sample holder 10 comprises a heater (not shown), which can heat a substrate 11 to hold the same at a proper high temperature.

Referring to Fig. 24, the basic operation of the apparatus 123 is now described. It is assumed that the substrate 11 is prepared from a polycrystalline quartz substrate, so that an axially oriented polycrystalline Si thin film is formed on the quartz substrate 11. It is also assumed that a polycrystalline Si thin film is previously formed on the quartz substrate 11 by a well-known method such as CVD (chemical vapor deposition). This polycrystalline Si thin film may have such an ordinary polycrystalline structure that respective crystal grains are oriented in arbitrary directions.

First, the substrate 11 is mounted on the sample holder 10. The heater provided in the sample holder 10 holds the substrate 11 at a temperature of 550 °C. Since this temperature is lower than the crystallization temperature of silicon, axially oriented polycrystalline Si once formed will not return to ordinary polycrystalline Si under this temperature. At the same time, this temperature is so high that ordinary polycrystalline Si can be grown into axially oriented polycrystalline Si from a nuclear of a seed crystal.

An ion current passing through an outlet 9 is converted to an atom current, which in turn is perpendicularly incident upon the surface of the substrate 11. For the same reason as that described in relation to the seventh preferred embodiment, an Ne atom current is selected as the atom current to be applied to the substrate 11, and energy of Ne plasma which is formed by an ECR ion source 2 is so set that energy of Ne atoms reaching the substrate 11 is lower than threshold energy in sputtering of Si.

Thus, the law of Bravais acts in a portion close to the surface of the polycrystalline Si thin film, whereby the Si atoms are rearranged in a portion close to the surface of the polycrystalline Si thin film so that a surface perpendicular to the direction of incidence of the Ne atom current which is applied to the polycrystalline Si thin film defines the densest crystal plane. Namely, a layer close to the surface of the polycrystalline Si tin film is converted to an axially oriented polycrystalline Si layer whose uniaxial direction is regulated so that the (111) plane is along its surface.

The temperature of the polycrystalline Si thin film is adjusted at 550 °, i.e., within a range suitable for growing a seed crystal, as described above. Thus, the axially oriented polycrystalline Si layer which is formed on the surface of the ordinary polycrystalline Si thin film serves as a seed crystal, to grow the axially oriented polycrystalline Si layer toward a deep portion of the ordinary polycrystalline Si thin film. Then, the overall region of the polycrystalline Si thin film is converted to an axially oriented polycrystalline Si layer. Thus, an axially oriented polycrystalline Si layer which is so oriented that the (111) plane is along its surface is formed on the quartz substrate 11.

Alternatively, an amorphous Si thin film may be previously formed on the substrate 11 in place of the ordinary polycrystalline Si thin film to be thereafter treated with the apparatus 123, thereby forming an axially oriented polycrystalline Si thin film.

Also in the apparatus 123, portions which may be irradiated with the Ne atom current or an Ne ion current before neutralization, such as at least surfaces of the inner wall of a reaction vessel 1 and the sample holder 10, for example, are made of materials causing no sputtering by the irradiation, such as Ta, W, Pt or the like shown in Table 2, for example, similarly to the apparatus 122. Therefore, no sputtering is caused in these members by irradiation with the Ne atom current or the Ne ion current, whereby the thin film is prevented from contamination with material elements forming these members.

While the structure and the operation of the apparatus 123 have been described with reference to formation of an Si thin film, it is also possible to form an axially oriented polycrystalline thin film of a material other than Si by the apparatus 123. For example, it is also possible to form a GaAs thin film. Also in this case, the surface of the sample holder 10 etc. is made of a material having higher threshold energy than that of the thin film. Alternatively, the surface of the sample holder 10 etc. may be made of the same material as that for the thin film, similarly to the apparatus 122. Further, the surface of the sample holder 10 etc. may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied.

⟨A-9. Eighth Preferred Embodiment⟩

An eighth preferred embodiment of the present invention is now described. A method according to this preferred embodiment is adapted to form an axially oriented polycrystalline thin film on a substrate 11 and to thereafter convert the same to a single-crystalline thin film by irradiating the film with atom currents from a plurality of directions, thereby forming a single-crystalline thin film on the substrate 11. To this end, the apparatus 122 according to the fourth preferred embodiment may be employed to form an axially oriented polycrystalline thin film on the substrate 11, so that this thin film is converted to a single-crystalline thin film through the apparatus 121 according to the seventh preferred embodiment, for example.

Alternatively, the apparatus 120 according to the eighth preferred embodiment may be employed to form an axially oriented polycrystalline thin film by executing supply of reaction gas and application of an atom current at first while removing the reflector 12e, so that the reflector 12e is thereafter set in the apparatus 120 to execute application of an atom current while heating the substrate 11 for converting the thin film to a single-crystalline thin film, thereby forming a single-crystalline thin film on the substrate 11.

Alternatively, a thin film having an amorphous structure or an ordinary polycrystalline structure may be previously formed on the substrate 11 by CVD or the like so that the thin film is thereafter converted to an axially oriented polycrystalline thin film through the apparatus 123 and thereafter the film is further converted to a single-crystalline thin film through the apparatus 121, thereby forming a single-crystalline thin film on the substrate 11.

Thus, in the method according to this preferred embodiment, an axially oriented polycrystalline thin film is previously formed before a single-crystalline thin film is formed on the substrate 11. Even if a portion which is hard to form a single-crystalline thin film is present on the substrate 11, therefore, mechanical and electrical properties of the thin film are not remarkably deteriorated since the portion is provided with an axially oriented polycrystalline thin film having characteristics which are close to those of a single-crystalline thin film. Namely, it is possible to obtain a thin film having properly excellent characteristics without precisely executing a step of forming a single-crystalline thin film.

This is particularly effective when it is difficult to uniformly irradiate a prescribed region of the substrate 11 with atom currents from a plurality of directions since the substrate 11 is not in the form of a flat plate but is in the form of a cube, or a screen having a thickness is formed on the surface of the substrate 11. Figs. 25 to 27 show such examples.

Fig. 25 is a sectional view typically illustrating such a state that the surface of a sample 170 comprising a substrate 11 having a cubic shape and an axially oriented polycrystalline Si thin film 171 previously formed thereon is irradiated with Ne atom currents from two directions. As shown in Fig. 25, the sample 170 has a cubic shape and hence the sample 170 itself serves as a screen for the atom currents. Consequently, a specific region of the axially oriented polycrystalline Si thin film 171 is irradiated with the Ne atom current from only one direction, and no irradiation from two directions is implemented.

Figs. 26 and 27 are sectional views typically showing steps of selectively forming a single-crystalline Si thin film on a substrate 11 through a masking member 172 in a process of fabricating a thin-film semiconductor integrated circuit. An amorphous or ordinary polycrystalline Si thin film 174 is previously formed on the substrate 11 by CVD or the like. Thereafter the apparatus 123 is employed to perpendicularly irradiate the upper surface of the Si thin film 174 with an Ne atom current through an opening of the masking member 172 which is made of SiO_2 or the like, thereby selectively forming an axially oriented polycrystalline Si thin film 171 immediately under the opening of the masking member 172 (Fig. 26).

Then, the apparatus 121 is employed to irradiate the upper surface of the Si thin film 171 with Ne atom currents from a plurality of directions through the opening of the masking member 172, thereby converting the axially oriented polycrystalline Si thin film 171 to a single-crystalline Si thin film (Fig. 27). At this time, a portion close to an edge of the opening of the masking member 172 is not sufficiently irradiated with the Ne atom currents from the plurality of directions since the masking member 172 has a constant thickness. Thus, the single-crystalline Si thin film is hardly formed in the portion close to the edge of the opening of the masking member 172. However, at least the axially oriented polycrystalline Si thin film is provided in this portion even if no single-crystalline Si thin film is formed, whereby it is possible to minimize deterioration of electrical properties such as carrier mobility.

In the method according to this preferred embodiment, one of the plurality of directions of incidence of the atom currents which are applied to carry out conversion to a single-crystalline thin film is preferably coincident with the direction of incidence of the atom current which is applied in advance for forming the axially oriented polycrystalline thin film. In this case, conversion to a single-crystalline thin film is carried out without changing the common uniaxial direction in the axially oriented polycrystalline thin film, whereby the step of conversion to a single-crystalline thin film smoothly progresses in a short time.

⟨A-10. Ninth Preferred Embodiment⟩

A ninth preferred embodiment of the present invention is now described.

5 ⟨A-10-1. Structure of Apparatus⟩

Fig. 28 is a front sectional view showing the overall structure of an apparatus 124 according to this preferred embodiment. This apparatus 124 is adapted to convert an amorphous, polycrystalline, or axially oriented polycrystalline thin film which is previously formed on a substrate 11 to a single-crystalline thin 10 film, thereby forming a single-crystalline thin film on the substrate 11.

This apparatus 124 is characteristically different from the apparatus 121 in a point that a reflecting unit 160 is set in place of the reflector 12e. The reflecting unit 160, which is adapted to generate a plurality of atom current components to be incident upon the substrate 11 at a plurality of prescribed angles of incidence, is set on a sample holder 10, to be located above the substrate 11. The sample holder 10 15 comprises a heater (not shown), which can heat the substrate 11 to maintain the same at a proper high temperature.

⟨A-10-2. Structure and Operation of Reflecting Unit⟩

20 The structure and the operation of the reflecting unit 160 are now described. Figs. 29 and 30 are a front sectional view and a plan sectional view showing the structure of the reflecting unit 160 respectively. The reflecting unit 160 illustrated in Figs. 29 and 30 is adapted to form a single crystal of a diamond structure such as single-crystalline Si. This reflecting unit 160 is arranged directly under an ion outlet 9 of an ECR ion source 2, i.e., downstream an atom current which is generated by the ECR ion source 2 to be 25 downwardly directed.

A screen plate 164 which can selectively screen the atom current supplied from the ECR ion source 2 is horizontally provided on an upper portion of the reflecting unit 160. The reflecting unit 160 is so set that a distance between the outlet 9 and this screen plate 164 is at a sufficient value, such as at least 14 cm, for example, for converting an ion current outputted from the ECR ion source 2 to a neutral atom current. 30 Namely, a substantially neutral atom current reaches the screen plate 164. Openings 162 are provided in this screen plate 164, to be in four-fold rotation symmetry about a central axis of the atom current from the ECR ion source 2. The atom current from the ECR ion source 2 passes only through the openings 162, to further flow downwardly.

A reflecting block 166 is set immediately under this screen plate 164. This reflecting block 166 is in the 35 form of a four-fold rotary-symmetrical cone whose symmetry axis is coincident with the central axis of the atom current, and four side surfaces of the cone are located immediately under the four openings 162 respectively. These side surfaces are not necessarily plane, but are curved in general. These four side surfaces serve as reflecting surfaces for reflecting the atom current. Namely, the atom current passing through the openings 162 is reflected by the four side surfaces of the reflecting block 166, whereby four 40 atom current components progressing toward directions separated from the central axis are obtained.

These four atom current components are divergent beams whose beam sections are two-dimensionally (planarly) enlarged. These four components pass through a rectifying member (rectifying means) 168 so that directions of progress thereof are accurately regulated in desired directions, to be thereafter incident upon four reflectors 169 respectively. The rectifying member 168, which is adapted to regulate the 45 directions of the atom current components radially from the side surfaces of the reflecting block 166 toward the reflecting plates 169, can be formed by a well-known technique.

These four reflectors 169 are arranged around the substrate 11, which is the target of irradiation, to be four-fold rotation symmetrical about the symmetry axis of the reflecting block 166 (Fig. 30 typically shows only one reflector 169. Fig. 30 also illustrates only an atom current which is incident upon and reflected by 50 an upper half portion of the single reflector 169). The atom current component which is incident upon each reflector 169 is again reflected by its reflecting surface. The reflecting surface of each reflector 169 has a shape of a proper concave surface. Therefore, the divergent atom current components are reflected by the reflecting surfaces and properly focused as the result, to form parallel beams which are uniformly applied to the overall upper surface of the substrate 11. Further, the parallel beams are incident upon the upper 55 surface of the substrate 11 from four directions at angles of incidence of 55°, for example.

(A-10-3. Operation of Apparatus 124)

Referring to Fig. 28, the operation of the apparatus 124 is now described. It is assumed that the substrate 11 is prepared from an amorphous or polycrystalline SiO_2 (quartz) substrate, so that a single-crystalline Si thin film (which includes an axially oriented polycrystalline Si thin film) is formed on the quartz substrate 11. A polycrystalline Si thin film is previously formed on the quartz substrate 11 by CVD (chemical vapor deposition), for example.

First, the substrate 11 is mounted between the sample holder 10 and the reflecting unit 160. The heater provided in the sample holder 10 holds the sample, i.e., the substrate 11 and the polycrystalline Si thin film, at a temperature of 550°C. Similarly to the apparatus 121, a gas which is introduced from an inert gas inlet pipe 7 is preferably prepared from inert Ne gas having smaller atomic weight than Si atoms.

Due to the action of an ECR ion source 2, an Ne atom current is supplied to the reflecting unit 160, to be incident upon the overall upper surface of the substrate 11 from four directions at angles of incidence of 55°, for example. In this case, the directions of incidence of the four Ne atom current components correspond to four directions which are perpendicular to four independent densest crystal planes of an Si single crystal to be formed, i.e., (111) planes. Similarly to the apparatus 121, energy of plasma which is formed by the ECR ion source 2 is so set that energy of the Ne atoms reaching the substrate 11 is lower than threshold energy in sputtering of Si by irradiation with the Ne atoms.

Thus, the law of Bravais acts on the polycrystalline Si thin film, whereby the Si atoms are rearranged in a portion close to the surface of the polycrystalline Si thin film so that surfaces perpendicular to the directions of incidence of the four components of the Ne atom current which is applied to the polycrystalline Si thin film define densest crystal planes. Namely, a layer in the vicinity of the polycrystalline Si thin film is converted to a single-crystalline Si layer having a regulated crystal orientation.

The temperature of the polycrystalline Si thin film is adjusted at 550°, i.e., within a range suitable for growing a seed crystal, as described above. Thus, the single-crystalline Si layer which is formed on the surface of the polycrystalline Si thin film serves as a seed crystal, to grow the single-crystalline Si layer toward a deep portion of the polycrystalline Si thin film. After a lapse of a constant time, the overall region of the polycrystalline Si thin film is converted to a single-crystalline Si layer. Thus, a single-crystalline Si layer having a regulated crystal orientation is formed on the quartz substrate 11. The single-crystalline Si thin film as formed is so oriented that the (100) plane is along its surface.

The angle of incidence of 55° shown in Fig. 29 is a mere example as a matter of course, and it is possible to introduce parallel beams into the substrate 11 at an arbitrary angle of incidence which is decided in response to the crystal structure of the desired single-crystalline thin film by properly changing the shapes and directions of the reflectors 169. Since the divergent beams are generated by the reflecting block 166, it is possible to uniformly irradiate a wide substrate 11 with parallel beams by properly adjusting the distances between the reflectors 169 and the symmetry axis of the reflecting block 166 in response to the width of the substrate 11.

Thus, according to this apparatus 124, it is possible to uniformly irradiate the overall surface of the substrate 11 having an area which is extremely larger than the section of each beam supplied from the ECR ion source 2 with atom current components at desired angles of incidence. Namely, it is possible to uniformly and efficiently form a desired single-crystalline thin film on the substrate 11 having a large area.

Further, it is possible to independently adjust the amounts of the four component beams passing through the openings 162 by independently adjusting the areas of the four openings 162 provided in the screen plate 164. Thus, it is possible to optimumly set the respective amounts of the four component beams which are applied to the upper surface of the substrate 11 from a plurality of directions. For example, it is possible to uniformly regulate the amounts of the four component beams. Thus, a high-quality single-crystalline thin film can be efficiently formed.

Similarly to the apparatus 121, at least surfaces of respective members of the reflecting unit 160 such as the reflecting block 168, the rectifying member 168 and the reflectors 169 which are irradiated with the atom current components may be made of materials such as Ta, W, Pt or the like having higher threshold energy in sputtering than the thin film to be formed. Alternatively, the surfaces of the respective members of the reflecting unit 160 may be made of the same material as that for the thin film, similarly to the apparatus 121. Further, the surfaces of the respective members of the reflecting unit 160 may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied.

⟨A-11. Tenth Preferred Embodiment⟩

An apparatus according to a tenth preferred embodiment of the present invention is now described. Fig. 31 is a front sectional view showing the overall structure of a beam irradiator according to this preferred embodiment. This apparatus 125 is adapted to form a polycrystalline thin film on a substrate 11 and to irradiate the same with an atom current at the same time, thereby sequentially converting the polycrystalline thin film as being grown to a single-crystalline thin film, similarly to the apparatus 120.

To this end, a reaction chamber 8 communicates with reaction gas supply pipes 13 in the apparatus 125, similarly to the apparatus 120. Reaction gases are supplied through the reaction gas supply pipes 13, for forming a film of a prescribed material on the substrate 11 by plasma CVD. The preferred embodiment shown in Fig. 31 is provided with three reaction gas supply pipes 13a, 13b and 13c. Other structural characteristics of this apparatus 125 are similar to those of the apparatus 124.

The apparatus 125 operates as follows: Similarly to the sixth preferred embodiment, it is assumed that the substrate 11 is prepared from polycrystalline SiO_2 (quartz), so that a thin film of single-crystalline Si is formed on the quartz substrate 11. The reaction gas supply pipes 13a, 13b and 13c supply SiH_4 (silane) gas for supplying Si, which is a main material for the single-crystalline Si, and B_2H_3 (diborane) gas and PH_3 (phosphine) gas for doping the substrate 11 with p-type and n-type impurities respectively. Ne gas is introduced from an inert gas inlet pipe 7 into a plasma chamber 4.

Due to the reaction gases supplied from the reaction gas supply pipes 13a, 13b and 13c and an Ne^+ ion current or an Ne atom current generated by an ECR ion source 2, plasma CVD reaction progresses on the upper surface of the substrate 11, thereby growing an Si thin film of an amorphous structure.

The Ne atom current downwardly flowing from the ECR ion source 2 is incident upon the overall surface of the Si thin film being formed on the upper surface of the substrate 11 from four directions having angles of incidence of 55°, for example, due to action of a reflecting unit 160. Similarly to the apparatus 120, energy of plasma which is formed by the ECR ion source 2 is so set that incident energy of the four components is lower than threshold energy with respect to Si. Thus, the law of Bravais acts on the amorphous Si thin film as being grown, whereby the amorphous Si thin film being grown by plasma CVD is sequentially converted to a single-crystalline Si thin film having a regulated crystal orientation. As the result, single-crystalline Si having a single crystal orientation is formed on the substrate 11.

Also in this apparatus 125, the reflecting unit 160 is so employed that it is possible to uniformly irradiate the overall surface of the substrate 11 having an area which is extremely larger than the section of each beam supplied from the ECR ion source 2 with atom current components at desired angles of incidence without scanning the substrate 11, due to employment of the reflecting unit 160. Namely, it is possible to uniformly and efficiently form a desired single-crystalline thin film on the substrate 11 having a large area.

⟨A-12. Eleventh Preferred Embodiment⟩

An apparatus 126 according to an eleventh preferred embodiment of the present invention is now described. Figs. 32 to 34 are a perspective view, a plan view and a front elevational view showing the apparatus 126 according to this preferred embodiment respectively. With reference to Figs. 32 to 34, the structure and the operation of the apparatus 126 according to this preferred embodiment are now described.

In this apparatus 126, an ECR ion source 2 is set in a horizontal state, to supply a gas beam in a horizontal direction which is parallel to the surface of a horizontally set substrate 11. A reflecting unit 180 is interposed in a path of the gas beam which is supplied from the ECR ion source 2 to reach the upper surface of the substrate 11.

In the reflecting unit 180, a reflecting block 186, a screen plate 184, a rectifying member 188 and a reflector 190 are successively arranged along the path of the gas beam. The reflecting block 186 is rotated/driven about its central axis which is in the form of a perpendicular prism. A distance between an outlet 9 and the reflecting block 186 is set at a sufficient length of at least 14 cm, for example, for converting an ion current which is outputted from the ECR ion source 2 to a neutral atom current. Thus, a substantially neutral atom current reaches the reflecting block 186.

Fig. 35 is a plan view for illustrating the operation of the reflecting block 186. As shown in Fig. 35, an atom current which is incident upon the reflecting block 186 is scattered to a number of directions in a horizontal plane by rotation of the reflecting block 186. Namely, the reflecting block 186 substantially generates divergent beams whose beam sections are enlarged linearly or in the form of strips, i.e., substantially one-dimensionally, with progress of the beams.

The screen plate 184 selectively passes only components of the divergent atom current having scattering angles in a specific range. The atom current components passed through the screen plate 184 are passed through the rectifying member 188, to be precisely regulated in directions of progress. The rectifying member 188 is structured similarly to the rectifying member 168. In place of the shape of a prism shown in Fig. 35, the reflecting block 186 may be in the form of a triangle pole, a hexagonal pole or the like, for example.

Referring again to Figs. 32 to 34, the atom current components passed through the rectifying member 188 are incident upon the reflector 190 which is in the form of a strip along the horizontal direction. A reflecting surface of the reflector 190 has a proper concave shape. Thus, the divergent atom current components are reflected by this reflecting surface and properly focused to form parallel beams, which are applied to the upper surface of the substrate 11 linearly or in the form of strips. Further, the parallel beams are incident upon the upper surface of the substrate 11 at angles of incidence of 35°, for example. As shown in Fig. 33, two sets of the members from the reflecting block 186 to the reflector 190 arranged along the path of the atom current are set. Thus, atom currents are incident upon the substrate 11 from opposite two directions at angles of incidence of 35° respectively.

Each atom current is scattered by each reflecting block 186 to be substantially one-dimensionally diverged, whereby it is possible to apply parallel beams to a linear or strip-shaped region having a width which is extremely larger than the diameter of the beam supplied from the ECR ion source 2 by sufficiently setting the distance between the reflecting block 186 and the reflector 190.

The apparatus 126 has a sample holder (not shown) for receiving the substrate 11, and this sample holder is horizontally movable by a horizontal moving mechanism (not shown). Following such horizontal movement of the sample holder, the substrate 11 is moved in parallel along a direction perpendicular to (intersecting with) the linear or strip-shaped region receiving the atom currents. Thus, it is possible to implement irradiation of the overall region of the substrate 11 by scanning the substrate 11. Due to such scanning of the substrate 11, it is possible to uniformly irradiate the wide substrate 11 with atom current components.

This apparatus 126 may comprise reaction gas supply pipes 13a, 13b and 13c similarly to the apparatus 120, to form a thin film of a prescribed material on the substrate 11 and to sequentially convert the thin film to a single crystal. Alternatively, the sample holder may be provided with a heater similarly to the apparatus 121, to convert a thin film of a prescribed material which is previously deposited on the substrate 11 to a single-crystalline thin film. Since the two atom currents are incident from opposite directions at the same angles of incidence of 35°, the single-crystalline thin film formed on the substrate 11 is so oriented that its (110) plane is along its surface.

It is possible to form a single-crystalline thin film which is so oriented that a crystal plane other than the (110) plane is along its surface, by changing the positional relation between the reflecting units 180, the angles of the reflectors 190 and the like. For example, it is possible to form a single-crystalline thin film which is so oriented that its (100) plane is along its surface by arranging at least two sets of reflecting units 180 so that central axes of atom currents from the reflecting blocks 186 toward the reflectors 190 are at angles of 90° or 180° and setting shapes and directions of the reflectors 190 so that angles of incidence of the atom currents incident upon the substrate 11 from the reflecting units 180 are 55°.

Further, it is possible to form a single-crystalline thin film which is so oriented that its (111) plane is along its surface by arranging at least two sets of three sets of of reflecting units 180 so that central axes of atom currents from the reflecting blocks 186 toward the reflectors 190 are each shifted by 120° and setting shapes and directions of the reflectors 190 so that angles of incidence of the atom currents incident upon the substrate 11 from the reflecting units 180 are at 70°.

Similarly to the apparatus 124, at least surfaces of respective members of the reflecting units 160 such as the reflecting blocks 168, the rectifying members 168 and the reflectors 169 which are irradiated with the atom current components may be made of materials such as Ta, W, Pt or the like having higher threshold energy in sputtering than the thin film to be formed. Alternatively, the surfaces of the respective members of the reflecting units 160 may be made of the same material as that for the thin film. Further, the surface of the respective members of the reflecting units 160 may be made of a material containing an element which is heavier than that forming the ion current or the atom current as applied.

⟨A-13. Twelfth Preferred Embodiment⟩

An apparatus 127 according to a twelfth preferred embodiment of the present invention is now described. Fig. 36 is a perspective view showing the structure of the apparatus 127 according to this preferred embodiment. As shown in Fig. 36, this apparatus 127 comprises a reflecting unit 191. This

reflecting unit 191 is characteristically different from the reflecting unit 180 in a point that the same has an electrostatic electrode 306 in place of the reflecting blocks 186. An ion current is incident upon the electrostatic electrode 196, in place of a neutral atom current. Namely, a distance between an outlet 9 and this electrostatic electrode 196 is set to be sufficiently short so that the ion current outputted from an ECR ion source 2 is hardly converted to a neutral atom current but incident upon the electrostatic electrode 196 as such.

The electrostatic electrode 196 is provided with an ac power source 197. This ac power source 197 supplies a fluctuation voltage which is formed by an alternating voltage superposed on a constant bias voltage to the electrostatic electrode 196. Consequently, the ion current which is incident upon the electrostatic electrode 196 is scattered into a number of directions within a horizontal plane by action of a fluctuating electrostatic field.

Thus, scattering of the ion current is implemented by the fluctuation voltage which is supplied by the ac power source 197 in this apparatus 127, whereby it is possible to easily suppress scattering of the ion current in unnecessary directions cut by screen plates 184. Namely, it is possible to efficiently apply the ion current which is supplied by the ECR ion source 2 to a substrate 11. Further, it is also possible to scatter the ion current to respective scattering directions with higher uniformity by setting the waveform of the fluctuation voltage supplied by the ac power source 197 in the form of a chopping wave, for example.

⟨A-14. Modifications of Fifth to Twelfth Preferred Embodiments⟩

(1) While the shapes of the reflecting blocks 166 and the arrangement of the reflectors 169 are selected to four-fold rotation symmetry in the sixth and tenth preferred embodiments, the same can alternatively be selected in two-fold or three-fold rotation symmetry, for example. Namely, it is possible to arbitrarily select the number of components of the atom current which are incident at different angles of incidence in response to the crystal structure of the desired single-crystalline thin film. The shape of the reflecting block 166 may be selected in a rotation symmetrical manner such as in the form of a cone. At this time, only a single reflecting block 166 is available regardless of the number of the directions of incidence upon the substrate 11. Thus, it is also possible to form a single-crystalline thin film having a crystal structure other than a diamond structure according to the inventive apparatus, while it is also possible to form a single-crystalline thin film having various crystal orientations in a single crystal structure. Further, the material for forming the single-crystalline thin film is not restricted to Si since it is possible to cope with an arbitrary crystal structure, whereby it is possible to form a semiconductor single-crystalline thin film of GaAs or GaN, for example.

(2) In each of the ninth and tenth preferred embodiments, each rectifying member 168 for rectifying the directions of the atom current components may be interposed in a path of the atom current which is reflected by the reflector 169 and directed toward the substrate 11, in place of the path of the atom current directed from the reflecting block 166 toward the reflector 169. Further, the rectifying members 168 may be interposed in both of these paths.

On the other hand, the apparatus may not be provided with the rectifying members 168. When the apparatus is provided with the rectifying members 168, however, it is possible to precisely set the directions of incidence of the atom current components upon the substrate 11 without strictly setting the shapes, arrangement etc. of the reflecting blocks 166 and the reflectors 169.

The above also applies to the rectifying members 188 in the eleventh and twelfth preferred embodiments.

(3) In each of the fourth to eleventh preferred embodiments, the ECR ion source 2 may be replaced by another beam source for generating a neutral atom current or a neutral molecular flow, or a neutral radical flow. A beam source for generating such a neutral atom or radical current has already been commercially available. Since a neutral atom or radical beam can be obtained by such a beam source, it is possible to form a single-crystalline thin film on an insulating substrate 11 with no requirement for means for neutralizing an ion current, similarly to the case of employing the ECR ion source 2.

(4) In each of the fourth to twelfth preferred embodiments, the ECR ion source 2 may be replaced by another ion source such as a Cage type or Kaufmann type source. In this case, however, the flow of the as-generated ion current may be diffused by repulsive force by static electricity between ions to be weakened in directivity, and hence means for neutralizing the ions or means such as a collimator for improving directivity of the ion current is preferably interposed in the path of the ion current.

Particularly when the substrate 11 is made of an electrically insulating material, means for neutralizing ions is preferably interposed in the path of the ion current, in order to prevent the substrate 11 from accumulation of electric charges inhibiting progress of irradiation. In the apparatus according to each

preferred embodiment comprising the ECR ion source 2, on the other hand, a neutral atom current can be easily obtained in a shape close to a parallel current with no means for neutralizing the ion current.

When means for neutralizing ions is set in the apparatus according to the twelfth preferred embodiment, the same is set downstream the electrostatic electrode 196.

5 (5) The beam irradiator described in each of the aforementioned preferred embodiments is not restricted to an apparatus for forming a single-crystalline thin film, but is also applicable to an apparatus for applying gas beams from a plurality of directions for another purpose. Particularly the apparatus shown in each of the ninth to twelfth preferred embodiments is suitable for a purpose of uniformly irradiating a wide substrate with gas beams from a plurality of directions.

10 (6) When the thin film to be formed contains N (nitrogen element) which is a gas under a normal temperature such as GaN in each of the fourth to twelfth preferred embodiments, the gas may be prepared from gaseous nitrogen. In this case, the characteristics of the thin film will not be deteriorated even if the gas remains in the thin film.

15 ⟨B. Preferred embodiments in Relation to Selective Formation and Further Efficient Formation of Single-Crystalline Thin Film⟩

On the basis of the aforementioned method, description is now made on preferred embodiments in relation to methods enabling selective formation of single-crystalline thin films on specific regions of
20 substrates and further efficient formation of single-crystalline thin films on substrates.

⟨B-1. Thirteenth Preferred embodiment⟩

Figs. 37 to 42 are process diagrams in relation to a method according to a thirteenth preferred
25 embodiment. First, an upper surface of an Si single-crystalline substrate 102 is oxidized to form an SiO_2 film 104 which is an insulator, as shown in Fig. 37. Further, an amorphous or polycrystalline Si thin film 106 is formed on the SiO_2 film 104 by CVD, for example.

Then, a thin film 108 of SiO_2 or Si_3N_4 is formed on the Si thin film 106 and thereafter this thin film 108 is selectively etched to form an opening in a desired specific region, as shown in Fig. 38. This thin film 108
30 having an opening serves as a masking material in a subsequent step. The selective etching is carried out by well-known photolithography sequentially through processes of resist application, pre-baking, exposure, development and post-baking. At this time, the exposure is carried out through a masking material having a prescribed pattern enabling selective etching, and separation of a resist material is carried out after the exposure. A portion of the Si thin film 106 which is exposed in the opening is subjected to washing by a
35 method such as the so-called reverse sputtering or the like.

Thereafter the apparatus 101 is employed to irradiate the overall upper surface of the Si single-crystalline substrate 102 with an Ne atom current 110 from directions which are perpendicular to a plurality of densest planes of a single-crystalline thin film to be formed with proper irradiation energy, as shown in Fig. 39. Ne atoms are lighter than Si which is an element forming the Si thin film 106 as irradiated and Si
40 which has the maximum atomic weight among elements forming the masking material 108 as irradiated, whereby the same hardly remain in the masking material 108 and the Si thin film 106 following the irradiation.

The Si thin film 106 is selectively irradiated with the Ne atom current only in the opening of the masking material 108. Therefore, the Si thin film 106 is selectively converted to a single-crystalline layer 112 having
45 a regulated crystal orientation in a region corresponding to the opening of the masking material 108, i.e., the aforementioned specific region, as shown in Fig. 40.

Then, the masking material 108 is remove and the upper surface is thermally oxidized to form an oxide film 114, as shown in Fig. 41. In general, a reaction rate of thermal oxidation in an amorphous or polycrystalline layer is larger by 2 to 5 times than that in a single-crystalline layer. Therefore, a portion of
50 the oxide film 114 located on the Si thin film 106 is larger in thickness by about 2 to 5 times than that located on the single-crystalline layer 112.

Thereafter the overall upper surface of the oxide film 114 is properly etched to expose the upper surface of the single-crystalline layer 112, as shown in Fig. 42. At this time, the oxide film 116 remains on the Si thin film 106. The single-crystalline layer 112 can be provided with a desired element such as a
55 transistor element, for example. At this time, the oxide film 116 serves as the so-called LOCOS (local oxidation of silicon) layer which isolates the element formed on the single-crystalline layer 112 from other elements. The Si single-crystalline substrate 102 itself is already provided therein with desired elements. Therefore, it is possible to implement a device having a three-dimensional structure by integrating a new

element into the single-crystalline layer 112. In the method according to this preferred embodiment, the LOCOS layer is formed on an amorphous or polycrystalline layer, whereby the same can be efficiently formed in a short time, to improve the throughput in an thermal oxidation device.

In the method according to this preferred embodiment, further, a single-crystalline thin film can be formed on the SiO_2 film 104 which is an insulator, whereby the element provided in the Si single-crystalline substrate 102 can be easily isolated from a new element provided thereon.

⟨B-2. Fourteenth Preferred embodiment⟩

Figs. 43 to 51 are process diagrams in relation to a fourteenth preferred embodiment. As shown in Fig. 43, a transistor is previously formed on a single-crystalline Si substrate. Namely, n-type source and drain layers 204 and 206 which are isolated from each other are selectively formed on an upper surface of a p-type single-crystalline Si substrate 202. Further, a gate electrode 210 is formed on the upper surface of the substrate 202 in a region corresponding to that between these layers 204 and 206, through a gate oxide film 208. Namely, this transistor is an n-channel MOS transistor. The gate oxide film 208 is made of SiO_2, and the gate electrode 210 is made of polycrystalline Si.

Then, an insulating film 212 of SiO_2 is formed entirely over the upper surfaces of the substrate 202 and the gate electrode 210, as shown in Fig. 44. Thereafter an amorphous or polycrystalline Si film 214 is formed on the overall surface of the insulating film 212, as shown in Fig. 45.

Then, the Si film 214 is selectively etched to be left only in a desired specific region. Fig. 46 shows an Si film 216 which is defined in the specific region by the selective etching.

Then, the apparatus 101 is employed to irradiate overall upper surfaces of the insulating film 212 and the Si film 216 with an Ne atom current 218 from directions which are perpendicular to a plurality of densest planes of a single-crystalline thin film to be formed with proper irradiation energy, as shown in Fig. 47. Ne atoms are lighter than Si forming the Si film 216 and the insulating film 212, whereby the same hardly remain in these layers following the irradiation. Due to this irradiation, the Si film 216 is converted to a single-crystalline Si thin film 220 having a regulated crystal orientation, as shown in Fig. 48. At this time, a region of the insulating film 212 which is exposed on the upper surface is also converted to a single-crystalline thin film.

Then, the single-crystalline Si thin film 220 is doped with an n-type impurity, to be converted to an n-type Si thin film, as shown in Fig. 48. Thereafter a gate oxide film 228 and a gate electrode 230 are selectively formed oil the upper surface of the n-type single-crystalline thin film 220. Further, these are employed as masks to selectively dope the upper surface of the single-crystalline Si thin film 220 with a p-type impurity, thereby forming a drain layer 224 and a source layer 226. Namely, these layers are formed by self alignment. Due to this step, the single-crystalline Si thin film 220 forms a p-channel MOS transistor.

Then, an insulating film 232 of SiO_2 or the like is formed over the entire upper surface. Then, desired portions of the insulating films 232 and 212 are selectively etched to form an opening serving as a contact hole. Further, a conductive wiring layer 234 of aluminum, for example, is applied onto the overall upper surface of the insulating film 232 including the contact hole, and thereafter the wiring layer 234 is selectively removed to couple the elements in a desired manner (Fig. 50).

As hereinabove described, it is possible to selectively form a single-crystalline layer on a desired specific region of the substrate 202 in the method according to this preferred embodiment. Further, it is possible to implement a device having a three-dimensional structure by forming a new element on the single-crystalline layer, since the substrate 202 itself is already provided with an element. In the method according to this preferred embodiment, a single-crystalline thin film can be formed on the insulating film 212 of SiO_2, whereby the element provided in the substrate 202 can be easily isolated from a new element provided thereon in the three-dimensional device.

Further, it is also possible to form a plurality of new elements on the substrate 202, as shown in Fig. 51. At this time, two new elements (two p-channel MOS transistors in Fig. 51) are provided in single-crystalline Si thin films 220 which are formed independently of each other. Thus, these elements can be easily isolated with no provision of a LOCOS layer or an isolation layer. Consequently, steps of manufacturing the device are simplified and the degree of integration of the elements is improved.

Although an n-type impurity is introduced into the selectively formed single-crystalline Si thin films 220 in the aforementioned preferred embodiment, the same may alternatively be introduced in the stage of the Si film 216, or into the overall surface of the Si film 214. In any method, it is possible to finally form the device of the three-dimensional structure shown in Fig. 50 or 51.

⟨B-3. Fifteenth Preferred embodiment⟩

As hereinabove described, the Si film 214 (Fig. 45) is selectively removed to form the Si film 216 (Fig. 46) and thereafter an Ne atom current is applied (Fig. 47) to convert the same to the single-crystalline Si thin film 220 (Fig. 48). Alternatively, the overall upper surface of the Si film 214 shown in Fig. 45 may be irradiated with the Ne atom current to be converted to a single-crystalline thin film, so that the Si film 214 is thereafter selectively removed to form the single-crystalline Si thin film 220 shown in Fig. 48. Subsequent steps are similar to those of the fourteenth preferred embodiment.

⟨B-4. Sixteenth Preferred embodiment⟩

As hereinabove described, the amorphous or polycrystalline Si film 214 is previously formed (Fig. 45) and thereafter irradiated with the Ne atom current, to be converted to a single-crystalline thin film in the fifteenth preferred embodiment. Alternatively, the apparatus 100 may be employed after the step shown in Fig. 43 is completed to grow an amorphous Si thin film on the insulating film 212 while simultaneously carrying out application of an Ne atom current, thereby forming a single-crystalline Si thin film on the insulating film 212. Thereafter the single-crystalline Si thin film is selectively removed, to form the single-crystalline Si thin film 220 shown in Fig. 48. Subsequent steps are similar to those of the fourteenth and fifteenth preferred embodiments.

⟨B-5. Seventeenth Preferred embodiment⟩

Figs. 52 to 60 are process diagrams in relation to a method according to a seventeenth preferred embodiment. As shown in Fig. 52, an amorphous or polycrystalline Si thin film is first formed on a substrate 502 which is made of SiO_2, by CVD or the like. Thereafter the apparatus 100 is employed to irradiate the Si thin film with an Ne atom current, thereby converting the Si thin film to a single-crystalline Si thin film 504 which is regulated in crystal orientation so that a (100) plane is exposed on the upper surface. Alternatively, the apparatus 101 may be employed in place of the apparatus 100, to grow an amorphous Si thin film on the substrate 502 while irradiating the same with an Ne atom current for forming the single-crystalline Si thin film 504.

Then, the upper surface of the single-crystalline Si thin film 504 is selectively thermally oxidized, to form LOCOS layers 506, as shown in Fig. 53. Thereafter p-type or n-type impurities are introduced into the respective ones of single-crystalline Si thin film regions 508, 510 and 512 which are isolated from each other by the LOCOS layers 506, thereby converting these single-crystalline Si thin film regions 508, 510 and 512 to p-type or n-type semiconductor regions, as shown in Fig. 54.

Then, gate oxide films 514 and 515 of SiO_2 and gate electrodes 516 and 517 of polycrystalline Si are formed on the upper surfaces of the single-crystalline Si thin film regions 512 and 510 respectively, as shown in Fig. 55. Thereafter these gate oxide films 514 and 515 and gate electrodes 516 and 517 are used as masks to selectively introduce n-type and p-type impurities into the single-crystalline Si thin film regions 512 and 510 from the upper surfaces, as shown in Fig. 56. Consequently, source and drain layers are formed in the single-crystalline Si thin film regions 512 and 510 respectively.

Then, an insulating film 526 of SiO_2 is formed on an upper surface portion excluding the upper surface of the
single-crystalline Si thin film region 508, as shown in Fig. 57. Thereafter the apparatus 101 is employed to apply an Ne atom current from the upper surface, as shown in Fig. 58. At this time, only the single-crystalline Si thin film region 508 which is not covered with the insulating film 526 of SiO_2 is selectively irradiated. Directions of irradiation are set in a plurality of directions which are perpendicular to a plurality of densest planes (111) of single-crystalline Si which is so oriented that one (111) plane is exposed on the upper surface. Thus, the single-crystalline Si thin film region 508 is converted to a single-crystalline Si layer 530 which is so regulated in crystal orientation that the (111) plane is exposed on the upper surface. Namely, the crystal orientation of the single-crystalline Si thin film region 508 is converted. The region 528 which is masked with the insulating film 526 of SiO_2 and not subjected to irradiation is a region to be provided with a CMOS element. On the other hand, the single-crystalline Si layer 530 which is converted in crystal orientation is provided with a pressure sensor, for example. Then, an insulating film 532 of SiO_2 is formed on the overall upper surface, as shown in Fig. 59. This insulating film 532 includes the insulating film 526. Thereafter a desired portion of the insulating film 532 is selectively etched to form an opening for serving as a contact hole. Further, a conductive wiring layer 534 of aluminum, for example, is applied to the overall upper surface of the insulating film 532 including the contact hole, and this wiring layer 534 is

thereafter selectively removed to couple the elements in a desired manner (Fig. 60).

Due to the aforementioned steps, a CMOS 528 and a pressure sensor 536 are formed in the single-crystalline Si thin film 504 by single-crystalline Si materials having different crystal orientations in a parallel manner. The single-crystalline Si forming the CMOS 528 is preferably oriented so that a (100) plane is along the major surface of the substrate, while the single-crystalline Si forming the pressure sensor is preferably oriented so that the (111) plane is along the major surface of the substrate. In the method according to this preferred embodiment, it is possible to form a composite device in which a plurality of elements having different preferable crystal orientations are provided in the same single-crystalline Si thin film. In the method according to this preferred embodiment, further, it is possible to form an element which is made from single-crystalline Si on the substrate 502 of SiO_2, which is not a single crystal. Namely, this method has such an advantage that the material for the substrate is not limited.

〈B-6. Eighteenth Preferred embodiment〉

As hereinabove described, an amorphous or polycrystalline Si thin film is formed on the substrate 502 by CVD or the like and thereafter the overall upper surface of this Si thin film is irradiated with an Ne atom current so that the overall region thereof is converted to the single-crystalline Si thin film 504 which is so oriented that the (100) plane is exposed on the upper surface (Fig. 52). Alternatively, a masking material 540 having a prescribed masking pattern may be formed on an upper surface to be thereafter irradiated with an Ne atom current, so that only a region of an Si thin film to be provided with a CMOS is selectively irradiated with the Ne atom current, as shown in Fig. 61. Thus, only the region to be provided with a CMOS is converted to a single-crystalline Si thin film 542 having an upper surface of a (100) plane, while another region 544 remains in the original state of the amorphous or polycrystalline Si thin film. Subsequent steps are similar to those of the seventeenth preferred embodiment.

The method according to the eighteenth preferred embodiment has an effect similar to that of the seventeenth preferred embodiment. Namely, it is possible to form a composite device in which a plurality of elements having different preferable crystal orientations are provided in the same single-crystalline Si thin film. Further, this preferred embodiment has such an advantage that the material for the substrate is not limited, similarly to the seventeenth preferred embodiment.

〈B-7. Nineteenth Preferred embodiment〉

Fig. 62 is a front elevational view showing the structure of a sample holder in an apparatus for forming a single-crystalline thin film according to a nineteenth preferred embodiment of the present invention. This sample holder is assembled into the apparatus 100 in place of the sample holder 10. In this sample holder, a reflector 12 is fixed to a fixed table 702 through supports 712. Further, a movable table 706 is horizontally slidably supported by the fixed table 702. A seating portion of this movable table 706 is fitted with a screw 708 which is rotated/driven by a motor 710, to be horizontally moved following rotation of the screw 708. This seating portion is provided with a horizontal driving mechanism (not shown) having a motor and a screw similarly to the fixed table 702, to horizontally drive an upper member of the movable table 706. A direction for sliding the seating portion is perpendicular to that for sliding the upper member. A substrate 11 to be irradiated is placed on the upper member. This substrate 11 is located under the reflector 12.

Fig. 63 is a plan view typically showing an operation of this sample holder. The substrate 11 is relatively scanned with respect to the reflector 12 along two orthogonal directions by action of the two horizontal driving mechanisms. Therefore, it is possible to homogeneously irradiate the overall surface of the substrate 11, which has a wider area as compared with an opening of the reflector 12 serving as an opening for passing beams, with the beams.

When this sample stand is employed, it is possible to efficiently apply the beams by employing an apparatus 101a for forming a single-crystalline thin film which comprises a magnetic lens 720, as shown in Fig. 64. The magnetic lens 720 is adapted to focus an ion current which is downwardly sprayed from an ion source 2 into the form of a strip. Fig. 65 is a model diagram showing such a state that an ion current is focused by the magnetic lens 720. Due to the action of the magnetic lens 720, the ion current has a strip-type sectional shape in the vicinity of the reflector 12f. Therefore, the reflector 12f also has a shape along this strip. Similarly to those in the apparatuses 100 and 101, the ion current is substantially converted to a neutral atom current in the vicinity of the reflector 12f. The substrate 11 is irradiated with components 726 of the atom current reflected from the reflector 12f and directly incident components 724. The angle of inclination of the reflector 12f is so adjusted that directions of incidence of these two components are orthogonal to a plurality of densest planes of a single-crystalline thin film to be formed respectively.

It is possible to efficiently irradiate a wide region on the substrate 11 in single scanning, by scanning the substrate 11 in a direction 728 which is perpendicular to the "strip of the atom current". Therefore, it is possible to attain irradiation of the substrate 11 having a wide area in a small number of scanning times. In other words, it is possible to form a single-crystalline thin film with higher efficiency by employing the apparatus 101a. This is particularly effective when the width of the substrate 11 is shorter than a major axis width of the "strip of the atom current". At this time, the substrate 11 may simply be scanned along one direction 728, whereby a single-crystalline thin film can be further efficiently formed. Further, the driving mechanism provided in the sample holder is sufficiently implemented only by a single driving mechanism which is integrated in the fixed table 702, whereby the sample holder is simplified in structure.

⟨B-8. Twentieth Preferred embodiment⟩

Fig. 66 is a front elevational view typically showing the structure of a reflector support which is provided in an apparatus for forming a single-crystalline thin film according to a twentieth preferred embodiment of the present invention. This reflector support rotatably supports an end of a reflector 802 by a hinge 804, while rotatably supporting another end by another hinge 806 which is provided on the forward end of a connecting bar 808. The connecting bar 808 is axially driven by a piston 810. Following the axial movement of the connecting bar 808, the reflector 802 is rotated about the hinge 804. Consequently, an angle θ of inclination of a reflecting surface is changed in the reflector 802. Namely, the angle of inclination is variable in the reflecting surface of the reflector 802 provided in this apparatus. Thus, it is possible to form single-crystalline thin films having various crystal orientations and crystal structures by employing a single apparatus. Namely, formation of various types of single-crystalline thin films can be economically attained.

Further, it is possible to efficiently form various types of single-crystalline thin films on a single substrate 11. This is because various types of single-crystalline thin films can be formed while inserting the substrate 11 in the apparatus. It is possible to instantaneously set a prescribed angle of inclination by controlling the operation of the piston 810 by a computer.

⟨B-9. Twenty-first Preferred embodiment⟩

Fig. 67 is a plan view typically showing the structure of a reflector support 902 which is provided in an apparatus for forming a single-crystalline thin film according to a twenty-first preferred embodiment of the present invention. This reflector support 902 comprises a plurality of arms 904 which are rotated/driven about vertical axes. Each one of a plurality of reflectors 906a to 906f, which are different from each other, is mounted on a forward end portion of each arm 904. The plurality of reflectors 906a to 906f are so formed that numbers or angles of incidence of atom current components which are incident upon a substrate 11 are different from each other. Namely, the reflectors 906a to 906f are different from each other in numbers of reflecting surfaces and angles of inclination. Since the arms 904 are rotated/driven, it is possible to arbitrarily select a desired reflector to be set in an irradiated region 908 which is irradiated with the atom current from the plurality of types of reflectors 906a to 906f.

Therefore, it is possible to form single-crystalline thin films having various crystal orientations and crystal structures only by a single apparatus, similarly to the apparatus according to the twentieth preferred embodiment. Namely, it is possible to economically form various types of single-crystalline thin films. Further, it is possible to efficiently form various types of single-crystalline thin films on a single substrate 11.

⟨B-10. Twenty-second Preferred embodiment⟩

The reflector(s) and the reflector support provided in each of the nineteenth to twenty-first preferred embodiments can also be employed in the apparatus 101, in place of the apparatus 100. Namely, the reflector(s) and the reflector support can be applied to both of an apparatus for forming an amorphous or polycrystalline thin film and thereafter converting the same to a single-crystalline film and an apparatus for simultaneously carrying out these operations.

⟨B-11. Twenty-third Preferred embodiment⟩

Fig. 68 is a plan view typically showing the structure of an apparatus for forming a single-crystalline thin film according to a twenty-third preferred embodiment of the present invention. In this apparatus, an etching unit portion 1104 for etching a substrate 11, a film forming unit portion 1106 for forming an amorphous or

polycrystalline thin film on the substrate 11, and an irradiation unit portion 1108 for irradiating the substrate 11 with an atom current are arranged around a carrier chamber 1102. Further, treatment chambers for storing the substrate 11 in the respective unit portions 1104, 1106 and 1108 communicate with each other through the carrier chamber 1102. The carrier chamber 1102 is provided with an inlet 1110 and an outlet 1112 for receiving and discharging the substrate 11 respectively. Both of the inlet 1110 and the outlet 1112 are provided with airtight switchable doors (not shown). The carrier chamber 1112 is provided with a carrier robot 1114, which receives and discharges the substrate 11 while automatically inserting and extracting the same into and from the respective treatment chambers.

In the apparatus according to this preferred embodiment, the respective treatment chambers communicate with each other, whereby it is possible to immediately start formation of a thin film after carrying out etching for removing an oxide film before forming a thin film on the substrate 11 while preventing new progress of oxidation. Thus, it is possible to reliably form a thin film having excellent and homogeneous characteristics while efficiently carrying out respective treatments. Further, it is possible to efficiently carry the substrate 11 into the respective treatment chambers due to provision of the carrier robot 1114.

⟨B-12. Twenty-fourth Preferred embodiment⟩

Fig. 69 is a front sectional view typically showing the structure of an apparatus for forming a single-crystalline thin film according to a twenty-fourth preferred embodiment of the present invention. This apparatus comprises two ECR ion sources 1204a and 1204b, in place of the reflector 12. Namely, atom currents which are supplied from the ECR ion sources 1204a and 1204b are directly incident upon the upper surface of a substrate 11. These ECR ion sources 1204a and 1204b are set to have prescribed angles with respect to the major surface of the substrate 11. Consequently, the atom currents are incident upon the upper surface of the substrate 11 in directions of incidence which are perpendicular to a plurality of densest planes of a single-crystalline thin film to be formed. It is possible to form a single-crystalline thin film on the substrate 11 also by employing such an apparatus having a plurality of beam sources, in place of the apparatus 100 comprising the reflector 12.

In this apparatus, a mechanism for adjusting the attitude of the substrate 11 is further added to a sample holder 1208 which is set in a treatment chamber 1202. Namely, the sample holder 1208 is rotatable in a horizontal plane, whereby it is possible to rotate the substrate 11 for directing an orientation flat 11a, which may be provided in the substrate 11, to a prescribed direction. When the substrate 11 which is placed on a carrier unit 1206 is carried through an inlet 1204 provided on a side surface of the treatment chamber 1202 of this apparatus and placed on the sample holder 1208, optical means detects the direction of the orientation flat 11a and the sample holder 1208 is rotated by a prescribed amount in order to correct the direction to a prescribed one. The amount of rotation is calculated by a control unit part (not shown) storing a computer therein.

The direction of the orientation flat 11a generally has a constant relation to the crystal orientation of a single-crystalline layer forming the substrate 11. Therefore, it is possible to set the crystal orientation of the single-crystalline layer forming the substrate 11 and that of a single-crystalline thin film to be newly formed thereon regularly in a desired relation by setting the orientation flat 11a in a prescribed direction. Thus, it is also possible to epitaxially form a new single-crystalline thin film on the single-crystalline layer forming the substrate 11, for example, by employing this apparatus.

Fig. 70 is a front sectional view typically showing the structure of another apparatus for forming a single-crystalline thin film according to the twenty-fourth preferred embodiment of the present invention. Also in this apparatus, it is possible to horizontally rotate a substrate 11 to adjust its attitude. Namely, a sample holder 1208 can be horizontally rotated by a rotation driving part 1214. This apparatus further comprises a crystal orientation detecting unit portion 1210 for detecting the crystal orientation of the substrate 11 having a single-crystalline structure. The crystal orientation detecting unit portion 1210 has a function of irradiating the surface of the substrate 11 with X-rays, for example, and catching a diffraction image thereof. An electric signal expressing the diffraction image obtained by the crystal orientation detecting unit portion 1210 is transmitted to a control part 1212 storing a computer therein. The control part 1212 decodes the diffraction image from this signal to calculate the crystal orientation in the substrate 11 while calculating difference between the same and a desired crystal orientation, and instructs an angle of rotation for correcting the orientation to the rotation driving part 1214. The rotation driving part 1214 rotates the sample holder 1208 along the instruction. The aforementioned operation eliminates the difference, to regularly set the crystal orientation of the single-crystalline layer forming the substrate 11 and that of the single-crystalline thin film to be newly formed thereon in a desired relation.

The apparatus shown in Fig. 70 has such an advantage that the crystal orientation can be adjusted with respect to an arbitrary single-crystalline substrate having no orientation flat 11a, dissimilarly to the apparatus shown in Fig. 69. Considering that the relation between the crystal orientation of the substrate 11 and the direction of the orientation flat 11a is not accurate in general, it can be said that the apparatus shown in Fig. 70 can adjust the crystal orientation in higher accuracy as compared with the apparatus shown in Fig. 69.

⟨B-13. Twenty-fifth Preferred embodiment⟩

Fig. 71 is a partially fragmented front elevational view typically showing a sample holder which is provided in an apparatus for forming a single-crystalline thin film according to a twenty-fifth preferred embodiment of the present invention. This sample holder is employed along with the apparatus 101. Namely, this sample holder is employed in an apparatus for growing an amorphous or polycrystalline thin film by supplying a reaction gas onto a substrate 11 while irradiating the same with an atom current. In this sample holder, a reflector 12 is fixedly supported on a fixed table 1302 through a support 1304. A rotatable table 1306 for receiving the substrate 11 is connected with a rotary shaft 1308, which is rotated/driven by an rotation/driving unit portion (not shown) thereby rotating the rotatable table 1306. Upon such rotation of the rotatable table 1306, the substrate 11 which is placed thereon is rotated. It is possible to eliminate inhomogeneity appearing in the thickness of the as-grown thin film due to inhomogeneity in a reaction system, i.e., inhomogeneity in distribution of a reaction gas onto the substrate 11 or that in temperature distribution on the substrate 11 by rotating the substrate 11 and properly changing its direction. On the other hand, relative positions of the reflector 12 and the substrate 11 are changed upon rotation of the substrate 11. When this sample holder is employed, therefore, application of the atom current is intermittently carried out so that the direction of the substrate 11 is changed to carry out only growth of a thin film, i.e., only film formation, with limitation to irradiation pauses. Further, the direction of the substrate 11 is returned to the original one before next irradiation is started. These operations are repeated to carry out film formation and conversion to a single crystal.

Fig. 72 is a plan view typically showing another example of the sample holder. This sample holder is adapted to implement treatment of the substrate 11 in a batch processing system, and employed in combination with the apparatus 100. In this sample holder, substrates 11 to be treated are placed on peripheral portions of a rotary shaft of a rotatable table 1310. Fig. 72 illustrates such an example that four substrates 11 are placed. Among these substrates 11, only that provided in a position of "A" in Fig. 72, for example, is irradiated with an atom current. A reaction gas is supplied in all positions "A" to "D".

When the rotatable table 1310 is intermittently rotated, the substrate 11 occupying the position "A" is subjected to both of irradiation and supply of the reaction gas. Namely, film formation and single crystallization progress at the same time. In the respective ones of the remaining positions "B" to "D", only supply of the reaction gas is carried out with progress of only film formation. Further, the directions of the substrates 11 are varied with the positions "A" to "D". When the substrates 11 successively itinerate the positions "A" to "D", therefore, it is possible to eliminate inhomogeneity in degree of film formation caused by inhomogeneity in a reaction system. Namely, it is possible to form a single-crystalline thin film having a uniform thickness on each substrate 11 also by employing this sample holder. Further, it is possible to regularly carry out irradiation with an atom current in the position "A". Therefore, it is possible to further efficiently form a single-crystalline thin film as compared with a case of employing the sample holder shown in Fig. 71.

⟨B-14. Twenty-sixth Preferred embodiment⟩

Fig. 73 is a front sectional view typically showing a sample holder which is provided in an apparatus for forming a single-crystalline thin film according to a twenty-sixth preferred embodiment of the present invention. In this sample holder, a reaction gas supply member 1412 defining a reaction gas supply path in its interior is rotatably mounted on a bottom portion of a treatment vessel 1402 while maintaining an airtight state. Therefore, this sample holder is suitably integrated in the apparatus 100 having no separate reaction gas supply system.

This reaction gas supply member 1412 is rotated/driven by a belt 1428. The reaction gas supply member 1412 is in a three layer structure provided with an inner pipe 1416 which is located on the innermost layer, an outer pipe 1414 which is located on the outermost layer, and an intermediate pipe 1418 which is located on the intermediate layer. Thus, the reaction gas supply member 1412 defines a supply path and an exhaust path for a reaction gas between the respective layers. Further, a reaction gas supply

port 1420 and a reaction gas discharge port 1426 are rotatably coupled to the reaction gas supply member 1412 through rotary seals 1430 and 1432 for maintaining airtightness respectively.

In addition, a support 1406 for fixedly supporting a sample fixing table 1404 is inserted in the interior of the reaction gas supply member 1412. A substrate 11 serving as a sample is placed on the sample fixing table 1404, while a heater 1408 for heating the sample is provided on a bottom surface of the sample fixing table 1404. This heater 1408 may be rotated at need, in order to improve temperature distribution on the substrate 11. The sample fixing table 1404 is so fixed that the same is not rotated following rotation of the reaction gas supply member 1412.

A reaction gas which is supplied from the reaction gas supply port 1420 passes through the supply path defined between the intermediate pipe 1418 and the inner pipe 1416, to be sprayed toward the upper surface of the substrate 11 from a reaction gas spray port 1422. A reacted residual gas enters another path which is defined between the outer pipe 1414 and the intermediate pipe 1417, i.e., the exhaust path from a reaction gas collection port 1424, and further passes this exhaust path to be discharged to the exterior from the reaction gas discharge port 1426. It is possible to homogeneously grow a prescribed thin film on the substrate 11 by rotating the reaction gas supply member 1412. Further, it is possible to continue the growth without interrupting irradiation with an atom current, since the substrate 11 is not rotated. Namely, it is possible to homogeneously form a film without interrupting single crystallization caused by irradiation with an atom current in this sample holder. Thus, it is possible to further efficiently form a single-crystalline thin film of a uniform thickness on the substrate 11.

⟨B-15. Twenty-seventh Preferred embodiment⟩

Fig. 74 is a front sectional view typically showing the structure of an apparatus for forming a single-crystalline thin film according to a twenty-seventh preferred embodiment of the present invention. This apparatus comprises two ECR ion sources 1204a and 1204b, similarly to the apparatus shown in Fig. 69. The feature of the apparatus according to this preferred embodiment resides in provision of control unit portions 1502 and 1504 for independently adjusting density levels of ion beams generated from the two ECR ion sources 1204a and 1204b. These control unit portions 1502 and 1504 separately, i.e., independently control the outputs of the two ECR ion sources 1204a and 1204b, whereby it is possible to easily optimize density levels of the ion beams supplied from the same. Thus, it is possible to stably form a high-quality single-crystalline thin film on the substrate 11.

⟨B-16. Twenty-eighth Preferred embodiment⟩

Fig. 75 is a front sectional view typically showing the structure of an apparatus for forming a single-crystalline thin film according to a twenty-eighth preferred embodiment of the present invention. This apparatus also comprises two ECR ion sources 1204a and 1204b, similarly to the apparatus shown in Fig. 74. The feature of the apparatus according to this preferred embodiment resides in that a bias voltage is applied across the two ECR ion sources 1204a and 1204b and a substrate 11, in a direction for accelerating ions. Namely, a dc voltage supply circuit is interposed in parallel in a series circuit of an RF power source 1602 for generating a high frequency and a matching circuit 1604 for ensuring impedance matching, i.e., a circuit for supplying a high frequency to the ECR ion sources 1204a and 1204b. The dc voltage supply circuit is formed by a series circuit of a dc power source 1606 and an inductor 1608 for blocking a high frequency.

Supply of the high frequency and that of the dc voltage are allotted to the two ECR ion sources 1204a and 1204b by time sharing through action of a switching relay 1610. These are alternately supplied to the two ECR ion sources 1204a and 1204b by time sharing, in order to prevent disturbance of a normal flow of an ion current caused by interference of dc voltages applied thereto.

In the apparatus according to this preferred embodiment, a bias voltage is applied across the ECR ion sources 1204a and 1204b and the substrate 11 in a direction for accelerating ions, whereby the atom current is advantageously improved in directivity. A similar effect is attained also when the bias voltage is simultaneously supplied to the two ECR ion sources 1204a and 1204b in place of the alternate supply by time sharing. Alternatively, two dc voltage supply circuits may be provided to independently supply bias voltages to the two ECR ion sources 1204a and 1204b respectively. In this case, it is possible to apply optimum bias voltages to the respective ECR ion sources 1204a and 1204b, whereby optimum irradiation conditions can be obtained.

⟨B-17. Twenty-ninth Preferred embodiment⟩

Fig. 76 is a front sectional view typically showing the structure of an apparatus for forming a single-crystalline thin film according to a twenty-ninth preferred embodiment of the present invention. This apparatus also comprises two ECR ion sources 1204a and 1204b, similarly to the apparatus shown in Fig. 75. The feature of the apparatus according to this preferred embodiment resides in that grids 1702 and 1704 to which bias voltages for adjusting ion extracting conditions are applied are provided in the vicinity of ion outlet ports of the two ECR ion sources 1204a and 1204b. Dc power sources 1706 and 1708 are interposed between the grids 1702 and 1704 and a substrate 11 respectively. The two grids 1702 and 1704 are separated from each other, so that the voltages applied thereto can be adjusted independently of each other.

When bias voltages are applied across the grids 1702 and 1704 and the substrate 11 in directions for accelerating ions, for example, an atom current is improved in directivity. In this apparatus, further, the levels of the bias voltages which are applied to the two grids 1702 and 1704 can be adjusted independently of each other, whereby it is possible to apply optimum bias voltages in response to operating states of the two ECR ion sources 1204a and 1204b. Thus, it is possible to efficiently form a high-quality single-crystalline thin film on the substrate 11.

While the invention has been shown and described in detail, the foregoing description is in all aspects illustrative and not restrictive. It is therefore understood that numerous modifications and variations can be devised without departing from the scope of the invention.

Claims

1. A method of forming a single-crystalline thin film, being adapted to form a single-crystalline thin film of a prescribed material on a substrate, by previously forming an amorphous thin film or a polycrystalline thin film of said prescribed material on said substrate and irradiating said amorphous thin film or said polycrystalline thin film with beams of neutral atoms or neutral molecules of low energy levels causing no sputtering of said prescribed material under a high temperature of not more than a crystallization temperature of said prescribed material from directions being perpendicular to a plurality of densest crystal planes, having different directions, in said single-crystalline thin film to be formed.

2. A method of forming a single-crystalline thin film in accordance with claim 1, wherein the atomic weights of atoms forming said beams are lower than the maximum one of the atomic weights of elements forming said prescribed material.

3. A method of forming a single-crystalline thin film in accordance with claim 1, wherein said beams are obtained by a single electron cyclotron resonance type ion generation source and a reflector being arranged in a path between said ion generation source and said amorphous thin film or said polycrystalline thin film.

4. A method of forming a single-crystalline thin film of a prescribed material on a polycrystalline substrate or an amorphous substrate using plasma chemical vapor deposition by supplying a reaction gas onto said substrate under a low temperature allowing no crystallization of said prescribed material with said plasma chemical vapor deposition alone while simultaneously irradiating said substrate with beams of a low energy gas causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed.

5. A method of forming a single-crystalline thin film in accordance with claim 4, wherein said gas is an inert gas.

6. A method of forming a single-crystalline thin film in accordance with claim 5, wherein the atomic weight of an element forming said inert gas is lower than the maximum one of the atomic weights of elements forming said prescribed material.

7. A method of forming a single-crystalline thin film in accordance with claim 4, wherein said prescribed material contains an element forming a gas material being in a gas state under ordinary temperatures, said beams of said gas being those of said gas material.

8. A method of forming a single-crystalline thin film in accordance with claim 4, wherein said reaction gas contains a reaction gas material being formed by an impurity element to be added to said prescribed material.

9. A method of forming a single-crystalline thin film in accordance with claim 8, wherein a plurality of types of said impurity elements are so employed that a plurality of types of reaction gas materials being formed by respective ones of said plurality of types of impurity elements are alternately supplied onto said substrate.

10. A method of forming a single-crystalline thin film in accordance with claim 4, wherein said beams of said gas are obtained by a single beam source and a reflector being arranged in a path between said beam source and said substrate.

11. A method of forming a single-crystalline thin film in accordance with claim 10, wherein said beam source is an ion generation source generating an ion beam of said gas, and said reflector is a metal reflector being substantially made of a metal.

12. A method of forming a single-crystalline thin film in accordance with claim 10, wherein said beam source is an electron cyclotron resonance type ion generation source.

13. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:
a container for storing said sample; and
a beam source for irradiating said target surface of said sample being set in a prescribed position of said container with said gas beam,
at least a surface of a portion irradiated with said beam being made of a material having threshold energy being higher than energy of said beam in sputtering by irradiation with said beam among an inner wall of said container and a member being stored in said container.

14. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:
a container for storing said sample; and
a beam source for irradiating said target surface of said sample being set in a prescribed position of said container with said gas beam,
at least a surface of a portion irradiated with said beam being made of a material having threshold energy with respect to sputtering being higher than that in said target surface of said sample among an inner wall of said container and a member being stored in said container.

15. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:
a container for storing said sample; and
a beam source for irradiating said target surface of said sample being set in a prescribed position of said container with said gas beam,
at least a surface of a portion irradiated with said beam being made of a material containing an element being larger in atomic weight than that forming said gas among an inner wall of said container and a member being stored in said container.

16. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:
a container for storing said sample; and
a beam source for irradiating said target surface of said sample being set in a prescribed position of said container with said gas beam,
at least a surface of a portion irradiated with said beam being made of the same material as that forming said target surface of said sample among an inner wall of said container and a member being stored in said container.

17. A beam irradiator in accordance with any of claims 13 to 16, wherein said member being stored in said container includes reflecting means being interposed in a path of said beam for separating said beam

into a plurality of components and irradiating said target surface of said sample with said plurality of components from directions being different from each other.

18. A beam irradiating method of irradiating a target surface of a sample with a gas beam, said method comprising:
a step of setting said sample in a prescribed position of a container; and
a step of irradiating said target surface of said sample being set in said container with said gas beam,
said target surface being irradiated with said beam at energy being lower than threshold energy of sputtering in a surface of a portion being irradiated with said beam among an inner wall of said container and a member being stored in said container.

19. A method of forming a single-crystalline thin film, being adapted to form a single-crystalline thin film of a prescribed material on a substrate, said method comprising:
a step of depositing said prescribed material on said substrate under a low temperature causing no crystallization of said prescribed material and irradiating said prescribed material being deposited with a gas beam of low energy causing no sputtering of said prescribed material from one direction, thereby forming an axially oriented polycrystalline thin film of said material; and
a step of irradiating said axially oriented polycrystalline thin film with gas beams of low energy causing no sputtering of said prescribed material under a high temperature below a crystallization temperature of said prescribed material from directions being perpendicular to a plurality of densest crystal planes of different directions in said single-crystalline thin film, thereby converting said axially oriented polycrystalline thin film to a single-crystalline thin film.

20. A method of forming a single-crystalline thin film, being adapted to form a single-crystalline thin film of a prescribed material on a substrate, said method comprising:
a step of depositing said prescribed material on said substrate thereby forming a thin film of said material;
a step of irradiating said thin film with a gas beam of low energy causing no sputtering of said prescribed material under a high temperature below a crystallization temperature of said prescribed material from one direction after said step, thereby converting said thin film to an axially oriented polycrystalline thin film; and
a step of irradiating said axially oriented polycrystalline thin film with gas beams of low energy causing no sputtering of said prescribed material under a high temperature below said crystallization temperature of said prescribed material from directions being perpendicular to a plurality of densest crystal planes of different directions in said single-crystalline thin film, thereby converting said axially oriented polycrystalline thin film to a single-crystalline thin film.

21. A method of forming a single-crystalline thin film in accordance with claim 19 or 20, wherein said direction of said gas beam in formation of said axially oriented polycrystalline thin film is identical to one of said plurality of directions of said gas beams in said conversion of said axially oriented polycrystalline thin film to said single-crystalline thin film.

22. A method of forming a single-crystalline thin film in accordance with claim 19 or 20, wherein said gas is an inert gas.

23. A method of forming a single-crystalline thin film in accordance with claim 22, wherein the atomic weight of an element forming said inert gas is lower than the maximum atomic weight among those of elements forming said prescribed material.

24. A method of forming a single-crystalline thin film in accordance with claim 19 or 20, wherein said prescribed material contains an element forming a gas material being a gas under a normal temperature, said gas beam being a beam of said gas material.

25. A method of forming a single-crystalline thin film in accordance with claim 19 or 20, wherein said gas beam is formed by an electron cyclotron resonance ion source.

26. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:

a single beam source for supplying said beam; and

reflecting means for reflecting said beam being supplied by said beam source, thereby enabling irradiation of said target surface with said gas in a plurality of prescribed directions of incidence,

said reflecting means comprising a reflector having a plurality of reflecting surfaces for reflecting said beam in a plurality of directions, and a screen being interposed in a path of said beam between said beam source and said reflecting surfaces for selectively passing said beam thereby preventing multiple reflection by said plurality of reflecting surfaces.

27. A beam irradiator in accordance with claim 26, wherein said screen further selectively passes said beam to uniformly irradiate said target surface with said beam.

28. A beam reflecting device for reflecting a gas beam being supplied from a single beam source thereby enabling irradiation of a target surface of a sample with said gas in a plurality of prescribed directions of incidence, said beam reflecting device comprising:

a reflector having a plurality of reflecting surfaces for reflecting said beam in a plurality of directions; and

a screen being interposed in a path of said beam between said beam source and said reflecting surfaces for selectively passing said beam thereby preventing multiple reflection by said plurality of reflecting surfaces.

29. A beam reflecting device in accordance with claim 28, wherein said screen further selectively passes said beam to uniformly irradiate said target surface with said beam.

30. A beam irradiator for irradiating a target surface of a sample with a gas beam, said beam irradiator comprising:

a single beam source for supplying said beam; and

reflecting means for reflecting said beam being supplied by said beam source, thereby enabling irradiation of said target surface with said gas in a plurality of prescribed directions of incidence,

said reflecting means comprising a first reflector being arranged in a path of said beam being supplied from said beam source for reflecting said beam in a plurality of directions thereby generating a plurality of divergent beams having beam sections being two-dimensionally enlarged with progress of said beams, and a second reflector having a concave reflecting surface for further reflecting said plurality of divergent beams to be incident upon said target surface substantially as parallel beams from a plurality of directions.

31. A beam irradiator in accordance with claim 30, wherein said reflecting means further comprises rectifying means being provided in a path of said beams between said first reflector and said substrate for regularizing directions of said beams.

32. A beam irradiator in accordance with claim 30, wherein said reflecting means further comprises beam distribution adjusting means being interposed in a path of said beam between said beam source and said first reflector for adjusting distribution of said beam on a section being perpendicular to said path, thereby adjusting the amounts of respective beam components being reflected by said first reflector in said plurality of directions.

33. A beam reflecting device for reflecting a gas beam being supplied from a single beam source thereby enabling irradiation of a target surface of a sample with said gas in a plurality of prescribed directions of incidence, said beam reflecting device comprising:

a first reflector for reflecting said beam in a plurality of directions thereby generating a plurality of divergent beams having beam sections being two-dimensionally enlarged with progress of said beams; and

a second reflector having a concave reflecting surface for further reflecting said plurality of divergent beams to be incident upon said target surface substantially as parallel beams from a plurality of directions.

34. A beam irradiator for irradiating a target surface of a sample with gas beams, said beam irradiator comprising:

a plurality of beam sources for supplying said gas beams; and

a plurality of reflecting means for reflecting said beams being supplied by said plurality of beam sources thereby enabling irradiation of a common region of said target surface with said gas in a plurality of prescribed directions of incidence,

each said reflecting means comprising a first reflector being arranged in a path of each said beam being supplied from each said beam source for reflecting said beam thereby generating a beam having a beam section being two-dimensionally enlarged with progress of said beam, and a second reflector having a concave reflecting surface for further reflecting said divergent beam to be incident upon linear or strip-shaped said common region of said target surface substantially as a parallel beam,

said beam irradiator further comprising moving means for scanning said sample in a direction intersecting with linear or strip-shaped said common region.

35. A beam irradiator in accordance with claim 34, wherein each said reflecting means further comprises rectifying means being provided in a path of each said beam between said first reflector and said substrate for regulating the direction of said beam.

36. A beam reflecting device for reflecting a gas beam being supplied from a beam source thereby enabling irradiation of a target surface of a sample with said gas in a prescribed direction of incidence, said beam reflecting device comprising:

a first reflector for reflecting said beam thereby generating a divergent beam having a beam section being two-dimensionally enlarged with progress of said beam; and

a second reflector having a concave reflecting surface for further reflecting said divergent beam to be incident upon a linear or strip-shaped region of said target surface substantially as a parallel beam.

37. A method of forming a single-crystalline thin film of a prescribed material, comprising:

(a) a step of forming an amorphous or polycrystalline thin film of said prescribed material on a substrate;

(b) a step of forming a masking material on said thin film;

(c) a step of selectively removing said masking material; and

(d) a step of irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed while utilizing selectively removed said masking material as a screen under a high temperature below the crystallization temperature of said prescribed material.

38. A method of forming a single-crystalline thin film in accordance with claim 37, wherein said steps (b) to (d) are carried out plural times while varying directions for applying said beams in said step (d), thereby selectively converting said thin film to a single crystal having a plurality of types of crystal orientations.

39. A method of forming a single-crystalline thin film of a prescribed material, comprising:

(a) a step of forming an amorphous or polycrystalline thin film of said prescribed material on a substrate;

(b) a step of forming a masking material on said thin film;

(c) a step of selectively removing said masking material;

(d) a step of etching said thin film while utilizing selectively removed said masking material as a screen, thereby selectively removing said thin film while leaving a specific region on said substrate; and

(e) a step of irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed under a high temperature below the crystallization temperature of said prescribed material.

40. A method of forming a single-crystalline thin film of a prescribed material, comprising:

(a) a step of forming an amorphous or polycrystalline thin film of said prescribed material on a substrate;

(b) a step of irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed under a high temperature below the crystallization temperature of said prescribed material;
5 (c) a step of forming a masking material on said thin film after said step (b);
(d) a step of selectively removing said masking material; and
(e) a step of etching said thin film while utilizing selectively removed said masking material as a screen, thereby selectively removing said thin film.

10 **41.** A method of forming a single-crystalline thin film of a prescribed material, comprising:
(a) a step of forming an amorphous or polycrystalline thin film of said prescribed material on a substrate;
(b) a step of irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes
15 having different directions in said single-crystalline thin film to be formed under a low temperature causing no crystallization of said prescribed material by said step (a) alone while carrying out said step (a);
(c) a step of forming a masking material on said thin film after said steps (a) and (b);
(d) a step of selectively removing said masking material; and
20 (e) a step of etching said thin film while utilizing selectively removed said masking material as a screen, thereby selectively removing said thin film.

42. A method of forming a single-crystalline thin film of a prescribed material, comprising:
(a) a step of forming an amorphous or polycrystalline thin film of said prescribed material on a
25 substrate;
(b) a step of irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed under a high temperature below the crystallization temperature of said prescribed material;
30 (c) a step of forming a masking material on said thin film after said step (b);
(d) a step of selectively removing said masking material; and
(e) a step of irradiating said substrate with said gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to said plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed, said
35 directions being different from those in said step (b), while utilizing selectively removed said masking material as a screen.

43. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:
40 irradiation means for irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed; and
substrate moving means for making said substrate scanned with respect to said irradiation means.

45 **44.** An apparatus for forming a single-crystalline thin film in accordance with claim 43, further comprising beam focusing means for bringing sections of said gas beams into strip shapes on said substrate.

45. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:
50 a single beam source for supplying a beam of a gas;
a reflector for reflecting at least a part of said beam being supplied by said beam source, thereby implementing irradiation of said substrate with said gas in a plurality of prescribed directions of incidence; and
reflector driving means for varying the angle of inclination of said reflector.

55

46. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:
a single beam source for supplying a beam of a gas;

a plurality of reflectors, each one of said plurality of reflectors reflecting at least a part of said beam being supplied by said beam source, thereby implementing irradiation of said substrate with said gas in a plurality of prescribed directions of incidence being related to the angle of inclination of said reflector; and

reflector exchange means for selecting a prescribed one from said plurality of reflectors and utilizing the same for reflecting said beam.

47. An apparatus for forming a single-crystalline thin film in accordance with claim 43, 45 or 46, further comprising film forming means for forming an amorphous or polycrystalline thin film of the same material as said single-crystalline thin film on said substrate.

48. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

etching means for etching a surface of said substrate;

film forming means for forming an amorphous or polycrystalline thin film of said prescribed material on said surface of said substrate; and

irradiation means for irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed,

treatment chambers for storing said substrate in said means communicating with each other,

said apparatus further comprising substrate carrying means for introducing and discharging said substrate into and from respective said treatment chambers.

49. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate having a single-crystalline structure, comprising:

irradiation means for irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed; and

attitude control means for controlling the attitude of said substrate for setting prescribed relations between directions of crystal axes of said substrate and directions of incidence of said beams.

50. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

film forming means for forming an amorphous or polycrystalline thin film of said prescribed material on said substrate by supplying a reaction gas;

irradiation means for irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed; and

substrate rotating means for rotating said substrate.

51. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

film forming means for forming an amorphous or polycrystalline thin film of said prescribed material on said substrate by supplying a reaction gas; and

irradiation means for irradiating said substrate with gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed,

said film forming means having supply system rotating means for rotating an end portion of a supply path for supplying said substrate with said reaction gas with respect to said substrate.

52. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

a plurality of irradiation means for irradiating said substrate with a plurality of gas beams of low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed respectively; and

control means for independently controlling operating conditions in said plurality of irradiation

means respectively.

53. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

irradiation means for irradiating said substrate with beams of a gas being supplied by an ion source at low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed; and

bias means for applying a bias voltage across said ion source and said substrate in a direction for accelerating ions.

54. An apparatus for forming a single-crystalline thin film of a prescribed material on a substrate, comprising:

irradiation means for irradiating said substrate with beams of a gas being supplied by an ion source at low energy levels causing no sputtering of said prescribed material from directions being perpendicular to a plurality of densest crystal planes having different directions in said single-crystalline thin film to be formed, a grid being provided in the vicinity of an ion outlet of said ion source; and

grid voltage applying means for applying a voltage to said grid for controlling conditions for extracting ions from said ion source.

55. A method of forming a single-crystalline thin film in accordance with any of claims 37 to 42, wherein the atomic weight of an element forming said gas is lower than the maximum one of the atomic weights of elements forming said prescribed material.

56. A method of forming a single-crystalline thin film in accordance with any of claims 37, 38 and 42, wherein the atomic weight of an element forming said gas is lower than the maximum one of the atomic weights of elements forming said masking material.

57. An apparatus for forming a single-crystalline thin film in accordance with any of claims 43 and 48 to 52, wherein said irradiation means comprises an electron cyclotron resonance type ion source, said gas beams being supplied by said ion source.

58. An apparatus for forming a single-crystalline thin film in accordance with claim 45 or 46, wherein said beam source is an electron cyclotron resonance type ion source.

59. An apparatus for forming a single-crystalline thin film in accordance with claim 53 or 54, wherein said beam source is an electron cyclotron resonance type ion source.

FIG. 1

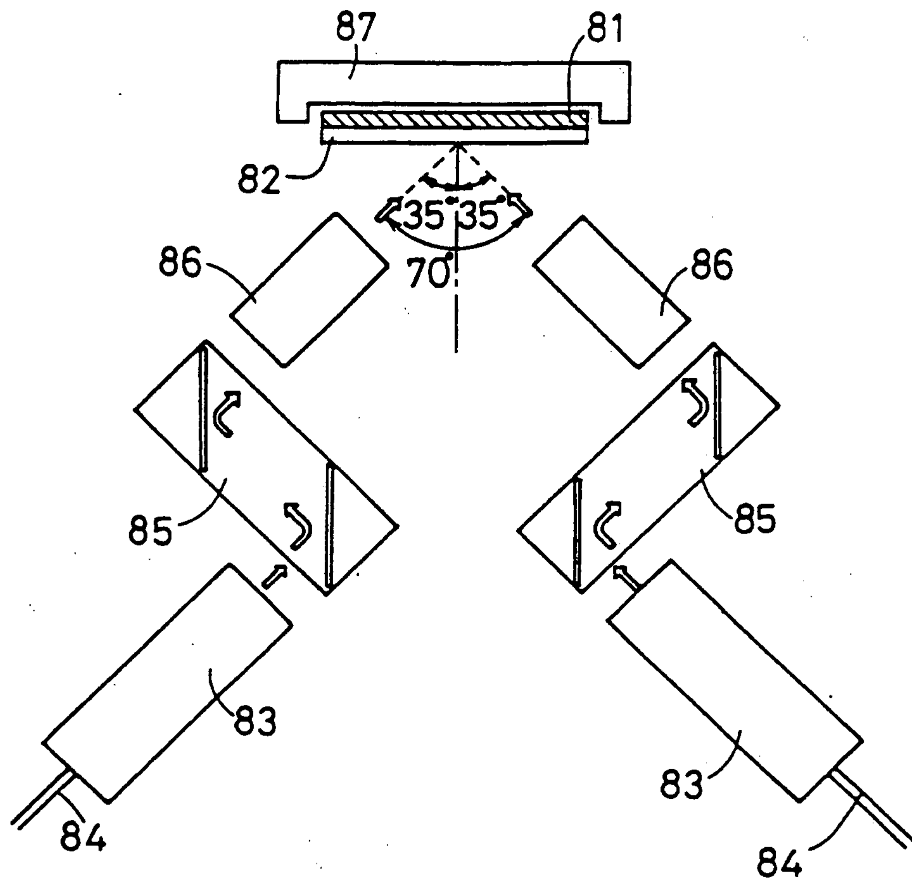


FIG.2A

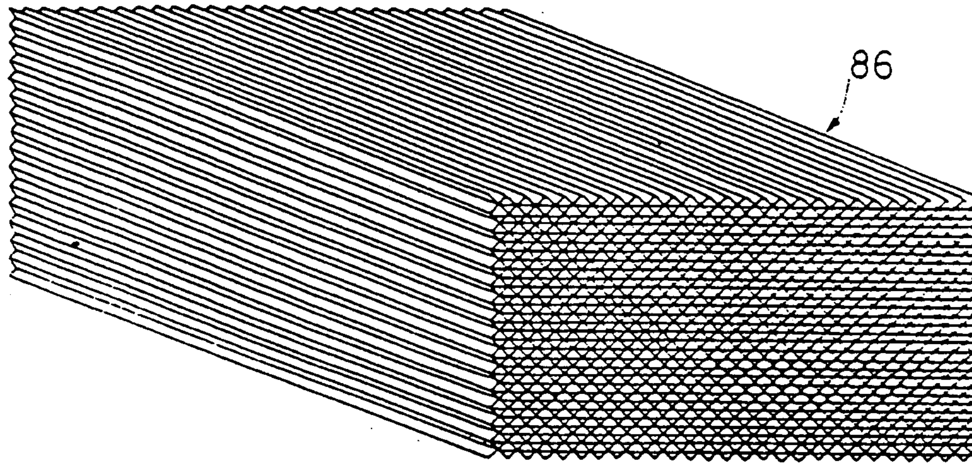


FIG.2B

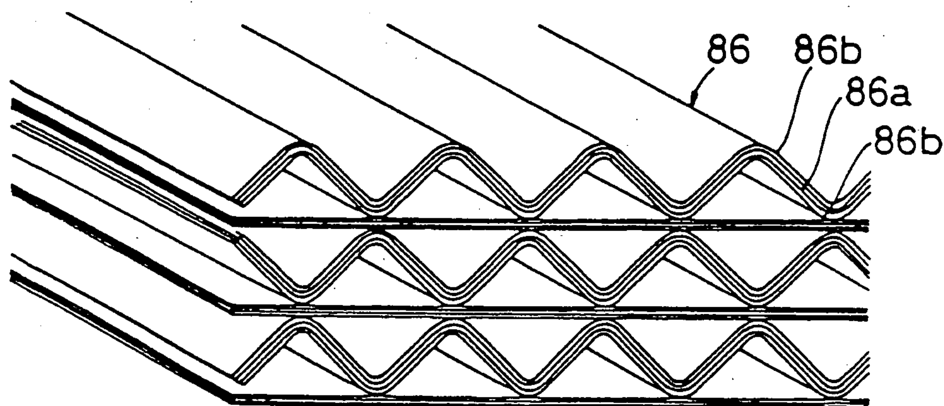


FIG.2C

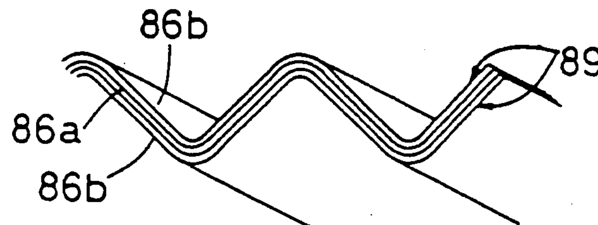


FIG.3A

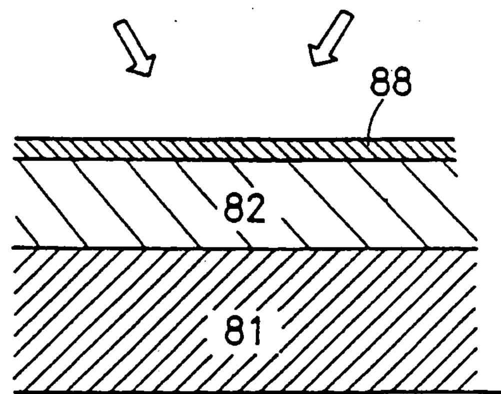
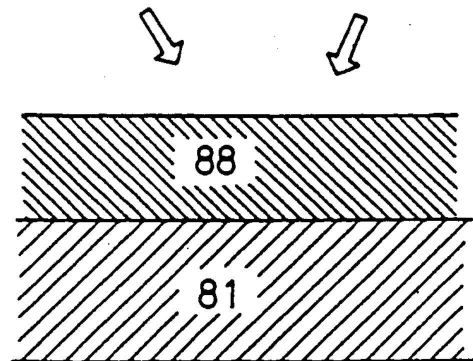


FIG.3B



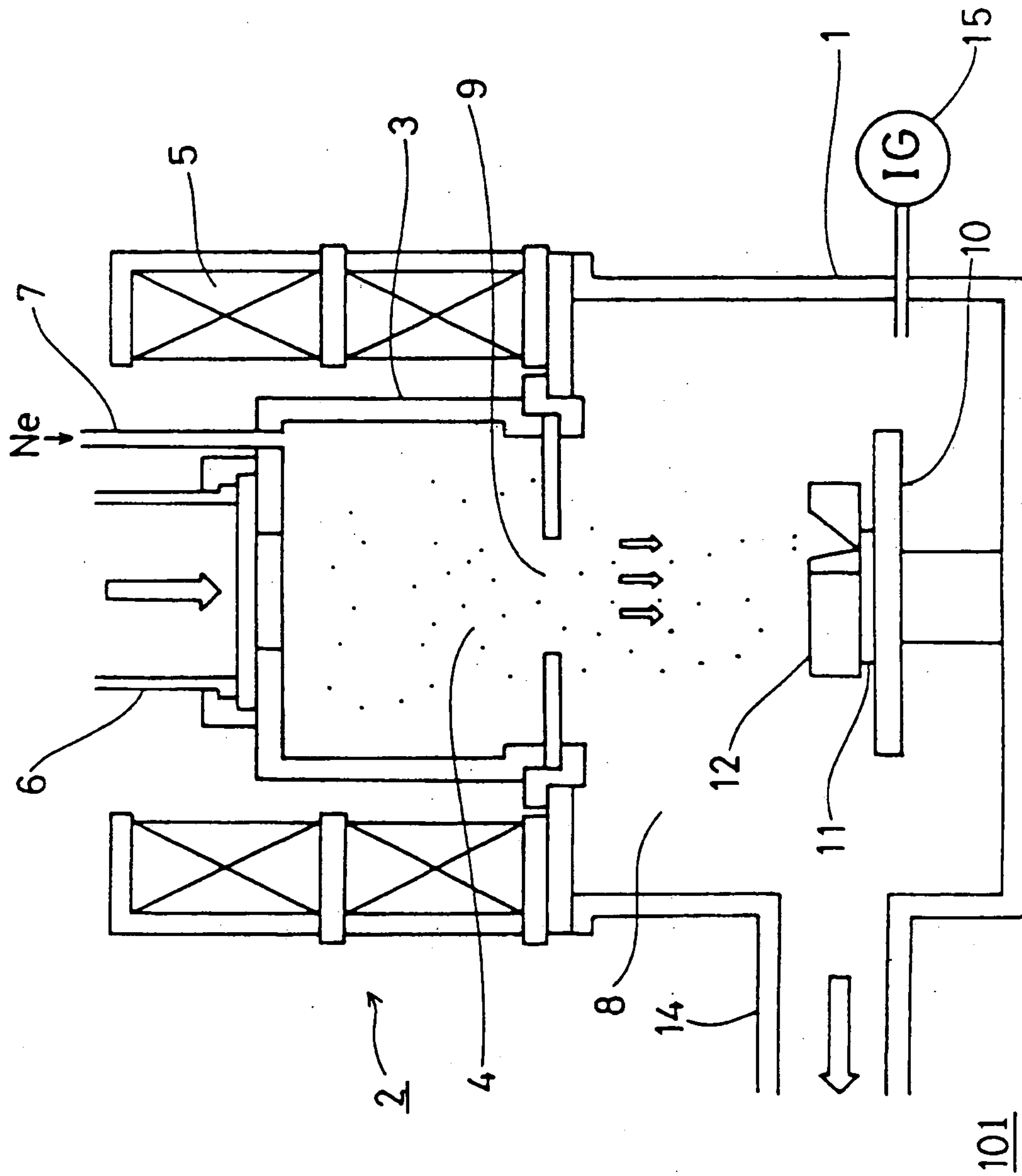


FIG. 4
Ne
IG
1
2
3
4
5
6
7
8
9
10
11
12
14
15
101

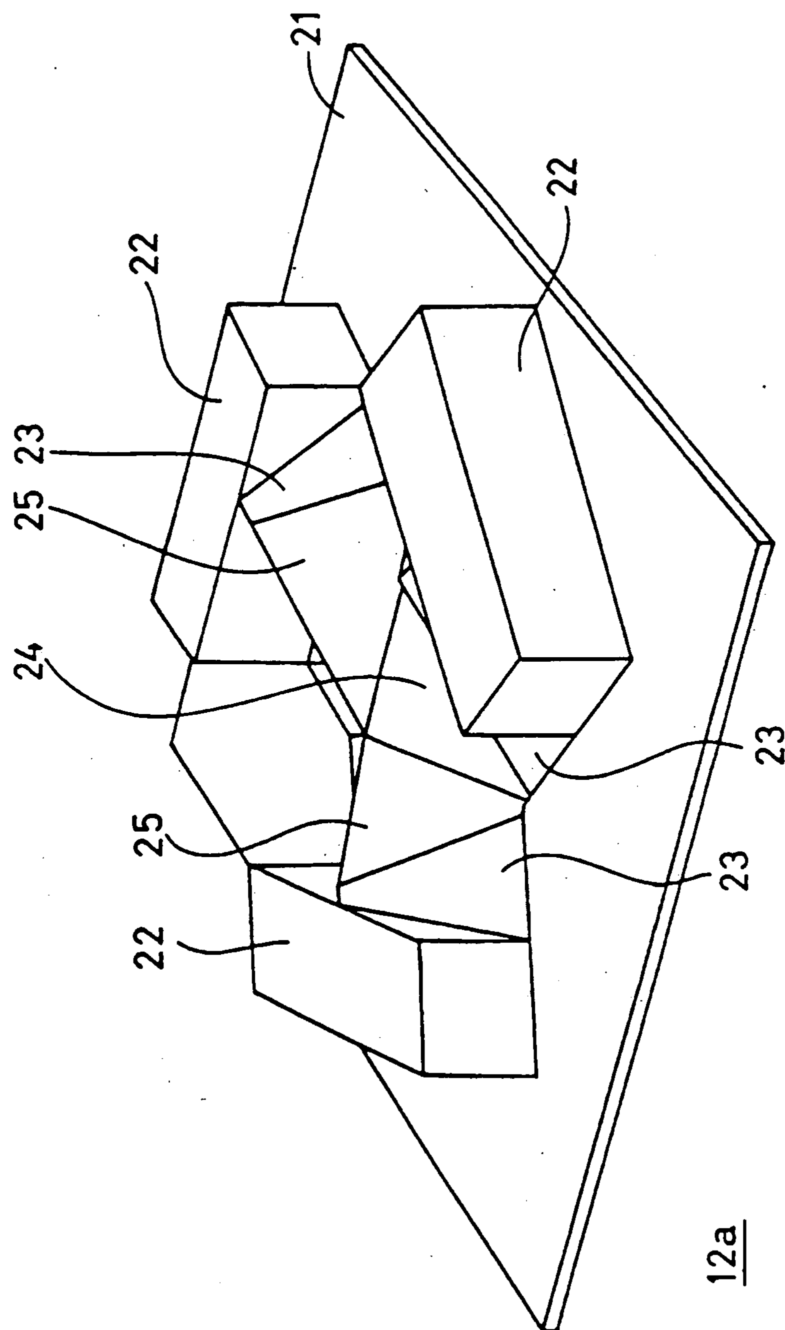


FIG. 5

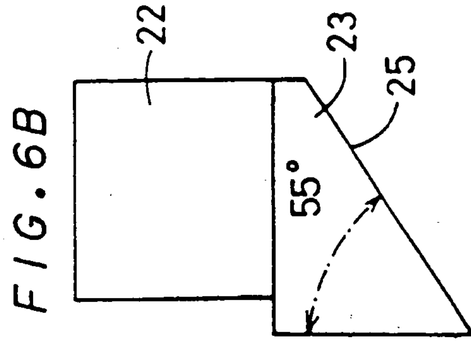


FIG.6B

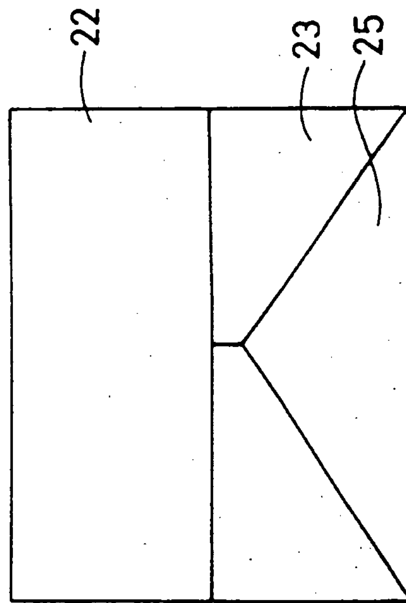


FIG.6A

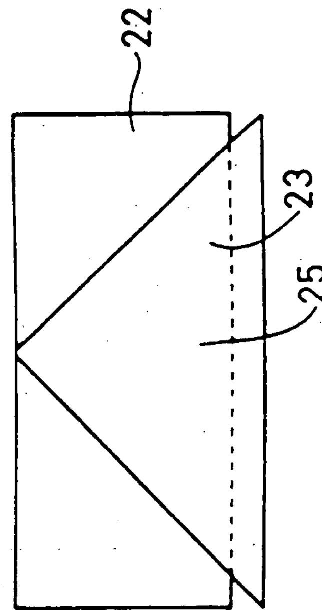


FIG.6C

12a

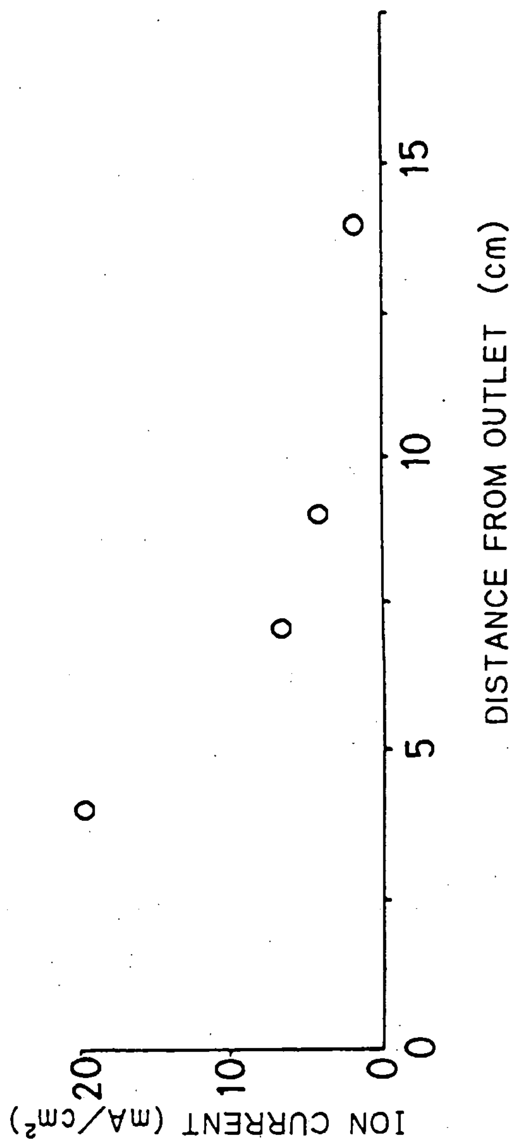


FIG. 7

FIG. 8

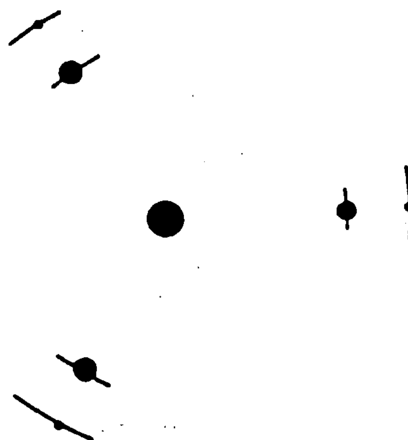
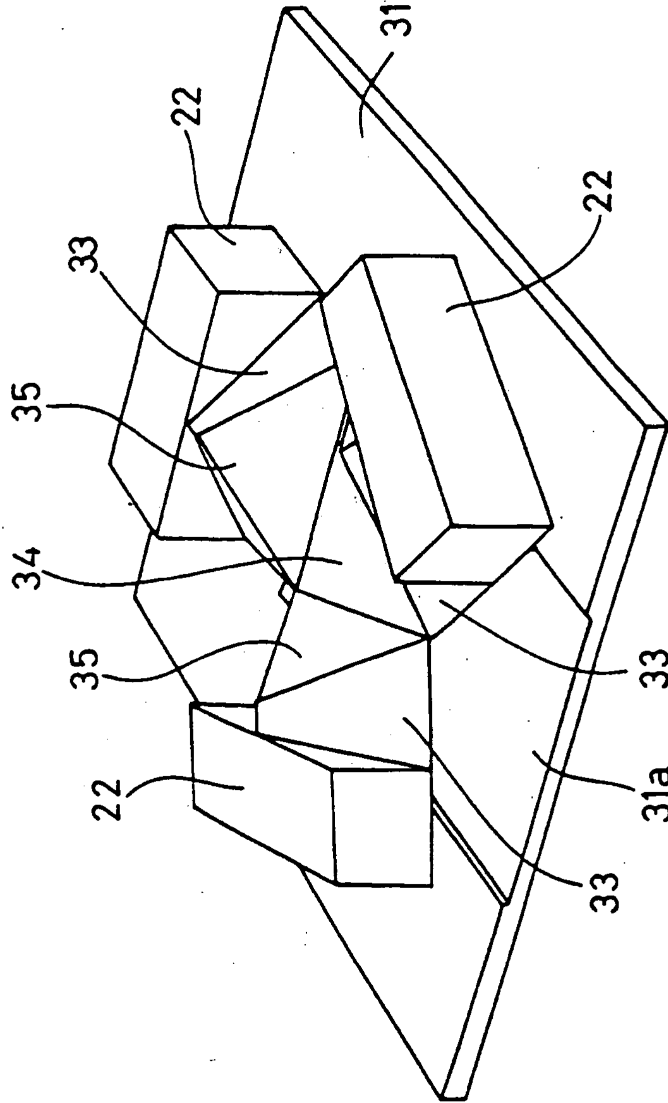


FIG. 9



12b

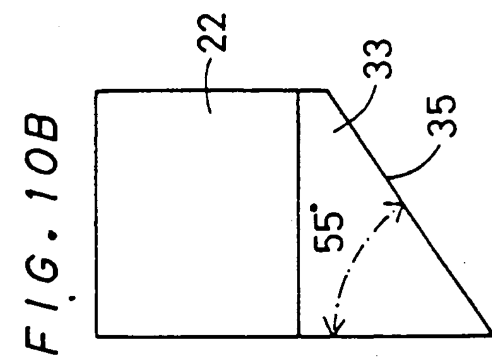


FIG. 10B

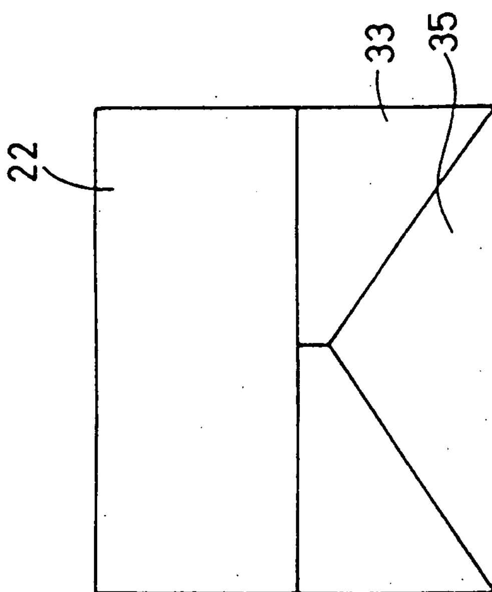


FIG. 10A

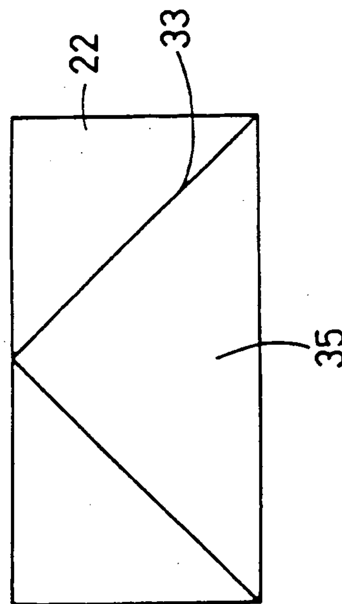


FIG. 10C

12b

FIG. 11A

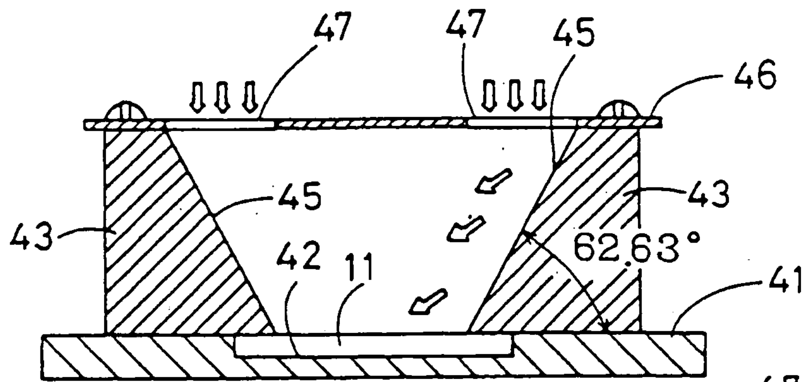
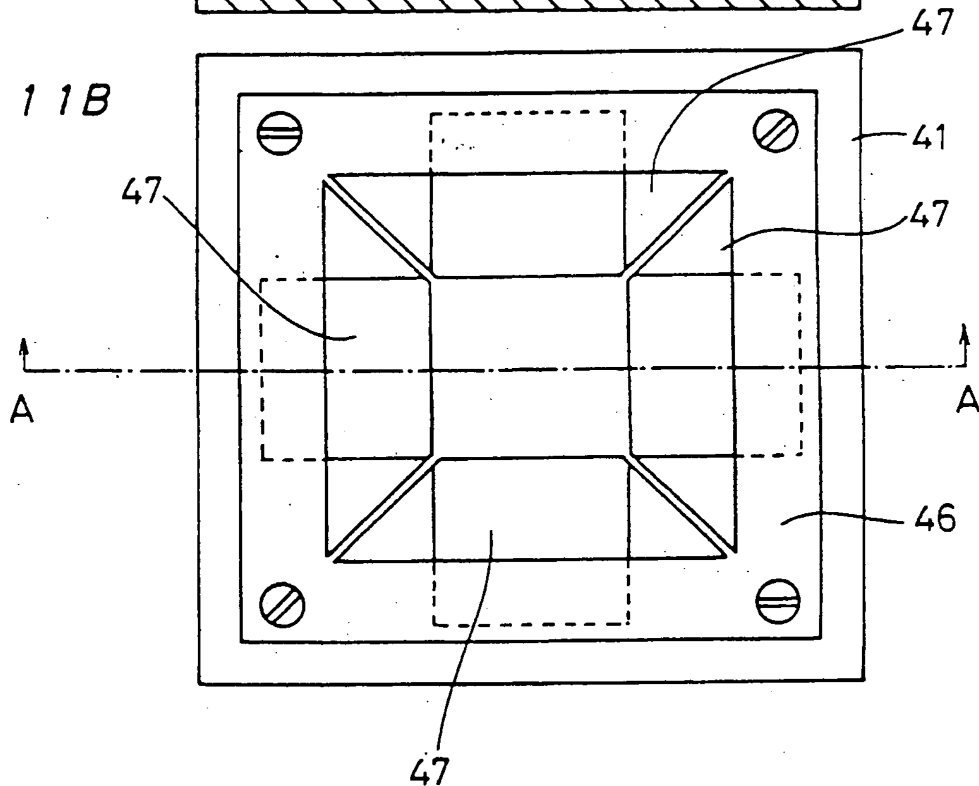


FIG. 11B



12c

FIG. 12A

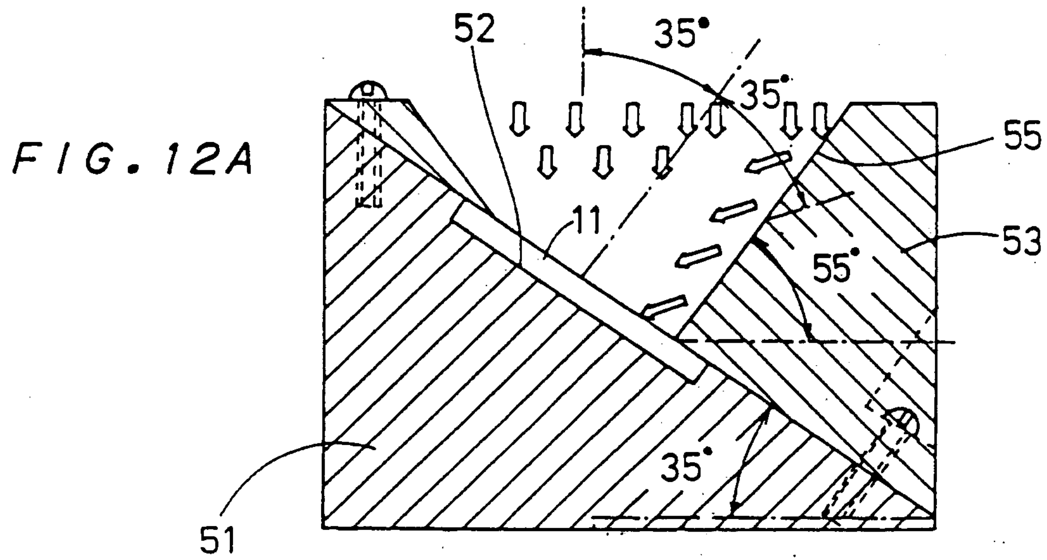
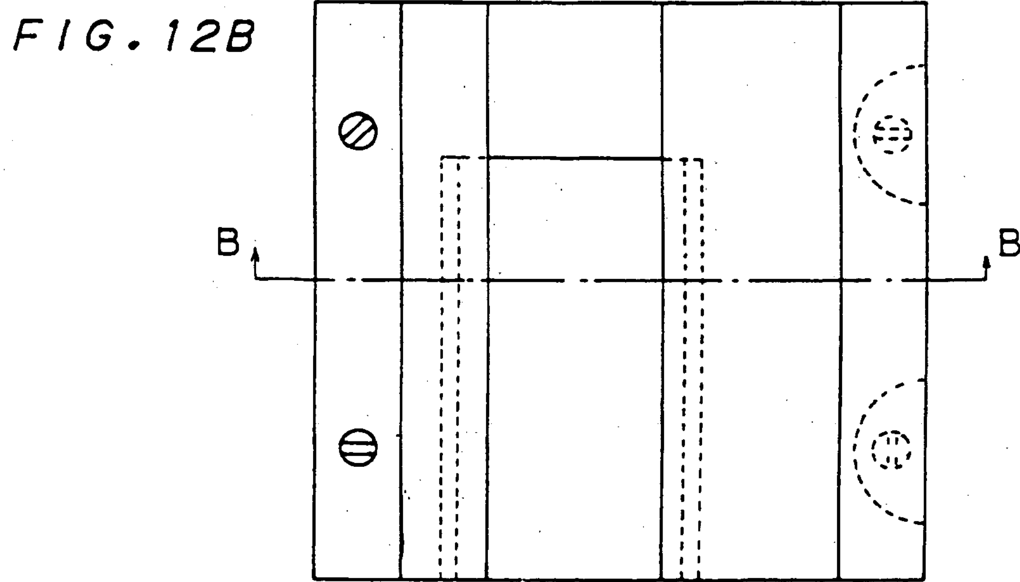
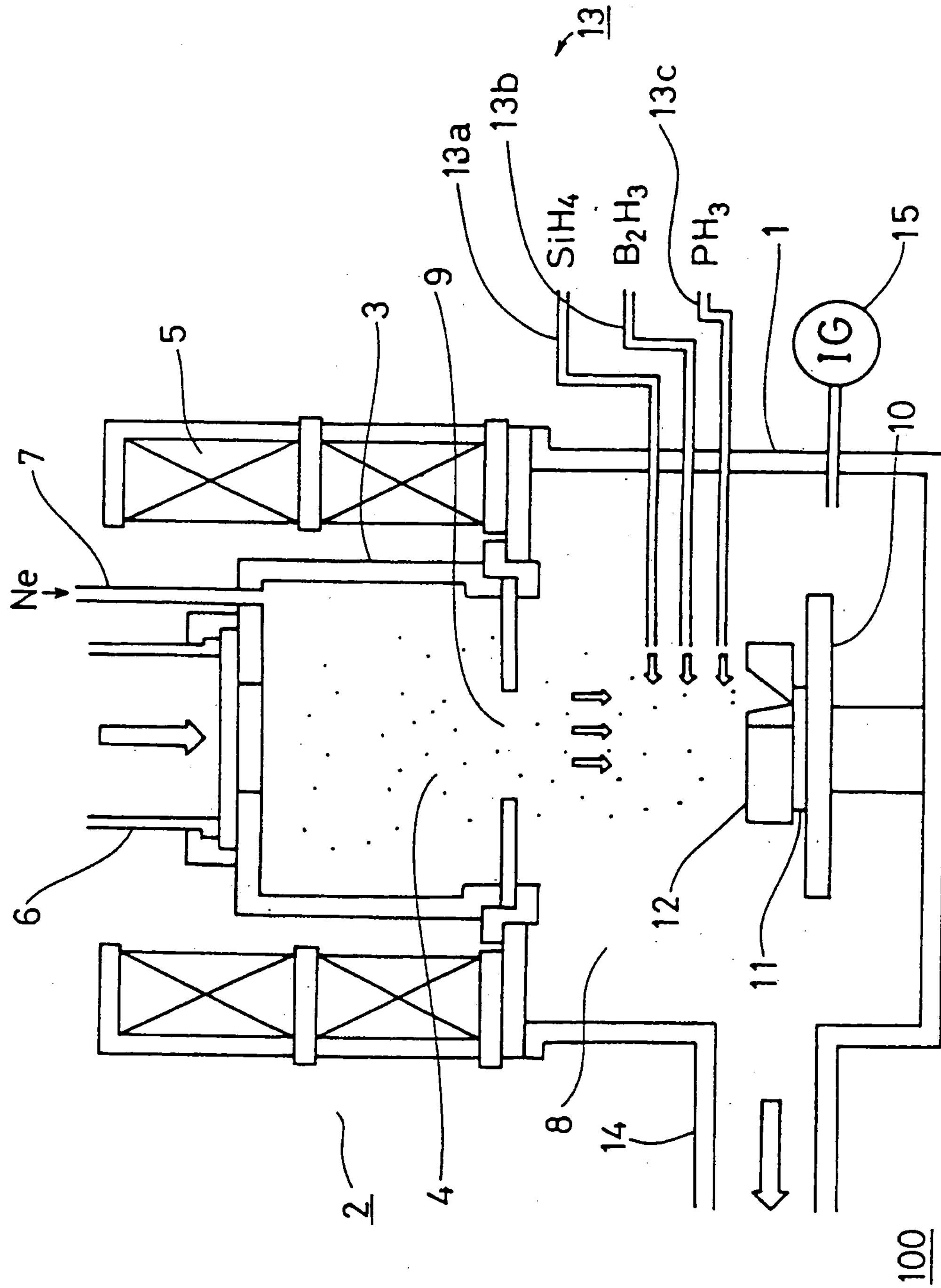


FIG. 12B



12d


F I G . 1 3
Ne
SiH4
B2H3
PH3
IG
13
13a
13b
13c
1
2
3
4
5
6
7
8
9
10
11
12
14
15
100

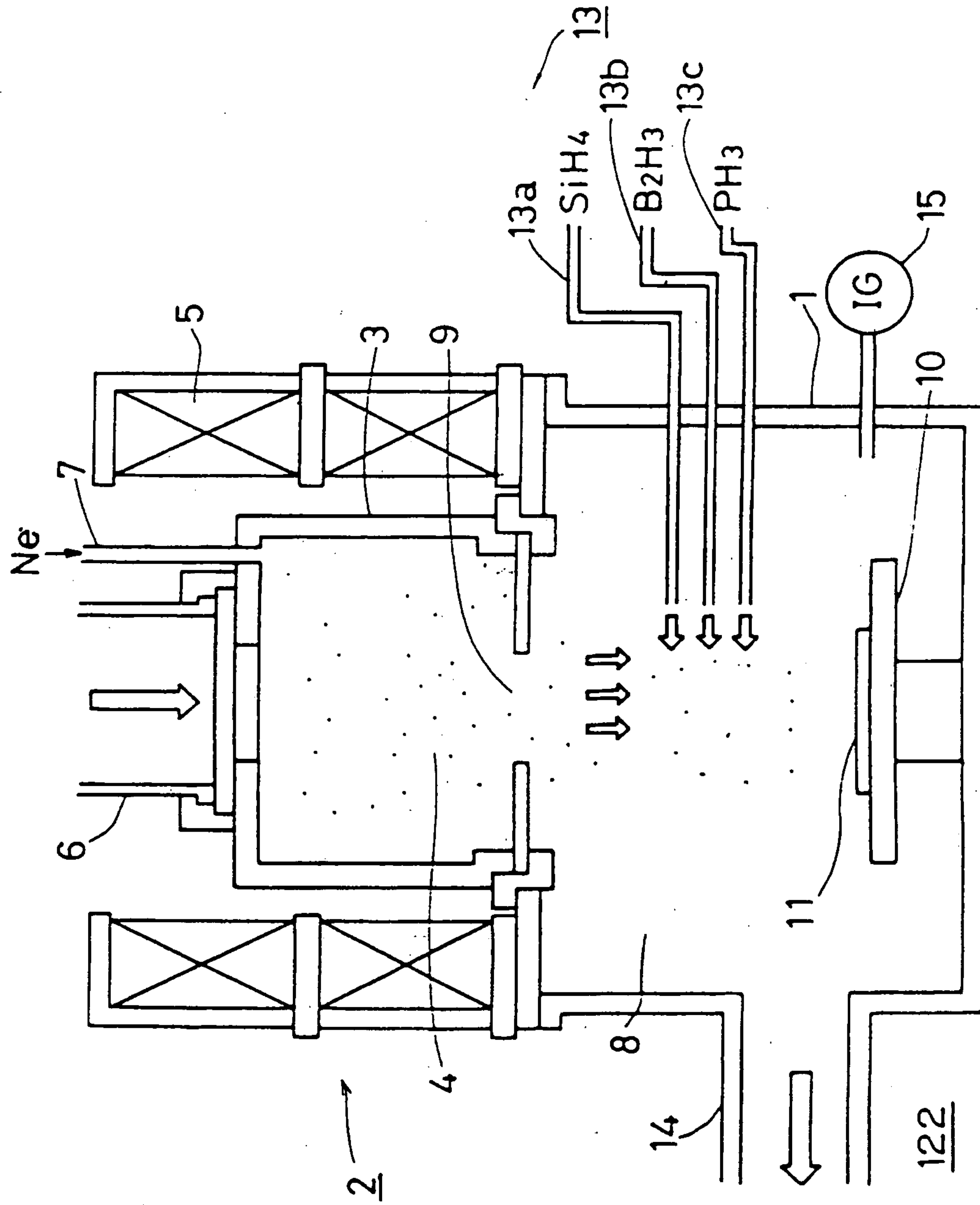
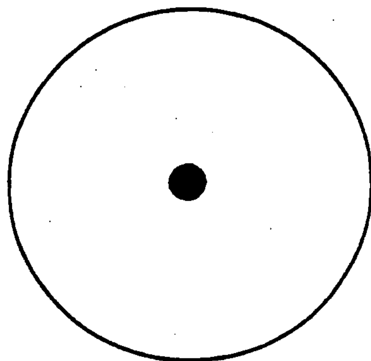


FIG. 14
Ne
13
13a
SiH4
13b
B2H3
13c
PH3
IG
15
1
10
5
3
9
7
6
11
8
4
2
14
122

FIG. 15



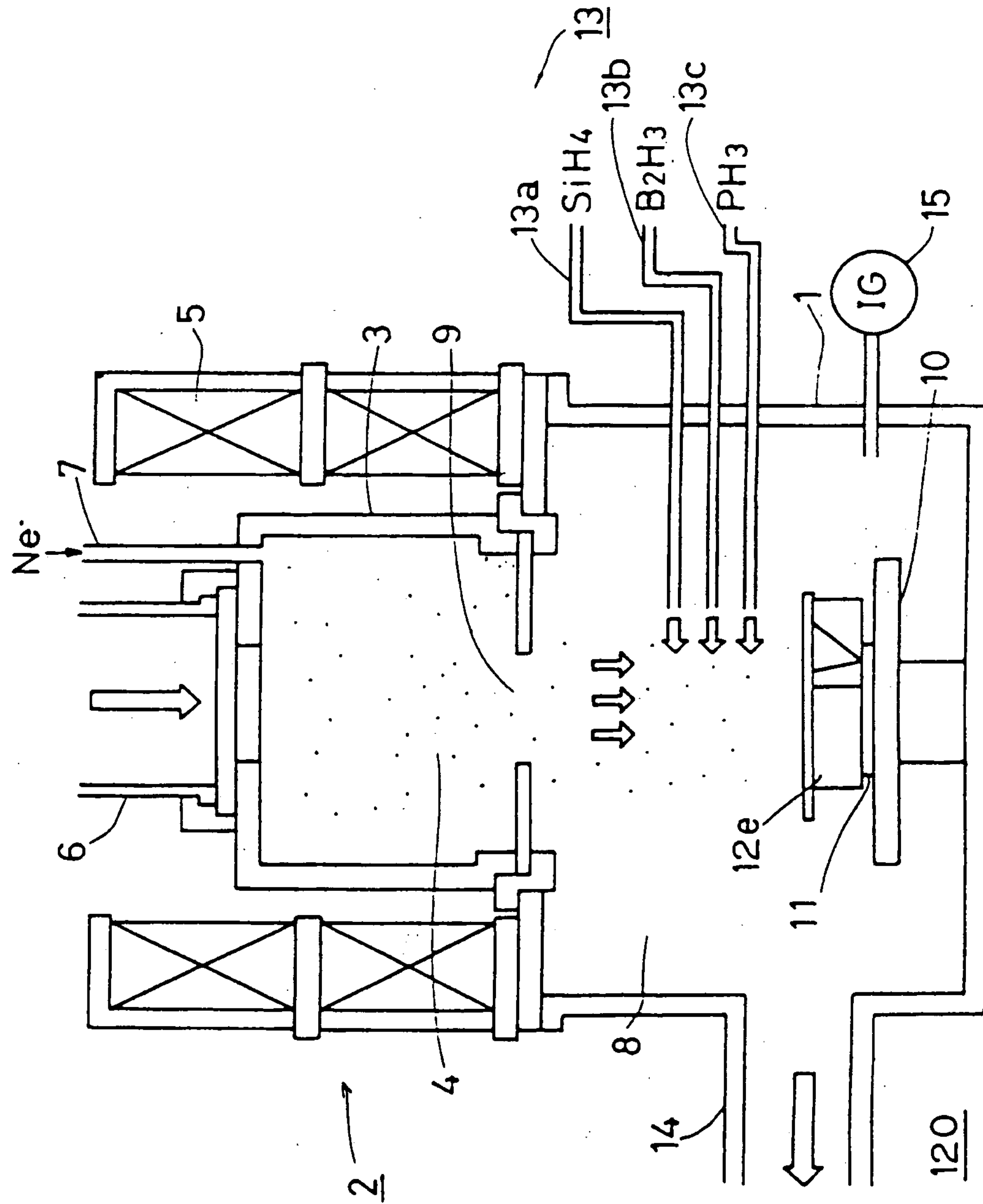


FIG. 16
13
13a
SiH4
13b
B2H3
13c
PH3
15
IG
1
10
5
3
9
7
Ne
6
12e
11
8
4
14
2
120

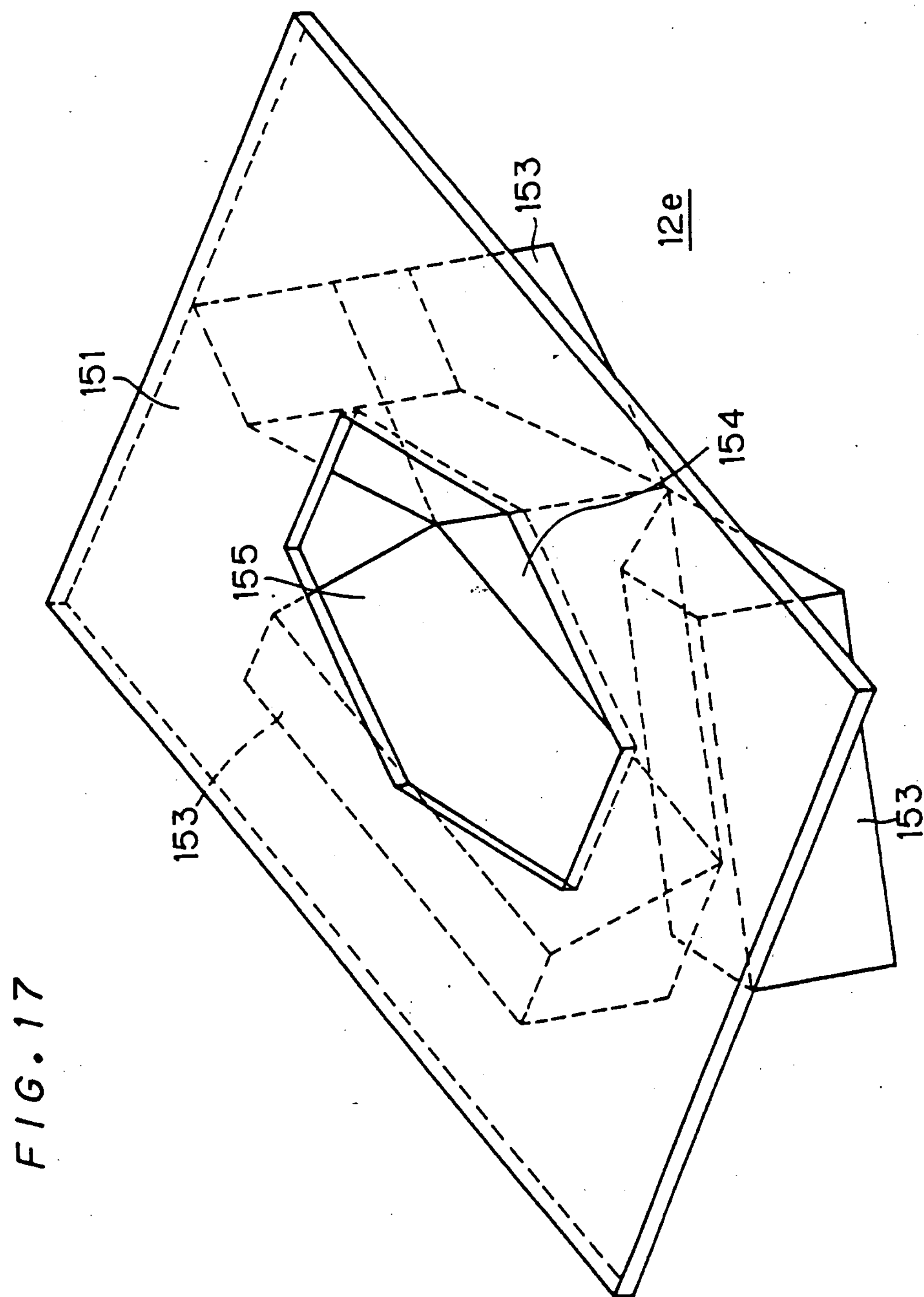


FIG. 17

FIG. 18

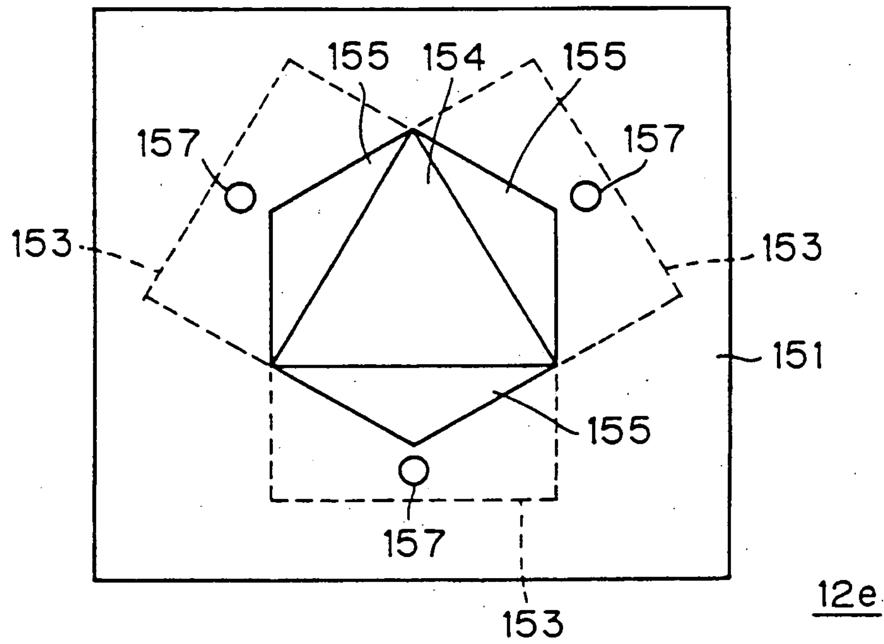


FIG. 19

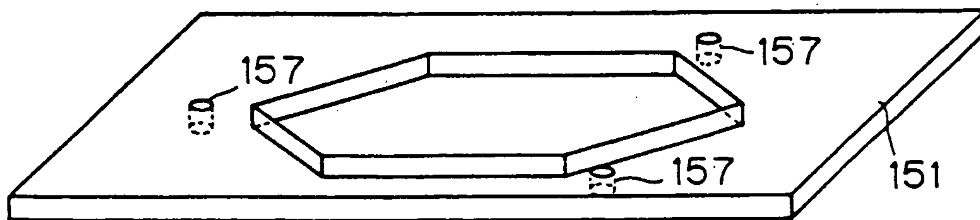


FIG.20

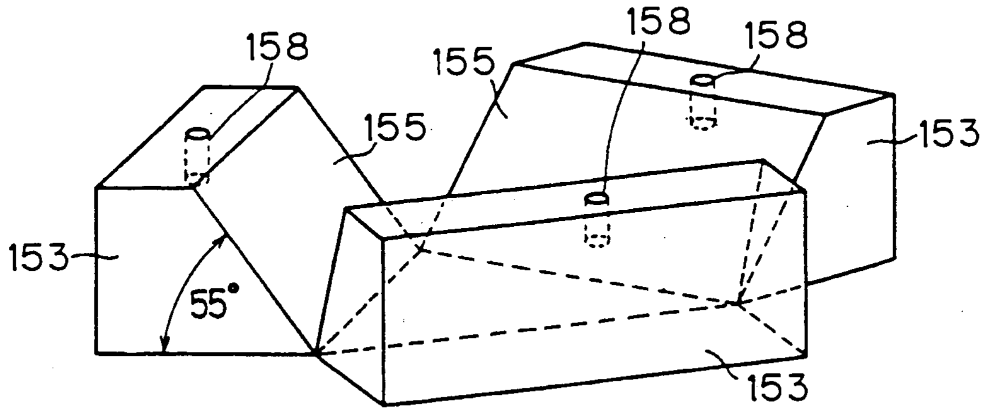


FIG.21

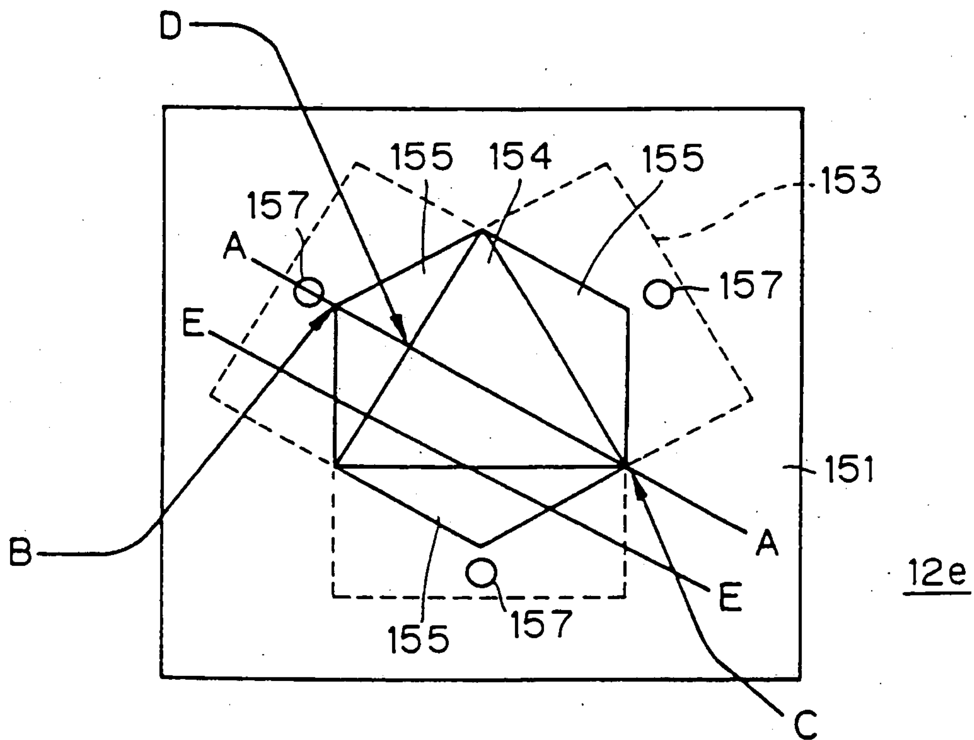
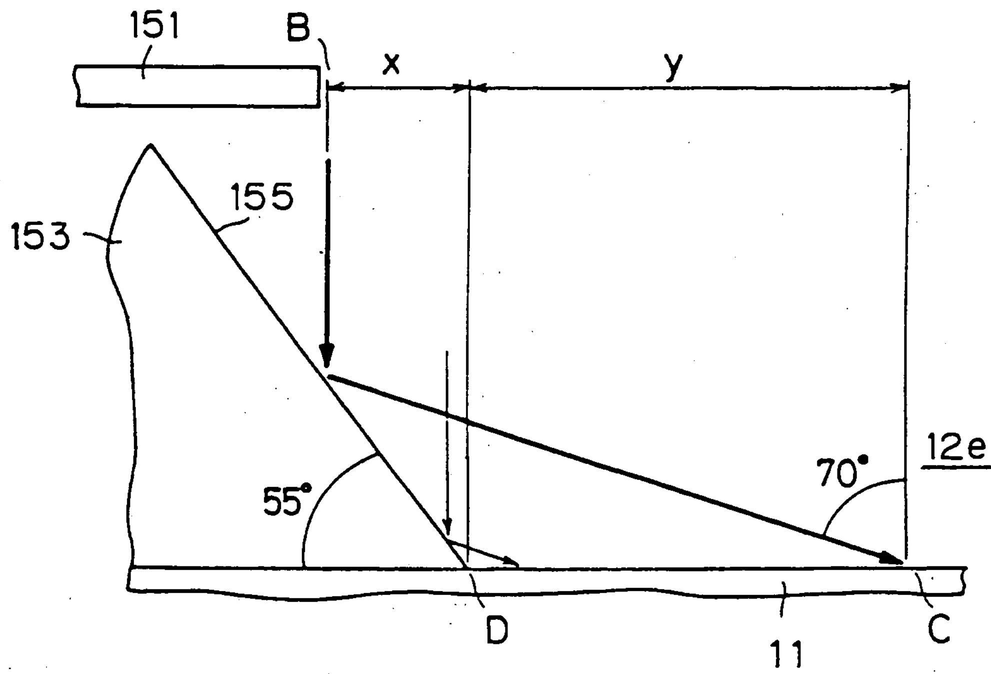
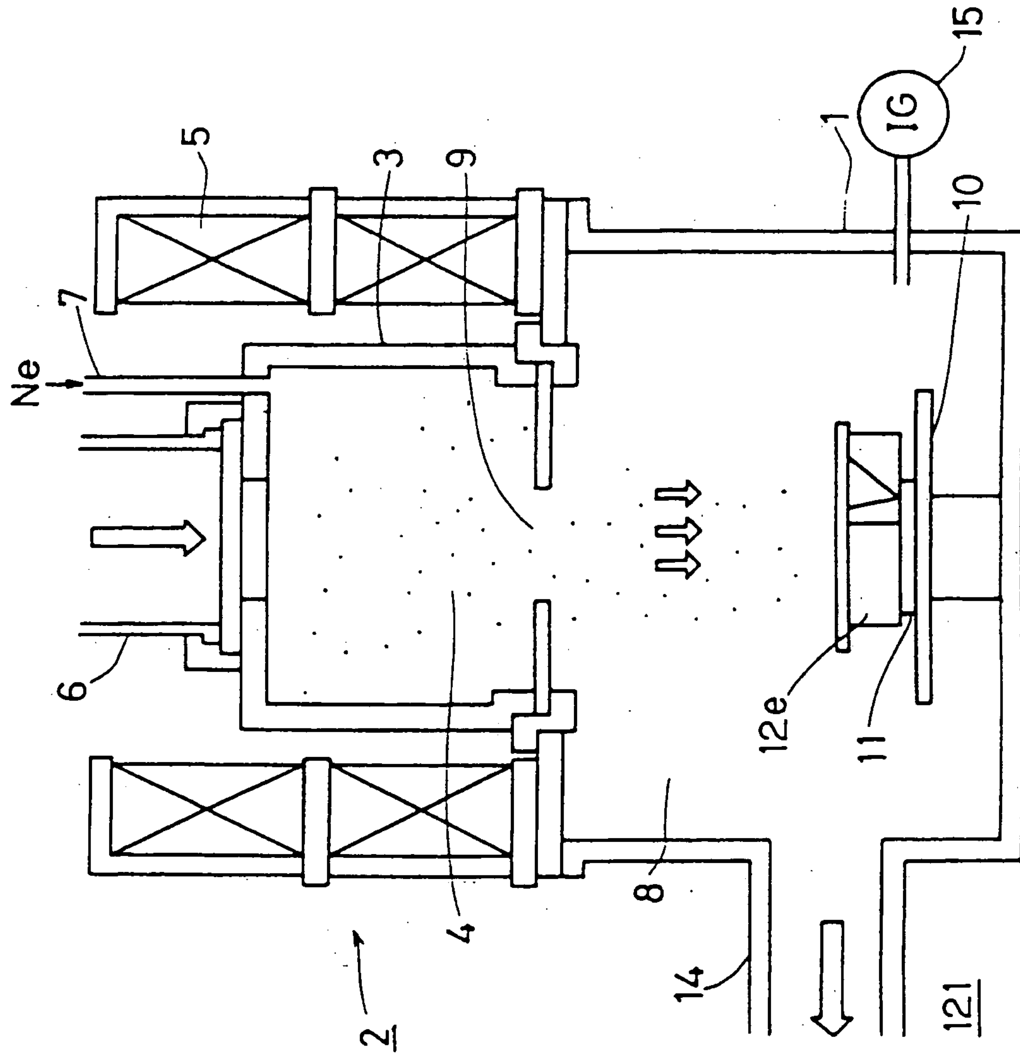


FIG.22




F I G . 2 3
5
3
9
7
Ne
1
IG
15
10
6
12e
11
8
4
14
2
121

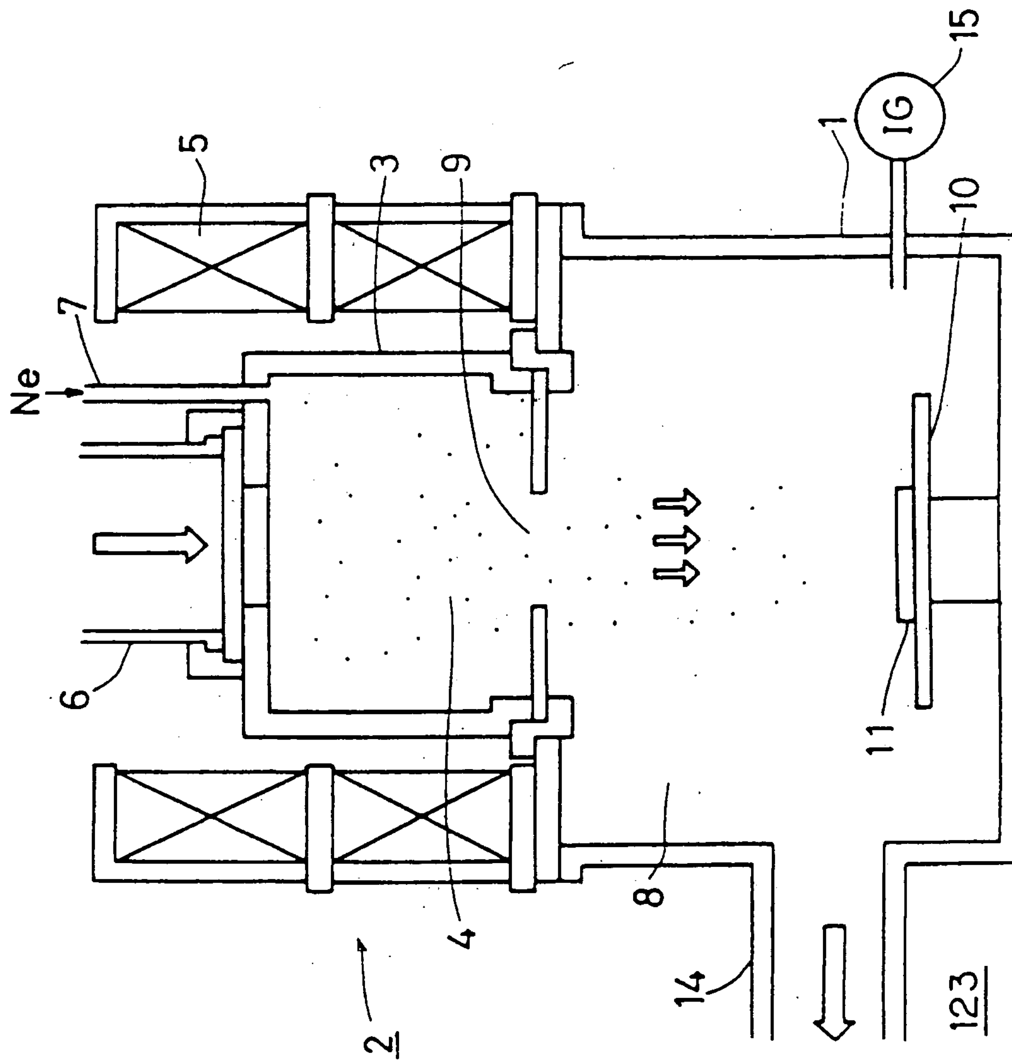


FIG.24
Ne
IG
1
2
3
4
5
6
7
8
9
10
11
14
15
123

FIG. 25

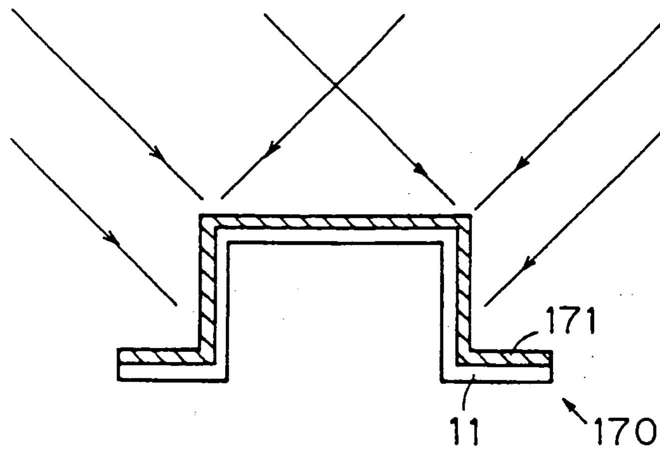


FIG. 26

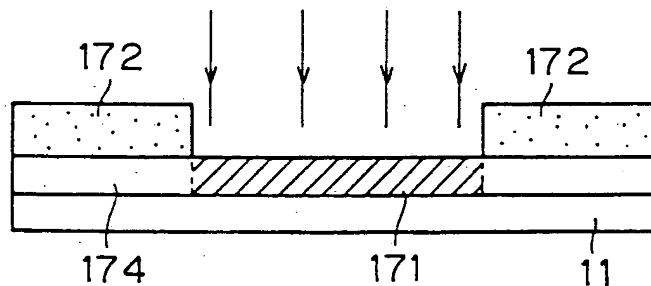
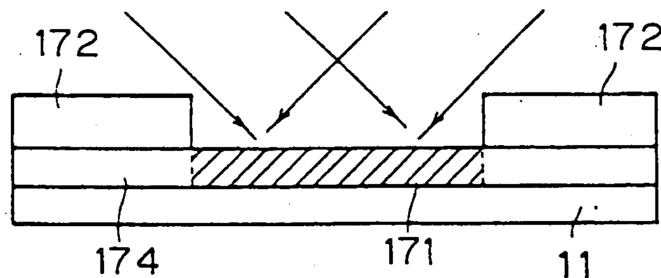


FIG. 27



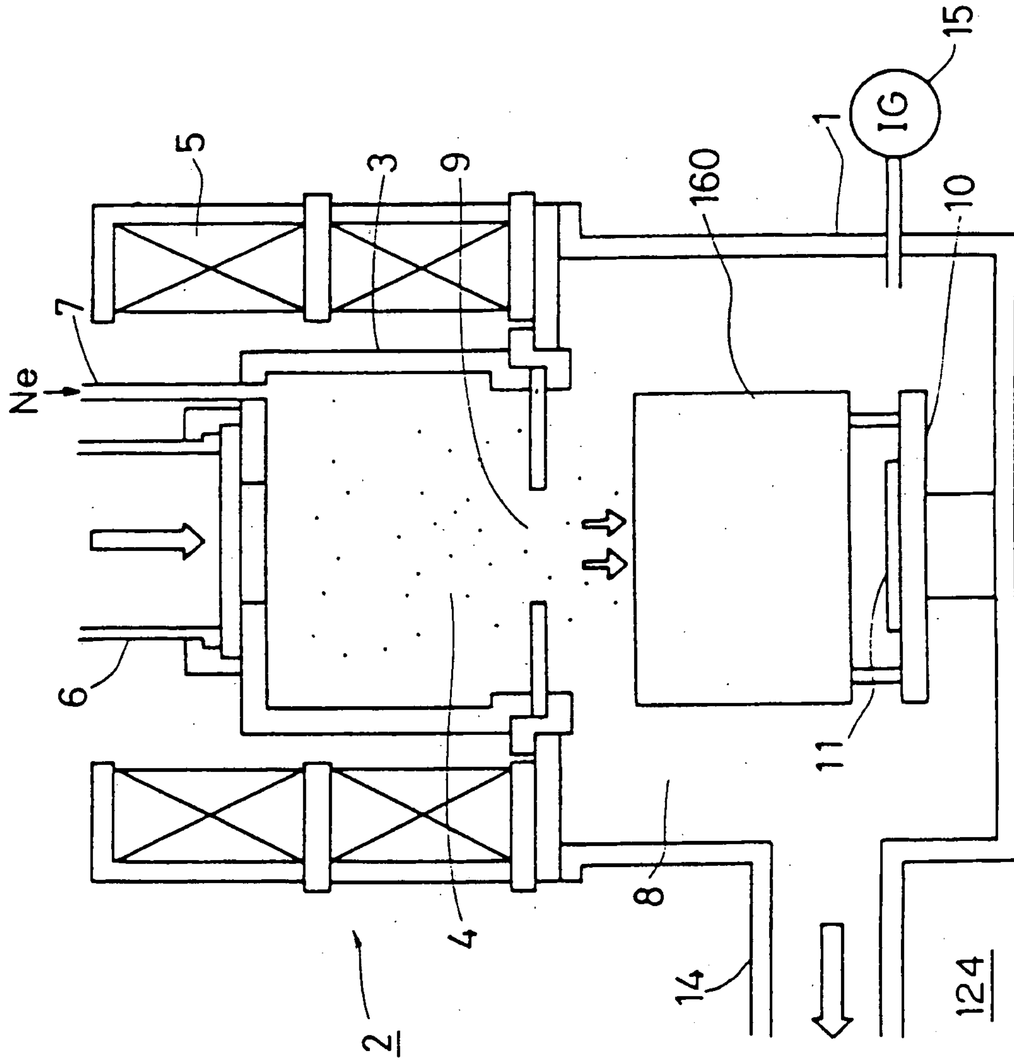

F I G . 28
Ne
7
6
5
3
9
160
1
IG
15
10
11
8
4
2
14
124

FIG.29

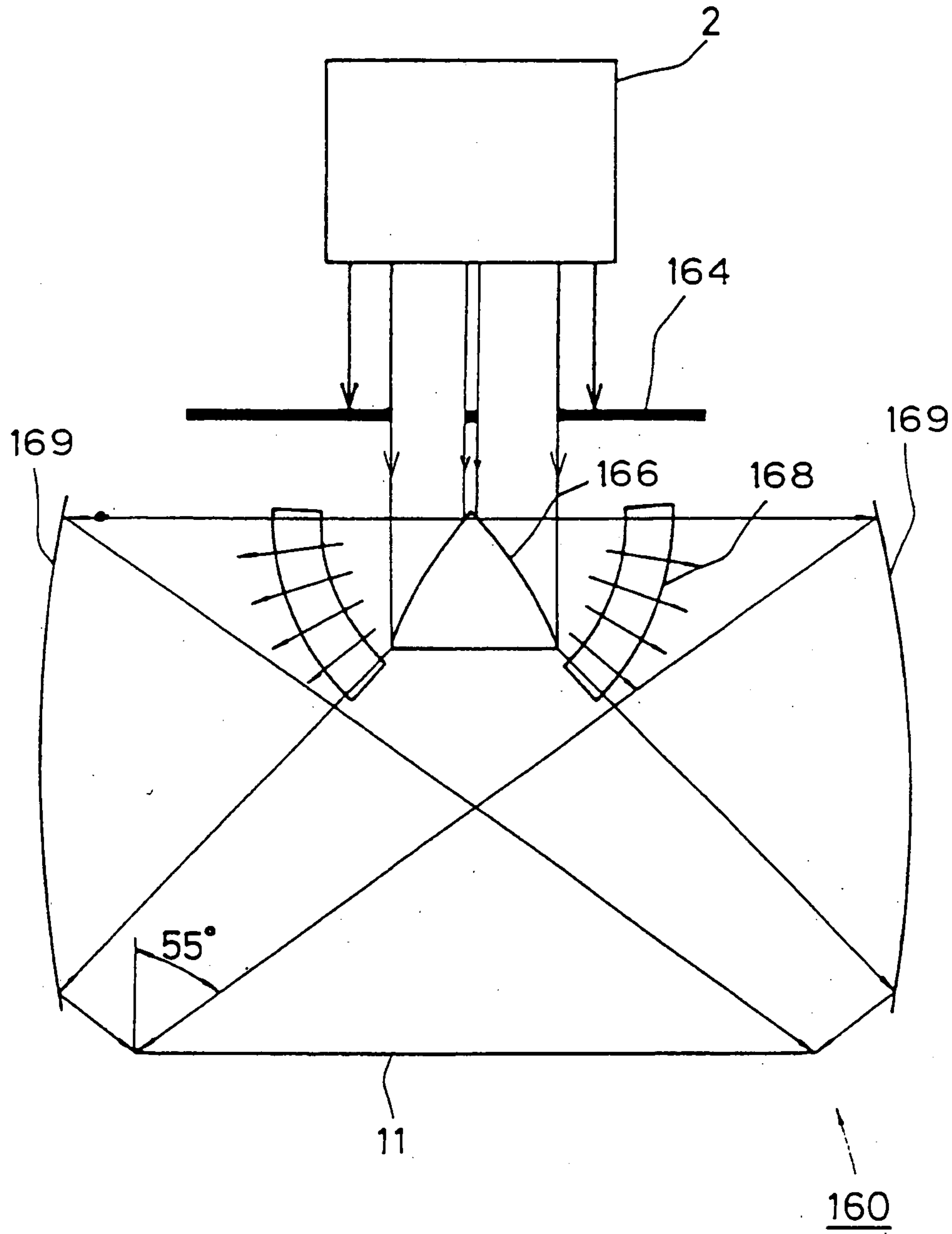
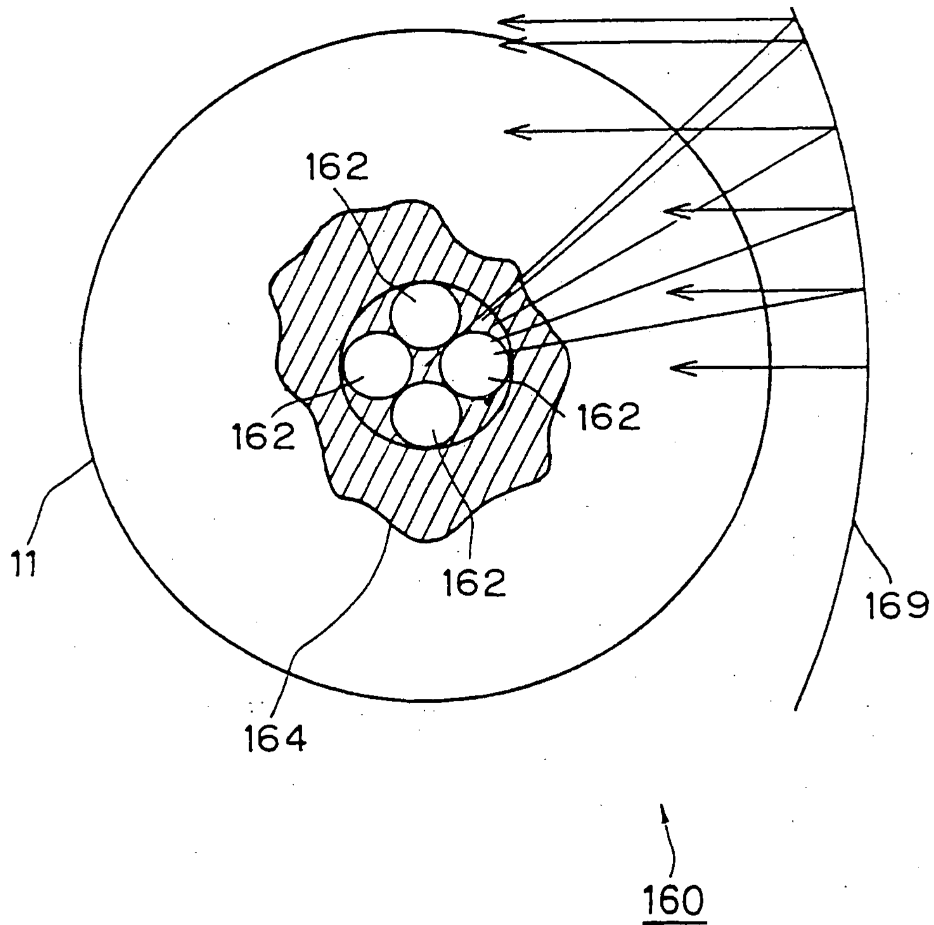


FIG.30



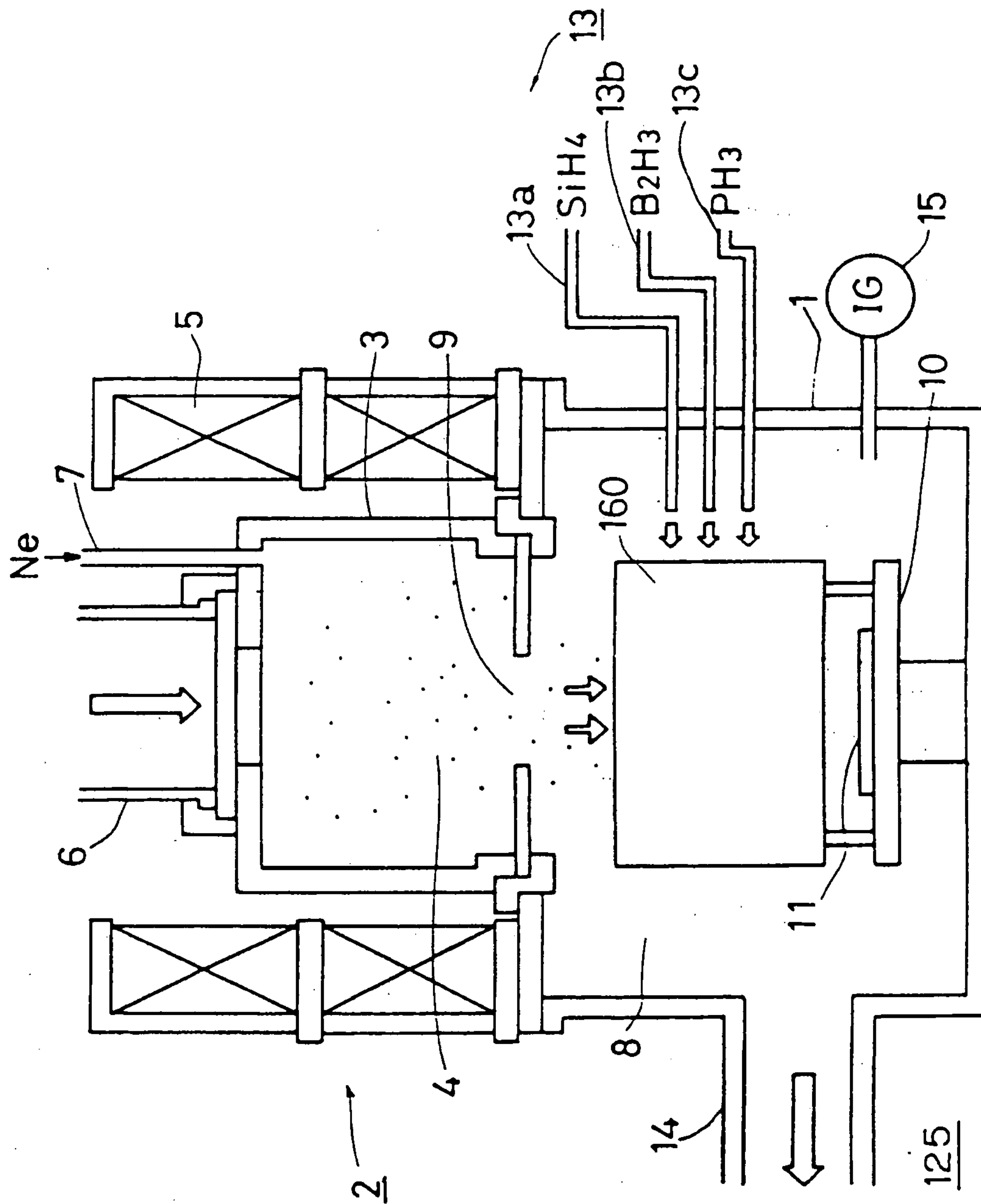


FIG.31

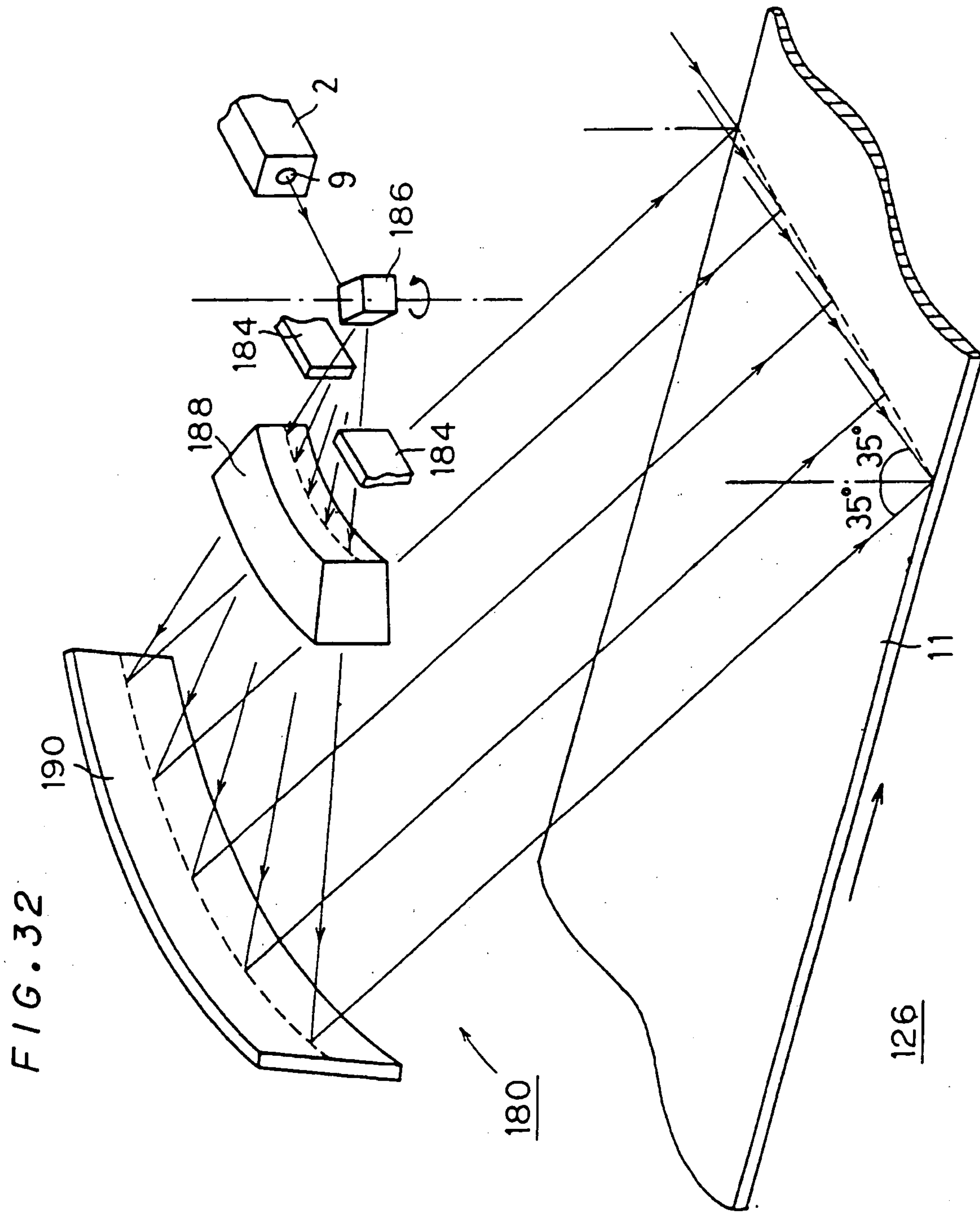


FIG.32
2
9
186
184
184
188
190
35°
35°
11
180
126

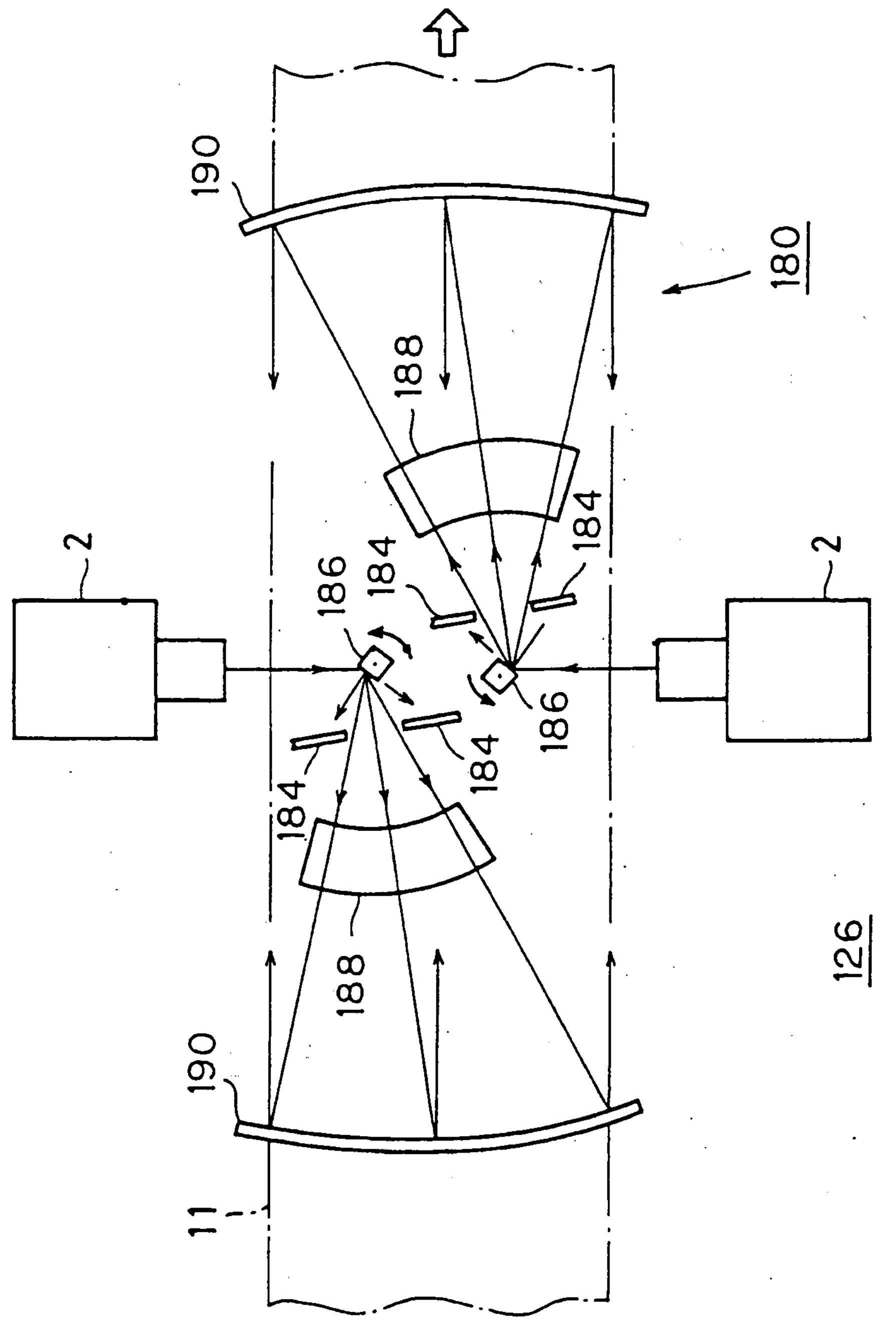


FIG. 33
190
188
184
186
2
180
126
11

FIG.34

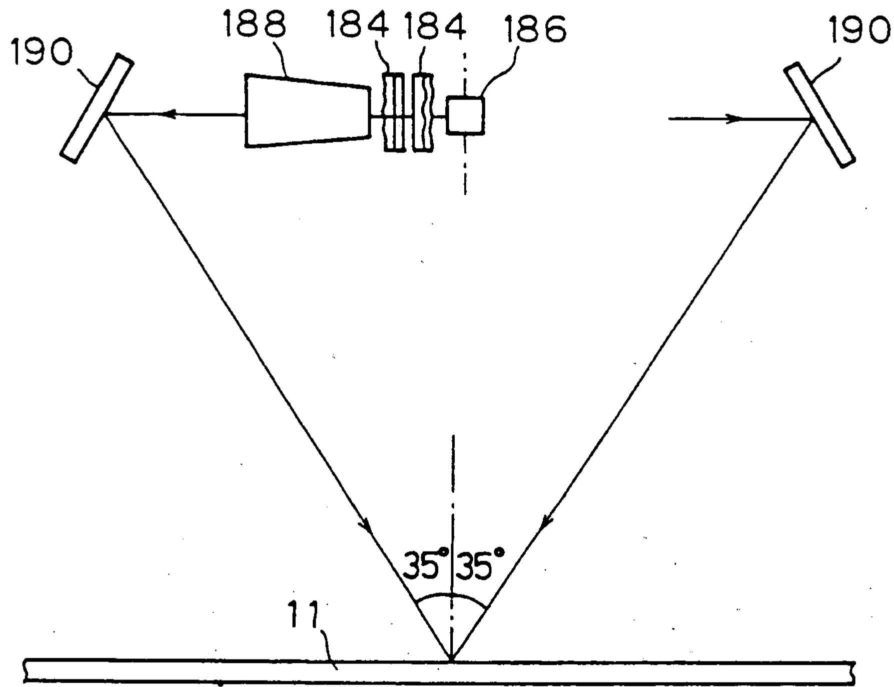
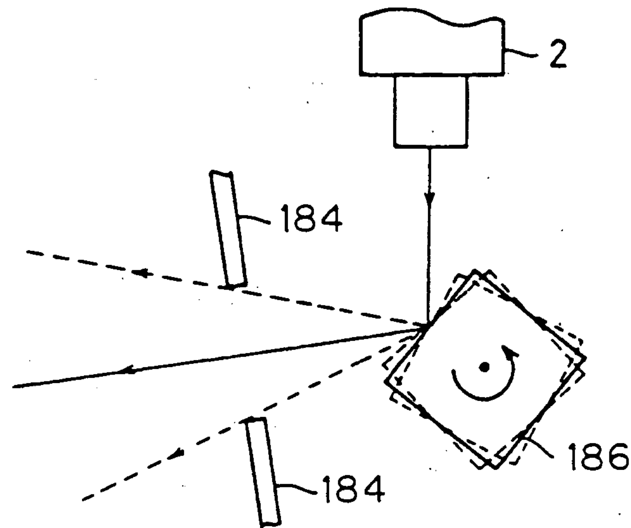


FIG.35



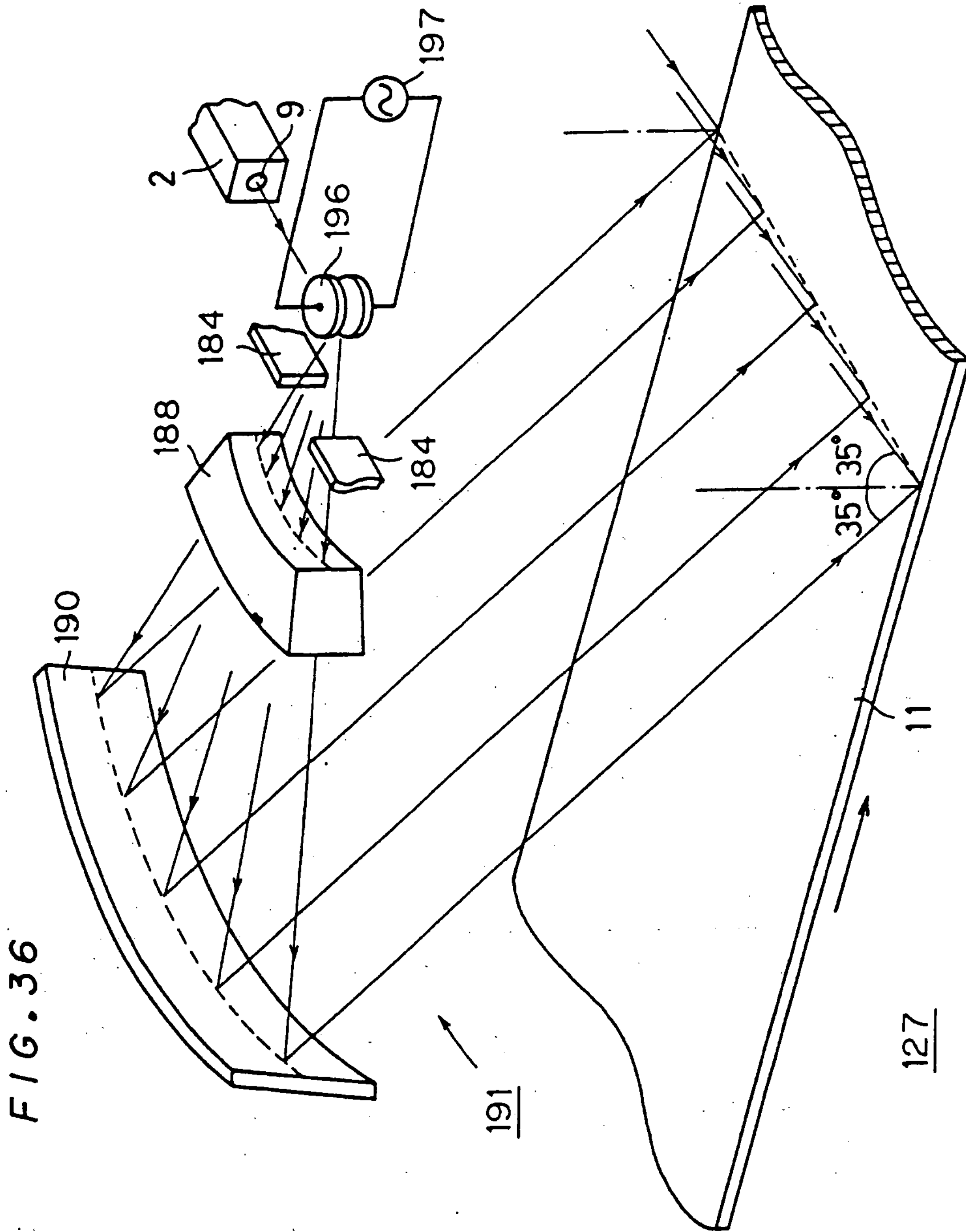


FIG.36
2
9
197
196
184
188
184
190
35°
35°
35°
11
191
127

FIG.37

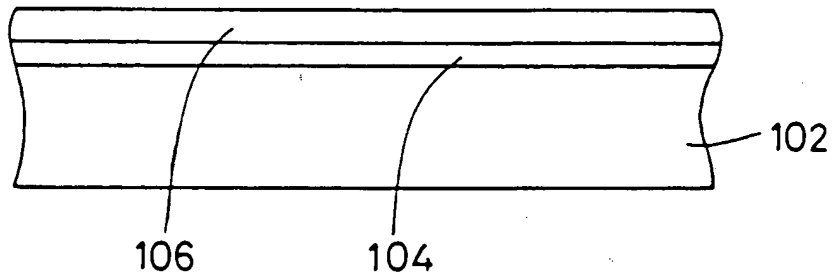


FIG.38

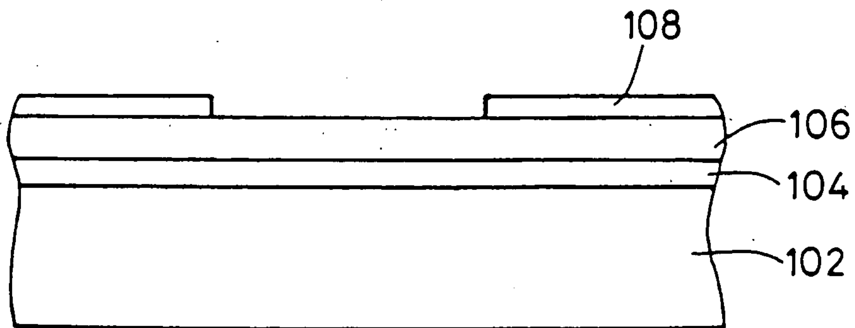


FIG. 39

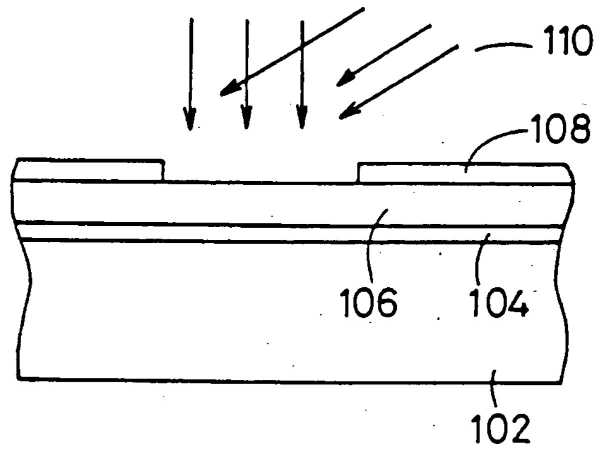


FIG. 40

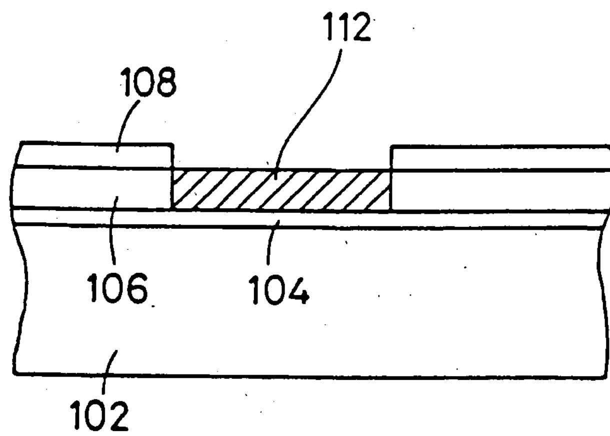


FIG.41

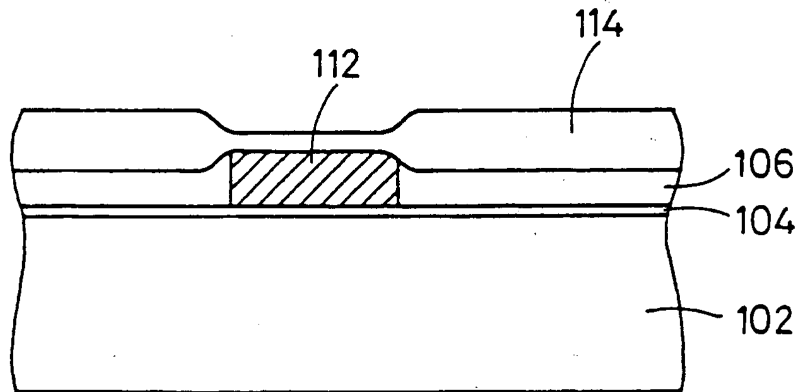


FIG.42

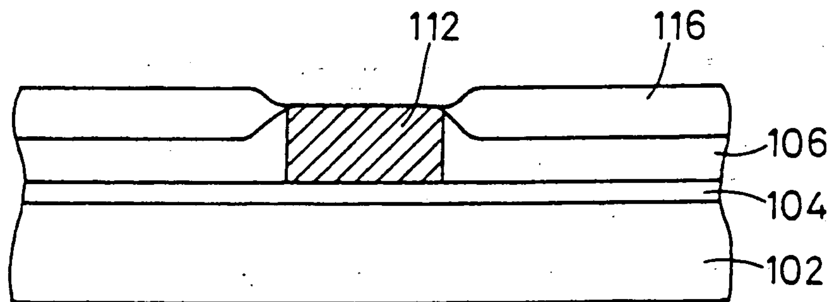


FIG.43

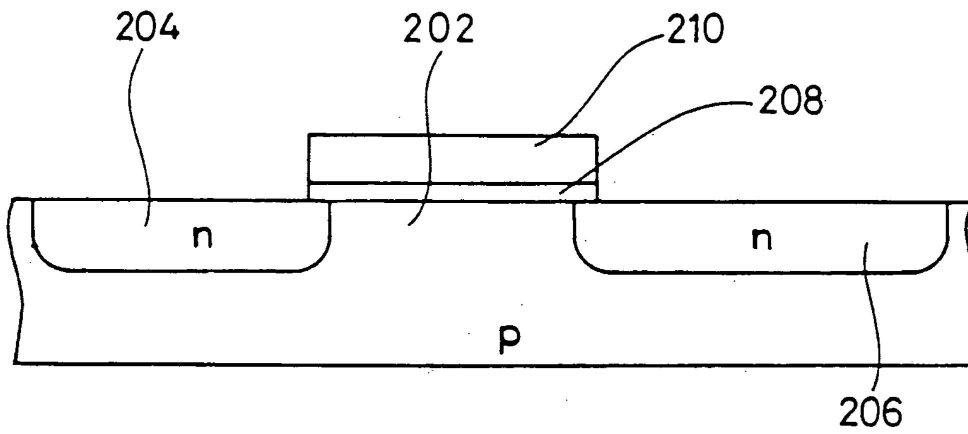


FIG.44

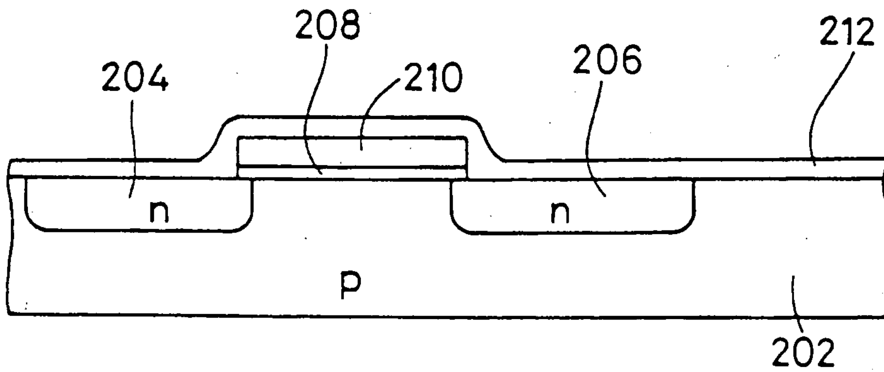


FIG. 45

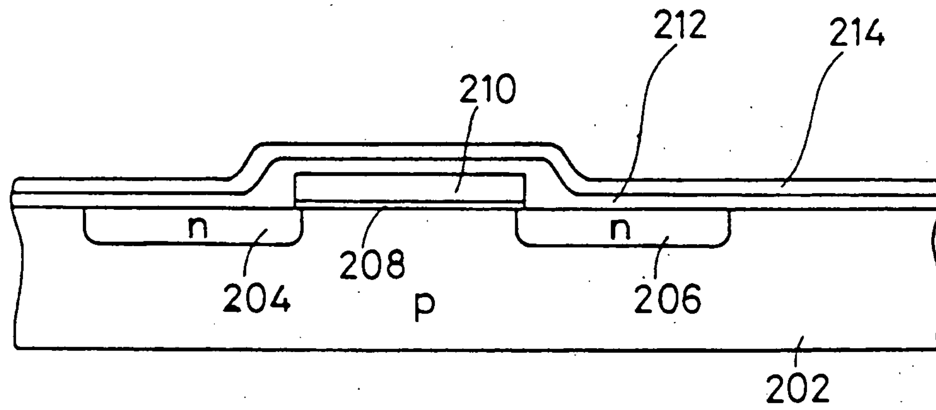
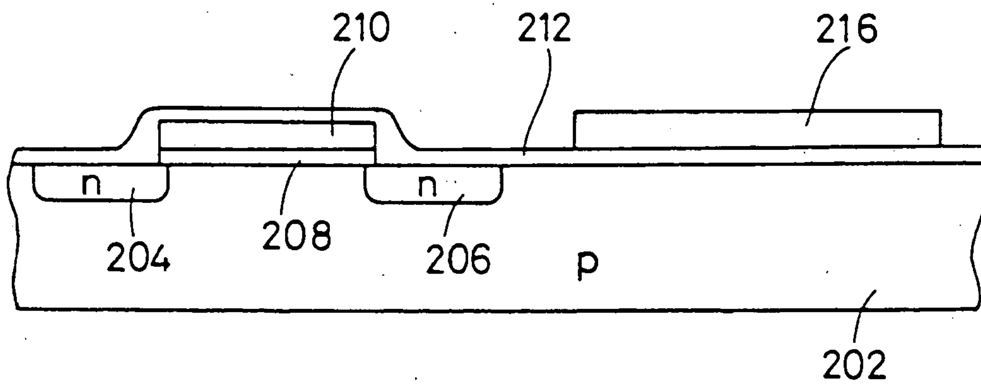


FIG. 46



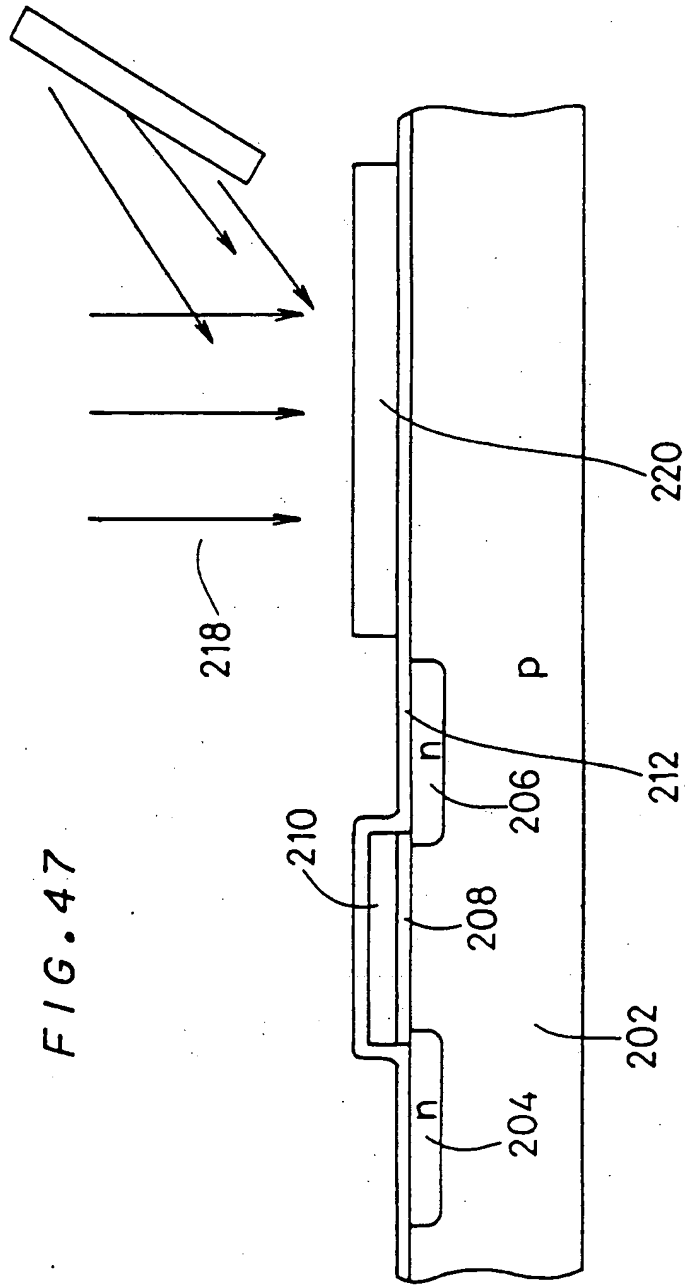


FIG.47

FIG. 48

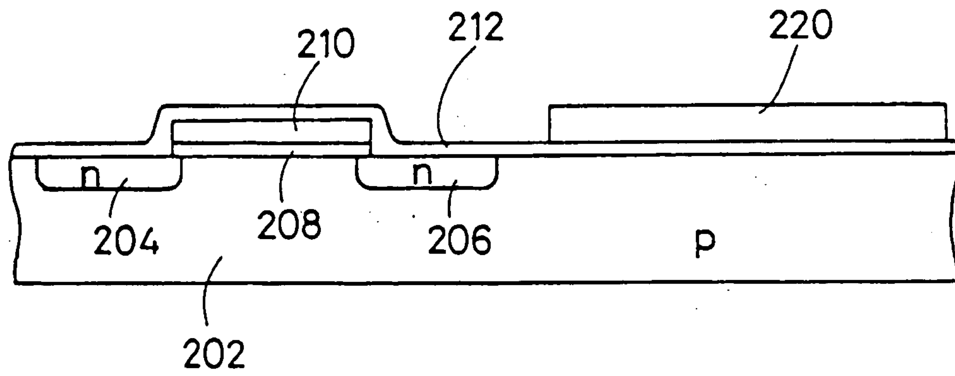


FIG. 49

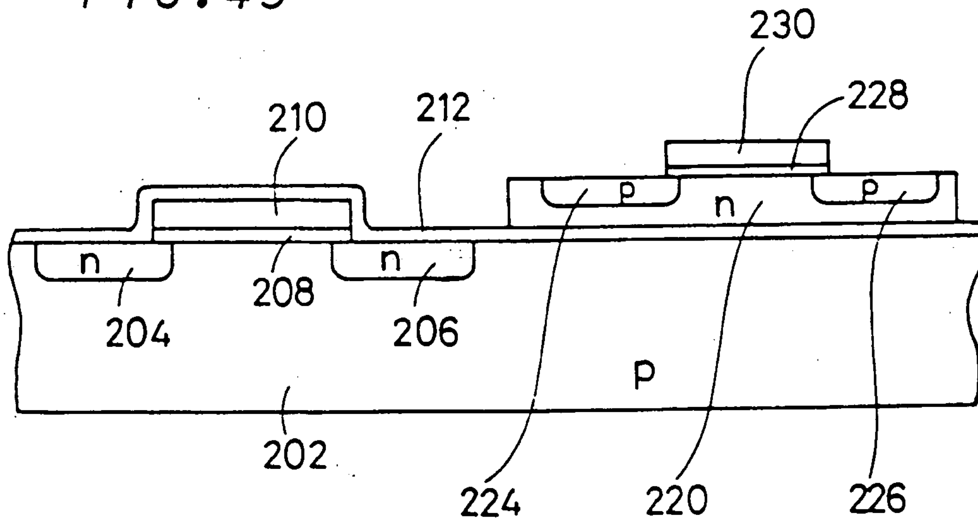


FIG.50

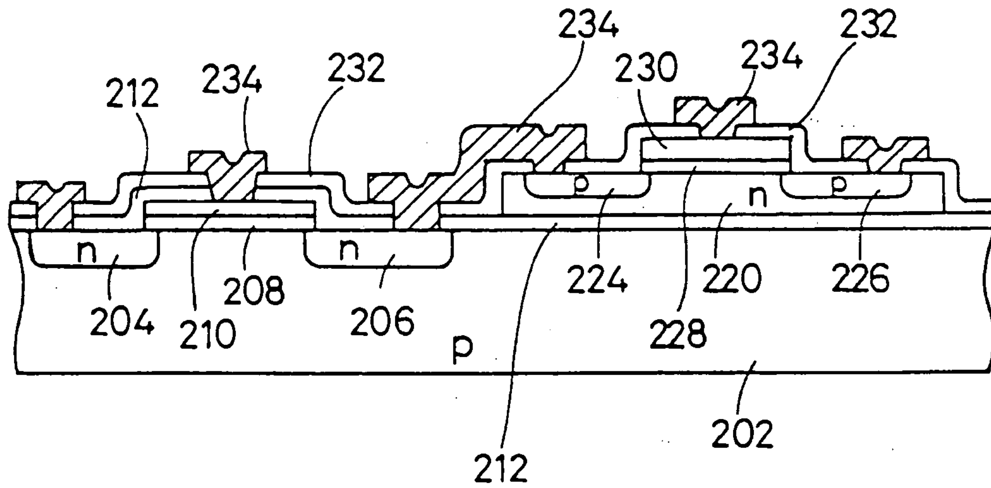


FIG.51

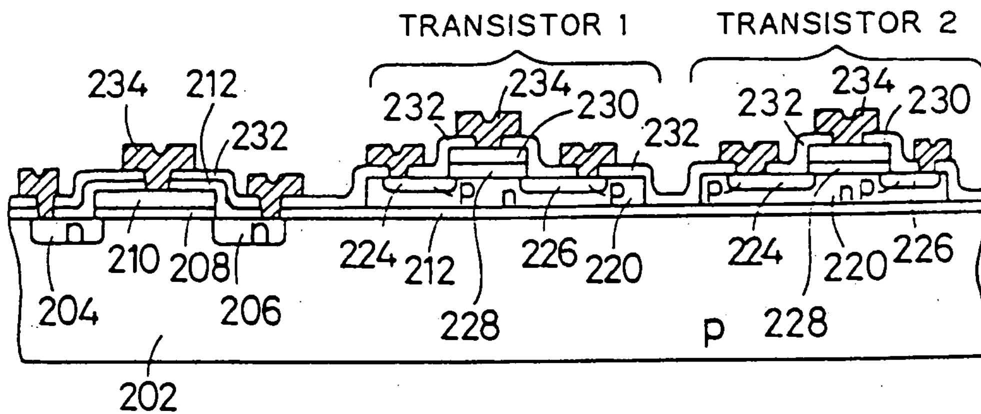


FIG.52

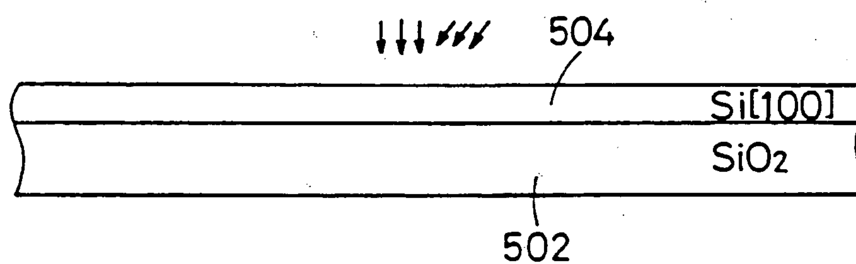


FIG.53

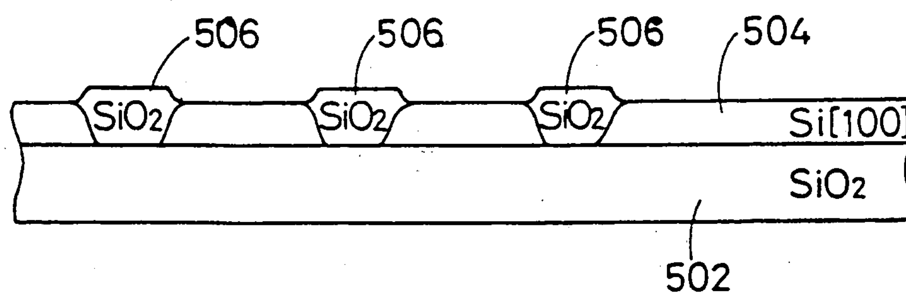


FIG.54

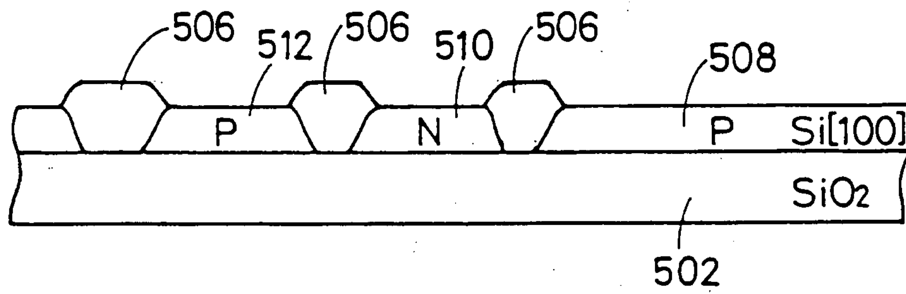


FIG.55

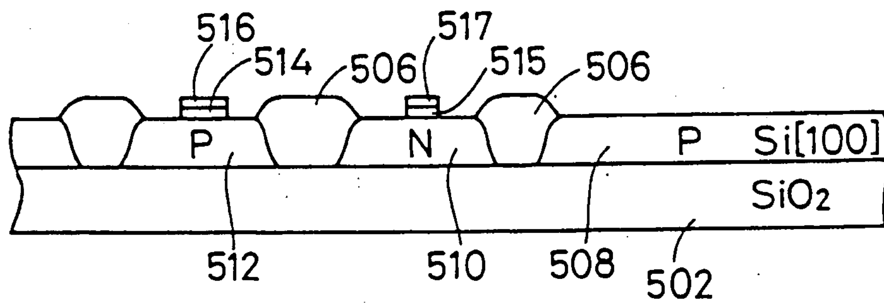


FIG.56

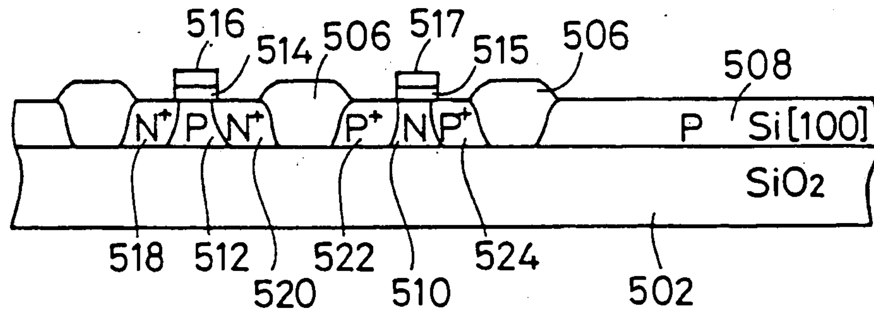
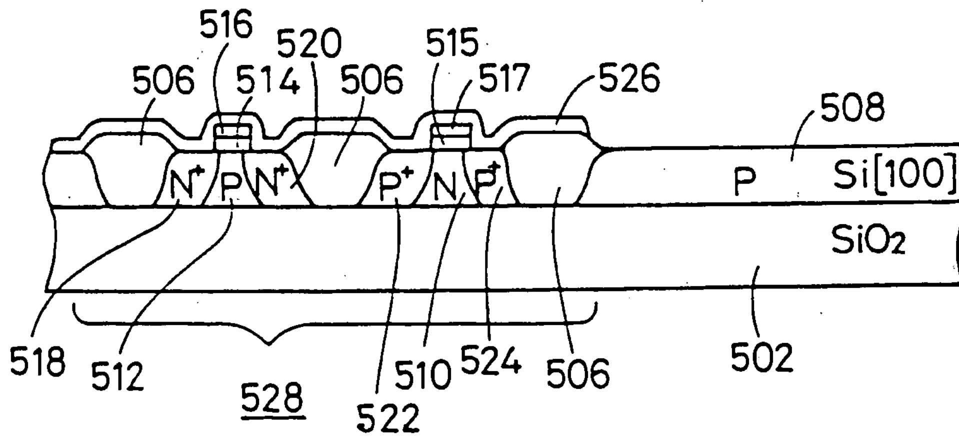
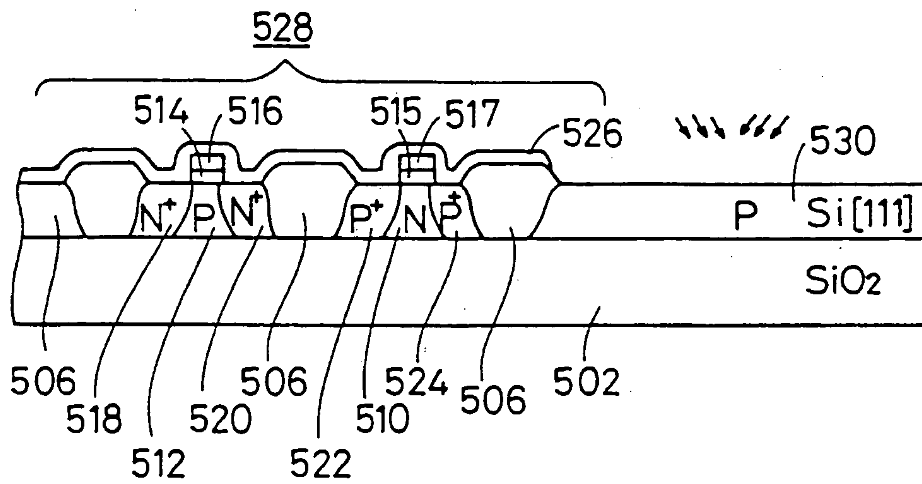


FIG.57



F I G . 58



F I G . 59

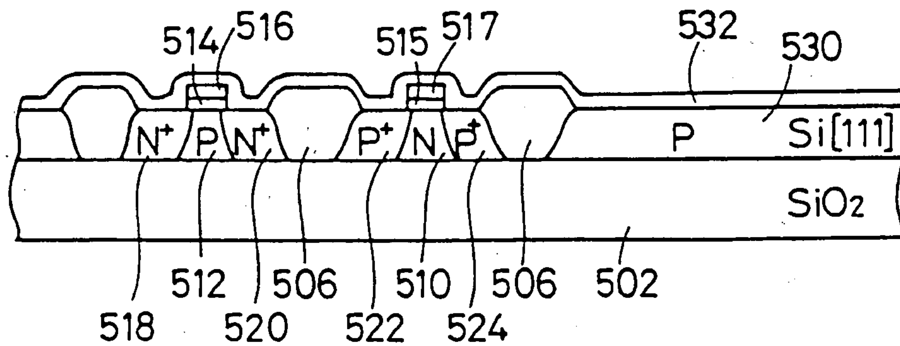


FIG.60

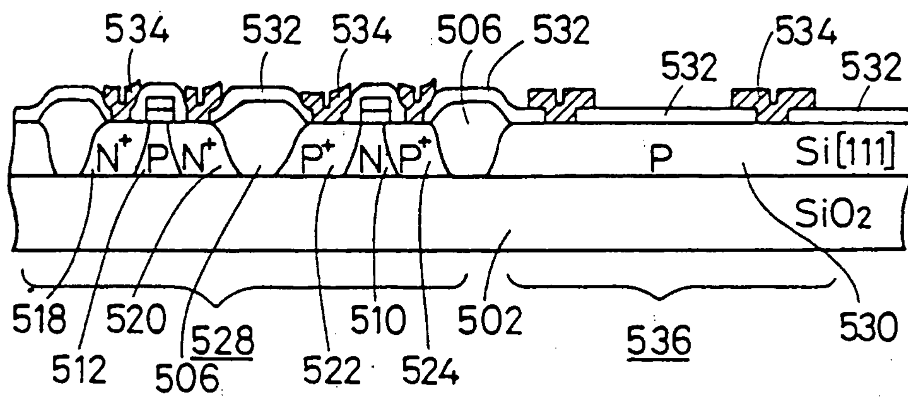


FIG.61

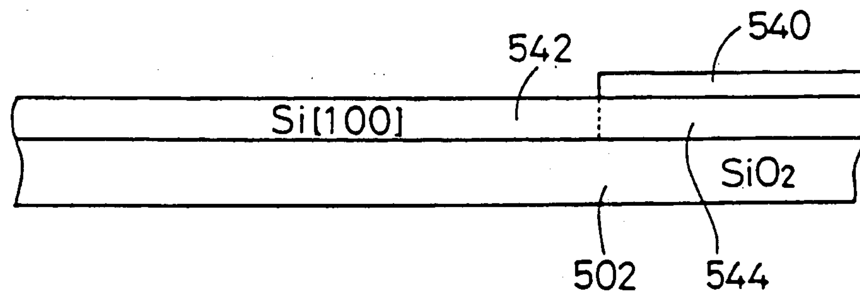


FIG.62

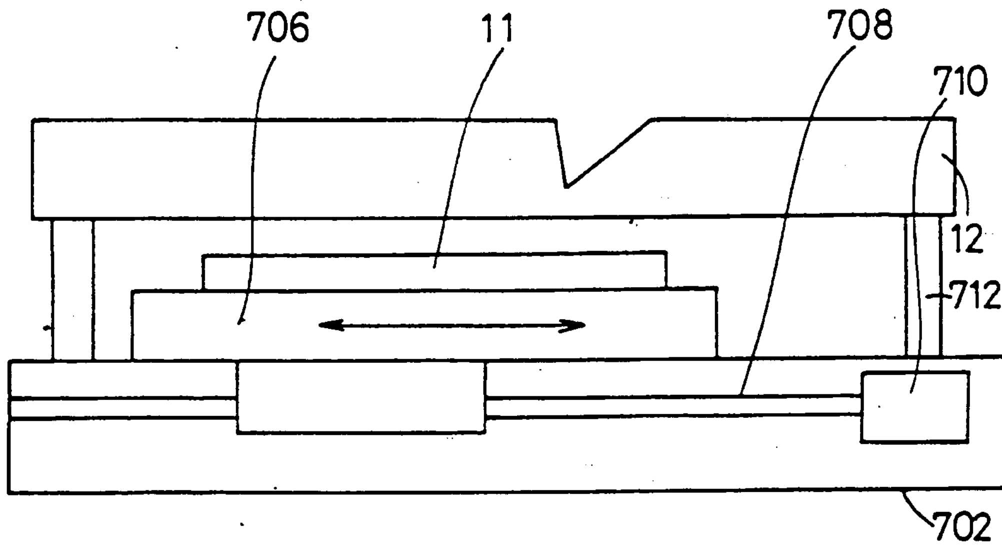
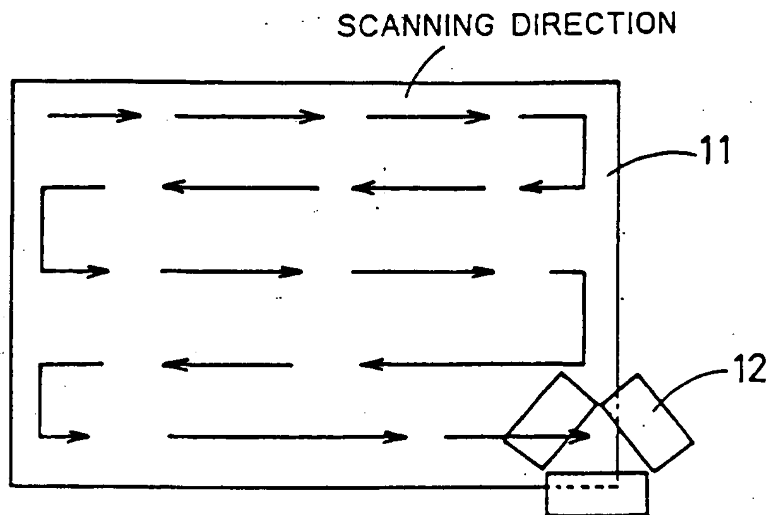


FIG.63



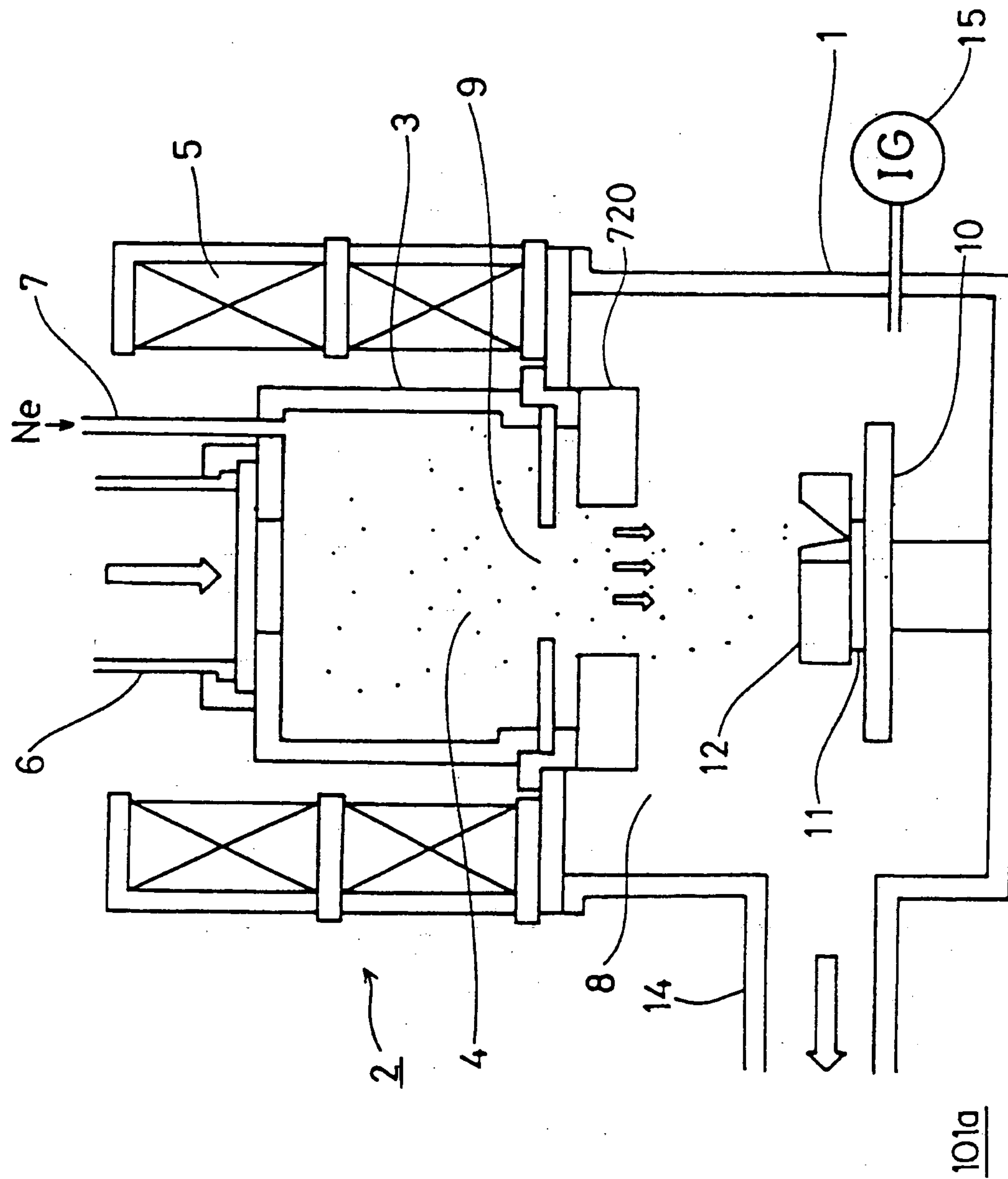


FIG.64
Ne
IG
1
2
3
4
5
6
7
8
9
10
11
12
14
15
720
101a

FIG. 65

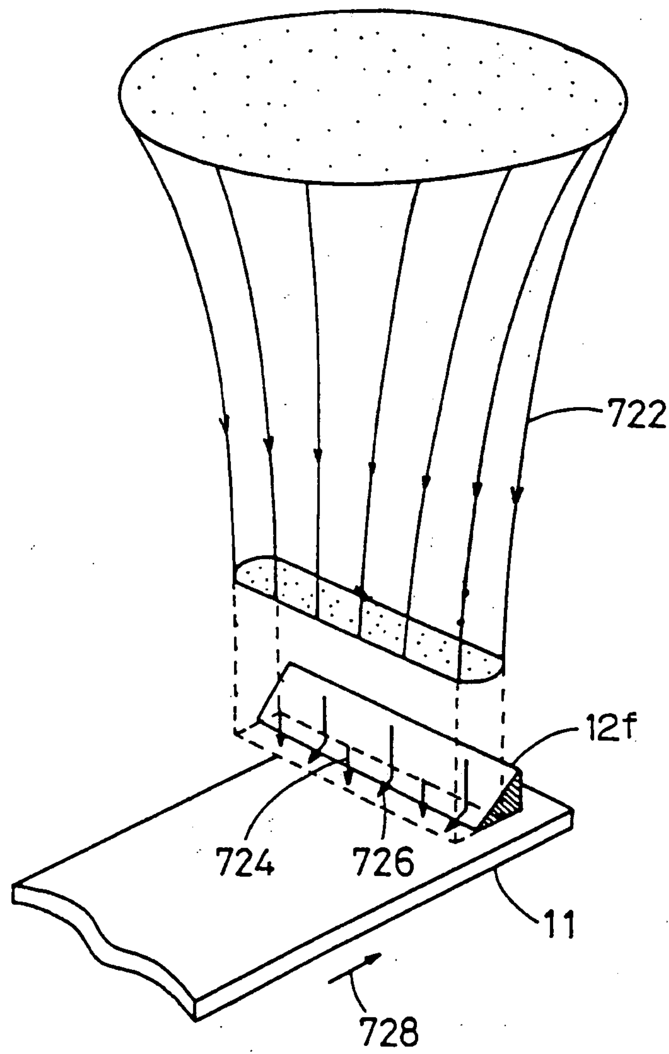


FIG.66

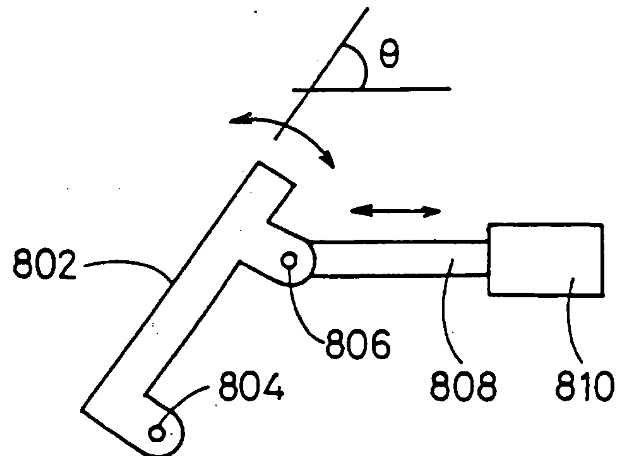


FIG.67

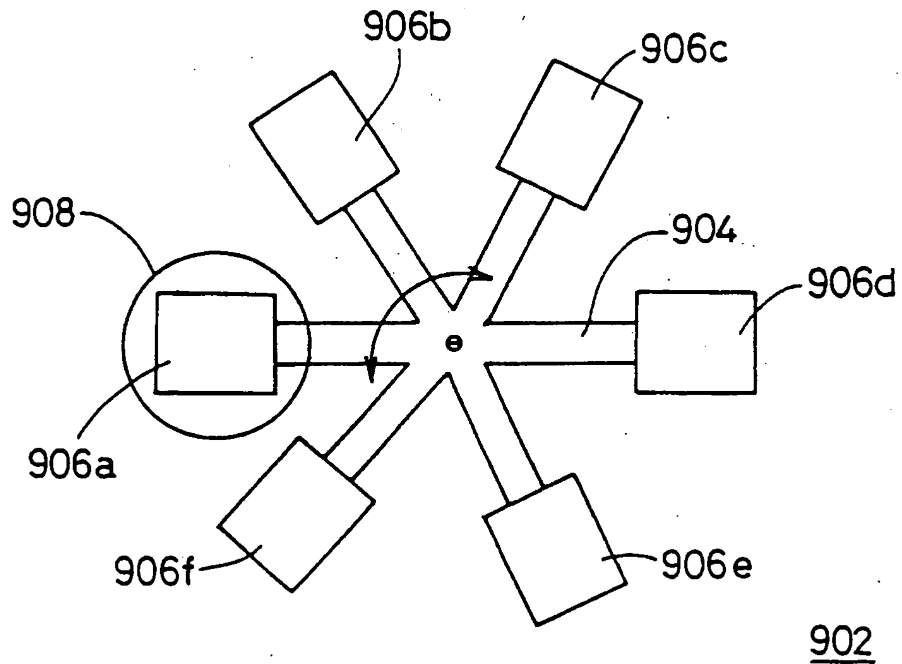


FIG. 68

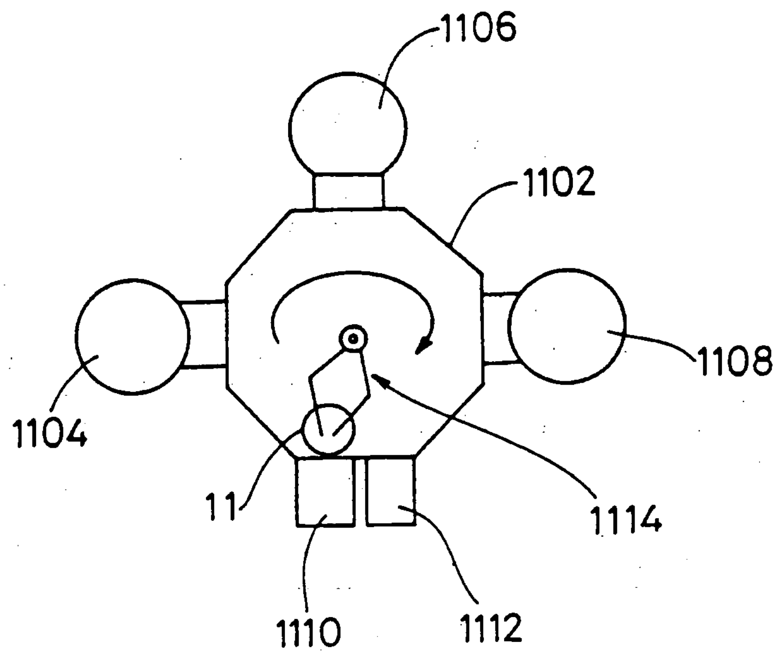
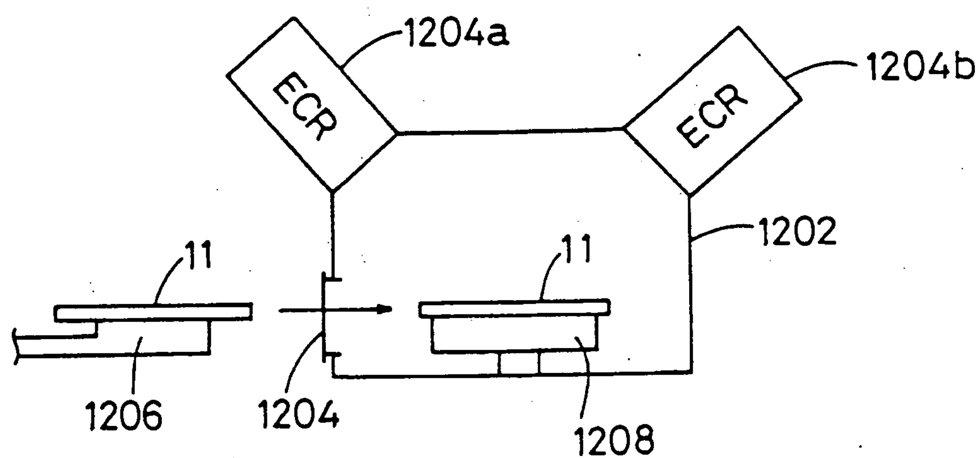


FIG.69



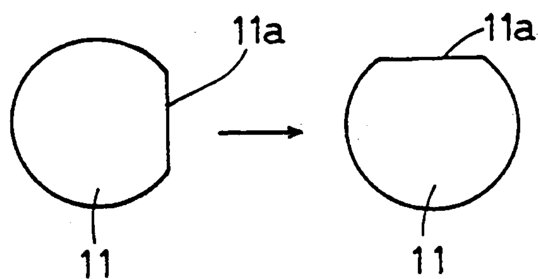


FIG.70

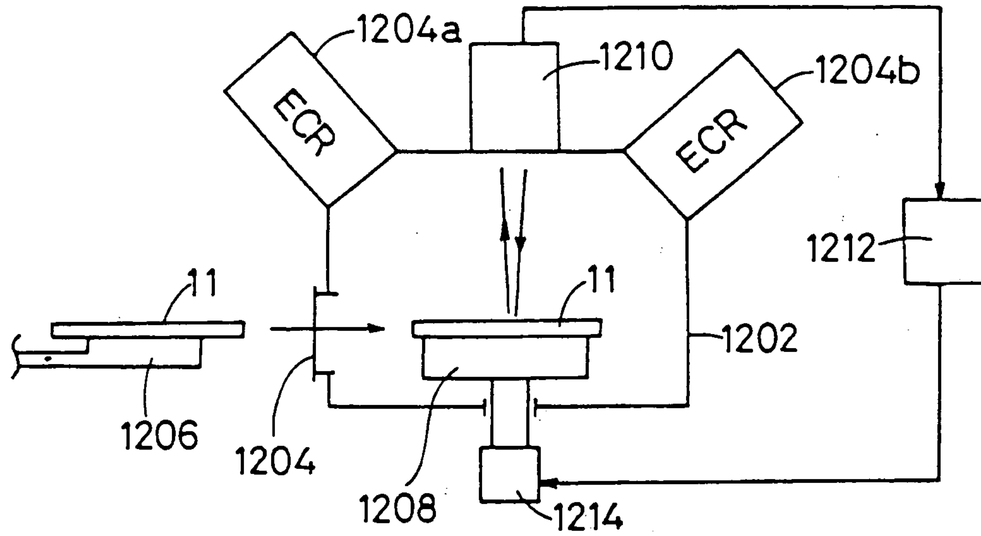


FIG.71

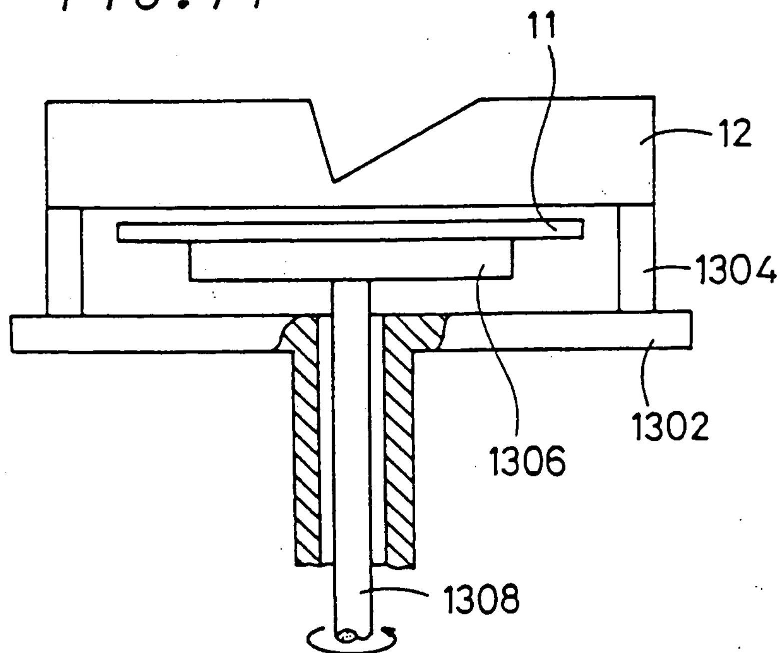


FIG. 72

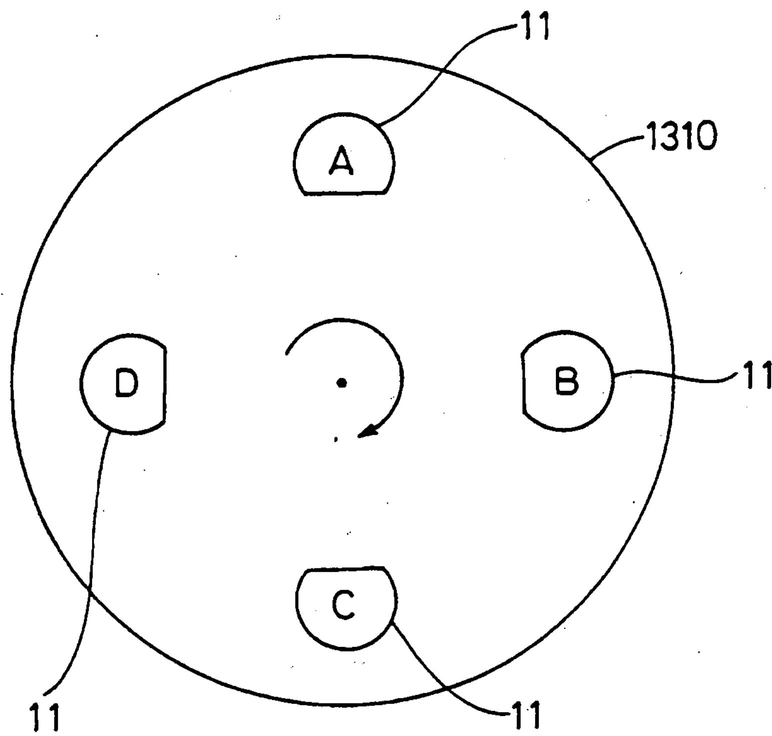


FIG.73

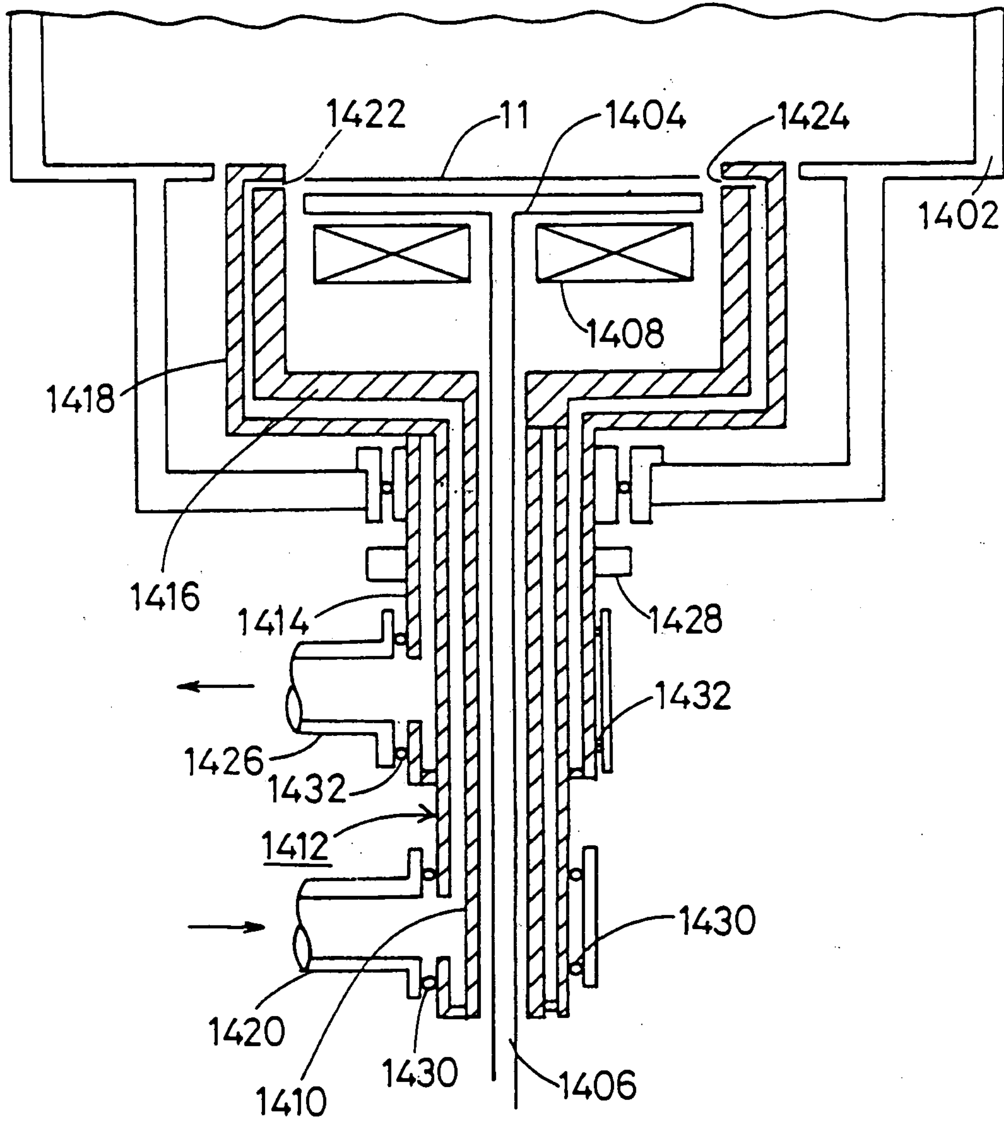


FIG.74

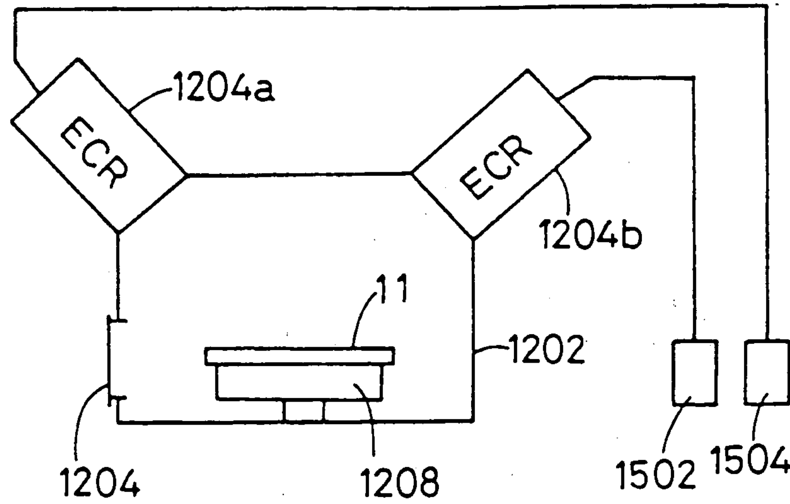


FIG.75

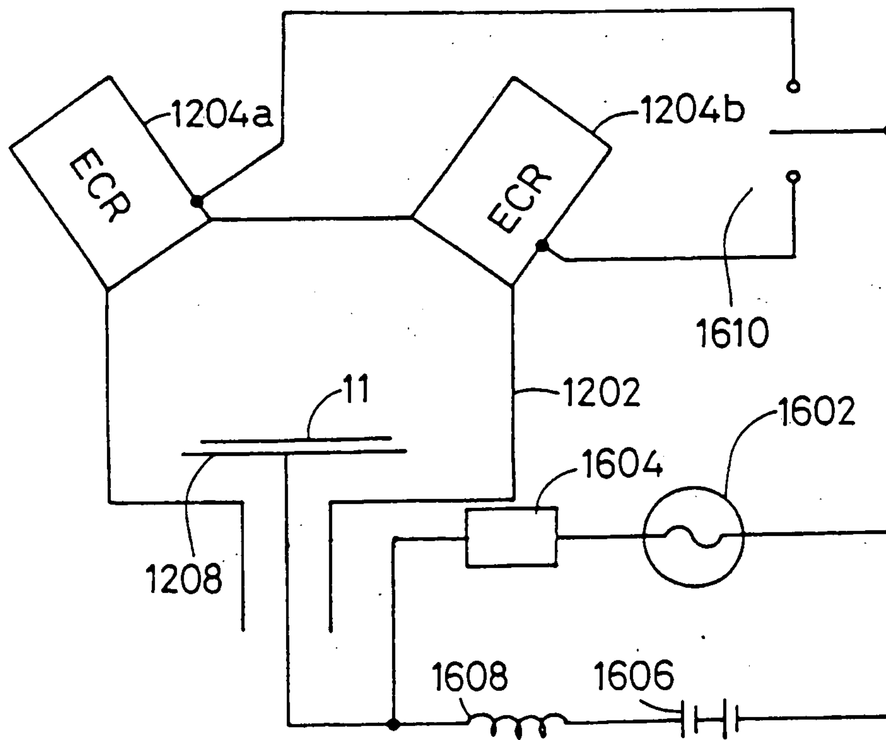
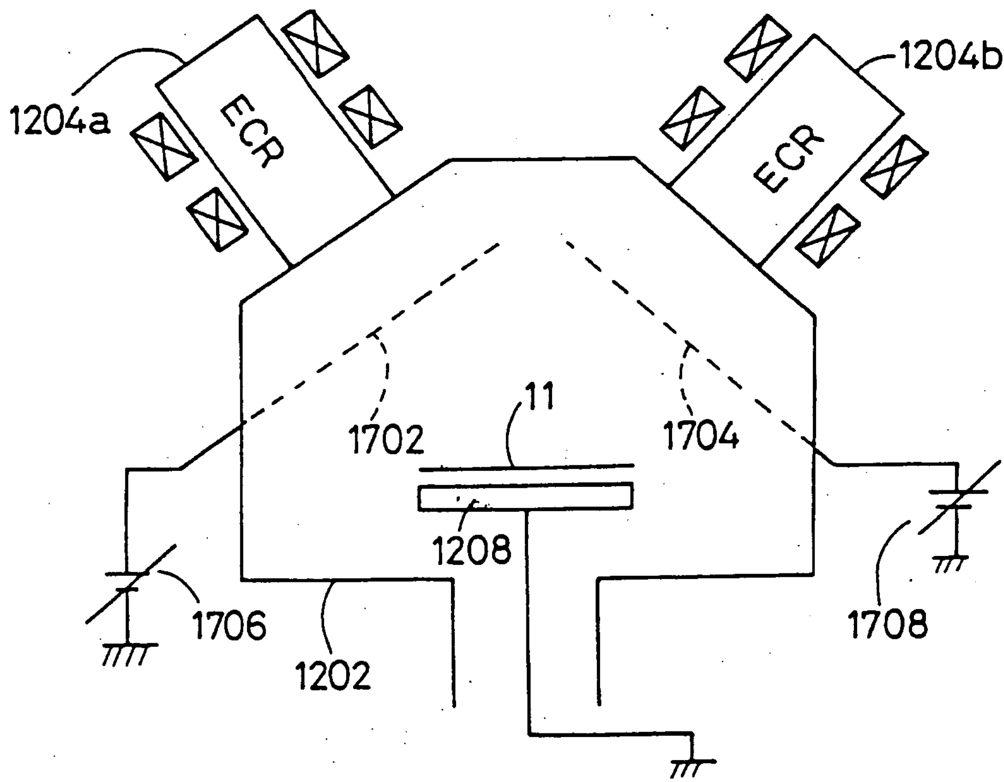


FIG.76



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 652 308 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
17.12.1997 Bulletin 1997/51

(43) Date of publication A2:
10.05.1995 Bulletin 1995/19

(21) Application number: 94116188.7

(22) Date of filing: 13.10.1994

(51) Int. Cl.[6]: C30B 23/02

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: 14.10.1993 JP 281748/93
20.10.1993 JP 285674/93
10.12.1993 JP 341281/93
29.03.1994 JP 58887/94

(71) Applicants:
- NEURALSYSTEMS CORPORATION
Tokyo-to (JP)
- MEGA CHIPS CORPORATION
Suita-shi, Osaka-fu (JP)

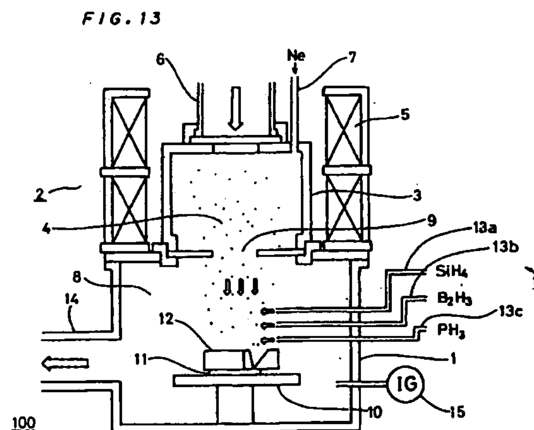
(72) Inventors:
- Asakawa, Toshifumi
Yamato-shi, Kanagawa-ken (JP)
- Shindo, Masahiro,
c/o Mega Chips Corporation
Suita-shi, Osaka-fu (JP)
- Yoshimizu, Toshikazu,
c/o Mega Chips Corporation
Suita-shi, Osaka-fu (JP)
- Ueyama, Sumiyoshi,
c/o Mega Chips Corporation
Suita-shi, Osaka-fu (JP)

(74) Representative:
KUHNEN, WACKER & PARTNER
Alois-Steinecker-Strasse 22
85354 Freising (DE)

(54) Method of and apparatus for forming single-crystalline thin film

(57) In order to form a single-crystalline thin film on a polycrystalline substrate using plasma CVD, a downwardly directed mainly neutral Ne atom current is formed by an ECR ion generator (2). A reaction gas such as silane gas which is supplied from a reaction gas inlet pipe (13) is sprayed onto an SiO_2 substrate (11) by an action of the Ne atom current, so that an amorphous Si thin film is grown on the substrate (11) by a plasma CVD reaction. At the same time, a part of the Ne atom current having high directivity is directly incident upon the substrate (11), while another part thereof is incident upon the substrate (11) after its course is bent by a reflector (12). The reflector (12) is so set that all directions of the parts of the Ne atom current which are incident upon the substrate (11) are perpendicular to densest planes of single-crystalline Si. Therefore, the as-grown amorphous Si is sequentially converted to a single-crystalline Si thin film having crystal axes which are so regulated that the densest planes are oriented perpendicularly to the respective directions of incidence, by an action of the law of Bravais. Thus, a single-crystalline thin film is formed on a polycrystalline substrate.

FIG. 13



EP 0 652 308 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 6188

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 107 (C-341), 22 April 1986 & JP 60 235788 A (HITACHI SEISAKUSHO KK), 22 November 1985, * abstract *	1	C30B23/02
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 543 (C-0783), 30 November 1990 & JP 02 229792 A (NIYUURARU SYST:KK), 12 September 1990, * abstract *	1	
L	PATENT ABSTRACTS OF JAPAN vol. 095, no. 003, 28 April 1995 & JP 06 340500 A (NIYUURARU SYST:KK), 13 December 1994, *DOCUMENT WHICH MAY THROW DOUBT ON THE PRIORITY CLAIMED* * abstract *		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C30B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 October 1997	Gregg, N

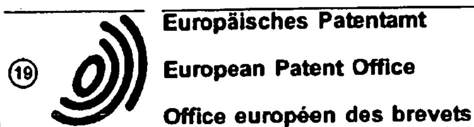
CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

(19) 

(11) Publication number : **0 510 883 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **92303476.3**

(22) Date of filing : **16.04.92**

(51) Int. Cl.[5] : **H01S 3/23,** H01S 3/17, H01S 3/091, G02B 6/12, C03C 15/00

(30) Priority : **25.04.91 US 691262**

(43) Date of publication of application : **28.10.92 Bulletin 92/44**

(84) Designated Contracting States : **DE FR GB**

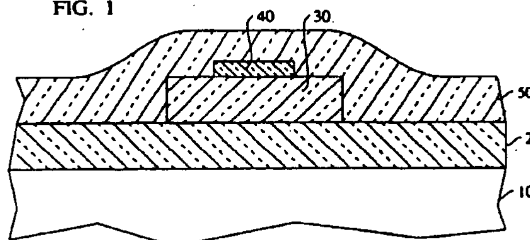
(71) Applicant : **AMERICAN TELEPHONE AND TELEGRAPH COMPANY**
550 Madison Avenue
New York, NY 10022 (US)

(72) Inventor : **Bruce, Allan James**
2351 Seneca Road
Westfield, New Jersey 07090 (US)
Inventor : **Shmulovich, Joseph**
82 Sagamore Drive
Murray Hill, New Jersey 07974 (US)
Inventor : **Wong, Amy**
169-51 25th Avenue
Whitestone, New York 11357 (US)
Inventor : **Wong, Yiu-Huen**
160 Woodland Avenue
Summit, New Jersey 07901 (US)

(74) Representative : **Watts, Christopher Malcolm Kelway, Dr. et al**
AT&T (UK) LTD. AT&T Intellectual Property Division 5 Mornington Road
Woodford Green Essex IG8 OTU (GB)

(54) **Planar optical device.**

(57) An active optical device comprises a glass, waveguiding structure (20,30,40,50) disposed on a substantially planar principal surface of a substrate (10). The structure includes a silica-based, erbium-doped active core (40). The active core has an erbium-to-silicon atomic ratio of at least about 0.01, an absolute erbium concentration of at least about 1.4×10^{20} atoms per cubic centimeter, and a radiative lifetime of the erbium lasing level of at least about 7 milliseconds. Also disclosed is a method for forming an active optical device, including the step of depositing an erbium-doped active core by sputtering.



EP 0 510 883 A2

Field of the Invention

This invention relates to active optical devices, such as amplifiers, that operate by stimulated emission in laser glass, and more particularly to devices made in the form of planar optical waveguides.

Art Background

Optical amplifiers are important in networks for distributing optical signals. Optical fiber amplifiers, made from glass that is doped with rare earth elements such as erbium, are a well-known example. For example, U. S. Patent No. 4,826,288, issued to R. J. Mansfield, et al. on May 2, 1989, describes one method for fabricating optical fibers having cores with relatively high rare earth content. However, for applications such as premises distribution of optical signals, where components need to be relatively small and device integration is desirable, it is advantageous to provide optical amplifiers in the form of planar waveguides deposited on silicon substrates. However, as currently envisioned, such devices are much shorter than optical fiber amplifiers, and the required level of doping is correspondingly much greater.

Attempts to deposit layers of glass at the high doping level appropriate for this purpose have been generally unsatisfactory. For example, a doped soot layer can be formed by chemical vapor deposition, and subsequently sintered to form a glass layer. A method for forming glass waveguides is described, for example, in U.S. Patent No. 4,425,146, issued to T. Izawa, et al., on January 10, 1984. A process forming sintered glasses containing rare earth dopants is described, for example, in U.S. Patent No. 4,826,288, issued to R. J. Mansfield, et al., on May 2, 1989. However, the sintering temperature required, which may be as much as about 1200°C, may promote phase separation and may damage underlying structures on the substrate. As a consequence, it would be advantageous to find a core glass composition that can be doped with erbium and incorporated in a waveguide amplifier without exposing the waveguide structure to potentially damaging, high temperatures.

Summary of the Invention

In a broad sense, the invention is an active optical device in the form of a planar optical waveguiding structure. The device includes an elongate, active glass core which comprises silicon, oxygen, and erbium, the erbium being at least partially in the form of Er^{3+} ions. The active core further comprises an alkali metal or alkaline earth metal in an effective quantity to prevent clustering of erbium atoms. The device further includes a glass cladding, means for coupling signal radiation into and out of the active core, and means for coupling pump radiation into the active core to pump the Er^{3+} ions. The cladding and core are formed such that they overlie a substantially planar principal surface of a substrate. In the active core, the erbium-to-silicon atomic ratio is at least about 0.01, the absolute erbium concentration is at least about 1.4 x 10^{20} atoms per cubic centimeter, and the erbium lasing level has a radiative lifetime of at least about 7 ms.

In another aspect, the invention is a method for forming an optical device on a silicon substrate having a substantially planar principal surface. The method includes, first, the step of forming a first layer of vitreous silicon dioxide on the principal surface. After that, a second layer of silica-based glass is deposited over the first layer by sputtering a target of silica-based glass containing sodium and erbium such that the second layer has a higher refractive index than the first layer. Significantly, the target composition is selected such that the core has an erbium-to-silicon atomic ratio of at least about 0.01 and a sodium-to-silicon atomic ratio in the approximate range 0.2 - 0.6, the absolute erbium concentration is at least about 1.4 x 10^{20} atoms per cubic centimeter, and the target composition is further selected such that a lasing level is associated with the erbium in the core, the lasing level having a radiative lifetime of at least about 7 ms. After the sputtering step, the second layer is annealed such that it is stabilized. A portion of the second layer is subsequently removed by etching, such that an elongate core is formed. After that, a third layer of phosphosilicate glass is deposited over the core such that the third layer has a smaller refractive index than the core.

Brief Description of the Drawings

FIG. 1 is a schematic, sectional end view of the inventive waveguiding structure, according to one embodiment.

FIG. 2 is a schematic, top view of the waveguiding structure of FIG. 1.

FIG. 3 is a schematic, sectional side view of the inventive waveguiding structure, according to an alternative embodiment.

FIG. 4 is a flowchart of the steps in an exemplary process for manufacturing the inventive waveguiding structure.

Detailed Description Of A Preferred Embodiment

The inventive optical amplifier is to be used to amplify optical signals by stimulated emission from Er^{3+} ions. As is well known in the art, the appropriate signal wavelength is about 1.55 μm. Various wavelengths of pump radiation are readily used to excite the Er^{3+} ions, as is described in greater detail below.

With reference to FIG. 1, a currently preferred embodiment of the inventive optical amplifier includes a silicon substrate 10, a lower cladding layer 20 overly-

BNSDOCID: <EP___0510883A2_I_>

ing the substrate, a passive core 30 overlying the lower cladding layer, an active core 40 overlying the passive core, and an upper cladding layer 50 overlying the active and passive cores and the lower cladding layer. In alternative embodiments of the invention, the passive core is omitted.

As is apparent in the figure, the two cores are substantially surrounded by the two cladding layers. The refractive indices of the upper and lower cladding layers are not necessarily equal to each other. However, they should both be smaller than the refractive index of the active core, and also smaller than the refractive index of the passive core. As a consequence of the refractive index differences, electromagnetic radiation of the signal wavelength and at least one pump wavelength is guided in both the active core and the passive core. (In general, the waveguiding properties of the active and passive cores are not distinctly separable. Thus, for example, radiation guided in the active core is not guided exclusively therein, but by an effective core to which the underlying passive core also contributes.)

Preferably, the active and passive cores function as single-mode waveguides, at least with respect to the signal wavelength. Thus, signal radiation is preferably guided exclusively in the fundamental mode. However, it should be noted that alternative embodiments are envisioned in which both the active and the passive cores function as multimode waveguides with respect to both the signal and pump radiation.

The refractive index of the active core is preferably somewhat greater than the refractive index of the passive core, in order to capture the greatest possible amount of light in the active core. (For example, active and passive cores are readily made having respective refractive indices of 1.50 and 1.45.) As a consequence of such refractive index difference, electromagnetic waves that are guided in the active core will have narrower mode profiles than waves guided in the passive core. Accordingly, it is advantageous in such situations to make the active core narrower than the passive core. Such a relatively narrow active core 40 is depicted in FIG. 1.

Lower cladding layer 20 is formed on an appropriately prepared, substantially planar principal surface of substrate 10, which is exemplarily a silicon wafer. Layer 20 is exemplarily a HIPOX layer; i.e., a layer of vitreous silicon dioxide that is grown by thermal oxidation of silicon under high pressure steam according to methods that are well-known in the art. The thickness of layer 20 should be greater than about 10 μm, because optical leakage may occur at substantially smaller thicknesses. A currently preferred thickness is about 15 μm.

Passive core 30 is exemplarily made from phosphosilicate glass. The phosphorus content, and concomitantly the refractive index, of the glass is selected (with reference to the compositions of layers 20 and 50 and active core 40) to provide the desired waveguiding properties, according to methods well known in the art. A useful range of glass compositions for passive core 30 consist of silica containing up to about 8 wt.% phosphorus, and the phosphorus content more typically lies in the range 4 - 8 wt.%. Core 30 is exemplarily deposited on layer 20 by low-pressure chemical vapor deposition, according to methods that are well-known in the art. The thickness of the passive core is exemplarily about 5 μm, and the width of the passive core is exemplarily about 7 μm.

Active core 40 is made from a silica-based glass having a relatively high concentration of erbium, e.g., glass having an erbium-to-silicon atomic ratio of at least about 0.01, preferably at least about 0.02, and still more preferably at least about 0.03. Furthermore, the absolute erbium concentration is at least about 1.4×10^{20} atoms per cubic centimeter. A smaller erbium-to-silicon ratio is undesirable because it could lead to an undesirably small value of signal gain per unit length of the amplifier.

Various glass-modifying chemical elements (hereafter, "modifiers") are advantageously added to the glass of the active core in order to increase the solubility of erbium in the glass, and thus to prevent clustering of erbium atoms at high concentrations. Certain modifiers have been found to increase erbium solubility while avoiding concentration-quenching effects, which would otherwise reduce the Er^{3+} radiative lifetime below about 7 ms at relatively high concentrations (i.e., at erbium-to-silicon atomic ratios greater than about 0.02). Modifiers that are useful in this regard include alkali metals such as sodium and alkaline earth metals such as calcium.

Modifiers are also usefully incorporated in the active core glass to control the homogeneous and inhomogeneous broadening of the Er^{3+} absorption and emission peaks. Such modifiers include alkali and alkaline earth metals, which in at least some cases tend to make the peaks narrower, and elements such as lanthanum, yttrium, and zirconium, which contribute high field-strength ions and tend to broaden the peaks. Modifiers (such as aluminum and gallium) that enhance the degree of cross linkage in the glass network may also increase the degree of inhomogeneous broadening. In some cases, such modifiers are advantageously added to offset the effects of other modifiers on the absorption and emission peaks.

Modifiers are also usefully incorporated in order to stabilize the glass against devitrification, crystallization, and attack by moisture during or after film deposition. Modifiers useful for that purpose include calcium, magnesium, aluminum, and lanthanum. (Because the active core glass typically has a greater thermal expansion coefficient than the underlying silicon and silica regions, it may also be advantageous to add modifiers that reduce the thermal expansion.)

Thus, for example, an active core glass with a rel-

BNSDOCID: <EP___0510883A2_I_>

atively high solubility for erbium is readily made by incorporating in silica glass an effective amount of sodium. An effective range for the sodium-to-silicon atomic ratio is from about 0.2 to about 0.6. An optional quantity of calcium, up to a calcium-to-silicon atomic ratio of about 0.2, is usefully incorporated in order to enhance erbium solubility and to stabilize the glass, as discussed above. An optional quantity of aluminum, up to an aluminum-to-silicon atomic ratio of about 0.1, is usefully incorporated in order to stabilize the glass. Similarly, optional quantities of other modifiers, such as those listed above, are usefully added in quantities that are limited, inter alia, by the ultimate refractive index desired and the relevant solubility limits.

An exemplary method for depositing active core 40 is by sputtering, as described in detail below. As noted, the refractive index of active core 40 should be greater than those of both cladding layers, and also greater than the refractive index of passive core 30. Significantly, the use of sputtering offers the advantage that the concentration of Er^{3+} ions can be made substantially uniform throughout the active core. Moreover, radiation damage (which can occur when erbium doping is performed by ion implantation) is avoided.

The thickness of the active core is exemplarily about 1.2 μm. If the active core is made substantially thinner than about 1.0 μm, there will be no guided mode at the signal wavelength. The width of the active core should be at least about 4 μm, and is exemplarily about 8 μm. The total length of the active core is typically 5 mm or more.

Upper cladding layer 50 is advantageously made from phosphosilicate glass, exemplarily by low-pressure chemical vapor deposition. In order to provide the desired index of refraction, an appropriate content of, e.g., phosphorus is selected according to methods well known in the art. An exemplary phosphorus content is about 2 wt.%. The thickness of the upper cladding layer is exemplarily about 5 μm.

In use, an optical signal at a wavelength of about 1.55 μm, and pump radiation at least at one wavelength shorter than 1.55 μm, are coupled into the passive core, and from the passive core into the active core. As is well-known in the art, pump radiation is absorbed by Er^{3+} ions in the active core, promoting at least some of them to the $^4I_{13/2}$ state, which is a lasing level of atomic excitation. The lasing level is not reached directly, but rather by optical excitation to any one of several excited states of still higher energy. The lasing level is reached by nonradiative decay from those higher states. Correspondingly, pump radiation is effective at any of a group of wavelengths, including 980 nm, 810 nm, 660 nm, 514 nm, and 1.48 μm.

In order for excitation of erbium ions, and resulting amplification, to take place, the signal and pump radiation must be coupled from the passive core into the active core, and vice versa. With reference to FIG. 2, this is readily achieved by providing the active core with tapers 60. That is, the active core has two terminal portions, each of which is progressively constricted as the corresponding end is approached. The constriction is in at least one dimension normal to the longitudinal axis of the core. The normal dimension may be transverse, as shown in FIG. 2, or, as depicted in FIG. 3, it may be vertical; i.e., normal to the orientation of the deposited layers.

In the preferred embodiment, the tapers 60 are adiabatic; that is, the signal radiation remains in the fundamental mode as it is coupled from the passive to the active core, and again when it is coupled from the active to the passive core. (In the preferred embodiment, the active and passive cores are, of course, single-mode waveguides with respect to the signal radiation.) As is well known in the art, a taper will be adiabatic only if it is relatively gradual. For example, a straight-sided taper in this context will generally be adiabatic if it has a reduction ratio of about 100:1; i.e., the original width (or depth) is constricted, in effect, down to zero over a length that is 100 times the original width (or depth). The length of each tapered region is exemplarily about 1 mm.

Shown in FIG. 3 is a flowchart representing an exemplary sequence of steps in the fabrication of the inventive optical amplifier. The enumeration of the process steps in the following discussion is made with reference to the figure.

In Step A, the lower cladding layer is first formed.

In Step B, a layer corresponding to the passive core is then deposited on the upper surface of the lower cladding layer.

In Step C, the workpiece is annealed in order to at least partially densify the deposited passive core layer. Appropriate annealing conditions will be readily apparent to a skilled practitioner in the art.

In Step D, the passive core is then formed by etching the passive core layer. Dry etching is preferable for this step.

In Step E, the workpiece is annealed in order to flow the passive core, reducing roughness that was caused by etching. Appropriate annealing conditions will be readily apparent to a skilled practitioner in the art.

In Step F, a layer corresponding to the active core is then deposited.

In Step G, the workpiece is annealed, exemplarily at 600°C for 2 hours in air. The purpose of this annealing step is to stabilize the deposited film (i.e., against subsequent changes in structure, optical properties, and susceptibility to chemical attack).

In Step H, the active core is then formed by etching away a portion of the active core layer. A preferred etching process for Step H is ion milling, because this process is relatively nonselective with regard to the

INSDOCID: <EP___0510883A2_I_>

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 821 of 1543

composition of the material being removed.

In optional Step I, the workpiece is desirably annealed in order to flow the active core, and thereby to reduce surface roughness created during Step H. Appropriate annealing conditions will be readily apparent to a skilled practitioner in the art.

In Step J, the workpiece is then annealed at a temperature of at least about 700°C for a duration of at least about 1 hour in a reactive atmosphere such as very dry oxygen. (An appropriate grade of oxygen for this purpose is research grade, i.e., 99.999% purity.) This step is believed to reduce contaminant levels.

In optional Step K, before the upper cladding layer is deposited, a protective film of an appropriate dielectric material is advantageously formed over the active core in order to prevent contamination of the active core by the upper cladding layer. Such contamination should be avoided because it can reduce the radiative lifetime of the Er^{3+} ions below acceptable limits. Protective films that are effective for that purpose can be, e.g., silicon dioxide or phosphorus silicate films formed by sputtering or evaporative deposition. Such a protective film, if used, should be at least about 1000 Å thick.

In Step L, the upper cladding layer is then deposited.

Etching steps D and H are carried out such that after etching is completed the remaining portions of the active and passive core layers describe at least one pair of elongated cores, comprising an active core overlying a passive core. The two cores have a common longitudinal axis. As is apparent in FIGs. 2 and 3, the active core is typically made smaller than the passive core in the longitudinal direction. As seen in FIG. 2, this leads to a pair of terminal passive core portions 70 not overlain by the active core. If the taper is formed with respect to the transverse direction, as shown in FIG. 2, the active core will also typically be smaller than the passive core in the transverse direction. However, if the taper is formed with respect to the vertical direction, as shown in FIG. 3, then the widths (i.e., in the transverse direction) of the active and passive cores are optionally made equal.

As noted above, an exemplary method of depositing the active core layer is by sputtering. According to this method, a glass target of a predetermined composition is provided. The silicon substrate and the target are both placed within a vacuum chamber that is evacuable to a pressure of about 3×10^{-7} torr or less. The chamber is evacuated, and oxygen and argon are admitted. A radio-frequency discharge is produced, which leads to evaporation of material from the target and redeposition of such material on the substrate, as is well-known in the art.

As noted above, it is desirable for the deposited active core layer to contain sodium or a similarly-behaving modifier, in order to prevent clustering of the erbium atoms. Sputtering of sodium-containing glass often has unsatisfactory results because the sodium content of the deposited glass often tends to fall far below the sodium content of the target. However, we have discovered that under appropriate sputtering conditions, the sodium content of the deposited glass can be made relatively close to that of the target. We have found the following conditions in the sputtering chamber to be desirable in that regard: a pressure of 8 - 50 μm, and preferably about 27 μm; an argon-to-oxygen flow ratio in the range 10:1 to 0.3:1, and preferably about 0.5:1; a substrate temperature that can range freely between about 25°C and about 70°C; and rf frequency of 13.6 MHz and power of about 50 W. We used a target 3 in. (7.6 cm) in diameter and a silicon-wafer substrate 4 in. (10.2 cm) in diameter. The target was situated 1 - 3 in. (2.5 - 7.6 cm) from the substrate, preferably about 3 in. (7.6 cm).

The radiative lifetime of the lasing level of the excited erbium ions is desirably at least about 7 ms. In order to achieve such relatively high lifetimes, it is particularly important to include, during formation of the device, Step J, annealing in a reactive atmosphere.

In use, the signal and the pump radiation are combined and injected into the amplifier, exemplarily by means of directional coupler or wavelength division multiplexer 80, shown in FIG. 2. The amplified signal is extracted, exemplarily by wavelength division demultiplexer 85 of FIG. 2, and unwanted pump radiation that would otherwise contaminate the amplified signal is eliminated, exemplarily by filtering. Such methods are well-known in the art, and need not be described here in detail.

The foregoing discussion is for illustrative purposes only, and is not intended to limit the scope of the invention to a single-pass optical amplifier. For example, a laser or parametric oscillator is readily made by incorporating at least one optical feedback element with the inventive waveguiding structure. An appropriate such element is, e.g., a mirror or a distributed Bragg reflector. Such an arrangement is readily envisioned with reference to FIG. 2, substituting a mirror or Bragg reflector for one or both of elements 80 and 85.

EXAMPLE

Erbium-doped glass films, varying in thickness from about 0.8 μm at the edge to about 1.5 μm at the center, were formed on 4-in. (10.2-cm) diameter silicon wafer substrates by sputter deposition, substantially as described above. In separate trials, three different target compositions were used. The target compositions will be described with reference to the general formula $SiO_2(Na_2O)_a(CaO)_b(Er_2O_3)_c$. The compositions of the resulting, sputter-deposited films will similarly be represented by $SiO_2(Na_2O)_{a'}(CaO)_{b'}(Er_2O_3)_{c'}$.

BNSDOCID: <EP___0510883A2_I_>

The first target had a=0.27, b=0.14, and c=0.028. The resulting sputter-deposited layer had a'=0.20, b'=0.117, and c'=0.0275. The second target had a=0.34, b=0.00, and c=0.033, resulting in a deposited layer with a'=0.30 and c'=0.036. The third target had a=0.265, b=0.00, and c=0.038, resulting in a deposited layer with a'=0.17 and c'=0.032. The deposited layers were analyzed by Rutherford backscattering. All three layers had erbium radiative lifetimes of about 10 milliseconds, and densities of about 6 x 10^{22} atoms per cubic centimeter.

Claims

1. An optical device, comprising:
   a) an elongate, active glass core which extends along a longitudinal axis and comprises silicon, oxygen, and erbium, the erbium being at least partially in the form of Er^{3+} ions, the active core having a refractive index;
   b) a glass cladding comprising at least one layer which at least partially surrounds the active core and has a refractive index which is smaller than the core refractive index;
   c) means for coupling signal radiation, having a signal wavelength, into the active core and means for coupling the signal radiation out of the active core; and
   d) means for coupling pump radiation into the active core such that pump radiation of an appropriate wavelength will excite at least some of the Er^{3+} ions to a lasing level, leading to amplification of the signal radiation by stimulated emission,
   CHARACTERIZED IN THAT
   e) the device further comprises a substrate having a substantially planar principal surface;
   f) the active core is a body that overlies a portion of the principal surface;
   g) the cladding comprises a lower cladding layer disposed between the active core and the principal surface, and an upper cladding layer which overlies and partially surrounds the active core;
   h) the active core further comprises an alkali metal or alkaline earth metal in an effective quantity to prevent clustering of erbium atoms;
   i) the active core has an erbium-to-silicon atomic ratio of at least about 0.01 and an absolute erbium concentration of at least about 1.4 x 10^{20} atoms per cubic centimeter, and
   j) the lasing level has a radiative lifetime of at least about 7 ms.

2. The optical device of claim 1, wherein the substrate comprises a silicon body.

3. The optical device of claim 1, wherein the active core has an erbium-to-silicon atomic ratio of at least about 0.02.

4. The optical device of claim 1, wherein the active glass core is adapted to guide the fundamental mode of the signal wavelength, and the means for coupling the signal radiation into and out of the active core are adapted to couple the signal radiation adiabatically.

5. The optical device of claim 1, wherein the concentration of Er^{3+} ions is substantially constant throughout the active core, and the active core is substantially free of radiation damage.

6. The optical device of claim 1, wherein the alkali metal or akaline earth metal comprises sodium, and the active core has a sodium-to-silicon atomic ratio in the approximate range 0.2 - 0.6.

7. The optical device of claim 1, wherein the alkali metal or akaline earth metal comprises calcium, and the active core has a calcium-to-silicon atomic ratio of not more than about 0.2.

8. The optical device of claim 4, further comprising an elongate, waveguiding, passive, glass core which extends along the longitudinal axis and is disposed between the lower cladding layer and the active core, the passive core being adapted to guide the fundamental mode of the signal radiation, means for coupling an optical signal and pump radiation into the passive core, and means for coupling signal radiation out of the passive core, wherein:
   the passive core is substantially free of erbiuin and has a refractive index that is smaller than the active core refractive index but larger than the upper and lower cladding refractive indices,
   the active core includes a central portion and two ends,
   and the means for coupling the signal radiation into and out of the active core comprise two further, tapered portions of the active core, each tapered portion extending between the central portion and an end and tapering toward the respective end such that the tapered portion is progressively constricted in at least one direction perpendicular to the longitudinal axis.

9. The optical device of claim 8, wherein the perpendicular direction is substantially parallel to the substrate principal surface.

10. The optical device of claim 8, wherein the perpendicular direction is substantially normal to the

BNSDOCID: <EP___0510883A2_I_>

substrate principal surface.

11. The optical device of claim 8, wherein the passive core comprises phosphosilicate glass, the upper cladding layer comprises phosphosilicate glass, and the lower cladding layer comprises thermal silicon dioxide.

12. The optical device of claim 1, further comprising at least one optical feedback element, such that the device can function as a laser.

13. The optical device of claim 1, further comprising at least one optical feedback element, such that the device can function as a parametric oscillator.

14. A method for forming an optical device on a substrate having a substantially planar principal surface, comprising:
 a) forming a first layer of vitreous silicon dioxide on the principal surface;
 b) depositing a second layer of silica-based glass over the first layer by sputtering a target of silica-based glass such that the second layer has a higher refractive index than the first layer,
 c) annealing the second layer such that it is stabilized;
 d) removing a portion of the second layer by etching, such that an elongate core, extending along the longitudinal axis, is formed, the core being adapted, after completion of the device, to guide electromagnetic radiation of at least a signal wavelength and a pump wavelength; and
 e) depositing a third layer of phosphosilicate glass over the core such that the third layer has a smaller refractive index than the core;
 CHARACTERIZED IN THAT
 f) the target further comprises sodium and erbium; and
 g) the target composition is selected such that the core has an erbium-to-silicon atomic ratio of at least about 0.01, a sodium-to-silicon atomic ratio in the approximate range 0.2 - 0.6, and an absolute erbium concentration of at least about 1.4×10^{20} atoms per cubic centimeter, and the target composition is further selected such that a lasing level is associated with the erbium in the core, the lasing level having a radiative lifetime of at least about 7 ms.

15. The method of claim 14, further comprising, after (d) and before (e), the step of forming a protective dielectric film over the core.

16. The method of claim 14, further comprising, after (d), the step of annealing the core such that roughness due to etching of the second layer is substantially removed.

17. The method of claim 14, further comprising, after (d), the step of annealing the core at a temperature of at least about 700°C for a duration of at least about 1 hour in a reactive atmosphere.

18. A method for forming an optical device on a substrate having a substantially planar principal surface, comprising:
 a) forming a first layer of silicon dioxide on the principal surface;
 b) depositing a second layer of phosphosilicate glass over the first layer such that the second layer has a higher refractive index than the first layer;
 c) annealing the second layer such that it is at least partially densified;
 d) removing a portion of the second layer by etching, such that an elongate lower core having a longitudinal axis is formed, the lower core being adapted, after completion of the device, to guide electromagnetic radiation of at least a signal wavelength and a pump wavelength;
 e) annealing the lower core such that roughness due to etching of the second layer is substantially removed;
 f) depositing a third layer of silica-based glass over the lower core by sputtering a target of silica-based glass such that the third layer has a higher refractive index than the lower core;
 g) annealing the third layer such that it is stabilized;
 h) removing a portion of the third layer by etching, such that an elongate upper core, extending along the longitudinal axis, is formed, the upper core being adapted, after completion of the device, to guide electromagnetic radiation of the signal and pump wavelengths;
 i) annealing the upper core at a temperature of at least about 700°C for a duration of at least about 1 hour in a reactive atmosphere; and
 j) depositing a fourth layer of phosphosilicate glass over the upper and lower cores such that the fourth layer has a smaller refractive index than the upper and lower cores;
 CHARACTERIZED IN THAT
 k) the target further comprises sodium and erbium; and
 l) the target composition is selected such that the third layer has an erbium-to-silicon atomic ratio of at least about 0.01, a sodium-to-silicon atomic ratio in the approximate range 0.2 - 0.6, and an absolute erbium concentration of at least about 1.4×10^{20} atoms per cubic cen-

BNSDOCID: <EP__0510883A2_I_>

timeter, and the target composition is further selected such that a lasing level is associated with the erbium in the third layer, the lasing level having a radiative lifetime of at least about 7 ms.

19. The method of claim 18 further comprising, after (i) and before (j), the step of forming a protective dielectric film over the active core.

20. The method of claim 17 or claim 18, wherein the reactive atmosphere comprises very dry oxygen.

21. The method of claim 18 a further comprising, after (h), the step of annealing the upper core such that roughness due to etching of the third layer is substantially removed.

BNSDOCID: <EP___0510883A2_I_>

FIG. 1

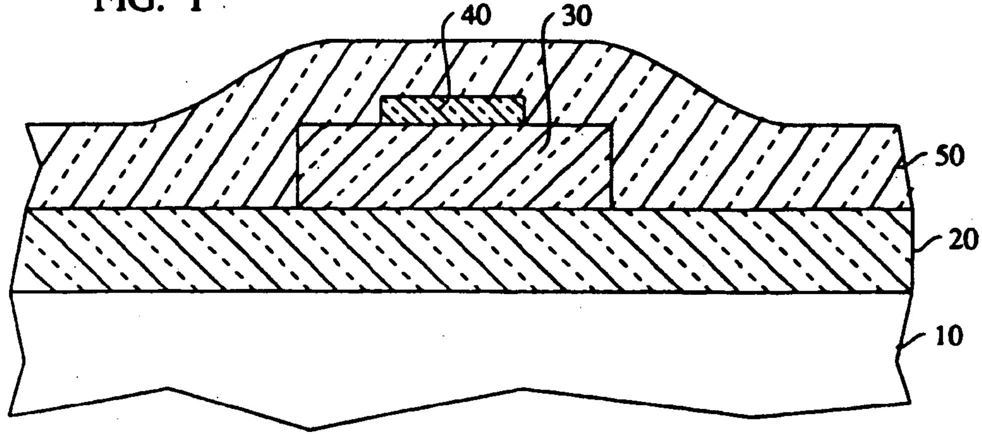


FIG. 2

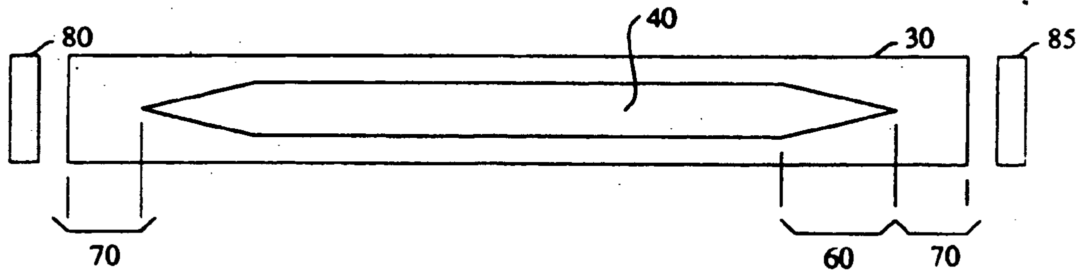
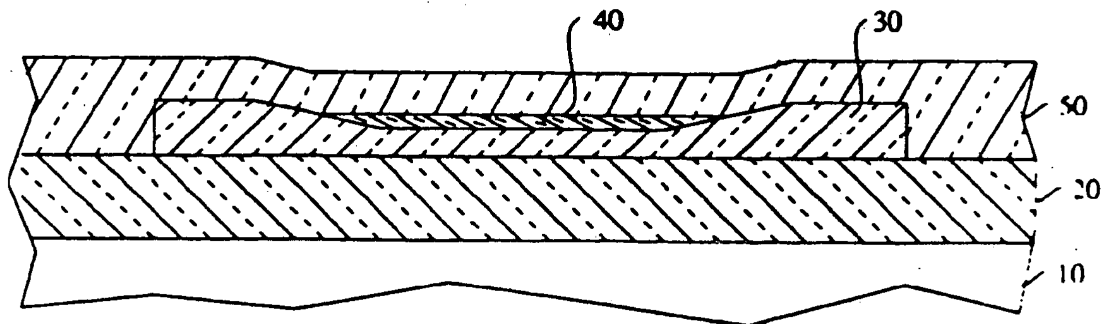
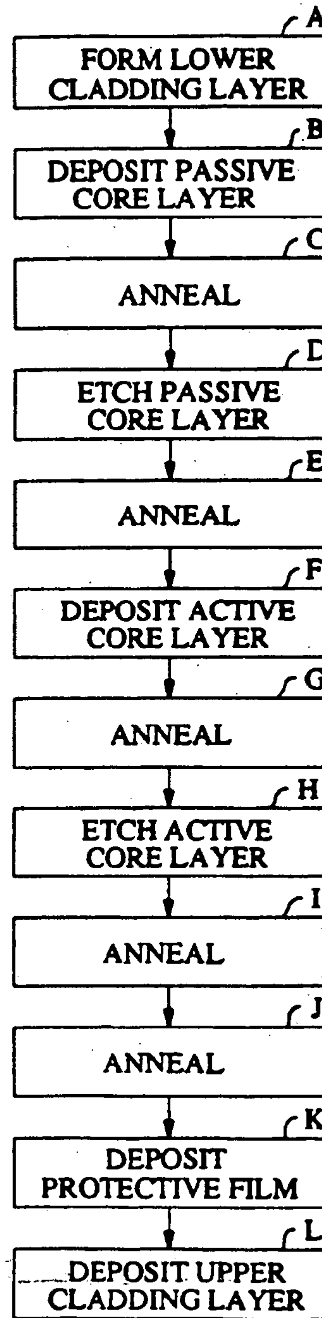


FIG. 3



BNSDOCID: <EP 0510883A2 I >

FIG. 4



BNSDOCID: <EP___0510883A2_I_>

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 07233469
PUBLICATION DATE : 05-09-95

APPLICATION DATE : 22-02-94
APPLICATION NUMBER : 06024420

APPLICANT : ASAHI GLASS CO LTD;

INVENTOR : SASAKI KENICHI;

INT.CL. : C23C 14/34 C04B 35/46 C23C 14/08

TITLE : TARGET, ITS PRODUCTION AND PRODUCTION OF HIGH-REFRACTIVE-INDEX FILM

ABSTRACT : PURPOSE: To produce a highly productive oxide sintered compact for a sputtering target having a low resistivity and a high content of oxygen by hot-pressing titanium dioxide powder in a nonoxidizing atmosphere and sintering the compact.

CONSTITUTION: The powder of titanium dioxide having 0.05-40μm grain diameter is hot-pressed at 1000-1300°C and 50-100kg/cm^2 in a nonoxidizing atmosphere of Ar, etc., to obtain an oxide sintered compact consisting essentially of TiO_x ($1<x<2$). A sputtering target having ≤10Ωcm resistivity at room temp. and contg. ≥35wt.% oxygen is formed from the sintered compact. A metal oxide other than TiO_x is incorporated, as required, into the target by <50%. The oxide of at least one kind among Cr, Ce, Zr, Y, Nb, Ta, Si, Al and B is preferably used for the metal oxide. DC sputtering is conducted by using the target to form a high-refractive-index uniform transparent film at a high rate.

COPYRIGHT: (C)1995,JPO

Document Summary

Preview Claims
Preview Full Text
Preview Full Image

Email Link:

Document ID: JP 02-054764 A2
Title: DEVICE FOR COATING SUBSTRATE WITH INSULATOR
Assignee: LEYBOLD AG
Inventor: SCHERER MICHAEL
LATZ RUDOLF
PATZ ULRICH
US Class:
Int'l Class: C23C 14/35 A
Issue Date: 02/23/1990
Filing Date: 06/22/1989

Abstract:

PURPOSE: To prevent the hindrance of the electrification on a target, by superposing the output voltage of an AC power source on the DC voltage of a DC power source and specifying the voltage of the AC power source to be applied on electrodes.

CONSTITUTION: The magnetron sputtering device is provided with the AC power source, which outputs voltages to be superposed on the DC voltage of the DC power source. The output of the AC power source impressed on the electrodes connected to the target is regulated to 5 to 20% of the output supplied to the electrodes by the DC power source. A high-frequency power source is used as the AC power source. As a result, an insulator, such as Al_2O_3, is deposited on the substrate at a high rate without receiving the hindrance by reactive sputtering.

(C)1990,JPO

Copyright © 1993-2000 Aurigin Systems, Inc.
Legal Notices

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 829 of 1543

⑲日本国特許庁（JP）　　⑪特許出願公開

⑫公開特許公報（A）　　平2-54764

⑤Int. Cl.⁵	識別記号	庁内整理番号	㊸公開 平成2年(1990)2月23日
C 23 C 14/35		8520-4K	

審査請求 未請求 請求項の数 17 （全9頁）

⑭発明の名称　基板を絶縁体で被覆する装置

㉑特　願　平1-158479
㉒出　願　平1(1989)6月22日
優先権主張　㉜1988年6月23日㉝西ドイツ(DE)㉛P38 21 207.2

⑫発明者　シエーラ-ミヒヤエル　ドイツ連邦共和国 ローデンバツハ D-6458 リンデンシユトラーセ 12
⑫発明者　ラツツ　ルドルフ　ドイツ連邦共和国 フランクフルト D-6000 マインツアー ラントシユトラーセ 326
⑫発明者　パツツ　ウルリツヒ　ドイツ連邦共和国 リンゼンゲリヒト 2 D-6464 ヴアルトシユトラーセ 26
⑪出願人　レイボルト アクチーエンゲゼルシヤフト　ドイツ連邦共和国 ハウナ 1 D-6450 ビルヘルム-ローン-シユトラーセ 25
⑭代理人　弁理士 鈴木 弘男

明　細　書

1．発明の名称

基板を絶縁体で被覆する装置

2．特許請求の範囲

（1）　ターゲットに接続された電極に接続された直流電源を有し、前記ターゲットから放出された粒子が基板上に堆積される導入物質との化合物を形成し、前記ターゲットには環状磁界が印加され、その磁力線は磁極部分においてターゲットの表面から出ていく、基板を絶縁体で被覆する装置において、前記直流電源の直流電圧に重畳される電圧を出力する交流電源を設け、前記電極に印加される前記交流電源の出力を前記直流電源によって前記電極に供給される出力の５％ないし２５％にしたことを特徴とする装置。

（２）　前記交流電源が高周波電源である請求項1に記載の装置。

（３）　前記高周波出力は前記直流出力の１０％である請求項１または２に記載の装置。

（４）　前記直流電源が第１および第２のインダクタを介して前記電極に接続された請求項１に記載の装置。

（５）　前記交流電源がコンデンサを介して前記電極に接続された請求項１に記載の装置。

（６）　前記直流電源と前記第１のインダクタとの間に一端を接地電位にしたコンデンサを接続した請求項４に記載の装置。

（７）　前記第１のインダクタと第２のインダクタとの間に一端を接地電位にしたコンデンサを接続した請求項４に記載の装置。

（８）　第１のコンテナと、この第１のコンテナの中に配置される第２のコンテナとを有し、第２のコンテナはダイヤフラムとしての開口を有し、被覆される基板は前記開口を通して前記ターゲットと対向し、１またはそれ以上の気体が第１および第２のコンテナの間の空間に導入される請求項1に記載の装置。

（９）　前記交流電源が１３．５６ＭＨｚの交流電圧を与える請求項１に記載の装置。

（１０）　前記ターゲットはアルミニウムから成

04/25/2002, EAST Version: 1.03.0002

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 830 of 1543

り、前記基板上に堆積される層はAl_2O_3から成る請求項1に記載の装置。

(11) 前記ターゲットはドーピングされたたとえば導電性シリコンから成り、前記基板上に堆積される層はSiO_2から成る請求項1に記載の装置。

(12) 前記ターゲットはアルミニウムから成り、前記基板上に堆積される層はAℓNから成る請求項1に記載の装置。

(13) 前記ターゲットはドーピングされたたとえば導電性シリコンから成り、前記基板に堆積される層はSi_3N_4から成る請求項1に記載の装置。

(14) 前記直流電源がターゲット物質の種類に応じて作動され、電流、電圧または出力電力が調整される請求項1に記載の装置。

(15) ターゲットにAℓ、SiまたはSnが使用されたときは、前記直流電源が優先的に作動されて電圧が調整される請求項1に記載の装置。

(16) アルゴン／酸素の雰囲気のもとで、Aℓ、Si、Sn、In／Snのターゲットがスパッタリングされるときは、前記直流電源が作動され電圧が調整される請求項1に記載の装置。

(17) アルゴン／窒素の雰囲気のもとで、Aℓ、Siのターゲットがスパッタリングされるときは、前記直流電源が作動され電圧が調整される請求項1に記載の装置。

3．発明の詳細な説明

（産業上の利用分野）

本発明は、基板を絶縁体で被覆する装置、とくにターゲットに電気的に接続された電極に接続された直流電源を有し、前記ターゲットから放出され微粉化された粒子が基板上に堆積される化合物を形成し、前記ターゲットには環状磁界が印加され、その磁力線は磁極部分においてターゲットの表面から出ていく装置に関する。

（従来技術）

スパッタリングまたは粉状化プロセスを用いて基板を金属で被覆することは、金属が良導電体であるため、比較的簡単である。しかし、導電性が全くないかあるいは非常に低い酸化物の層で基板を被覆することは非常に難しい。この困難さにもかかわらず、基板上に酸化物および他の絶縁体を堆積させるためには、直流スパッタリング手段を用いて金属粒子を発生させ、それらを反応的な雰囲気下で酸化物に転化し基板上に堆積させている。

この処理において、金属粒子の酸化物への転化は基板のすぐ近くであってスパッタリング陰極から離れた所で起こる。これは陰極上に酸化物が堆積しそれに伴なってスパッタリング率が低下するのを防ぐためである。それにもかかわらず、実際には陰極に酸化物を全く付着させないことはできず、スパッタリング率は徐々にかなり低下する。

スパッタリングがマグネトロン陰極を用いて行なわれるときは、磁力線の曲率が最大であるところでスパッタリングは最も激しく、スパッタ溝が発生する。これらの場所における激しいスパッタリングは酸化物の堆積を防止する。ターゲットのこれらの部分は全くスパッタリングされないかまたは非常にゆっくり行なわれる。しかし非導電性の誘電体膜が反応的気体の影響のもとで形成される。これらの成長部分は静電気的に帯電され、ターゲット表面上の瞬時放電の開始点となり、結局、ターゲットとプラズマまたはターゲットとターゲットの周りの物質との間の放電の開始点となる。放電中は放電アークを消すために陰極電流を一時的に減少させなければならない。しかし、それによって放電が最終的にやむまで不安定状態が生じる。

直流電流によるマグネトロン・スパッタリングにおいては、純粋な二極管スパッタリングとは対照的にターゲットに反応生成物が部分的に付着するのを防ぐことはできず、せいぜい磁界を最適化して低くおさえることができるだけである。

この問題を解決するための手始めとして、直流電圧の代りに周波数の高い交流電圧をターゲット電極と基板との間に与えることがある。反応的な

04/25/2002, EAST Version: 1.03.0002

雰囲気下でこの高周波マグネトロン・スパッタリングを行なえばターゲット表面での放電も起こらないし、静電的な帯電も起こらない。しかしながら、純粋な高周波スパッタリングにおいては、スパッタリング率が比較的低い。

しかし、高周波電圧を重ねた直流電圧を用い、基板上にタンタルおよびタンタル酸化物を堆積させるスパッタリング処理も知られている（F. Vratny「高周波を重ねた直流スパッタリングによるタンタルおよびタンタル酸化物の堆積」1968年10月 7日～11日薄膜誘電体に関する会議資料、J. Electrochem. Soc. 114-5,505,1967 からの再複製）。直流電流と交流電流が結合された電界はプラズマ密度を高め、反応的スパッタリング中に陰極上に誘電体膜が形成されるのを防止する。それにより、０．５～２ミリトルのスパッタリング圧力下で約８０Å／分のタンタル堆積率を達成することができ、１０～２０ミリトルの圧力下ではタンタル堆積率を２倍に増大させることができる。純粋な酸素の下における反応的スパッタリングの過程では、Ta_2O_5およびMnO_2を被覆するのに５０～１００Å／分の堆積率が得られる。

この堆積率の増加は、高周波電界においては帯電粒子が振動運動を行なうという事実によって説明することができる。重畳電界の影響により移動する電子は直流電界中における電子よりも長い距離を移動する。この長い移動距離は電子と気体原子との衝突の確率を増加させ、これは与えられた圧力下での陰極への正イオンの流入密度を増加させることになる。このことはスパッタリング率および層堆積を増加させる効果をもつ。気体中で電子がどのように反応するかは、気体圧力すなわち電子の自由路長、高周波電界の周波数および電極配置に依存する。低い圧力のもとでは、平均自由路長が電極間の距離より長ければ、電子は励起されてほとんど気体との衝突なしに電極間を移動する。たとえば１０ミリトルの圧力のもとではアルゴン中の電子は０．４ｅＶのエネルギーを有し、平均自由路長は従来の電極間の距離とほぼ一致する１０cmである。電子の平均自由路長が電極間の距離より短い圧力のもとで電界の周波数が気体の衝突周波数より低いときは、電子は各々振動して数回衝突し、電界の位相に合わせて移動しようとする。この例としては低周波交流スパッタリングおよび低周波直流／交流スパッタリングがある。このとき電子は連続して陰極および基板に突入する。高い周波数では電子は気体の衝突の間で小さな振幅で多く振動することができる。この場合電子は静止しているようにみえ、その結果強力なプラズマができる。このプラズマは重畳された直流電界で引き上げることができる。さらに高い周波数たとえばマイクロ波の範囲では、電子は電気的および磁気的成分を有する定在波の影響を受ける。この影響のため、電子は空間の条件たとえば電極寸法の関数および定在波を発生する周波数などに応じて空間中で分散する。

さらに、高周波電界があるため、電気的な負性気体による反応的スパッタリング中に陰極上に誘電体の被覆が堆積するのを防止する。イオン濃度は高周波電界を通して維持され、陰極への電子の衝突は大量の絶縁被覆が形成される可能性を減少させる。イオン化の確率が増え、気体の絶縁破壊強度が小さくなることにより、高周波電界においては二極管スパッタリング中の通常の圧力より低いスパッタリング圧力のもとで作用することができる。

上述した公知の装置は二極管スパッタリングあるいは二極管粉状化に関するものである。それはまた直流および交流電圧を電極に印加する公知の装置にも言えることである。しかし、二極管スパッタリングは仮に交流の重ね合せを利用したとしても多くの適用例において堆積率が低いという欠点がある。マグネトロン陰極を用いた上記スパッタリングは実質的により高いスパッタリング率を有する。

マグネトロン・スパッタリングとマイクロ波放射を結合することもまた公知である（米国特許４６１０７７０号＝ヨーロッパ特許０１４８５０４号）。この場合のマイクロ波放射は、マグネト

04/25/2002, EAST Version: 1.03.0002

ロン電極の環状力線が位置している所だけターゲットがスパッタリングされないのを防止しようとするものである。このようにスパッタリング率を上昇させ、ターゲットの腐食を狭い限られた部分だけでなく防止するために、スパッタリング領域をかなり増加させる。この目的を達するために、同軸状に配置された2個の永久磁石を用いてミラー磁界を発生させる。このとき磁石間では磁力線が拡散し、磁石の近くでは再び収縮する磁束分布となる。この場合の欠点は中空の導波管または同等の手段を用いたマイクロ波の放射が高価であること、また永久磁石の構造が複雑であることである。

さらに、基板ホルダとターゲットホルダが高周波の高電圧電源と接続され、－３０Ｖから－１００Ｖ好ましくは－７０Ｖ±１０Ｖのバイアス電圧がスパッタリング手段によって薄いドープ金属層を製造する方法が知られている（ドイツ特許２９０９８０４号）。この方法は電気的性質が正確に定義された抵抗層の再現可能な堆積に関するもので、ここでは上記抵抗層は純粋な二極管高周波スパッタリングによって製造される。この公知の方法は良導電体である化合物が放出されるので、アークの問題に関するものでなく、さらに直流電源も使用されない。

さらに、中和装置を有するイオンビーム処理装置が知られている。この装置では基板ホルダおよび／またはターゲット上の電荷が不確定な状態になるのを避けるため、中和装置が熱放出電子の形成で使用され、さらに正電位が基板および／またはターゲットに印加される。反応的スパッタリングの問題とくに絶縁体の反応的スパッタリングの問題については触れていない。

アルミニウムをエッチングする別の二極管方法によれば、直流電源および高周波発生器が並列に接続され、これらの共通の出力電圧は２つの相対する電極に印加される（ドイツ特許３１４０６７５号）。このケースの場合も運動量の伝達による反応的なスパッタリングの問題は述べられていない。

（発明の目的および構成）

本発明は永久磁石の磁力線が環状に形成されてスパッタリングされる物質に印加される従来のマグネトロン・スパッタリング装置において、ターゲット上の帯電が妨げられるのを防止することを目的とする。

この目的を達するために、直流電源の直流電圧に交流電源の出力電圧を重ね、電極に与えられる交流電源の電圧を、直流電源によって電極に与えられる電圧の５％ないし２５％にするように構成した。

本発明によって得られる利点は、SiO_2、Al_2O_3、Si_3N_4またはAlNなどの絶縁体を従来のマグネトロン陰極を用いた反応的スパッタリングを使って何ら妨害を受けることなく高い率で堆積できるということである。

反応的直流スパッタリングの全ての利点は保有されている。なぜなら、重畳高周波成分はターゲット上の電位差を減少させ、それによりターゲット上で帯電効果を妨害することは避けられる。このため永久アークにより放電が終了することが保証される。このことは高周波成分が、第１にプラズマ密度を増加させることによってスパッタリング率を増加させ、第２にターゲットの非導電領域から離れたスパッタリングに役立つという意味ではない。むしろ反応的マグネトロン・スパッタリング中に不可避的に形成される非導電性のターゲット部分上に帯電効果の妨害を生じさせないということである。このため、直流電圧はターゲット上の帯電効果の妨害を避けるように高周波電圧によって変調される。

（実施例）

以下、本発明の一実施例を図面に基づいて詳細に説明する。

第１図には基板１が示され、この基板１には絶縁体の薄い層２が設けられる。基板１に対向してスパッタリングされるべきターゲット３が配置されている。ターゲット３は断面がＵ字形のエレメント４を介して電極５と接続されている。電極５はヨーク６上に接地され、ヨーク６とエレメント

04/25/2002, EAST Version: 1.03.0002

4との間には永久磁石7，8，9が設けられている。

永久磁石7，8，9の磁極は、外側の2つの永久磁石7および9のS極と真中の永久磁石8のN極がターゲット3を通してほぼ円弧状の磁界を形成するように、ターゲット3に交互に向けられている。この磁界はターゲット3の前のプラズマを圧縮して、磁界がその円弧の最高点のところで磁界の密度が最大になる。プラズマ中のイオンは、直流電源10から供給される直流電圧により形成される電界によって加速される。直流電源10のマイナス極は2個のインダクタ11および12を介して電極5に接続されている。電界はターゲット3の表面と垂直に形成され、プラズマの正イオンはターゲット3の方向に加速される。これによって、多数の原子や粒子がターゲット3から放出される。とくに領域13および14から放出され、そこで磁界は最大となる。放出された原子または粒子は基板1の方向へ移動し、薄い層2となって堆積される。

ターゲット物質が金属であって基板上に酸化膜を被覆するときは、ターゲット3から放出された粒子は空間15において特定の気体と反応する。この気体はガスタンク16および17からバルブ18，19およびパイプ22，23を経て、入口弁20，21を介して空間15に導入される。この空間15は2つのコンテナ24および25によって形成され、コンテナ25は基板1を収容し、他方のコンテナ24は基板1の前で終わり、ダイヤフラム26を形成している。コンテナ24，25およびコンテナ25の底に載置された基板1は共に接地されている。直流電源10の第2の極27もまた接地され、第1の極28はインダクタ11および12から離れてコンデンサ29に接続され、コンデンサ29は接地されている。

さらに、端子31を有する高周波電源30は直流電源10のそばにあって、可変コンデンサ33および34を介して電極5に接続されている。可変コンデンサ33および34の接続点にはインダクタ35の一端が接続され、その他端は接地されている。インダクタ11および12の接続点はコンデンサ32に接続され、コンデンサ32は接地されている。高周波電源30の第2の端子36も接地されている。

コンデンサ29および32とその間に接続されたインダクタ11とによって高周波の通過を妨げるローパスフィルタを形成している。インダクタ12によってその効果をさらに強めている。コンデンサ33および34とインダクタ35によって高周波を陰極5に印加する回路を形成している。これらは同時にハイパスフィルタとして機能する。すなわち直流電圧は高周波電源30には印加されない。

第1図の装置のおける気体は実際には第1および第2のコンテナ25および24の間の空間に入るが、それは陰極5の周りのガス分配システムを通して第2のコンテナ24へ導入することもできる。

第1図の装置を制御するために、測定データおよび出力制御命令を処理する処理制御コンピュータが用いられる。この処理制御コンピュータにたとえば処理室25内の分圧の測定値が与えられる。これらのデータおよび他のデータに基づいて、コンピュータはたとえばバルブ18および19を通って流入する気体を制御し、陰極5における直流と交流の電圧の割合を設定する。処理制御コンピュータは他の全ての変数たとえば陰極電流、高周波出力および磁電強度を制御することができる。このような処理制御コンピュータはよく知られているので、その構成についての説明は省略する。

第1図には高周波の供給がどのように調整されるか示されていない。しかし、特定の値を予め設定し出力が常にこの設定値に調整されるように調整回路を構成することは公知である。

第2図は直流だけによるスパッタリング中に生じた過程を示す図である。これらの過程は以下に説明する本発明による装置の実施例の作用を理解する上で重要である。第2図は気体圧力が7×

04/25/2002, EAST Version: 1.03.0002

10^{-2}ミリバールのアルゴンの純不活性ガスの雰囲気下のものであり、この図から直流陰極電流は明らかに直流陰極電圧の関数であることがわかる。電圧の上昇に伴ない導電性プラズマが形成されて抵抗値が減少するので、電流Ｊ＝ｆ（Ｕ）はほぼ放物線状に増加する。スパッタリング率ＲはÅ／Ｓで表わされ、スパッタリング出力の増加に伴ない直線的に上昇し、直線Ｒ＝ｆ（Ｐｅｌ）によって表わされる。出力密度１０Ｗ／cm^2に対応するスパッタリング出力が４４０Ｗのとき、スパッタリング率は５０Å／ｓである。

第３図には、陰極電圧の関数としての陰極電流および直流のときに予め設定したアルゴンおよび酸素流入の場合における酸素分圧と陰極電圧の相関が示されている。第３図の測定曲線は酸素の流量f_{O_2}が６．７ＳＣＣＭ／分で一定のときに記録されたものである。ここでＳＳＣＭ／分は標準的なcm^3／分と一致する。

第２図とは対照的に、第３図は反応的な直流スパッタリング時の状態を示している。電流－電圧特性から電圧を増加させたときの電流Ｊは依然として明らかに電圧の関数であることがわかる。電圧を増加させると電流は初め非常に急激に上昇するが、その後最大値に達し、そこから減少し次いで再びいく分増加する。しかし、電圧を約６００Ｖの高電圧から減少させると、電流は初め電圧の減少に伴ない減少する。しかし、最初の金属ターゲットの状態を仮定すると、電圧がさらに下がると電流は大きく上昇し、このとき基板上の酸化物の形成は増加していることがわかる。３５０Ｖ以下になると、電流は再び急に減少し、酸素分圧が大きく上昇する。約４５０Ｖから３５０Ｖまでの範囲では、ターゲット上に堆積するAl_2O_3の２次電子発生量は、アルゴンイオンの衝撃によって上昇する。これとは対照的に、３５０Ｖ以下においてはターゲットは酸素分子で被覆されターゲット上にAl_2O_3が形成されることはない。この酸素分子はアルゴンの衝突イオンによって放出され、２次電子効果は低下する。反応的直流動作の欠点は、基板上に吸収のない層を形成する陰極電圧の範囲（約３００Ｖないし４００Ｖの範囲）が不安定な範囲であることであり、その中で悖く後に火花やプラズマ損失が起こる。したがって動作点を早く動かして放電が止まらないようにしなければならない。

すでに述べたように、陰極電流Ｊは明らかに陰極電圧の関数であり、各々の電圧値には確実に１つの電流値が対応する。しかし、その逆は言えない。もし第３図の縦軸と横軸を交換し、縦軸に電圧Ｕをとり、横軸に電流Ｊをとると、電圧曲線は１つの電流値が２つの電圧値をとるＳ字形を描く。

第４図には酸素分圧および直流電流の陰極電圧の関数としての放電電流が第３図と同じ条件のもとで示されているが、今度は高周波変調された陰極電圧が使用されている。ここでの変調周波数は１３．５６Ｈｚであり、高周波の振幅は１４０Ｖ，陰極における有効電力は一定で２０Ｗである。吸収のないAl_2O_3の層は４２５Ｖ以下で得られ、これは第３図の純直流電流の場合と似ている。しかし、放電は完全に安定しておりアークはない。実験では約４２０Ｖの動作点において、放電は火花が起こることなく数時間行なわれた。５００Ｖから３５０Ｖの間では第３図および第４図の電圧－電流特性は数パーセント以内の偏差で一致している。第３図と比べると、第４図で観察することができる連続した強い電流の増加は次のように説明できよう。すなわち、高周波成分は初めターゲット表面上の酸素分子の吸収を防止するが、２次電子の発生量の増加は邪魔されない。２次電子が増加すると確かに衝突によるイオン化を通してイオン流量が増加するが、初めは陰極からの電子流量が増加することによってイオン流量が増加する。この効果は動作範囲を広げスパッタリング率は電圧の低下に伴ないわずかしか変化しない。この電圧低下は酸素分圧の比較的わずかな増加によて示される。４２０Ｖの動作点ではAl_2O_3のスパッタリング率は約４７０Ｗの電力で２５Å／秒であり、これは純粋な金属の場合と比較すると半分に低下しただけである。２８０

04/25/2002, EAST Version: 1.03.0002

V以下では電流は大きく減少し、これはスパッタリングの酸素による被覆および低い電圧におけるスパッタリング効果の減少のためである。500V以上では高周波成分を有する電圧で流れる電流は第3図の純直流電流の場合より小さい。明らかにここではプラズマの影響を受けている。

第5図は電極5に印加される変調電圧を示している。これは－420Vの直流電圧に振幅140Vの高周波電圧を重ねたものである。この電圧は処理室のアルゴン圧が7×10^{-3}ミリバールのとき、アルミニウムがスパッタリングされ酸素との酸化が起こる場合は、優先的に印加される。高周波の有効電力は20Wに設定され電極5を流れる直流電流は約1.14Aである。

第6図は純アルゴン雰囲気下における電流電圧特性を示し、ここにはプラズマについての高周波の効果がはっきり示されている。純直流動作における電流電圧特性を示す測定値はX印で表わされ、変調電圧での電流電圧特性を示す測定印は○印で表わされている。陰極5での高周波電力はここで約20Wである。この有効電力は純直流の場合および高周波の場合のスパッタリング率を比較して決定された。第6図においては2つの本質的な事項が認められる。すなわち、直流マグネトロン放電のための典型的な電力密度10W/cm²（第6図においては約600V/0.8A）から開始して、同一の直流電圧のときの直流の放電電流は重畳高周波電力20Wのときすでに、ゼロになっている。すなわち、変調振幅が約140Vのとき電流は0.18Aだけ減少する。

磁界に支持された直流マグネトロン放電用として、直流電力の約5%の高周波変調は強烈な効果を有している。直流出力電力は約100W（＝2.3W/cm²）減少される。明らかに高周波電界は陰極5の前で循環している電子のドリフト電流を妨害する。高周波電界に追随できる電子はさらに陰極5から取り除かれる。このことは電子の衝突確率が減少することを意味する。これと関連して電子のドリフト損失も減少する。

この結果は純二極管スパッタリング動作中のブラトニー（Vratny）の観測と矛盾する。それによれば二極管高周波変調された直流電圧が印加されると、直流放電電流が著しく増加するという。ブラトニーによって示された高周波電力約200Wは所与の直流電流および高周波電力の約43%である。これが実際に陰極上に効果のある高周波電力であるかどうかは述べられていない。

第6図において、直流陰極電圧の減少に伴ない、高周波変調のときの直流放電電流はゆっくりと減少を続ける。350V以下のときの直流放電電流は純直流の放電より大きい値である。純直流電流の放電は290Vでなくなるが、高周波変調放電の直流成分は減少して純高周波放電の固有直流電位である140Vでゼロになる。

このようにマグネトロンの場合、純高周波の放電の直流電位と純直流の放電範囲との間において、高周波変調の直流を用いた場合、直流電流成分の増加が観察される。反応的処理にとって2番目に重要であるこの範囲において、高周波放電の高いイオン化効果が決定される。

純二極管スパッタリングにおけるブラトニーによる結論および観察は一般に本発明にとってはあまり重要ではないこの効果に関連している。

定電力の高周波変調による直流マグネトロン放電で広い範囲において、直流電流を減少させることのほとんど予見できず実際には歓迎されない効果は、反応動作中に増加された第2電子発生量によりターゲットを部分的に酸化することで十分補償される。この効果の程度は使用される物質および気体に依る。アルゴン/酸素の雰囲気中におけるAℓ、Si、Snおよびアルゴル/窒素の雰囲気中におけるAℓおよびSiについてはその効果は実験によってすでに確認ずみである。

4．図面の簡単な説明

第1図は本発明による装置の基本的構成図、第2図は公知の直流マグネトロン・スパッタリング装置において圧力7×10^{-3}ミリバールのもとで、陰極電圧の関数としての陰極電流、スパッタリング率およびスパッタリング出力を示す図、第3図はアルゴン圧7×10^{-3}ミリバール、酸素流

04/25/2002, EAST Version: 1.03.0002

量6．7ＳＣＣＭ／分で一定およびアルミニウムのターゲットのもとにおける直流陰極電圧の関数としての陰極電流および酸素分圧を示す図、第4図はアルゴン圧7×10^{-3}ミリバール、酸素流量6．7ＳＣＣＭ／分で一定、振幅140Ｖの重畳高周波電圧およびアルミニウムのターゲットのもとで直流陰極電圧の関数としての陰極電流および酸素分圧を示す図、第5図は交流電圧が重ねられた直流陰極電圧を示す図、第6図は純アルゴン雰囲気下において直流陰極電圧および直流電圧と重畳交流電圧との結合電圧の関数としての陰極電流を示す図である。

1…基板、2…絶縁層、3…ターゲット、5…陰極、7，8，9…永久磁石、10…直流電源、24，25…コンテナ、30…高周波電源

特許出願人　レイボルト　アクチーエンゲゼルシャフト
代理人　弁理士　鈴木弘男

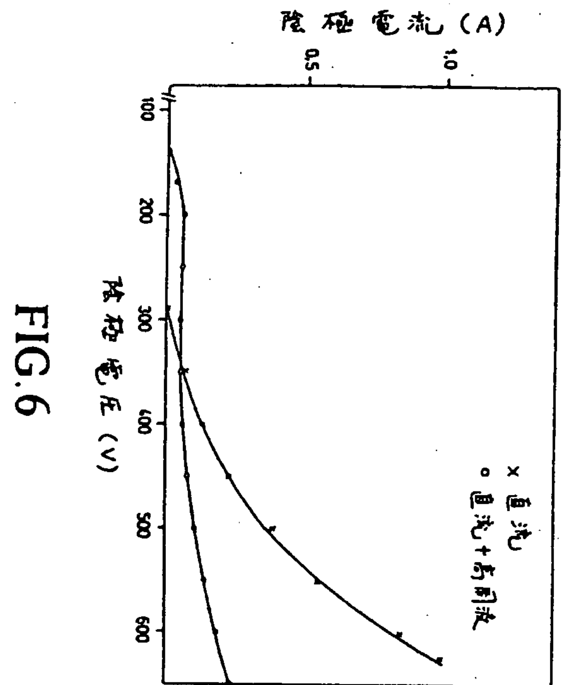


FIG.6

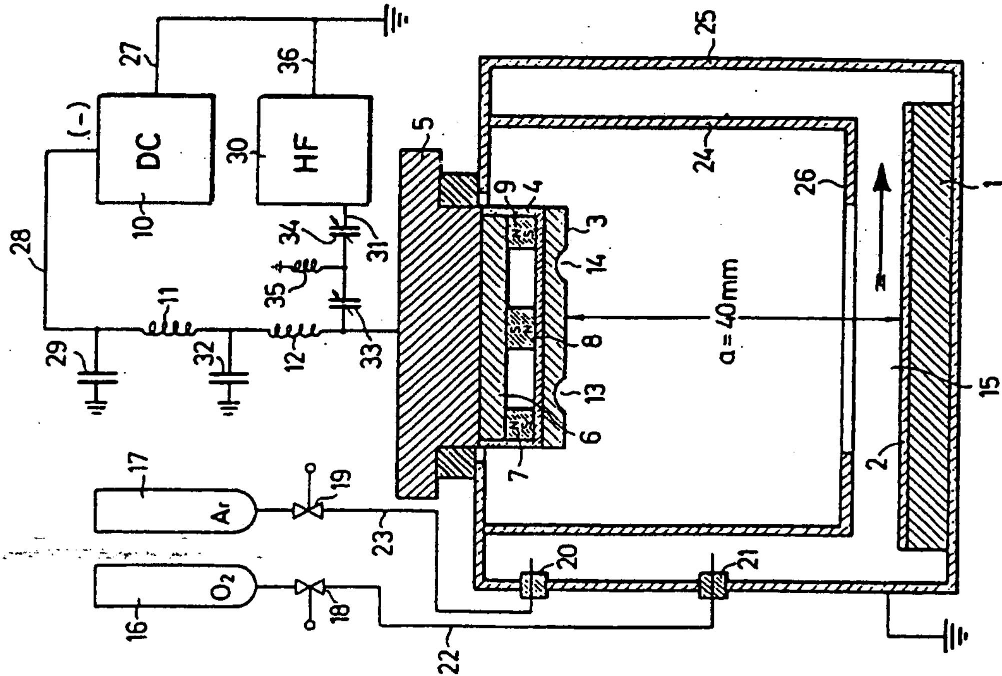


FIG.1

04/25/2002, EAST Version: 1.03.0002

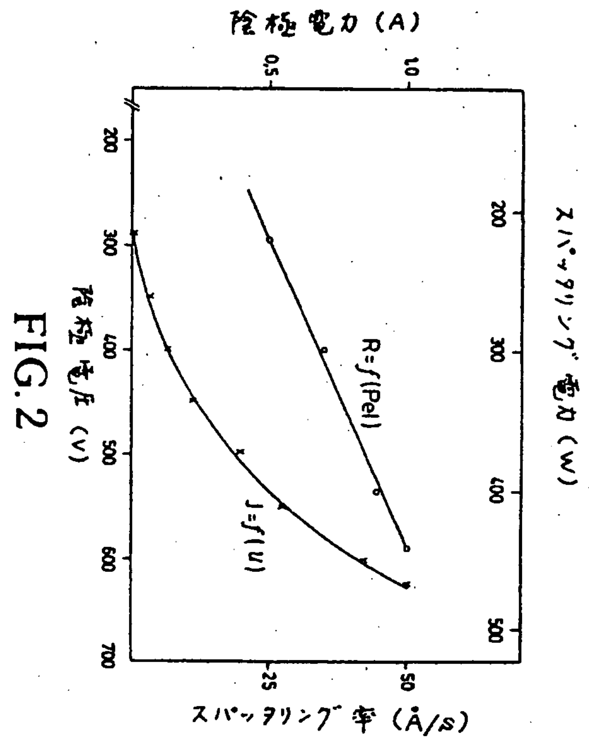


FIG.2

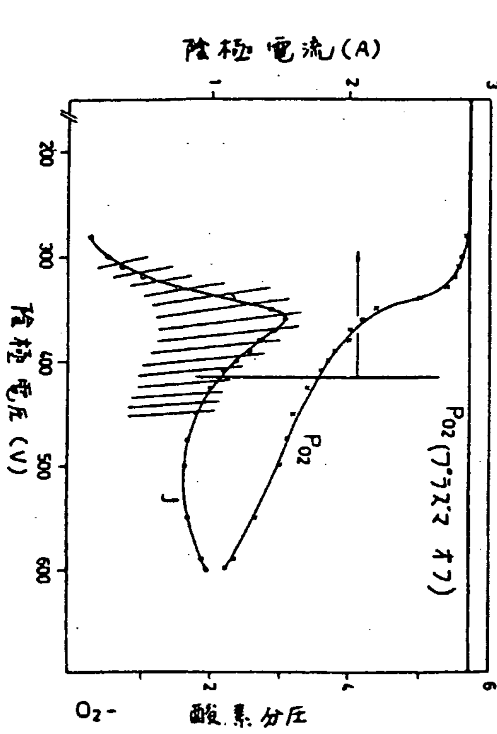


FIG.3

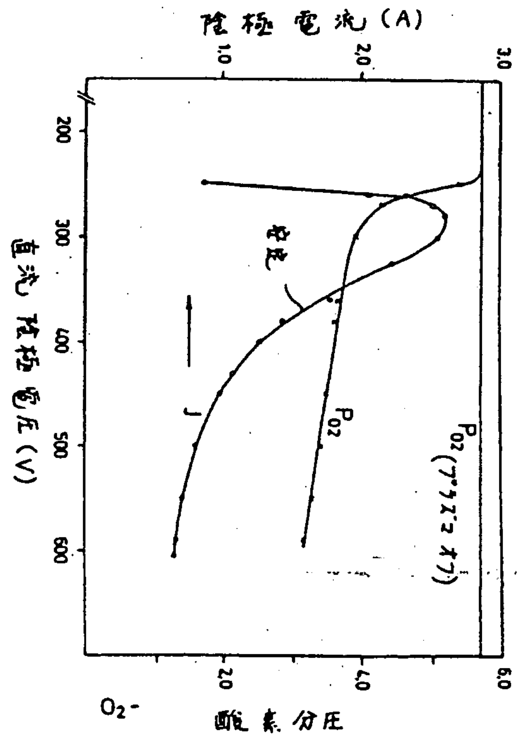


FIG.4

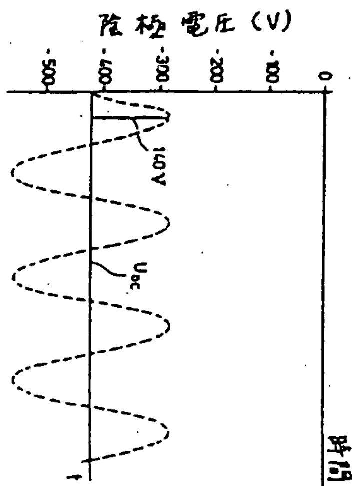


FIG.5

04/25/2002, EAST Version: 1.03.0002

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C03C 13/04, H01S 3/06	A1	(11) International Publication Number: WO 00/21898 (43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/KR99/00609

(22) International Filing Date: 11 October 1999 (11.10.99)

(30) Priority Data:
1998/42713 13 October 1998 (13.10.98) KR

(71) Applicant: SAMSUNG ELECTRONICS CO., LTD. [KR/KR]; 416, Maetan-dong, Paldal-gu, Suwon-city, Kyunggi-do 442-373 (KR).

(72) Inventors: HEO, Jong; 8-401, Kyosoo Apt., Jigok-dong, Nam-gu, Pohang-city, Kyungsangbuk-do 790-390 (KR). LEE, Dong-chin; 7/1, 94-10, Onchun 1-dong, Tongrae-gu, Pusan 607-061 (KR). PARK, Se-ho; 246-55, Junggok 1-dong, Kwangjin-gu, Seoul 143-221 (KR). JUNG, Sun-tae; 602-1503, Taeyoung Apt., 1075, Hogae-dong, Tongan-gu, Anyang-city, Kyungki-do 431-080 (KR). KIM, Hyoun-soo; 801-1002 Jinheung Apt., Imae-dong, Bundang-gu, Sungnam-city, Kyungki-do 463-060 (KR).

(74) Agent: LEE, Young-pil; The Cheonghwa Building, 1571-18, Seocho-dong, Seocho-gu, Seoul 137-073 (KR).

(81) Designated States: AU, CA, CN, JP, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: OPTICAL FIBER FOR LIGHT AMPLIFIER

(57) Abstract

An optical fiber used for an optical amplifier, which is formed by doping glass with rare-earth ions. Both praseodymium ions (Pr^{+3}) and erbium ions (Er^{+3}) are used as the rare-earth ions, and the glass is a fluoride glass or a sulfide glass. The optical fiber can be used at both wavelengths of 1.3 μm and 1.55 μm. The light amplification efficiency of an optical amplifier made of the optical fiber can be improved compared to an optical amplifier formed of only Pr^{+3} or only Er^{+3}.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	Country	Code	Country	Code	Country	Code	Country
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

OPTICAL FIBER FOR LIGHT AMPLIFIER

Technical Field

The present invention relates to optical fibers for use in a light amplifier,
5 and more particularly, to an optical fiber for use in a light amplifier which can be used at wavelengths of both 1.3 μm and 1.55 μm.

Background Art

The wavelength of light used in optical communications has been
10 shifted from a wavelength of 1.3 μm to a wavelength of 1.55 μm. In general, praseodymium ions (Pr^{+3}) which are used to dope an optical fiber, are used to amplify an optical signal having a wavelength of 1.3 μm while erbium ion (Er^{+3}) which are used to dope an optical fiber, are used to amplify an optical signal having a wavelength of 1.55 μm.

15 U.S. Patent No. 5,486,947 discloses an optical fiber for use in an optical amplifier, which are capable of operating with optical sufficient optical gain at the 1.3 μm wavelength. The optical fiber is a fluoride glass optical fiber containing rare earth metal ions in a core glass, wherein the refractive index difference between the core and a cladding layer is above 1.4%, and the glass
20 contains lead difluoride (PbF_2) in a proportion of 25 mol % or less based on the total composition for forming the glass.

Now, both wavelengths of 1.3 μm and 1.55 μm are used in many optical communications related fields. Thus, different parts which are suitable for each wavelength, are required to construct an optical circuit, so that
25 development cost increases in addition to switching cost for switching the wavelengths.

Disclosure of the Invention

An object of the present invention is to provide an optical fiber for use
30 in an optical amplifier, which can be used for both the 1.3 μm and 1.55 μm bands.

According to an aspect of the present invention, there is provided an optical fiber for an optical amplifier, which is formed by doping glass with rare-earth ions, wherein both praseodymium ions (Pr^{+3}) and erbium ions (Er^{+3}) are used as the rare-earth ions, and the glass is a fluoride glass or a sulfide glass.

5 Preferably, the content of Pr^{+3} is 100~1000 ppm and the content of Er^{+3} is 100~5000 ppm. If the Pr^{+3} and Er^{+3} content is outside the above range, light amplification efficiency is undesirably lowered. Also, the mixing ratio of Pr^{+3} to Er^{+3}, by weight, may be between 1:1 and 1:3. If the ratio of Pr^{+3} to Er^{+3} exceeds the above ratio, fluorescence emission quantity at the wavelength of 10 1.55 μm is decreased. Conversely, if the ratio of Pr^{+3} to Er^{+3} is less than the above ratio, the amplification at the wavelength of 1.3 μm unfavorably decreased.

Brief Description of the Drawings

15 FIG. 1 shows the fluorescence emission spectrum at wavelengths of 1.3 μm and 1.55 μm according to the amount of Er^{+3} in optical fibers, when a laser beam having a wavelength of 980 nm is irradiated onto an optical fiber which is formed by doping glass made of $Ge_{29}As_8Ga_1S_{62}$ with Pr^{+3} and Er^{+3}, wherein the fluorescence emission at the wavelength of 1.3 μm is caused by the 20 electron transition of Pr^{3+} from the $^1G_4$ level to the $^3H_5$ level in Pr^{+3} doped fibers, and that at the wavelength of 1.55 μm is caused by the transition $^4I_{13/2}$ → $^4I_{15/2}$ in Er^{3+} doped fibers ;

FIG. 2 is a graph showing the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level and of Er^{+3} at the $^4I_{13}/2$ level and $^4I_{11}/2$ level according to the amount of 25 Er^{+3} in optical fibers, when a laser beam having a wavelength of 980 nm is irradiated onto an optical fiber which is formed by doping a $Ge_{29}As_8Ga_1S_{62}$ glass with Pr^{+3} and Er^{+3};

FIG. 3 is a diagram illustrating energy transfer between Pr^{+3} and Er^{+3} ions;

30 FIG. 4 shows the fluorescence emission spectrum at the wavelength of 1.3 μm by the electron transition of Pr^{+3} from the $^1G_4$ level to the $^3H_5$ level when a laser beam having a wavelength of 1020 nm is irradiated onto an optical fiber which is formed by doping a $Ge_{29}As_8Ga_1S_{62}$ glass with Pr^{+3};

FIG. 5 shows the fluorescence emission spectrum at the wavelength of 1.55 μm by the electron transition of Er^{+3} from the $^4I_{13/2}$ level to the $^4I_{15/2}$ level when a laser beam having a wavelength of 980 nm is irradiated onto an optical fiber which is formed by doping a $Ge_{29}As_8Ga_1S_{62}$ glass with Er^{+3}; and

5 FIG. 6 shows the fluorescence emission spectrum at the wavelengths of 1.3 μm and 1.55 μm according to the amount of Pr^{+3} in optical fibers, when a laser beam having a wavelength of 980 nm is irradiated onto an optical fiber which is formed by doping a $Ge_{29}As_8Ga_1S_{62}$ glass with Pr^{+3} and Er^{+3}, wherein the fluorescence emission at the wavelength of 1.3 μm is due to the electron

10 transition of Pr^{3+} from the $^1G_4$ level to the $^3H_5$ level, and that at the wavelength of 1.55 μm is due to the electron transition of Er^{3+} from the $^4I_{13/2}$ level to the $^4I_{15/2}$ level.

Best mode for carrying out the Invention

15 The present invention provides an optical fiber for use in a light amplifier, which can be used at wavelengths of both 1.3 μm and 1.55 μm, by using a laser beam having a wavelength of 980 nm as a light source for exciting an optical fiber formed of Pr^{+3} and Er^{+3}. In the present invention, the term "fibers" refers ro shapes with a wide range of diameters, not merely thin

20 fibers. For example, a fiber may have diameter of 5 to 100mm. In the present invention, the fiber contains Pr^{+3} and Er^{+3}, wherein the maximum absorption peak of Er^{+3} in a laser beam having wavelength 980 nm is at the $^4I_{11/2}$ level. In this case, two ions are simultaneously excited, so that Pr^{+3} emits fluorescence at 1.3 μm and Er^{+3} emits fluorescence at 1.55 μm. In particular,

25 as shown in FIG. 3, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level is elongated due to the energy transfer from Er^{+3}, so that light amplification efficiency is improved compared to a conventional optical fiber containing only Pr^{+3}.

Preferably, in the present invention, a fluoride or sulfide glass is used

30 to minimize lattice vibration relaxation of Pr^{+3} from the $^1G_4$ level to $^3F_4$ level. The fluoride glass may be a ZBLAN glass which is a fluoride containing zirconium (Zr), barium (Ba), lanthanum (La), aluminum (Al) and sodium (Na), and the sulfide glass may be a germanium-arsenic-gallium-sulfur (Ge-As-Ga-

S) or Ge-As-S glass. Here, using the sulfide glass can further minimize the lattice vibration relaxation of Pr^{+3} from the $^1G_4$ level to the $^3F_4$ level compared to the case of using the fluoride glass. However, using the fluoride glass rather than a sulfide glass generally makes the manufacture of optical fiber easier.

5 In order to maximize the light amplification efficiency at both wavelengths of 1.3 μm and 1.55 μm, the mixing weight ratio of Pr^{+3} and Er^{+3} is adjusted to be between 1:1 and 1:3.

Hereinafter, the present invention will be described using the following examples. However, these examples are merely illustrative and the present

10 invention is not limited thereto.

Comparative Example 1

Ge, As, Ga and S having a purity of 99.999% or more, were weighted in an atomic ratio of 29:8:1:62 in a glove box where the content of hydroxy

15 (OH) group and oxygen was maintained to be 10 ppm or less, and Pr metal powder was added in amount of 300 ppm to give the Pr^{+3}.

After filling a SiO_2 test tube with the above composition, the test tube was left under a vacuum condition of 0.1 mTorr for a predetermined period of time. Then, the test tube was made airtight by sealing it with an oxy-propane

20 flame.

Following this, the test tube was put into a rocking furnace such that the composition comprised in the test tube was completely mixed, and the resultant was kept at 950°C for 12 hours. Then, the test tube was quenched in air, and heated in a furnace which was set at 400°C for 1 hour. After the

25 heating process, the test tube was slowly cooled to room temperature and broken into pieces, resulting in an optical fiber formed of a Pr^{+3}-doped sulfide glass of $Ge_{29}As_8Ga_1S_{62}$ in which the amount of lattice vibration relaxation was slight. The optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished.

30 Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 1017 nm as a source of light excitation. At this wavelength, Pr^{+3} at the $^1G_4$ level showed a maximum light absorption.

As a result, the fluorescence emission at a wavelength of 1.3 μm, which was caused by electron transition of Pr^{+3} from the $^1G_4$ level to $^3H_5$ level, was observed (see FIG. 4), and the fluorescence lifetime was 305 μsec (see FIG. 2).

5

Comparative Example 2

An optical fiber was manufactured in the same manner as in Comparative Example 1 except that Er^{+3} was used instead of Pr^{+3}. Er_2S_3 was used as the source of Er^{+3}. Then, the optical fiber was cut into a disc
10 shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

15 As a result, the fluorescence emission at a wavelength of 1.55 μm, which was caused by electron transition of Er^{+3} from the $^4I_{13/2}$ level to $^4I_{15/2}$ level, was observed (see FIG. 5), and the fluorescence lifetime at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 2100 μsec and 3400 μsec, respectively (see FIG. 2)

20 Example 1

An optical fiber was manufactured in the same manner as in Comparative Example 1 except that Er^{+3} was further added in the amount of 300 ppm together with 300 ppm of Pr^{+3}. Then, the optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and
25 polished. Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by
30 electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see

FIG. 1 (a)). The intensify of fluorescence was increased at each wavelength compared to that of Comparative Examples 1-2. Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was 605 μsec, and the fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 824 μsec and 3120 μsec,
5 respectively (see FIG. 2).

According to Example 1, as shown in FIG. 3, the simultaneous fluorescence emission at the wavelengths of 1.3 μm and 1.55 μm was due to the effective energy transfer indicated by "b". Thus, the optical fiber obtained in Example 1 can be used at wavelengths of both 1.3 μm and 1.55
10 μm.

Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was markedly elongated to 605 μsec compared to Comparative Example 1, and the light amplification efficiency at the wavelength of 1.3 μm was further improved by adding both Pr^{+3} and Er^{+3}. However, the fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$
15 level was 3120 μsec, which is lower than in Comparative Example 2, thus lowering light amplification efficiency. This is due to the energy transfer indicated by "e".

Example 2

20 An optical fiber was manufactured in the same manner as in Comparative Example 1 except that 500 ppm of Er^{+3} was further added together with 300 ppm of Pr^{+3}. Then, the optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. Then, the fluorescence spectrum and fluorescence lifetime of the resultant
25 were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was
30 caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see FIG. 1 (b)). The intensify of fluorescence was increased at each wavelength

compared to that of the Comparative Examples 1-2. Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was 760 μsec, and the fluorescent lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 1740 μsec and 2910 μsec, respectively (see FIG. 2).

5 According to Example 2, as shown in FIG. 3, the simultaneous fluorescence emission at the wavelengths of 1.3 μm and 1.55 μm was due to the effective energy transfer indicated by "b". Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was markedly elongated to 760 μsec compared to Comparative Example 1 and Example 1, and the fluorescence 10 lifetime of Er^{+3} at the $^4I_{13/2}$ level was decreased to 2910 μsec, compared to Comparative Example 2 and Example 1.

From the above result, it can be understood that the energy transfer indicated by "b" and "e" occur more effectively as the content of Er^{+3} increases. However, the fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$ level was 15 increased to 1740 μsec, compared to Example 1. As a result, it was concluded that as Er^{+3}, which is not involved in the energy transfer indicated by "b", increases, the energy transfer degree in the direction indicated by "b" decreases.

20 <u>Example 3</u>

An optical fiber was manufactured in the same manner as in Comparative Example 1 except that 700 ppm of Er^{+3} was further added together with 300 ppm of Pr^{+3}. Then, the optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. 25 Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by 30 electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see

FIG. 1 (c)). The intensify of fluorescence was increased at each wavelength compared to that of Examples 1-2. Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was 769 μsec, and the fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 1760 μsec and 2920 μsec, respectively (see FIG. 2).

5 According to Example 3, as the content of Er^{+3} increased, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was slightly increased. This was due to an increase in energy transfer indicated by "b" shown in FIG. 3. However, because Er^{3+} was contributed for elongating the fluorescence lifetime at the $^4I_{11/2}$ and $^4I_{13/2}$ levels, the ratio of Er^{+3} associated with the

10 energy transfer indicated by "b" and "e" was decreased, thus resulting in a slight increase in fluorescence lifetime of Pr^{+3} at the $^1G_4$ level. That is, the light amplification efficiency at the wavelength of 1.55 μm showed a tendency to increases with an increase in the fluorescence lifetime of Er^{+3} at the $^4I_{13/2}$ level.

15

Example 4

An optical fiber was manufactured in the same manner as in Comparative Example 1 except that 1000 ppm of Er^{+3} was further added together with 300 ppm of Pr^{+3}. Then, the optical fiber was cut into a disc

20 shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

25 As a result, the fluorescence emission of Pr^{+3}, which was caused by electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see FIG. 1 (d)). The intensify of fluorescence was increased at each wavelength

30 compared to that of Examples 1-3. Also, the fluorescence lifetime of Pr^{+3} at the $^1G_4$ level was 881 μsec, and the fluorescent lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 2030 μsec and 3340 μsec, respectively (see FIG. 2).

According to Example 4, as shown in FIG. 3, the simultaneous fluorescence emission at the wavelength of 1.3 μm by Pr^{+3} at the $^1G_4$ level, and at the wavelength of 1.55 μm by Er^{+3} at the $^4I_{13/2}$ level, was due to effective energy transfer indicated by "b". Also, the fluorescence lifetime of
5 Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels showed the maximum levels. Thus, it can be understood that the mixing ratio of Pr^{+3} and Er^{3} in this embodiment shows the maximum light amplification efficiency at both 1.3 μm and 1.55 μm.

10 Example 5

An optical fiber was manufactured by the same manner as in Comparative Example 1 except that 1500 ppm of Er^{+3} was further added together with 300 ppm of Pr^{+3}. Then, the optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished.
15 Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by
20 electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see FIG. 1 (e)). The intensify of fluorescence was saturated, i.e., at the maximum level, at each wavelength. Also, the fluorescence lifetime of Pr^{+3}
25 at the $^1G_4$ level was 794 μsec, and the fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was 1870 μsec and 3240 μsec, respectively (see FIG. 2).

According to Example 5, as shown in FIG. 3, the simultaneous fluorescence emission at the wavelength of 1.3 μm by Pr^{+3} at the $^1G_4$ level and at the wavelength of 1.55 μm by Er^{+3} at the $^4I_{13/2}$ level was due to
30 effective energy transfer indicated by "b". The fluorescence lifetime of Er^{+3} at the $^4I_{11/2}$ and $^4I_{13/2}$ levels was slightly decreased compared to Example 4, because the energy transfer indicated by "b" and "e" were saturated.

Example 6

Ge, Ga and S having a purity of 99.999% or more, were weighted in an atomic ratio of 25:5:70 in a glove box where the content of hydroxy (OH) group and oxygen was maintained to be 10 ppm or less, and 300 ppm of
5 Pr^{+3} and 300 ppm of Er^{+3} were added.

After filling a SiO_2 test tube with the composition, the test tube was left under a vacuum condition of 0.1 mTorr for a predetermined period of time. Then, the test tube was made airtight by sealing it with an oxy-propane flame.

10 Following this, the test tube was put into a rocking furnace such that the composition comprised in the test tube was completely mixed, and the resultant was kept at 950°C for 12 hours. Then, the test tube was quenched in air, and heated in a fumace which was set at 260°C for 1 hour. After the heating process, the test tube was slowly cooled to room temperature and
15 broken into pieces, resulting in an optical fiber formed of a Pr^{+3} and Er^{+3} doped sulfide glass of $Ge_{25}Ga_5S_{70}$ in which the amount of lattice vibration relaxation was slight.

The optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. Then, the fluorescence
20 spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by
25 electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see FIG. 6 (a)).

According to Example 6, it can be understood that both a Ge-GA-S
30 glass doped with Pr^{+3} and Er^{+3} and a Ge-As-Ga-S glass doped with Pr^{+3} and Er^{+3} can be used as a material of an optical amplifier which can be used at both 1.3 μm and 1.55 μm.

Example 7

An optical fiber was manufactured in the same manner as in Example 6 except that the amount of Pr^{+3} was increased to 500 ppm. Then, the optical fiber was cut into a disc shape (having a diameter of 10 mm and a thickness of 3 mm) and polished. Then, the fluorescence spectrum and fluorescence lifetime of the resultant were measured using a laser beam having a wavelength of 980 nm as a source of light excitation. At this wavelength, Er^{+3} at the $^4I_{11/2}$ level showed a maximum light absorption.

As a result, the fluorescence emission of Pr^{+3}, which was caused by electron transition from $^1G_4$ level to $^3H_5$ level and that of Er^{+3}, which was caused by electron transition from $^4I_{13/2}$ level to $^4I_{15/2}$ level were observed simultaneously at the wavelengths of 1.3 μm and 1.55 μm, respectively (see FIG. 6 (b)). Also, as the amount of Pr^{+3} was increased, energy transfer in directions indicated by "b" and "e" in FIG. 3 increased. As a result, the fluorescence intensity of Pr^{+3} at the $^1G_4$ level increased at the wavelength of 1.3 μm, whereas that of Er^{+3} at the $^4I_{13/2}$ level decreased at the wavelength of 1.55 μm. However, the rate at which the fluorescence intensity increases at 1.3 μm is slower than the rate at which the fluorescence intensity decreases at 1.55 μm, and thus it can be inferred that the energy transfer indicated by "e" is more rapid than that indicated by "b".

Summing up the results, it can be understood that increasing the concentration of Pr^{+3} is undesirable.

Industrial Applicability

As described above, the optical fiber used in an optical amplifier according to the present invention can be applied to both wavelengths of 1.3 μm and 1.55 μm, improving light amplification efficiency compared to a conventional optical fiber amplifier containing only Pr^{+3}.

What is claimed is:

1. An optical fiber for an optical amplifier, which is formed by doping glass with rare-earth ions, wherein both praseodymium ions (Pr^{+3}) and erbium ions (Er^{+3}) are used as the rare-earth ions, and the glass is a
5 fluoride glass or a sulfide glass.

2. The optical fiber of claim 1, wherein the sulfide glass is a germanium-arsenic-gallium-sulfide (Ge-As-Ga-S) glass or a Ge-As-S glass.

10 3. The optical fiber of claim 1, wherein the fluoride glass is a ZBLAN glass containing zirconium (Zr), barium (Ba), lanthanum (La), aluminum (Al) and sodium (Na).

4. The optical fiber of claim 1, wherein the mixing weight ratio of
15 Pr^{+3} to Er^{+3} is between 1:1 and 1:3.

5. The optical fiber of claim 1, wherein a laser having a wavelength capable of absorbing Er^{+3} is used as a light source for exciting the optical fiber.

20

6. The optical fiber of claim 1, wherein the content of Pr^{+3} is 100~1000 ppm and the content of Er^{+3} is 100~5000 ppm.

FIG. 1

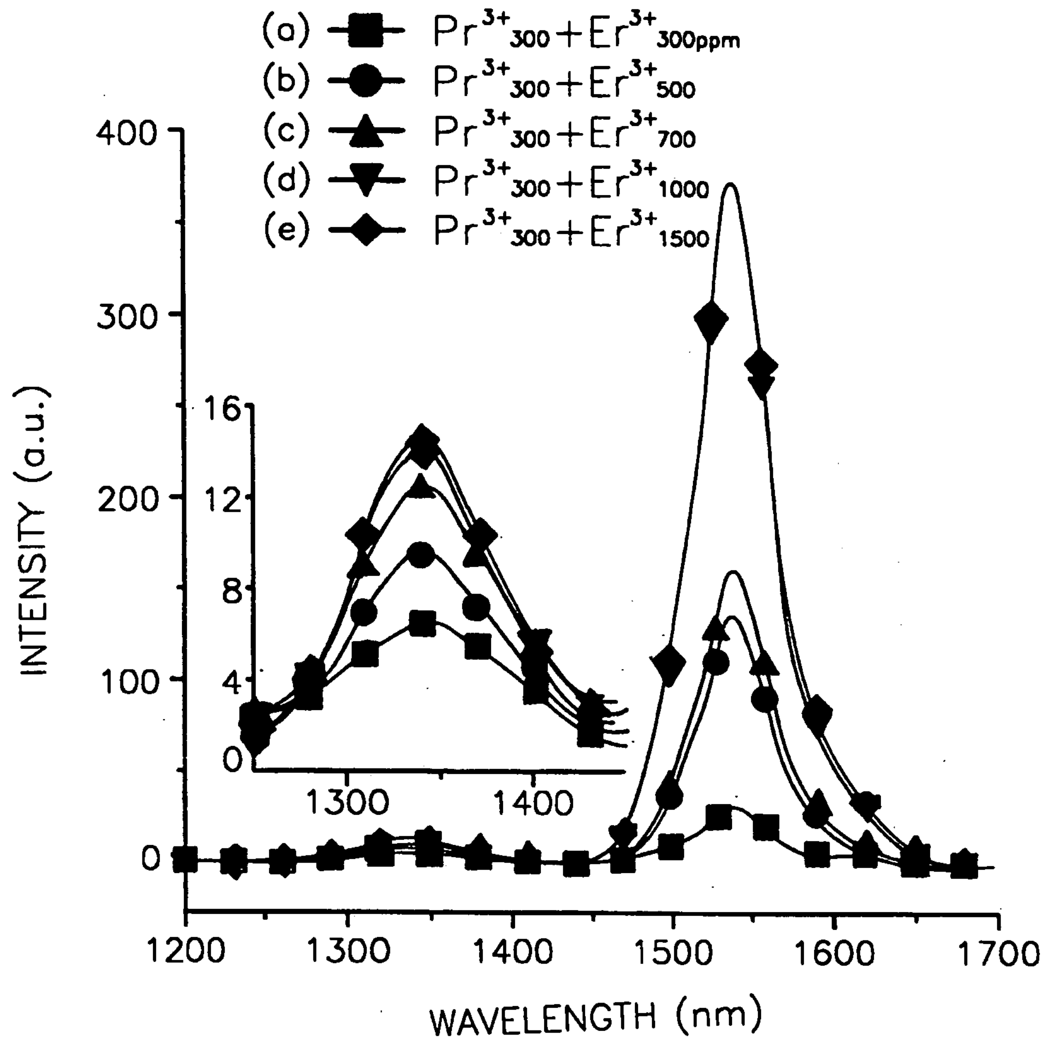


FIG. 2

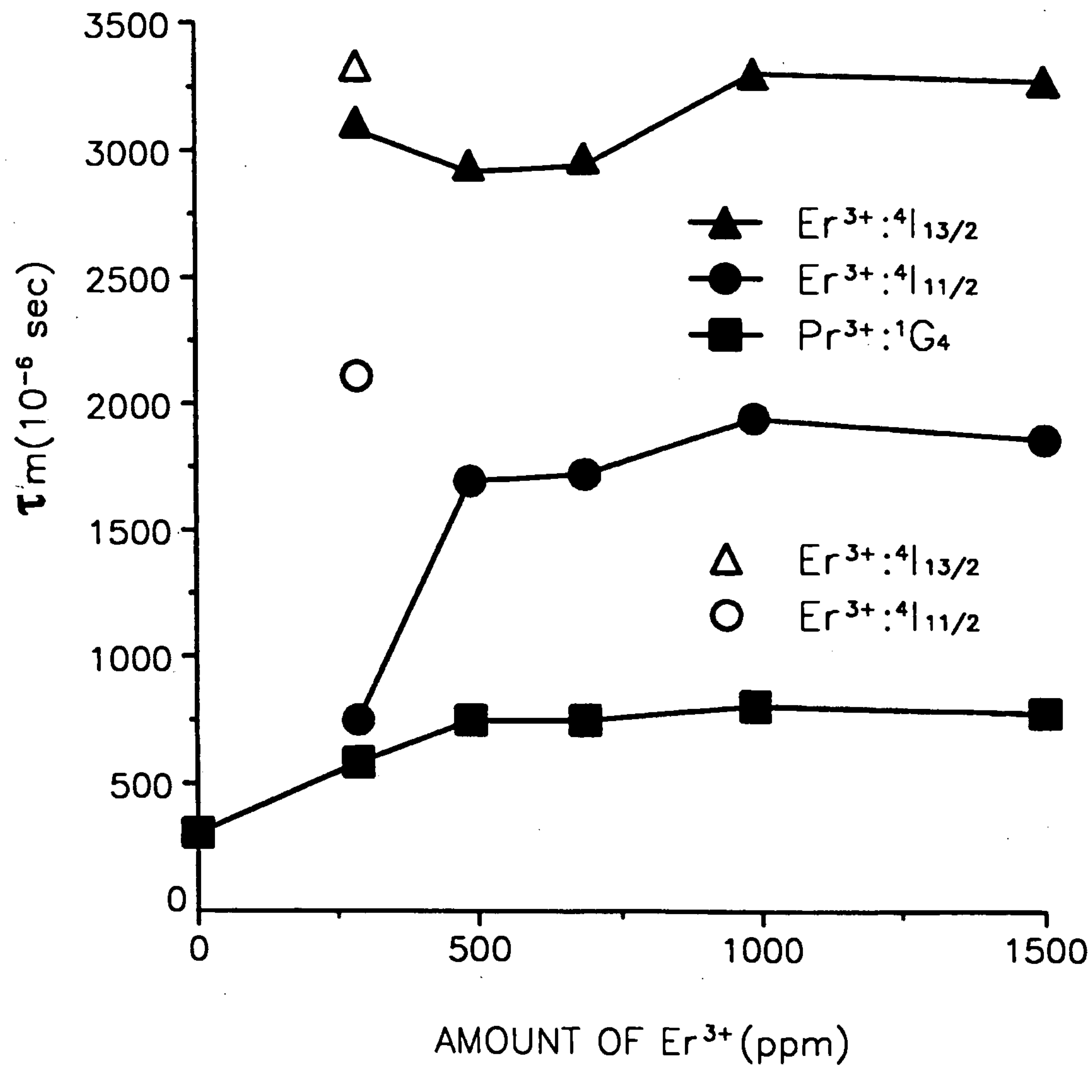


FIG. 3

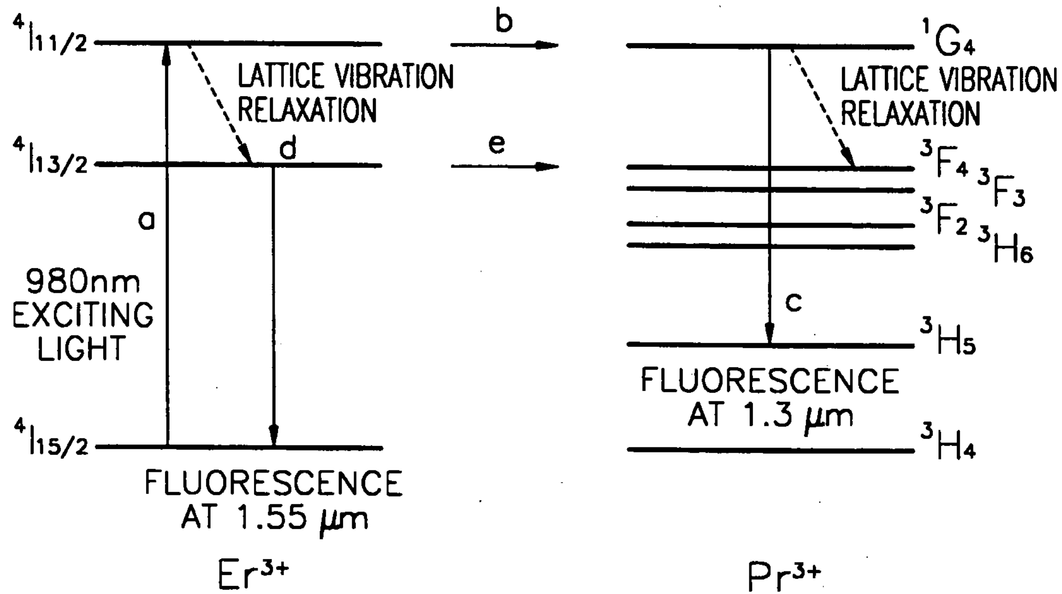


FIG. 4

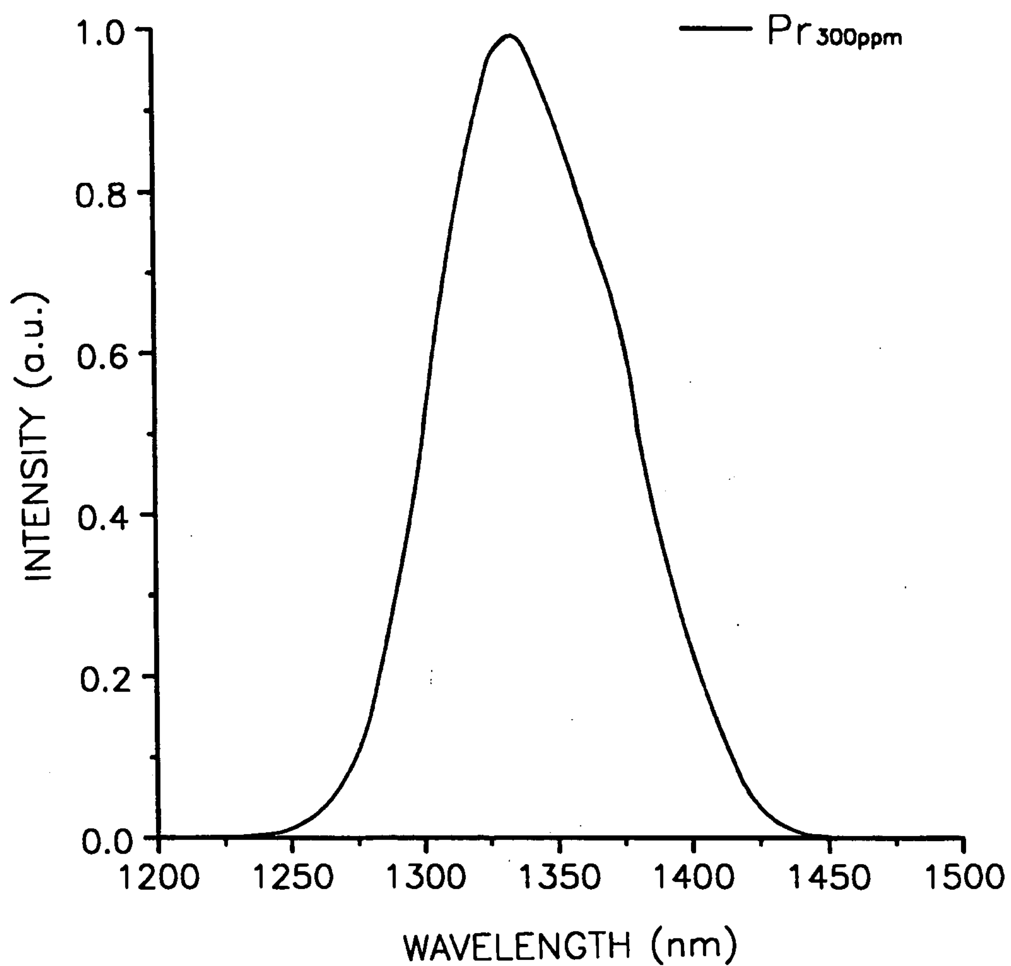


FIG. 5

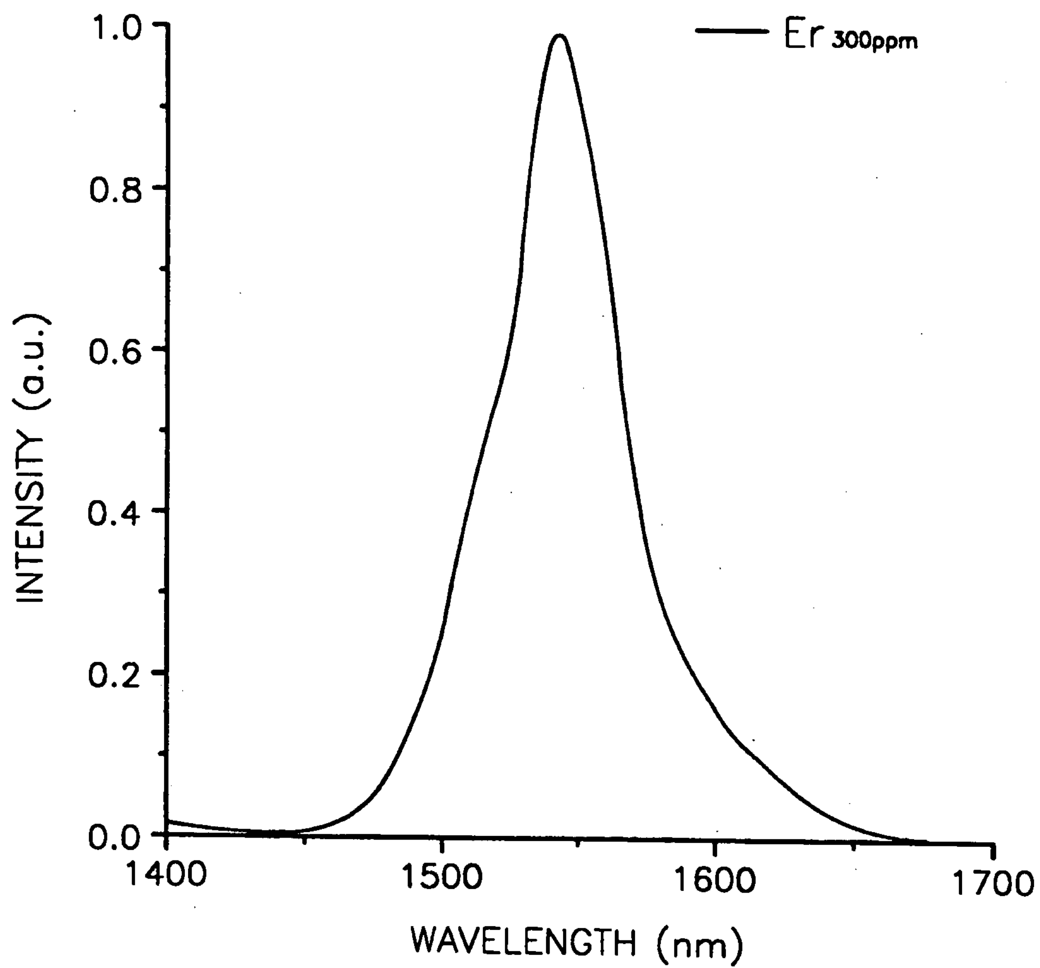
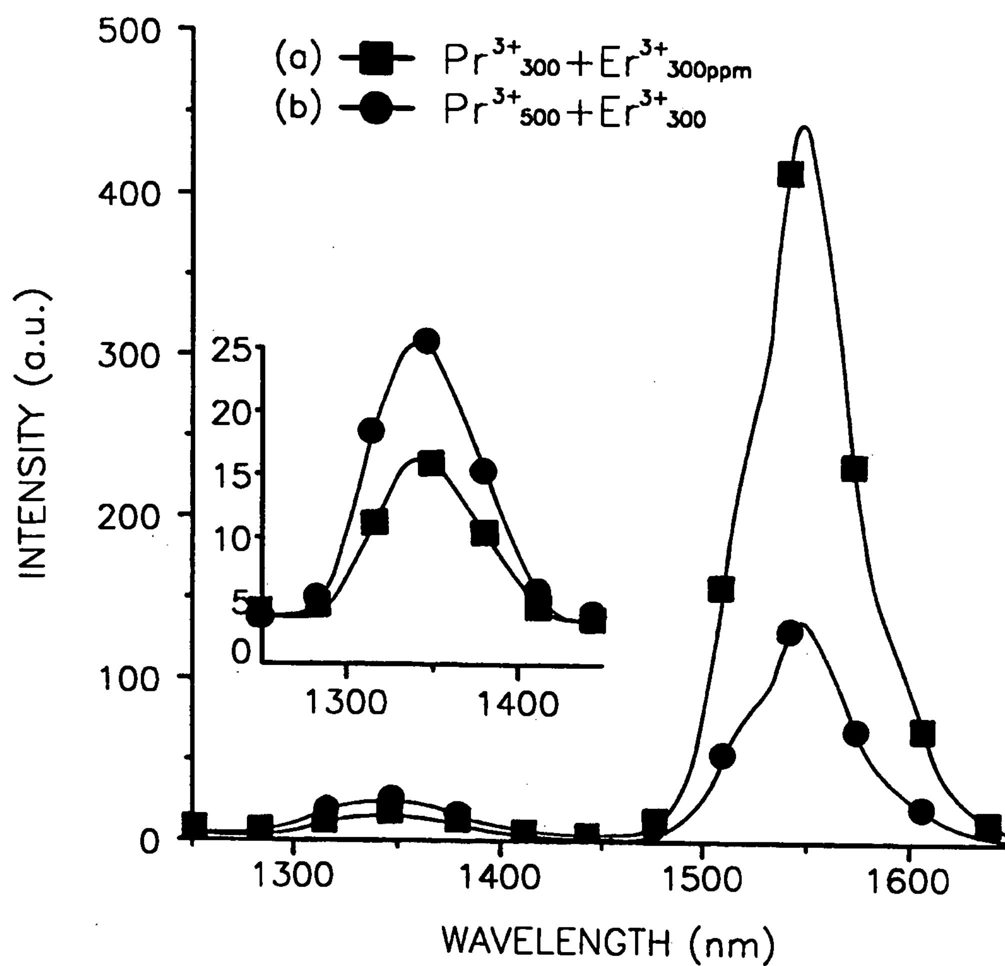


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00609

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C 03 C 13/04; H 01 S 3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C 03 C; H 01 S

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5486947 A (OHISHI et al.), 23 January 1996 (23.01.96), abstract; column 2, line 45 - column 3, line 58; example 29.	1,3-6
A	EP 0511069 A1 (ALCATEL N.V.), 28 October 1992 (28.10.92), claim 1; column 2, lines 1-9.	1,3
A	JP 08-104533 A (NIPPON TELEGRAPH), 23 April 1996 (23.04.96), (abstract), [online] [retrieved on 24 November 1999 (24.11.99)]. Retrieved from: EPO PAJ Database.	1

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
„L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed
„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 1999 (24.11.99)	18 February 2000 (18.02.00)
Name and mailing adress of the ISA/AT Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer Hauswirth Telephone No. 1/53424/136

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00609

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US A 5486947	23-01-1996	US A 5351335	27-09-1994
		DE C0 69223720	05-02-1998
		DE T2 69223720	23-04-1998
		EP A2 535798	07-04-1993
		EP A3 535798	15-09-1993
		EP A2 733600	25-09-1996
		EP A3 733600	02-01-1997
		EP B1 535798	29-12-1997
		EP B1 733600	12-01-2000
		JP A2 6069584	11-03-1994
		JP B2 2772349	02-07-1998
EP A1 511069	28-10-1992	AT E 122180	15-05-1995
EP B1 511069	03-05-1995	CA AA 2066549	23-10-1992
		CA AA 2066549	22-10-1993
		CA C 2066549	31-12-1996
		DE C0 69202296	08-06-1995
		DE T2 69202296	07-09-1995
		ES T3 2071451	16-06-1995
		FR A1 2675592	23-10-1992
		FR B1 2675592	16-07-1993
		JP A2 5183227	23-07-1993
		US A 5185847	09-02-1993
JP A2 8104533	23-04-1996	none	

Best Available Copy

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 092 689 A1

(12) EUROPÄISCHE PATENTANMELDUNG

(43) Veröffentlichungstag:
18.04.2001 Patentblatt 2001/16

(51) Int. Cl.[7]: C03C 17/36

(21) Anmeldenummer: 00119591.6

(22) Anmeldetag: 07.09.2000

(84) Benannte Vertragsstaaten:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Benannte Erstreckungsstaaten:
AL LT LV MK RO SI

(30) Priorität: 11.10.1999 DE 19948839

(71) Anmelder: BPS Alzenau GmbH
63754 Alzenau (DE)

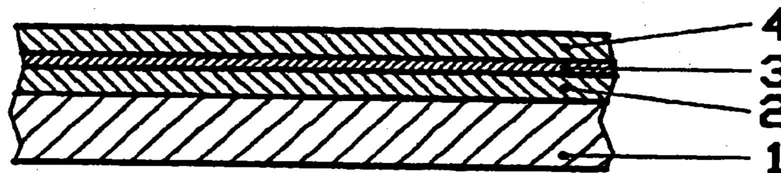
(72) Erfinder:
- Stollenwerk, Johannes, Prof. Dr.
51503 Rösrath (DE)
- Köppel, Andreas
63695 Glauburg (DE)
- Bender, Marcus
35606 Solms (DE)

(74) Vertreter:
Herrmann-Trentepohl, Werner, Dipl.-Ing.
Patentanwälte
Herrmann-Trentepohl
Grosse - Bockhorni & Partner
Forstenrieder Allee 59
81476 München (DE)

(54) **Leitende transparente Schichten und Verfahren zu ihrer Herstellung**

(57) Auf einem Substrat aus Glas (1) ist eine Grundschicht (2) aus Indium-Cer-Oxid und darauf eine dünne Kupfer enthaltende Silberschicht (3), beide hergestellt durch DC-Zerstäubung, aufgebracht. Darauf befindet sich eine weitere Indium-Cer-Oxidschicht (4), welche durch AC-überlagerte DC-Zerstäubung hergestellt wird. Dieses Schichtsystem weist sehr niedere Flächenwiderstände bei gleichzeitig hoher Durchlässigkeit im sichtbaren Spektralbereich, also einen hohen Haackeschen Gütefaktor auf.

Fig.1



Printed by Xerox (UK) Business Services
2.16.7 (HRS)/3.6

BNSDOCID: <EP_______1092689A1_I_>

Best Available Copy

Beschreibung

[0001] Die Erfindung betrifft leitende transparente Schichten nach dem Oberbegriff des Patentanspruches 1 sowie ein Verfahren zur Herstellung dieser leitenden transparenten Schichten nach Patentanspruch 6.

[0002] Leitende transparente Schichten werden heute in der Displaytechnik, in der Optoelektronik sowie als Architekturglas vielfältig eingesetzt. Dabei wird einerseits eine möglichst hohe Transmission im sichtbaren Spektralbereich und andererseits eine möglichst hohe Leitfähigkeit beziehungsweise ein möglichst niederer Flächenwiderstand angestrebt. Als Mass für die Güte leitender transparenter Schichten kann der Haackesche Gütefaktor $\Phi_{TC} = T^{10}/R_S$, definiert in Journal of Applied Physics, Vol. 47, Seite 4086 bis 4089 (1976), verwendet werden. Dabei bedeuten T die optische Transmission der Schicht (als Bruchteil der auffallenden Strahlung) und R_S den Flächenwiderstand in Ω_{sq}. So besitzt beispielsweise eine Schicht mit einer Transmission von 90% und einem Flächenwiderstand von 3 Ω_{sq} einen Haackeschen Gütefaktor von 0,116 Ω^{-1}. Eine Schicht mit einer Transmission von 80% und einem Flächenwiderstand von 5 Ω_{sq} besitzt einen Gütefaktor von 0,021 Ω^{-1}.

[0003] Eine weitere wichtige Eigenschaft eines solchen Schichtsystems ist seine Ätzbarkeit. Diese hängt von seiner chemischen Zusammensetzung und seiner Dicke ab. Fur eine kurze Ätzzeit und gute Kantenschärfe ist es wichtig, dass die Schichtdicke möglichst klein ist, d.h. unter 100 nm beträgt.

[0004] Zur Erzielung hoher Gütefaktoren ist es vorteilhaft, Schichtsysteme aus oxidischen und metallischen Schichten zu kombinieren. So ist es bekannt, sehr dünne Silberschichten zwischen dünne Oxidschichten einzulagern. Durch die Einlagerung zwischen Oxidschichten wird die Silberschicht einerseits stabilisiert und geschützt, andererseits wird gleichzeitig ihre Reflexion vermindert und dadurch die Transmission erhöht. Diese Schichtkombinationen besitzen ferner den Vorteil einer geringen Gesamtschichtdicke, nämlich 100 nm oder weniger, verglichen mit einer Schicht aus Indium-Zinn-Oxid mit vergleichbarem Flächenwiderstand, die eine Dicke von über 500 nm aufweist (S. H. Shin und Koautoren, Thin Solid Films 341 (1999) 225 - 229). Damit können Ätzprozesse, wie sie bei der Herstellung von Displays üblich sind, schneller und mit geringerer Unterätzung hergestellt werden.

[0005] Solche Schichtsyteme sind z. B. beschrieben in: EP 0 599 071 A1, JP 10062602 A und im Artikel von K. K. Choi und Koautoren, Thin Solid Films 341 (1999) 152 - 155.

[0006] In der EP 0 599 071 A1 wird ein Schichtsystem mit der Schichtfolge Indium-Zinn-Oxid, Silber bzw. verschiedene Silberlegierungen, Indium-Zinn-Oxid beschrieben. Durch einstündige Temperung bei 300°C lassen sich Schichten mit einem Flächenwiderstand von 3,2 Ω_{sq} und gleichzeitig guter Transmission im sichtbaren Bereich herstellen. Für die Wellenlängen 435, 545 und 610 nm ergibt sich ein gemittelter Haackescher Gütefaktor von 0,066. Nachteilig ist jedoch die für Displayanwendungen nötige nachträgliche Temperaturbehandlung, da diese einen zusätzlichen Arbeitsschritt bedeutet.

[0007] In der JP 10062602 A wird ein ähnliches Schichtsystem beschrieben. Hier wird eine dünne Silberschicht mit mindestens 1,5 At.-% Goldbeimengung zwischen Oxidschichten, bestehend aus Zinnoxid und Indiumoxid sowie geringen Beimengungen anderer Oxide, eingebettet. Damit werden Schichten mit einem Flächenwiderstand von 4 - 20 Ω_{sq} und hoher Durchlässigkeit bei 550 nm erhalten. Die erhöhten Kosten durch die Goldbeimengung und der relativ hohe Flächenwiderstand müssen als Nachteile angesehen werden.

[0008] In Thin Solid Films 341 beschreiben K. K. Choi und Koautoren ein Schichtsystem bestehend aus Indium-Zinn-Oxid gefolgt von einer Silberschicht und als Deckschicht wiederum Indium-Zinn-Oxid. Zur Verbesserung der Leitfähigkeit werden die Schichten aus Indium-Zinn-Oxid bei 200°C, die Silberschicht jedoch bei Raumtemperatur abgeschieden. Doch durch die Erwärmung vor Abscheidung der zweiten Schicht aus Indium-Zinn-Oxid werden die Eigenschaften der Silberschicht bezüglich optischer Transmission und elektrischer Leitfähigkeit ungünstig beeinflusst. Im besten Fall wurden Schichten mit einem Flächenwiderstand von 4 Ω_{sq} und einer Transmission von 90% bei 550 nm erzielt.

[0009] Es ist weiterhin bekannt, dass bei spezieller Wahl der Materialien und Beschichtungsparameter transparente leitende Schichtsysteme mit 2,93 Ω_{sq} und Transmissionswerten (gegen Luft gemessen) von 89,2 % bei 435 nm, 92,4 % bei 545 nm und 82,2 % bei 610 nm mit einer Gesamtschichtdicke von 86,5 nm hergestellt werden können. Dieser transparente Leiter besitzt für die drei genannten Wellenlängen einen mittleren Haackeschen Gütefaktor von 0,104 Ohm^{-1}.

[0010] Im Displaybereich für grossflächige flache LCD-Displays oder Computermonitore mit Bilddiagonalen vorzugsweise über 17" werden nun transparente Elektroden mit noch niedererem Flächenwiderstand bei gleichzeitig hoher Durchlässigkeit im sichtbaren Bereich, d. h. einem hohem Haackeschem Gütefaktor, benötigt. Dies ist durch die Bildgrösse, die hohe Auflösung und Pixelzahl sowie die höhere Geschwindigkeit dieser Displays bedingt. Diese Anforderungen können mit den bisher bekannten Verfahren nicht mehr erfüllt werden.

[0011] Die vorliegende Erfindung macht sich zur Aufgabe, die Nachteile des Standes der Technik zu beheben, insbesondere einen noch niedereren Flächenwiderstand bei einem hohen Haackeschen Gütefaktor zu erreichen.

[0012] Diese Aufgabe wird gelöst durch ein Schichtsystem nach Anspruch 1 sowie durch ein Verfahren nach Anspruch 6. Die abhängigen Patentansprüche beschreiben weitere bevorzugte Ausführungen der

BNSDOCID: <EP_______1092689A1_I_>

Best Available Copy

Erfindung.

[0013] Ein erfindungsgemässes Schichtsystem nach Anspruch 1 umfasst mindestens 2 Oxidschichten und eine dazwischen gelagerte Silberschicht und weist einen Flächenwiderstand von weniger als 2,9 Ω_{sq}, vorzugsweise 2,5 Ω_{sq} und geringer auf, bei einem über die Wellenlängen 435, 545 und 610 nm gemittelten Haakkeschen Gütefaktor von grösser als 0,085 Ω^{-1}.

[0014] Dabei ist es aus Gründen der Farbneutralität günstig, wenn bei einem Flächenwiderstand von 2,5 Ω_{sq} die optische Transmission bei 435 nm mindestens 89 %, bei 545 um mindestens 88 % und bei 610 nm mindestens 75 % beträgt. Damit ist gewährleistet, dass die Beschichtung in Durchsicht möglichst neutral erscheint.

[0015] Besonders gute Ergebnisse werden erzielt, wenn die Dicke der beiden Oxidschichten vorteilhafterweise unter 50 nm, vorzugsweise zwischen 30 und 40 nm, und die Dicke der Silberschicht unter 20 nm, vorzugsweise bei 15 nm, gewählt wird.

[0016] Die Entspiegelungswirkung der Oxidschichten wird besonders gut, wenn die Oxidschicht neben Indium 5 bis 10 At.-% Cer enthält.

[0017] Die Stabilität der Silberschicht wird durch Beigabe von bis zu 10 Gew.-% Kupfer erhöht. Besonders wirksam zeigten sich Beigaben von 0,5 bis 3 % und insbesondere 0,5 bis 1 %.

[0018] Bei der Herstellung des beschriebenen Schichtsystems ist es entscheidend, wie in Anspruch 6 und weiteren abhängigen Ansprüchen beschrieben, dass die Aufbringung der zweiten Oxidschicht nicht mit reiner DC Zerstaubung, sondern mit einer gepulsten DC-Zerstaubung oder mit einer AC-überlagerten DC-Zerstaubung erfolgt. Die AC-Überlagerung wird beispielsweise dadurch erzeugt, dass das Ausgangssignal über ein Filter auf die mit einer DC-Stromversorgung gespeiste Sputterquelle eingekoppelt wird. Eine weitere Möglichkeit besteht beispielsweise auch darin, die DC-Stromversorgung entsprechend zu modulieren oder zu tasten (choppern). Es sind also verschiedene Modulationen möglich.

[0019] Die AC-Frequenz sollte zwischen 1 und 50 MHz, vorzugsweise zwischen 10 und 20 MHz, liegen, um besonders gute Ergebnisse zu erreichen.

[0020] Im Weiteren wird mit Vorteil der AC-Anteil, definiert durch das Verhältnis der eingespeisten DC- und AC-Leistung, zwischen 10 und 90 %, vorzugsweise zwischen 30 und 50 %, eingestellt.

[0021] Besonders geeignet erwies sich eine totale Leistungsdichte (AC und DC) von 1 bis 3 W/cm^2, vorzugsweise von 2 bis 2.2 W/cm^2.

[0022] Als Zerstäubungsmethode wird Magnetronsputtern bevorzugt.

[0023] Die Vorteile dieses Verfahrens können wie folgt zusammengefasst werden:

[0024] Durch die Erhaltung der guten Leitfähigkeit der dünnen Silberschicht durch die Art der Aufbringung der zweiten Oxidschicht kann die optische Transmission hoch gehalten werden. Ohne das erfindungsgemässe Vorgehen müsste zur Erzielung dieser Leitfähigkeit die Dicke der Silberschicht erhöht werden, was unvermeidlich zu einer deutlicheren Verringerung der Transmission und damit zu einer wesentlichen Verschlechterung des Haackeschen Gütefaktors führen würde.

[0025] Die Herstellung solcher Schichten an Hand des erfindungsgemässen Verfahrens soll nun an dem nachfolgenden Beispiel beschrieben werden.

[0026] Die Glas-Substrate aus herkömmlichem dünnen Floatglas oder Maschinenglas werden in herkömmlicher Weise gereinigt und dann in eine Zerstäubungsanlage eingebracht. Die Vakuumkammer wird abgepumpt und nach Erreichung des nötigen Vakuums mit der Aufstäubung der ersten Oxidschicht aus Indium- und Ceroxid begonnen. Diese Oxidschicht wird teilreaktiv von einem Oxidtarget abgestäubt, d. h. in einer Argonatmosphäre von ca. 2,2x10^{-3} hPa mit einer Beimischung von Sauerstoff von maximal 5 %. Dieser Zerstäubungsprozess ist ein reiner DC-Prozess. Typische Zerstäubungsraten sind 5 bis 8 nmxm/minxcm^{2}W. Anschliessend erfolgt als reiner nicht-reaktiver DC-Prozess das Aufstäuben der Silberschicht. Hier liegen die typischen Zerstäubungsraten bei 12 bis 15 nmxm/minxcm^2/W. Ihm schliesst sich das Aufstäuben der zweiten Oxidschicht mit einer AC-überlagerten DC-Zerstäubung an. Dabei liegt der AC-Anteil, definiert durch das Verhältnis der eingespeisten DC- und AC-Leistung, zwischen 30 und 50 %. Die AC-Frequenz liegt bei 13,56 MHz. Nach Beendigung des Zerstäubungsprozesses werden die beschichteten Gläser durch eine Schleuse oder durch Fluten der Kammer an Luft ausgebracht. In einem anschliessenden Ätzprozess werden die Substrate dann strukturiert und zu Displays weiterverarbeitet.

[0027] Im folgenden ist die Erfindung in den Figuren 1 und 2 an Hand von Ausführungsbeispielen erläutert.

Fig. 1 zeigt schematisch und im Querschnitt ein erfindungsgemässes Schichtsystem.

Fig. 2 zeigt die im sichtbaren Spektralbereich gegen Luft gemessene optische Transmission eines erfindungsgemässen Schichtsystems mit einem Flächenwiderstand von 2,5 Ω_{sq}.

[0028] In der Fig. 1 bedeuten 1 das Glassubstrat, auf welches das erfindungsgemässe Schichtsystem aufgebracht wird, 2 eine Indium-Cer-Oxidschicht, 3 eine Kupfer-dotierte Silber-Schicht, und 4 eine abschliessende Indium-Cer-Oxidschicht.

[0029] Das Glassubstrat 1 ist z. B. ein handelsübliches Floatglas mit 1,1 mm Dicke. Es können aber auch andere Glasdicken und andere Gläser, z. B. Maschinenglas, benützt werden.

[0030] Darauf wird durch teilreaktive DC-Zerstäubung von einem Oxidtarget, bestehend aus vorzugsweise 90 bis 95 At.-% Indium und 5 bis 10 At.-% Cer,

BNSDOCID: <EP______1092689A1_I_>

Best Available Copy

eine Oxidschicht 2 mit der geometrischen Dicke von 30 bis 37 nm abgeschieden.

[0031] Auf diese Oxidschicht 2 wird eine Silberschicht 3 mit 0,5 bis 10 % Kupfer-Beimengung, vorzugsweise 0,5 bis 3% und insbesondere 0,5 bis 1% Kupfer, in einem reinen DC-Zerstäubungsprozess in einer Argonatmosphäre in einer Dicke von 15 nm aufgebracht.

[0032] Auf die Schicht 3 aus Silber/Kupfer wird direkt eine zweite Indium-Cer-Oxidschicht 4, ebenfalls mit der geometrischen Dicke von 30 bis 37 nm, abgeschieden. Dies erfolgt jedoch mit einem AC-überlagerten DC-Zerstäubungsprozess. Dabei liegt der AC-Anteil, definiert durch das Verhältnis der eingespeisten DC- und AC-Leistung, zwischen 10 und 90 %, vorzugsweise zwischen 30 und 50 %. Die AC-Frequenz liegt zwischen 1 und 50 MHz, vorzugsweise zwischen 10 und 20 MHz.

[0033] Optional kann nach der Silber/Kupfer-Schicht eine Schutzschicht aus Oxiden von Titan- oder Nickellegierungen mittels DC-Magnetron-Zerstäubung aufgebracht werden.

[0034] In der Fig. 2 ist die optische Durchlässigkeit (gemessen gegen Luft) eines erfindungsgemässen Schichtsystems mit einem Flächenwiderstand von 2,5 Ω_{sq} in Abhängigkeit von der Wellenlänge im Spektralbereich 400 bis 800 nm dargestellt. Bei 435 nm werden 89,8 %, bei 545 nm 88,4 % und bei 610 nm 75,4 % erreicht. Der über diese drei Wellenlängen gemittelte Haackesche Gütefaktor beträgt 0,092 Ω^{-1}.

Patentansprüche

1. Leitendes transparentes Schichtsystem mit zwei Oxidschichten (2,4) und einer dazwischen gelagerten Silber-Schicht (3) auf einem Substrat (1), **dadurch gekennzeichnet, dass** bei einem Flächenwiderstand R_s von < 2,9 Ω_{sq}., vorzugsweise < 2,5 Ω_{sq} und weniger, der mittlere Haackesche Gütefaktor des Schichtsystems für die Wellenlängen 435, 545 und 610 nm ($\Phi_{Tc}=T^{10}/R_s$)>0,085Ω^{-1}beträgt.

2. Schichtsystem nach Anspruch 1, **dadurch gekennzeichnet, dass** bei einem Flächenwiderstand von 2,5 Ω_{sq} die Durchlässigkeit T bei 435 nm mindestens 89 %, bei 545 nm mindestens 88 % und bei 610 nm mindestens75%beträgt.

3. Schichtsystem nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die Dicke des Schichtsystems < 100 nm, vorzugsweise 80 bis 90 nm beträgt, wobei die Dicke der Silberschicht (3) bei < 20 nm, vorzugsweise bei 15 nm, und die Dicke der beiden Oxidschichten (2,4) bei < 50 nm, vorzugsweise zwischen 30 und 40 nm, liegt.

4. Schichtsystem nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die Oxidschichten (2,4) Indium und Cer enthalten, vorzugsweise 90 bis 95 At.-% Indium und 5 bis 10 At.-% Cer.

5. Schichtsystem nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die Silber-Schicht (3) bis zu 10 Gew.-% Kupfer enthält, vorzugsweise im Bereich o.5 bis 3 % und insbesondere 0,5 bis 1 %.

6. Verfahren zur Herstellung eines leitenden transparenten Schichtsystems nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** bei der Aufbringung der zweiten Oxidschicht (4) eine gepulste DC-Zerstäubung oder eine AC-überlagerte DC-Zerstäubung verwendet wird.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** eine AC-Überlagerung mit einer Frequenz zwischen 1 und 50 MHz, vorzugsweise zwischen 10 und 20 MHz vorgenommen wird.

8. Verfahren nach Anspruch 6 und 7, **dadurch gekennzeichnet, dass** der AC-Anteil, definiert durch das Verhältnis der eingespeisten DC- und AC-Leistung, zwischen 10 und 90 %, vorzugsweise zwischen 30 und 50 % liegt.

9. Verfahren nach Anspruch 6, 7 und 8, **dadurch gekennzeichnet, dass** die totale Leistungsdichte (AC und DC) im Bereich 1 bis 3 W/cm^2, vorzugsweise aber bei 2 bis 2.2 W/cm^2 liegt.

10. Verfahren nach Anspruch 6 bis 9, **dadurch gekennzeichnet, dass** als Zerstäubungsverfahren Magnetronzerstäubung gewählt wird.

11. Leitendes transparentes Schichtsystem nach Anspruch 1 bis 5, **dadurch gekennzeichnet, dass** es nach dem Verfahren nach den Ansprüchen 6 bis 10 gefertigt wurde.

12. Leitendes transparentes Schichtsystem als transparente Elektroden für grossflächige Displays nach Anspruch 1 bis 5, **dadurch gekennzeichnet, dass** es nach dem Verfahren nach den Ansprüchen 6 bis 10 gefertigt wurde.

BNSDOCID: <EP________1092689A1_I_>

Best Available Copy

Fig.1

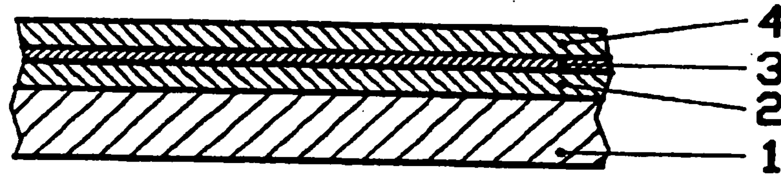
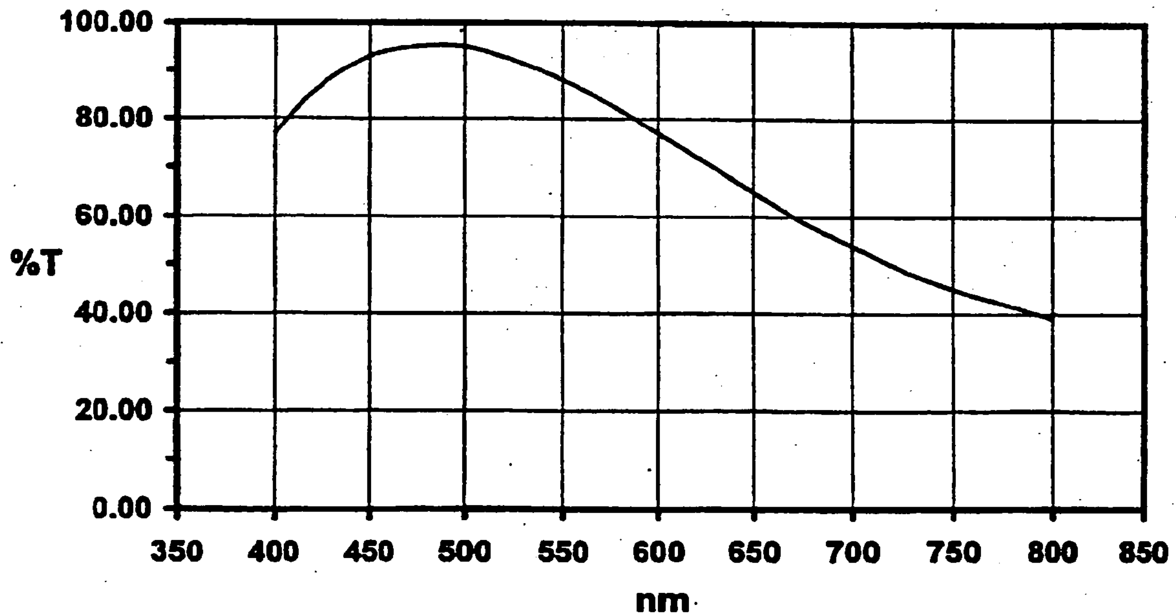


Fig.2



BNSDOCID: <EP_____1092689A1_I_>

Best Available Copy

Europäisches Patentamt

EUROPÄISCHER TEILRECHERCHENBERICHT

der nach Regel 45 des Europäischen Patent-übereinkommens für das weitere Verfahren als europäischer Recherchenbericht gilt

Nummer der Anmeldung
EP 00 11 9591

EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.7)
X	US 4 565 719 A (HIGGINS PATRICK K ET AL) 21. Januar 1986 (1986-01-21) * Anspruch 1; Tabelle 3 * ---	4	C03C17/36
X	GB 2 126 256 A (TOYODA CHUO KENKYUSHO KK) 21. März 1984 (1984-03-21) * Ansprüche 1-15; Beispiel 1 * ---	4-12	
A	DATABASE WPI Section Ch, Week 199015 Derwent Publications Ltd., London, GB; Class A32, AN 1990-113453 XP002159490 & JP 02 066158 A (UNITIKA LTD), 6. März 1990 (1990-03-06) * Zusammenfassung * ---	4	
P,A	GB 2 344 600 A (SONY CORP) 14. Juni 2000 (2000-06-14) * Ansprüche 1-4 * -----	4,5	

RECHERCHIERTE SACHGEBIETE (Int.Cl.7)

C03C

UNVOLLSTÄNDIGE RECHERCHE

Die Recherchenabteilung ist der Auffassung, daß ein oder mehrere Ansprüche, den Vorschriften des EPÜ in einem solchen Umfang nicht entspricht bzw. entsprechen, daß sinnvolle Ermittlungen über den Stand der Technik für diese Ansprüche nicht, bzw. nur teilweise, möglich sind.

Vollständig recherchierte Patentansprüche:

Unvollständig recherchierte Patentansprüche:

Nicht recherchierte Patentansprüche:

Grund für die Beschränkung der Recherche:

Siehe Ergänzungsblatt C

Recherchenort	Abschlußdatum der Recherche	Prüfer
DEN HAAG	6. Februar 2001	Reedijk, A

KATEGORIE DER GENANNTEN DOKUMENTEN

X : von besonderer Bedeutung allein betrachtet
Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
A : technologischer Hintergrund
O : nichtschriftliche Offenbarung
P : Zwischenliteratur

T : der Erfindung zugrunde liegende Theorien oder Grundsätze
E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist
D : in der Anmeldung angeführtes Dokument
L : aus anderen Gründen angeführtes Dokument

& : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument

EPO FORM 1503 03.82 (P04C09)

BNSDOCID: <EP_______1092689A1_I_>

Best Available Copy

Europäisches Patentamt

UNVOLLSTÄNDIGE RECHERCHE
ERGÄNZUNGSBLATT C

Nummer der Anmeldung
EP 00 11 9591

Vollständig recherchierte Ansprüche:
4-12

Nicht recherchierte Ansprüche:
1-3

Grund für die Beschränkung der Recherche:

Die geltenden Patentansprüche 1-3 sind auf ein Produkt , das (u.a.) mittels folgender Parameter definiert wird, zu beziehen:
P1: Haackesche Gütefaktor bei einem Flächenwiderstandsbereich.
Die Verwendung dieser Parameter muss im gegebenen Zusammenhang als Mangel an Klarheit im Sinne von Art. 84 EPÜ erscheinen. Es ist unmöglich, die vom Anmelder gewählten Parameter mit dem zu vergleichen, was der Stand der Technik hierzu offenbart. Der Mangel an Klarheit ist dergestalt, daß er eine sinnvolle vollständige Recherche unmöglich macht. Daher wurde die Recherche beschränkt auf die Teile mit Bezug auf Ausführungsbeispiele, wie sie in der Beschreibung auf Seite 4 und Patentansprüche 4-12 erwähnt sind.

BNSDOCID: <EP_________1092689A1_I_>

Best Available Copy

ANHANG ZUM EUROPÄISCHEN RECHERCHENBERICHT ÜBER DIE EUROPÄISCHE PATENTANMELDUNG NR. EP 00 11 9591

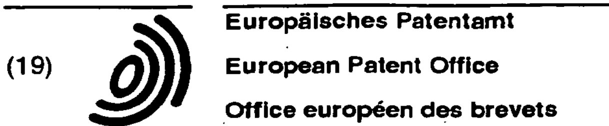
In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten europäischen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

06-02-2001

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
US 4565719 A	21-01-1986	CA 1243523 A	25-10-1988
		EP 0106223 A	25-04-1984
		JP 59131449 A	28-07-1984
GB 2126256 A	21-03-1984	JP 59031147 A	20-02-1984
		DE 3329504 A	23-02-1984
JP 2066158 A	06-03-1990	KEINE	
GB 2344600 A	14-06-2000	JP 2000171601 A	23-06-2000
		NL 1013664 A	13-06-2000

EPO FORM P0461

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82


(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 068 899 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.01.2001 Bulletin 2001/03

(51) Int Cl.7: B01J 35/00, B01J 37/34

(21) Application number: 00114185.2

(22) Date of filing: 13.07.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 14.07.1999 JP 20059499

(71) Applicant: Nippon Sheet Glass Co., Ltd.
Osaka-shi, Osaka (JP)

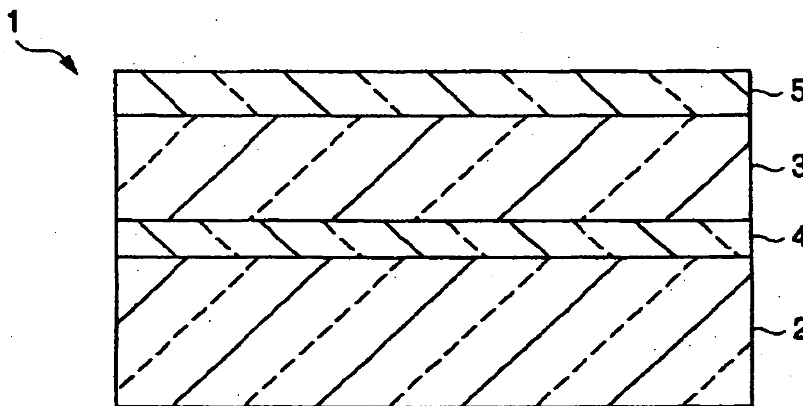
(72) Inventors:
- Ogino, Etsuo
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)
- Mori, Kenji
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)
- Kijima, Yoshifumi
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)
- Kawahara, Tetsuro
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)
- Doushita, Kazuhiro
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)
- Inomata, Hiroyuki
3-chome, Chuo-ku, Osaka-shi, Osaka (JP)

(74) Representative: HOFFMANN - EITLE
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) **Multilayer structure and process for producing the same**

(57) A conductive sinter obtained from a mixture of titanium oxide particles and 2.5% by weight niobium oxide particles is used as a target in direct current sputtering to form a photocatalytically active film mainly comprising titanium oxide on a glass substrate. The target has a surface resistance of 500 Ω/□ or lower and the sputtering is conducted while heating the substrate at 230°C. The photocatalytically active film is based on an amorphous matrix. This process is free from problems of a conventional process in which a photocatalytically active titanium oxide film is deposited by reactive sputtering using titanium metal as a target. The problems are that the substrate needs to be heated to 350°C or higher and that the deposited film does not have high photocatalytic activity.

FIG. 1



Best Available Copy

EP 1 068 899 A1

Description

FIELD OF THE INVENTION

5

[0001] The present invention relates to a multilayer structure which functions as a photocatalyst and can render its surface hydrophilic upon irradiation with ultraviolet rays or visible rays. The present invention further relates to a process for producing the same.

BACKGROUND OF THE INVENTION

10

[0002] Members comprising a substrate coated with a titanium oxide film functioning as a photocatalyst are used in various applications. Such members are applicable to various articles so as to take advantage of the hydrophilicity resulting from their photocatalytic function for various purposes such as, e.g., antifogging, cleaning by rain, cleaning by water washing, and antifouling. For example, in the case of articles wherein the substrate is a glass plate, such as, e.g., windshields and sideview mirrors for vehicles, window glasses for buildings, and mirrors, a technique is used in which the substrate is coated with a photocatalyst film whose surface becomes hydrophilic and is thereby prevented from being clouded with steam or covered with adherent waterdrops.

15

[0003] JP-A-10-278165 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a technique in which a metal target comprising titanium as the main component is used to conduct sputtering in an oxygen-containing atmosphere and the resulting deposit is heated to thereby form on a glass plate a photocatalyst film having anatase crystals and excellent resistance to abrasion and wearing.

20

[0004] However, in order for the technique described above to form a titanium oxide film having photocatalytic activity, it is necessary that a titanium oxide film should be deposited on a substrate heated to 300°C or higher or that a titanium oxide film which has been deposited on a substrate having room temperature should be heated to a temperature as high as 600°C or higher. Furthermore, there has been a problem that in the reactive sputtering in which a titanium metal target is used in an oxygen-containing atmosphere, the glow discharge becomes unstable as an electrically insulating oxide accumulates on the titanium metal surface and, as a result, a titanium oxide film cannot be stably obtained.

25

[0005] JP-A-10-310653 discloses a technique in which an anatase titanium oxide film or rutile titanium oxide film is deposited on a glass plate by the sol coating method, organic titanate method, electron beam vapor deposition method, or the like. There is a description therein to the effect that the energy band gap between the conductive band and the valence band in a titanium oxide film functioning as a photocatalyst is regulated by incorporating a metal oxide selected from ruthenium oxide, cobalt oxide, cerium oxide, chromium oxide, rhodium oxide, and vanadium oxide to thereby effectively obtain hydrophilicity.

30

35

[0006] However, the technique described above has had a problem that a step of heating at a temperature as high as 350°C or higher is necessary for obtaining a crystalline titanium oxide film having photocatalytic activity, resulting in a complicated production process.

[0007] JP-A-1-92176 discloses a technique in which a titanium oxide photocatalyst film is deposited on a glass plate by reactive sputtering using titanium metal as a sputtering target and this titanium oxide film is doped with ions of a metal such as niobium, cobalt, or chromium by ion implantation to improve catalytic activity.

40

[0008] However, the technique described above has had drawbacks that an expensive ion injector is necessary for injecting metal ions in a glass by ion injection, and that it is virtually difficult to deposit a photocatalytically active film on a glass having a relatively large area, such as a window glass for buildings, etc., on an industrial scale.

45

SUMMARY OF THE INVENTION

[0009] The present invention has been achieved in order to overcome the problems described above.

[0010] One object of the present invention is to provide a multilayer structure comprising a substrate and formed thereon a film having satisfactory photocatalytic activity and practical antifouling properties.

50

[0011] Another object of the present invention is to provide a process for producing a multilayer structure comprising a substrate and formed thereon a film having photocatalytic activity and antifouling properties.

[0012] According to the first embodiment of the present invention provides, there is provided a process for producing a multilayer structure comprising a substrate and formed thereon a film mainly comprising titanium oxide and having photocatalytic activity, which comprises sputtering a conductive sinter target obtained by sintering a mixture of particles of titanium oxide and particles of at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide, in an atmosphere capable of having a regulated vacuum to form the film mainly comprising titanium oxide and having photocatalytic activity on the substrate.

55

SDOCID: <EP_______1068899A1_I_>

[0013] The film mainly comprising titanium oxide (hereinafter referred to as "titanium oxide film") in the present invention is obtained by sputtering, in an atmosphere capable of having a regulated vacuum, a conductive target obtained by sintering a mixture of particles of titanium oxide as the main component and particles of at least one metal oxide, as a minor component, selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide. The surrounding gas when sputtering that can be used is an inert gas such as argon or a mixed gas comprising an inert gas and oxygen.

[0014] Especially when an oxygen-containing atmosphere having a reduced pressure is used in order to sputter a titanium oxide film which does not have a considerable deficiency of oxygen as compared with the stoichiometric amount and is transparent in the visible region, the target surface is inhibited from being covered with an electrically insulating substance because a small oxygen amount is sufficient for the atmosphere.

[0015] The target used in the present invention, which is an oxide sinter containing titanium oxide as the main component, is electrically conductive in such a degree that electric current can flow through the surface thereof. It is preferred that a direct current glow discharge be used to bombard the conductive target and thereby deposit a film. This is because a direct current power source, which is relatively inexpensive, can be used to generate a stable glow discharge and deposit a photocatalytically active titanium oxide film on a substrate.

[0016] The target having conductivity for use in the present invention can be obtained by sufficiently mixing particles, preferably fine particles, of titanium oxide with particles, preferably fine particles, of at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, tin oxide, chromium oxide and copper oxide, and forming the powder mixture into a given shape by pressure molding. Conventional cold pressing or hot pressing method can be used for this pressure molding.

[0017] The conductivity of the target for use in the present invention is preferably such that the surface resistance thereof is 500 Ω/□ or lower, in order to maintain a glow discharge for sputtering the target over a long period of time to thereby form a titanium oxide film in a stable manner. If the surface resistance exceeds 500 Ω/□ ; it is not preferable in that the glow discharge is apt to be interrupted. From the standpoint of even more stably maintaining a glow discharge over a long period of time, the surface resistance of the target is more preferably 50 Ω/□ or lower.

[0018] In the present invention, the formation of a photocatalytically active titanium oxide film is preferably conducted at a substrate temperature of 170°C or higher. If the substrate temperature is lower than 170°C, it is undesirable in that the titanium oxide film obtained has insufficient resistance to abrasion and wearing and has low photocatalytic activity. From this standpoint, the substrate temperature is more preferably 200°C or higher.

[0019] On the other hand, if the substrate temperature exceeds 270°C during film formation, the titanium oxide film tends to have a higher degree of anatase crystal orientation and, unexpectedly, the photocatalytic activity thereof decreases gradually. From this standpoint, the substrate temperature during film deposition is preferably 270°C or lower, more preferably 250°C or lower.

[0020] Preferred metal oxides to be contained in titanium oxide in the present invention are niobium oxide, vanadium oxide and tantalum oxide because these metal oxides are effective not only in relatively easily maintaining a glow discharge necessary for sputtering the sinter target but in obtaining a titanium oxide film having enhanced photocatalytic activity. Of those, niobium oxide is most preferable.

[0021] The oxygen content of the sputtering gas atmosphere (gas composition introduced into the film-formation chamber) is preferably less than 80 vol%, more preferably less than 60 vol%, from the standpoint of increasing the deposition rate of film formation.

[0022] According to the second embodiment of the present invention, there is provided a multilayer structure comprising a substrate and formed thereon a film mainly comprising titanium oxide and having photocatalytic activity (hereinafter referred to as "titanium oxide film"), wherein the film contains as a minor component at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide and is substantially amorphous when analyzed by X-ray diffraction method.

[0023] In the case where the titanium oxide film formed is composed of crystals, many grain boundaries are present therein. Electron-hole pairs which have been excited by light in the titanium oxide film are trapped by many lattice defects present on those grain boundaries, so that the number of electron-hole pairs present on the film surface, which contribute to photocatalytic activity, is reduced. Because of this, such a titanium oxide film has reduced photocatalytic activity. In contrast, the multilayer structure of the present invention is reduced in the trapping since it mainly comprises an amorphous matrix. This constitution is thought to bring about a high photoexcitation efficiency. The multilayer structure of the present invention therefore has high photocatalytic activity.

[0024] The titanium oxide film is characterized in that it is less apt to have a crystalline structure because the titanium oxide contains a small amount of one or more metal oxides. The film thickness of the titanium oxide film is preferably 150 nm to 500 nm.

[0025] In the present invention, the content of the metal oxide(s) as a minor component in the titanium oxide is preferably 1% by weight or higher, more preferably 2.5% by weight or higher. If the content of metal oxides as a minor component in the film is lower than 1% by weight, it is undesirable in that not only stable photocatalytic activity is difficult

to obtain but also the target is less apt to retain conductivity (electricity-passing properties) in a degree so as to conduct sputtering in a stable manner, making it difficult to stably form a titanium oxide film.

[0026] On the other hand, the content of the metal oxide(s) as a minor component is preferably 10% by weight or lower, more preferably 5% by weight or lower. This is because if the content of the metal oxide(s) exceeds 10% by weight, the content of titanium oxide decreases in relative amount, resulting in lowering photocatalytic activity.

[0027] In the present invention, preferred metal oxides as the minor component are niobium oxide, vanadium oxide and tantalum oxide from the standpoints of obtaining high photocatalytic activity and forming a stable glow discharge to form a titanium oxide film with satisfactory reproducibility. Especially preferred from such standpoints is niobium oxide.

[0028] Usable substrates include ones made of inorganic materials such as glasses and ceramics and ones made of organic materials such as plastics because in the process of the present invention, film formation on substrates is possible at relatively low temperature. Examples of applications of such substrates include window glasses for buildings and vehicles, exterior and interior materials for buildings, Braun tubes, PDP displays, liquid-crystal display panels, optical recording media, magnetic recording media, and members or housings of domestic electrical appliances or OA apparatus.

[0029] In the case where a glass plate, especially one containing alkali components, such as a soda-lime silicate composition, is used as a substrate, it is preferred to dispose, between this glass substrate and a titanium oxide film, a primer film serving to prevent the alkali components of the substrate from dissolving in the titanium oxide film. From the standpoint of further improving antifouling properties, it is preferred to partly or wholly coat the titanium oxide film of the present invention with a hydrophilic film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] Fig. 1 is a sectional view showing one embodiment of the multilayer structure according to the present invention.

[0031] Fig. 2 is a graphic presentation showing the influence of substrate temperature during titanium oxide film formation on residual triolein amount.

[0032] Fig. 3 is a graphic presentation showing the influence of substrate temperature during titanium oxide film formation on the crystalline structure of the film.

[0033] Reference Numerals in the drawings are as follows:

1: Multilayer structure of the present invention
2: Glass substrate
3: Photocatalytically active film mainly comprising titanium oxide
4: Primer film
5: Hydrophilic film

DETAILED DESCRIPTION OF THE INVENTION

[0034] Embodiments of the present invention will be explained in detail below.

[0035] Fig. 1 is a sectional view showing one embodiment of the multilayer structure according to the present invention. This multilayer structure 1 comprises a glass substrate 2 and, superposed on one side thereof in this order, a primer film 4 comprising silicon dioxide serving to prevent alkali dissolution, a titanium oxide film 3 having photocatalytic activity, and a hydrophilic film 5. Fig. 2 is a graphic presentation showing the influence of the substrate temperature during titanium oxide film formation on the residual triolein amount. Fig. 3 is a graphic presentation showing the influence of the substrate temperature during titanium oxide film formation on the crystalline structure of the film.

[0036] Examples of the glass substrate include plates made of a soda-lime silicate glass, alkali borosilicate glass and aluminoborosilicate glass. Examples of plastic substrates include substrates made of a polycarbonate resin, acrylic resin and polystyrene resin. In the case of using a substrate containing an alkali component, e.g., sodium ions, as in a soda-lime silicate glass, it is preferred to dispose a film of a metal oxide such as silicon dioxide as an alkali dissolution preventive film between the substrate and a titanium oxide film in order to prevent the alkali component, which is apt to move within the glass, from coming into the titanium oxide film from the glass. Silicon dioxide can be film-formed by conventional technique such as sputtering, CVD or a method using an aqueous solution containing hydrosilicofluoric acid supersaturated with silicon dioxide. The thickness of this silicon dioxide film is preferably from 10 to 100 nm.

[0037] The sinter target used in forming a photocatalytically active titanium oxide film according to the present invention is produced by, for example, the following manner. Titanium oxide and niobium oxide each are regulated so as to have a particle diameter of from about 0.01 to 50 μm. The niobium oxide is mixed with the titanium oxide in an amount of from 1 to 10% by weight based on the weight of the titanium oxide, and this mixture is molded into a given

DOCID: <EP________1068899A1_I_>

shape by cold isostatic pressing in water in which the powder mixture is pressed at 3 t/cm^2. The resulting molded product is degreased at 400 to 500°C, preliminarily burned in an oxygen atmosphere at 1300 to 1500°C for 4 to 6 hours, and then subjected to hot isostatic pressing at 1,350 to 1,450°C under a pressure of about 100 MPa in an atmosphere comprising argon and oxygen.

5 **[0038]** Conductivity is imparted to the sputtering target according to the present invention to such a degree that the target is not charged during sputtering with a direct current glow discharge. From the standpoint of easily obtaining such target surface conductivity, preferred metal oxides for use as the minor component are niobium oxide, vanadium oxide and tantalum oxide. Especially preferred is niobium oxide.

[0039] By using the oxide sinter target which is not charged, sputtering can be conducted with a direct current glow 10 discharge. The partial oxygen pressure of the atmosphere used for this sputtering may be lower than that in the reactive sputtering method in which titanium metal is used as a target. Even when the sputtering is conducted over a long period of time, the accumulation of an electrically insulating substance on the target surface can be inhibited. The sputtering atmosphere is regulated so as to have a pressure of from 1 to 5 mTorr in magnetron sputtering (MS) or dual magnetron sputtering (DMS). For maintaining this pressure, the gas to be introduced into the film-formation chamber is preferably 15 regulated so as to have a composition having an oxygen content of from 0.5 to 10% by volume.

[0040] The primer film used as an alkali dissolution preventive film in the present invention may be a film of a metal oxide or a film of a nitride. Especially preferred are silicon dioxide, silicon nitride and silicon oxynitride because these compounds show satisfactory adhesiveness to glass plates and titanium oxide films.

[0041] In the present invention, both hydrophilicity and antifouling properties can be imparted to the substrate more 20 satisfactorily by coating the titanium oxide film with a hydrophilic film transparent to ultraviolet or visible light. Preferred examples of this hydrophilic film include silicon dioxide films or films containing silicon dioxide as the main component.

[0042] Methods for forming the primer film or hydrophilic film are not particularly limited, and conventional methods can be used, such as sputtering, CVD using an organosilane as a starting material, and a method using an aqueous hydrosilicofluoric acid solution supersaturated with silicon dioxide.

25 **[0043]** The present invention will be explained in more detail below by reference to the following Examples and Comparative Examples, but it should be understood that the invention is not construed as being limited thereto. In each of those Examples and Comparative Examples, the following conditions were used in forming a titanium oxide film.

Target size: 38 cm (length) x 13 cm (width) x 6 mm (thickness)
30 Sputtering power: 3 kW
Pressure of sputtering atmosphere: 3 mTorr
Gas introduced: argon/oxygen mixed gas or oxygen gas
Substrate heating: various temperatures according to experiments in the range of from room temperature (about 25°C) to 350°C.

35

EXAMPLE 1

[0044] A mixture of 2.5% by weight niobium oxide and 97.5% by weight titanium oxide was molded into the shape shown above by cold isostatic pressing in water at a pressure of 3 t/cm^2. This molded product was degreased at 450°C, 40 preliminarily burned in an oxygen atmosphere at 1,400°C for 5 hours, and then subjected to hot isostatic pressing at 1,400°C under a pressure of about 100 MPa in an atmosphere composed of argon and a small proportion of oxygen.

[0045] The oxide sinter target thus obtained had a surface resistance of 5 Ω/□. Using this target, a titanium oxide film having a thickness of 250 nm was formed on a 30 cm-square float glass plate having a soda-lime silicate composition under the film-formation conditions shown in Table 1. The substrate temperature during film-formation was reg-45 ulated to 230°C. Thus, Sample 1 was obtained. The titanium oxide film of the multilayer structure obtained was examined for photocatalytic performance (triolein-decomposing ability and contact angle with water) and crystalline state. Antifouling performance also was evaluated.

[0046] The examination and evaluation methods are as follows.

[0047] Film crystallinity: Crystalline state of the film was judged based on X-ray diffraction peaks obtained with CuK_{α} 50 line (50 kV, 200 mA).

[0048] Triolein-decomposing ability: The side coated with the titanium oxide film was coated with about 2 mg of triolein. The film side of this sample was then irradiated with black light (containing ultraviolet) at an intensity of 3 mW/cm^2. After 43 hours, the residual triolein amount was determined and shown in terms of %.

[0049] Antifouling performance: The multilayer structure was exposed outdoors for 2 months, and the surface thereof 55 was then visually examined. The adhesion of fouling substances, such as waterdrop marks resulting from rain or dust particles, was evaluated and indicated by O, Δ or ×. The results of this comparative evaluation, in which the fouled state of the glass plate not coated with a titanium oxide film is taken as ×, are shown in Table 1.

×: Considerable adhesion of fouling substances derived from waterdrops, etc., and the sample looked white in terms of reflected light.
Δ: Slightly reduced adhesion of fouling substances.
O: Even more reduced adhesion of fouling substances, and the sample looked less white in terms of reflected light.

5

[0050] The results of the evaluation of Sample 1 obtained are shown in Table 1. Table 1 shows the following.
[0051] In X-ray diffraction analysis, no diffraction peak characteristic of crystals was observed in the titanium oxide film of Sample 1. The film was hence found to be amorphous. This titanium oxide film had a residual triolein amount of 0% and a contact angle with pure water of as small as 9 degrees, showing that the surface thereof was satisfactorily hydrophilic. Furthermore, the antifouling performance thereof was rated as O, which is the best.

10

EXAMPLES 2 TO 4

[0052] Multilayer structure Samples 2 to 4 were produced in the same manner as in Example 1, except that the content of niobium oxide was changed to 1.0% by weight, 5.0% by weight and 10.0% by weight, respectively. The evaluation results for these samples are shown in Table 1. In each sample, the titanium oxide film was amorphous when analyzed by the X-ray diffraction method, and the surface thereof was hydrophilic and had an antifouling effect based on photocatalytic function.

15

20

Table 1

Sample No.	Titanium oxide target			Titanium oxide film			
	Minor metal oxide		Surface resistance (Ω/□)	Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
	Ingredient	Content (wt%)					
Sample 1	Nb_2O_5	2.5	10	amorphous	0	9	O
Sample 2	Nb_2O_5	1.0	5	amorphous	4	11	O
Sample 3	Nb_2O_5	5.0	10	amorphous	2	9	O
Sample 4	Nb_2O_5	10.0	20	amorphous	6	11	O
(Notes) Substrate temperature: 230°C Titanium oxide film thickness: 250 nm							

25

30

35

40

EXAMPLE 5

[0053] A multilayer structure sample was produced in the same manner as in Example 1, except that prior to the titanium oxide film formation, a primer film of silicon dioxide having a thickness of 50 nm was formed by high-frequency sputtering using quartz glass as a target. Multilayer structure Sample 5 thus obtained was subjected to the film evaluations in the same manner as in Example 1, and the results obtained are shown in Table 2.

45

EXAMPLE 6

[0054] A multilayer structure sample was produced in the same manner as in Example 3. Thereafter, a hydrophilic film of silicon dioxide was formed on the titanium oxide film of the sample by high-frequency sputtering using quartz glass as a target. Multilayer structure Sample 6 thus obtained was subjected to the film evaluations in the same manner as in Example 1, and the results obtained are shown in Table 2. The results for Sample 1, which had neither a primer film nor a hydrophilic film, are also shown in Table 2 for the sake of comparison.
[0055] Table 2 shows that Sample 5 and Sample 6 both had satisfactory triolein-decomposing ability and that especially in Sample 6, the surface of the multilayer structure had improved hydrophilicity.

50

55

DOCID: <EP_____1068899A1_I_>

Table 2

Sample No.	Primer film		Hydrophilic film		Titanium oxide film			
	Material	Thickness (nm)	Material	Thickness (nm)	Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
Sample 5	SiO_2	50	none		amorphous	0	9	O
Sample 6	SiO_2	50	SiO_2	10	amorphous	27	7	O
Sample 1	none		none		amorphous	0	9	O

(Notes) Nb_2O_5 content: 2.5 wt%
Substrate temperature: 230°C
Substrate thickness: 250 nm

EXAMPLES 7 TO 12

[0056] Multilayer structure Samples 7 to 12 were produced in the same manner as in Example 1, except that the niobium oxide was replaced with each of the various metal oxides shown in Table 3. These multilayer structures were examined for photocatalytic performance in the same manner as in Example 1, and the results obtained are shown in Table 3. The titanium oxide sinter targets respectively containing those metal oxides each had such a surface resistance that a glow discharge could be stably generated. It was further found that the multilayer structures obtained had satisfactory photocatalytic performance and antifouling performance based on it.

Table 3

Sample No.	Titanium oxide target			Titanium oxide film			
	Minor metal oxide		Surface resistance (Ω/□)	Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
	Ingredient	Content (wt%)					
Sample 7	Ta_2O_5	2.5	10	amorphous	7	10	○
Sample 8	V_2O_5	2.5	5	amorphous	8	10	○
Sample 9	ZrO_2	2.5	30	amorphous	5	10	○
Sample 10	SnO_2	2.5	15	amorphous	9	11	○
Sample 11	Cr_2O_3	2.5	30	amorphous	10	12	○
Sample 12	CuO	2.5	15	amorphous	8	11	○
(Notes) Film thickness: 250 nm Substrate temperature: 230°C							

EXAMPLES 13 TO 16

[0057] Multilayer structure samples were produced in the same manner as in Example 1, except that the substrate temperature was changed to 170°C, 200°C, 250°C and 270°C, respectively, for the purpose of examining the influence of the substrate temperature during film deposition on the photocatalytic activity of the titanium oxide film. The evaluation results for the samples obtained are shown in Table 4 together with the results for Sample 1.

COMPARATIVE EXAMPLES 1 TO 4

[0058] Multilayer structure samples were produced in the same manner as in Example 1, except that the substrate temperature was changed to room temperature (no heating), 150°C, 300°C and 350°C, respectively. The evaluation results for Comparative Samples 1 to 4 thus obtained are shown-in Table 4.

DOCID: <EP_______1068899A1_I_>

Table 4

Sample No.	Titanium oxide target		Substrate		Titanium oxide film			
	Minor metal oxide		Temperature (°C)	Thickness (nm)	Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
	Ingredient	Content (wt%)						
Comparative Sample 1	Nb_2O_5	2.5	room temp	250	amorphous	96	22	×
Comparative Sample 2	Nb_2O_5	2.5	150	250	amorphous	93	21	×
Sample 13	Nb_2O_5	2.5	170	250	amorphous	25	13	O
Sample 14	Nb_2O_5	2.5	200	250	amorphous	9	11	O
Sample 1	Nb_2O_5	2.5	230	250	amorphous	0	9	O
Sample 15	Nb_2O_5	2.5	250	250	amorphous	6	9	O
Sample 16	Nb_2O_5	2.5	270	250	amorphous	9	10	O
Comparative Sample 3	Nb_2O_5	2.5	300	250	anatase	32	14	Δ
Comparative Sample 4	Nb_2O_5	2.5	350	250	anatase	73	17	Δ

[0059] Table 4 shows that from the standpoint of imparting sufficient photocatalytic activity to the titanium oxide film, the substrate temperature during film formation is preferably 170°C or higher and 270°C or lower. Fig. 2 shows a plot of the relationship between the found values of residual triolein amount shown in Table 4 and the substrate temperatures during film formation shown in Table 4. As the substrate temperature rises beyond 150°C, the residual triolein amount abruptly decreases, i.e., photocatalytic activity increases. On the other hand, as the substrate temperature lowers from 350°C, the residual triolein amount decreases, i.e., photocatalytic activity increases. It can be seen from this relationship that high photocatalytic activity is obtained when the substrate temperature is from 170 to 270°C, and even higher catalytic activity (a reduced residual triolein amount) is obtained when the substrate temperature is from 200 to 250°C.

[0060] Fig. 3 shows X-ray diffraction charts for the titanium oxide films of the samples for which substrate temperatures of room temperature (no substrate heating), 150°C, 230°C and 300°C had been used, respectively. In the samples for which substrate temperatures of 300°C and 350°C had been used respectively, the diffraction peak attributable to the (101) plane of anatase crystals was observed. In contrast, the sample for which the substrate had not been heated and the samples for which substrate temperatures of 150°C and 230°C had respectively been used each showed no diffraction peak, showing that the titanium oxide films of these samples were substantially amorphous.

[0061] From the Examples and Comparative Examples given above, it could be seen that when a titanium oxide film is formed at substrate temperatures not lower than 300°C, the titanium oxide film deposited is not amorphous but composed of anatase crystals and this titanium oxide film has reduced photocatalytic activity (an increased residual triolein amount). Namely, it was found that a titanium oxide film having satisfactory photocatalytic activity is obtained at relatively low temperatures (nearly the same as or lower than the heat resistance temperatures of organic resin materials and the like, which are around 250°C).

[0062] The samples for which substrate temperatures of room temperature and 150°C had been used had low photocatalytic activity whereas the samples for which substrate temperatures ranging from 170°C to 270°C had been used had high photocatalytic activity, despite the fact that these two groups of samples had such a common property that the titanium oxide film was amorphous when analyzed by the X-ray diffraction method. Although the reason for this has not been elucidated, it is presumed that in each of the samples in the latter group, microcrystals not detectable by the X-ray diffraction method are present in the amorphous matrix and make some contribution to photocatalytic activity.

EXAMPLES 17 TO 19

[0063] Multilayer structure Samples 17 to 19 were produced in the same manner as in Example 1, except that the thickness of the titanium oxide film was changed to 50 nm, 100 nm and 500 nm, respectively, for the purpose of examining the influence of titanium oxide film thickness on photocatalytic performance. The evaluation results for these samples are shown in Table 5 together with the results for Sample 1. It was found that as the film thickness increases, both the value of residual triolein amount, as a measure of triolein-decomposing ability, and the value of contact angle with water decrease.

Table 5

Sample No.	Titanium oxide target		Substrate		Titanium oxide film			
	Minor metal oxide		Temperature (°C)	Thickness (nm)	Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
	Ingredient	Content (wt%)						
Sample 17	Nb_2O_5	2.5	230	50	amorphous	91	21	×
Sample 18	Nb_2O_5	2.5	230	100	amorphous	57	16	Δ
Sample 1	Nb_2O_5	2.5	230	250	amorphous	0	9	○
Sample 19	Nb_2O_5	2.5	230	500	amorphous	0	8	○

EXAMPLE 20

[0064] Mmultilayer structure Sample 20 was produced in the same manner as in Example 1, except that the composition of the surrounding gas was changed in order to examine the influence of the sputtering gas atmosphere (gas composition introduced into the film-formation chamber) used for titanium oxide film formation on photocatalytic performance. The results of the examinations of the titanium oxide film obtained are shown in Table 6 together with the results for Sample 1. It was found that a high oxygen concentration in the atmosphere gives a titanium oxide film comprising anatase crystals and having reduced triolein-decomposing ability. Namely, this experiment showed that for forming a titanium oxide film having high photocatalytic activity, it is advantageous to conduct film formation in an atmosphere containing a small amount of oxygen.

Table 6

Sample No.	Titanium oxide target	Substrate temperature (°C)	Surrounding gas composition, oxygen/ argon (volt)	Titanium oxide film			
	Nb_2O_5 amount (wt%)			Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
Sample 20	2.5	230	60/40	anatase	50	17	Δ
Sample 1	2.5	230	6/94	amorphous	0	9	○

COMPARATIVE EXAMPLE 5

[0065] Using titanium metal as a target, a titanium oxide film having a thickness of 250 nm was formed by direct-current sputtering on a 30 cm-square float glass plate having a soda-lime silicate composition under the conditions shown in Table 7 to produce a multilayer structure. The gas composition of the atmosphere used for sputtering was regulated so as to have an oxygen content of 100% in order to secure transparency of the titanium oxide. Comparative Sample 5 of multilayer structure thus obtained was evaluated. As a result, the sample had poor triolein-decomposing ability as shown in Table 7.

COMPARATIVE EXAMPLE 6

[0066] Sputtering was conducted in the same manner as in Comparative Example 5, except that the substrate temperature was changed to 350°C. Thus, Comparative Sample 6 of multilayer structure was produced. Although the titanium oxide film of this multilayer structure had an anatase crystal structure, it had low triolein-decomposing ability (a large residual triolein amount) and insufficient antifouling performance.

DOCID: <EP________1068899A1_I_>

Table 7

Sample No.	Target	Substrate temperature (°C)	Surrounding gas composition, oxygen/ argon (vol%)	Titanium oxide film			
				Crystallinity	Triolein-decomposing ability, residual amount (%)	Contact angle with water (degree)	Anti-fouling performance
Comparative Sample 5	titanium metal	230	100/0	anatase	89	22	×
Comparative Sample 6	titanium metal	350	100/0	anatase	75	19	Δ

[0067] The above results show that in order for the conventional reactive sputtering method using titanium metal as a target to obtain a titanium oxide film having photocatalytic activity, the substrate should be heated to a temperature as high as 350°C, and that the photocatalytic activity thus obtained is not so high. The results further show that a titanium oxide film having photocatalytic activity cannot be obtained at a substrate temperature of 230°C, i.e., a titanium oxide film having high catalytic activity cannot be obtained at low temperatures.

[0068] The above Examples and Comparative Examples demonstrate that according to the process of the present invention for producing a multilayer structure, films having high catalytic activity can be obtained at relatively low substrate temperatures of 270°C or lower. The Examples further demonstrate that the photocatalytically active titanium oxide films obtained have antifouling properties and are practically useful.

[0069] According to the process of the present invention for producing a multilayer structure, a photocatalytically active titanium oxide film is formed on a substrate by sputtering in an atmosphere capable of having a regulated vacuum using a conductive sinter target obtained by sintering a mixture of particles of titanium oxide and particles of at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide. Consequently, a multilayer structure having a photocatalytically active film can be produced at high rate without the necessity of heating the substrate at high temperature.

[0070] As a result, it has become possible to produce a multilayer structure using a large glass plate as a substrate, such as a window glass, using a sputtering apparatus having a simplified heating mechanism. The equipment cost can hence be reduced.

[0071] Since lower substrate temperatures can be used in substrate heating, a photocatalytically active film can be formed on organic resin substrates and the like.

[0072] Furthermore, by regulating the conductivity of the sinter target so that the surface resistance thereof is 500 Ω/□ or lower, not only a multilayer structure can be produced with a direct current glow discharge continuing stably, but also a film having enhanced catalytic activity can be obtained when the substrate is heated to 170 to 270°C.

[0073] The multilayer structure of the present invention has a titanium oxide film which contains as a minor component at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide, and which is substantially amorphous when analyzed by the X-ray diffraction method. Due to this constitution, the multilayer structure has high photocatalytic activity.

[0074] By regulating the content of the metal oxide(s) as the minor component to 1 to 10% by weight, the titanium oxide film can be an amorphous film having high photocatalytic activity.

[0075] Furthermore, by interposing, between the substrate and the titanium oxide film, a primer film which serves to prevent any alkali component of the substrate from dissolving in the titanium oxide film, the photocatalytic activity of the multilayer structure can be made to last over long period of time. Moreover, by partly or wholly coating the titanium oxide film with a hydrophilic film, the surface of the multilayer structure can be made more hydrophilic and the antifouling properties can be enhanced.

Claims

1. A process for producing a multilayer structure comprising a substrate and formed thereon a film mainly comprising titanium oxide and having photocatalytic activity, which comprises forming the film by sputtering a conductive sinter target obtained by sintering a mixture of particles of titanium oxide and particles of at least one metal oxide selected from the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide, in an atmosphere capable of having a regulated vacuum.

2. The process for producing a multilayer structure as claimed in claim 1, wherein the target has a conductivity such that the surface resistance thereof is 500 Ω/□ or lower, and the sputtering is conducted with a direct current glow discharge.

3. The process for producing a multilayer structure as claimed in claim 1, wherein the film mainly comprising titanium oxide is formed while heating the substrate at a temperature of from 170 to 270°C.

4. The process for producing a multilayer structure as claimed in claim 3, wherein the film mainly comprising titanium oxide is formed while heating the substrate at a temperature of from 200 to 250°C.

5. The process for producing a multilayer structure as claimed in claim 1, wherein the metal oxide is niobium oxide.

6. A multilayer structure comprising a substrate and formed thereon a film mainly comprising titanium oxide and having photocatalytic activity, said film containing as a minor component at least one metal oxide selected from

XOCID: <EP_______1068899A1_I_>

the group consisting of niobium oxide, tantalum oxide, vanadium oxide, zirconium oxide, tin oxide, chromium oxide and copper oxide, and being substantially amorphous when analyzed by the X-ray diffraction method.

7. The multilayer structure as claimed in claim 6, wherein the substantially amorphous film mainly comprising titanium oxide comprises an amorphous matrix containing microcrystals.

8. The multilayer structure as claimed in claim 6, wherein the content of the metal oxide as the minor component in the film mainly comprising titanium oxide is from 1 to 10% by weight.

9. The multilayer structure as claimed in claim 8, wherein the metal oxide as the minor component is niobium oxide.

10. The multilayer structure as claimed in claim 6, which has, interposed between the substrate and the film consisting mainly of titanium oxide, a primer film which serves to prevent any alkali component of the substrate from dissolving in the film mainly comprising titanium oxide.

11. The multilayer structure as claimed in claim 6, wherein the film mainly comprising titanium oxide is coated with a hydrophilic film.

12. The multilayer structure as claimed in claim 11, wherein the primer film and the hydrophilic film each is a film of silicon dioxide.

FIG. 1

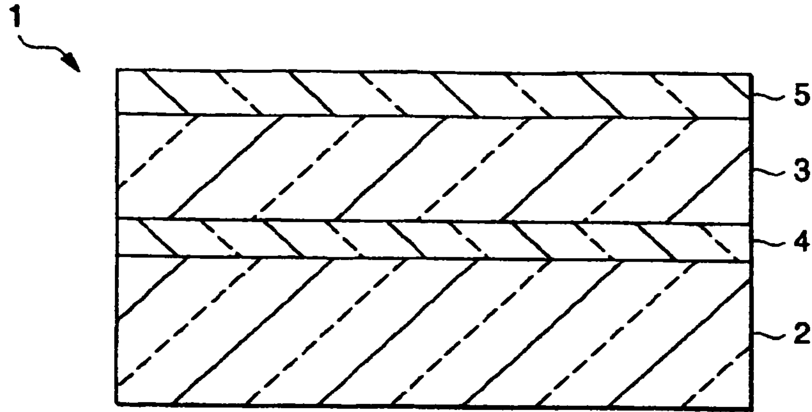
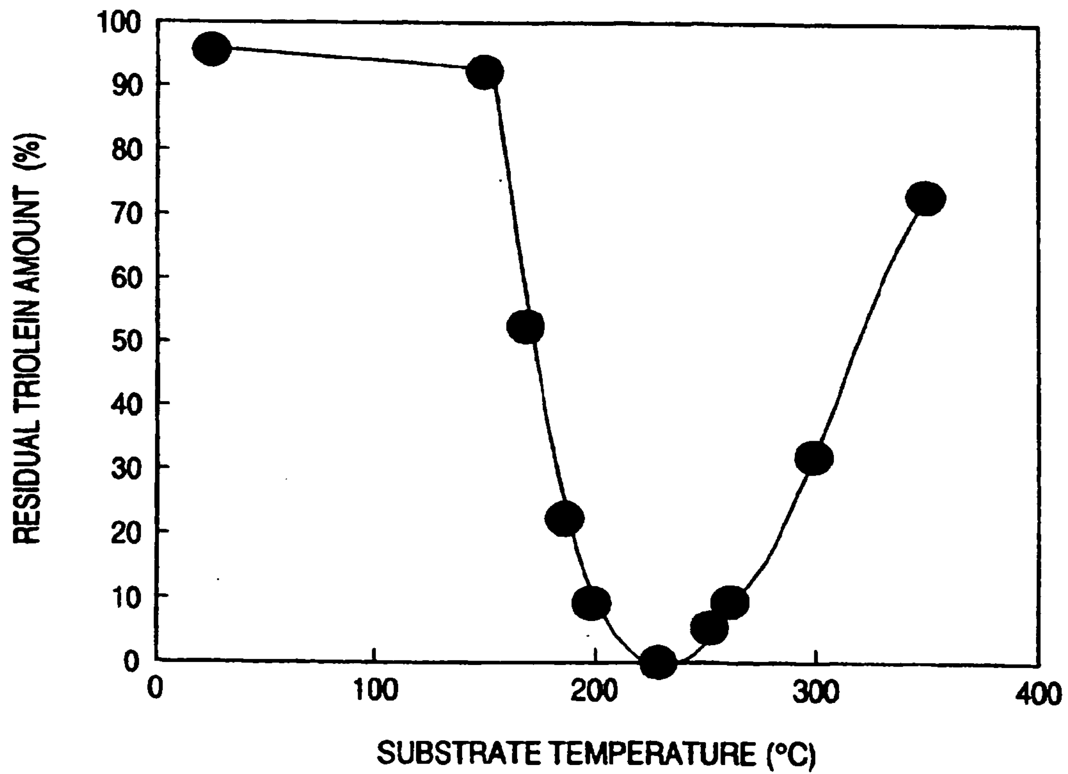


FIG. 2



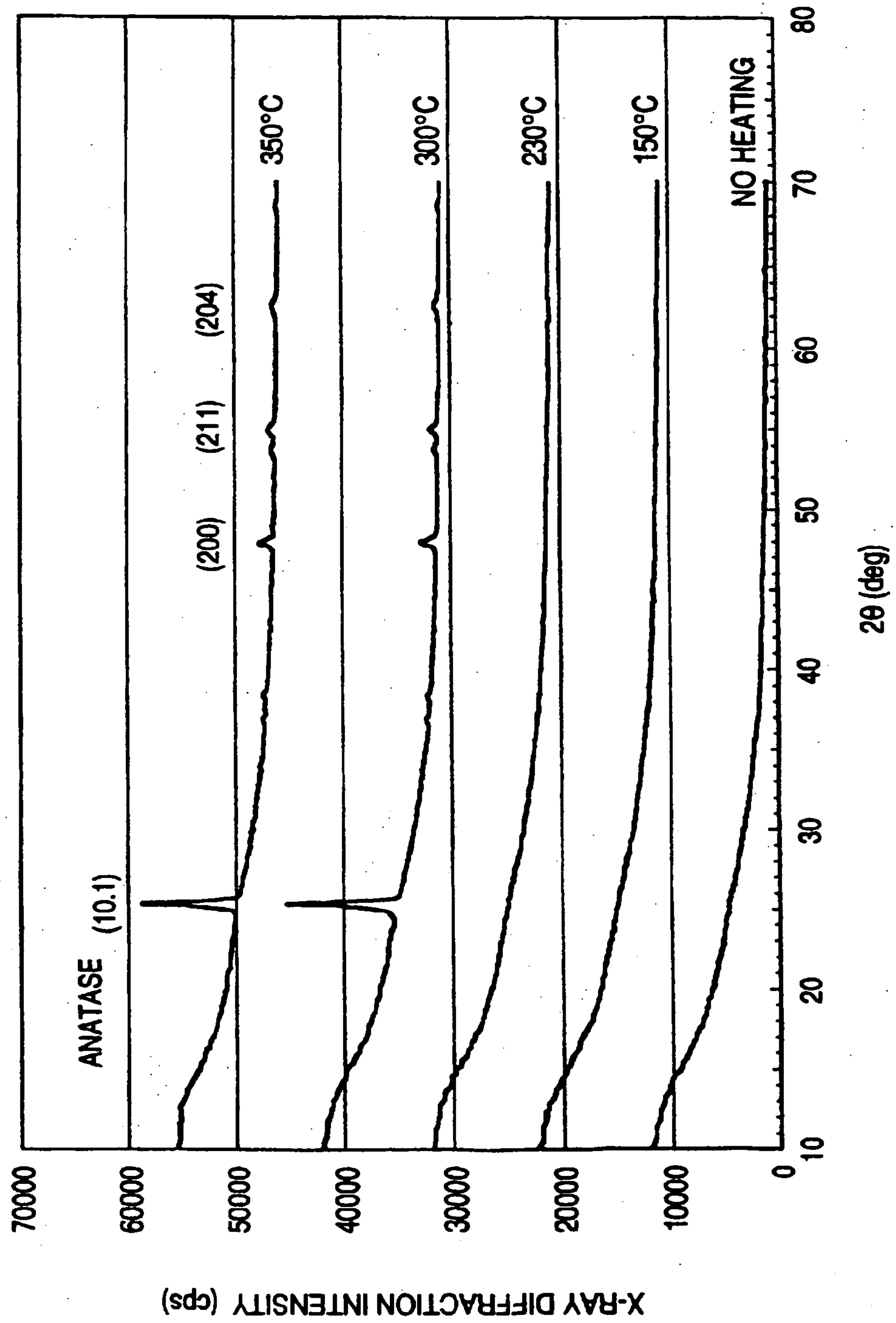


FIG. 3

EP 1 068 899 A1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 4185

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	DATABASE WPI Section Ch, Week 199930 Derwent Publications Ltd., London, GB; Class D15, AN 1999-352578 XP002149112 & JP 11 130434 A (BRIDGESTONE CORP), 18 May 1999 (1999-05-18) * abstract *		B01J35/00 B01J37/34
A	DATABASE WPI Section Ch, Week 199924 Derwent Publications Ltd., London, GB; Class D15, AN 1999-283348 XP002149113 & JP 11 092176 A (BRIDGESTONE CORP), 6 April 1999 (1999-04-06) * abstract *		
A	DATABASE WPI Section Ch, Week 199901 Derwent Publications Ltd., London, GB; Class J04, AN 1999-003984 XP002149114 & JP 10 278165 A (ASAHI GLASS CO LTD), 20 October 1998 (1998-10-20) * abstract *		TECHNICAL FIELDS SEARCHED (Int.Cl.7) B01J
A	DATABASE WPI Section Ch, Week 199706 Derwent Publications Ltd., London, GB; Class D15, AN 1997-060199 XP002149115 & JP 08 309204 A (BRIDGESTONE CORP), 26 November 1996 (1996-11-26) * abstract *		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 October 2000	Thion, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

DOCID: <EP_______1068899A1_I_>

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 11 4185

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-10-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11130434 A	18-05-1999	NONE	
JP 11092176 A	06-04-1999	NONE	
JP 10278165 A	20-10-1998	NONE	
JP 8309204 A	26-11-1996	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)

HIS PAGE BLANK (USPTO)

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☑ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☑ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ____________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

Best Available Copy

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 639 655 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **94111669.1**

(22) Date of filing: **26.07.94**

(51) Int. Cl.[6]: **C23C 14/00**, C23C 14/34, H01J 37/32

(30) Priority: **28.07.93 JP 205704/93**

(43) Date of publication of application: **22.02.95 Bulletin 95/08**

(84) Designated Contracting States: **BE DE FR GB**

(71) Applicant: **ASAHI GLASS COMPANY LTD.**
1-2, Marunouchi 2-chome
Chiyoda-ku
Tokyo 100 (JP)

(72) Inventor: **Shimizu, Junichi, Asahi Glass Company Ltd.**
Chuo Kenkyusho,
1150, Hazawa-cho,
Kanagawa-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Watanabe, Shujiro, Asahi Glass Company Ltd.**
Chuo Kenkyusho,
1150, Hazawa-cho,
Kanagawa-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Takaki, Satoru, AG TECHNOLOGY CO., LTD.**
1160, Matsubara
Hazawa-cho,
Kanagawa-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Osaki, Hisashi, Asahi Glass Company Ltd.**
Chuo Kenkyusho,
1150, Hazawa-cho,
Kanagawa-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Oyama, Takuji, Asahi Glass Company Ltd.**
Chuo Kenkyusho,
1150, Hazawa-cho,
Kanagawa-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Ando, Eiichi, Asahi Glass Company Ltd.**
Kashima Kojo,
25, Oaza-higashiwada,
Kamisu-cho,
Kashima-gun,
Ibaraki-ken (JP)

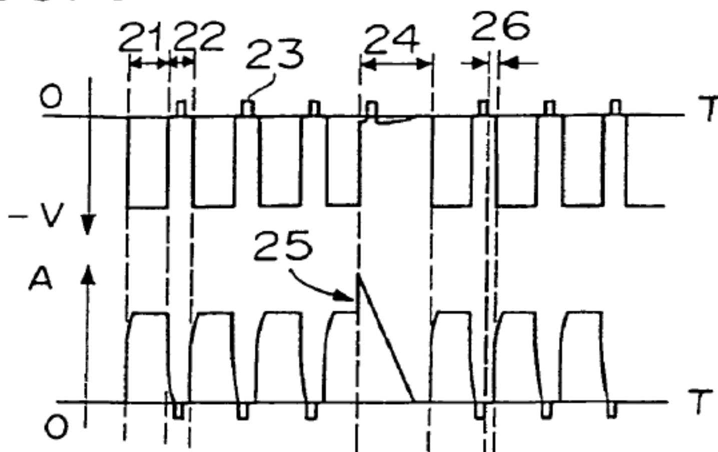
(74) Representative: **Wächtershäuser, Günter, Prof. Dr.**
Patentanwalt
Tal 29
D-80331 München (DE)

(54) Method and apparatus for sputtering.

(57) A sputtering method comprises applying a negative voltage intermittently in a constant periodic cycle to a cathode disposed in a vacuum chamber, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 μs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

EP 0 639 655 A1

FIGURE 2



The present invention relates to a sputtering method in which a pulse-like DC voltage is applied, a film-deposition method by sputtering, an apparatus for obtaining sputtering and a power processing portion for sputtering.

A cathode for DC sputtering (hereinbelow, referred to as sputtering) can not be used for forming a film of high quality at a high deposition rate unless a problem of abnormal discharge is overcome.

Various causes are considered concerning the abnormal discharge occurring around the cathode (hereinbelow, referred to as arcing). As one of the causes, electric charges are accumulated on a small insulating substance, which is deposited or grown on the surface of a target material, and the electric charges cause arcing to a potentially opposite site, e.g. a substrate on which a film is to be formed, an anode electrode, the inner wall of a vacuum chamber or the surface of the target.

The arcing occurs frequently in a case that an insulating film is produced from a conductive target material by reactive sputtering. When the arcing is generated, arcing energy concentrates locally to a portion of the target surface in a reactive gas atmosphere, this forming an insulation or insulations, whereby the arcing happens frequently in a series. Accordingly, a stable glow discharge effective to sputtering can not be maintained; a sputtering rate becomes unstable and the production of films of uniform quality is impossible. Occasionally, a substrate on which a film is formed is damaged by arcing, or a mechanical component constituting a cathode or a target material or a cathode is molten by arcing.

In order to avoid the above-mentioned disadvantage, a method of using electric power of a high frequency such as 13.56 MHz has been used.

Recently, a technique of preventing arcing by using a waveform proposed in Japanese Unexamined Patent Publication Nos. 148644/1993 and 331634/1993 or using a device to obtain such waveform (the device is commercialized as SPARC-LE by Advanced Energy in U.S.A. Namely, the waveform having a frequency of several kHz which is comparable to the effect obtained by a discharge in 13.56 MHz by applying a pulse-like positive electric potential of about 5 µs-10 µs is applied in a periodic cycle to a cathode so that positive electric charges accumulated on a small insulating substance, which is deposited or grown on the surface of a target material are neutralized by attracting electrons in plasma.

Recently, another technique of neutralization of a potential difference on the target surface has been developed as seen in U.S.P. 5,082,546. Namely, an alternating current having an intermediate frequency such as several tens kHz is applied to a pair of closely disposed cathodes to ignite glow discharges between the two cathodes alternately. In this case, when the electric potential of the cathodes is negative, sputtering is conducted, and when the electric potential is positive, positive electric charges accumulated on a small insulating substance, which is deposited or grown on the surface of a target material are neutralized by attracting electrons in plasma.

The sputtering method using a radio frequency power source having 13.56 MHz is believed to suppress arcing because an insulation can be sputtered. However, it is difficult to form a sputtering apparatus using a radio frequency power source of 13.56 MHz because a power source having an output of 10 kW or more is large and expensive, and an impedance-matching circuit of high voltage and large current is needed.

A sputtering method wherein DC power is used to apply a positive potential intermittently and the power is intermittently off is a useful technique because a potential difference on the target surface can be neutralized and the generation of arcing at the initial stage can be suppressed. Thus, the generation of arcing could be effectively suppressed in comparison with the ordinary DC sputtering method. However, this method has no ability of sputtering an insulating substance unlike the sputtering method using 13.56 MHz, and accordingly, arcing occurs when a continuous discharge is conducted for a long time. When the arcing is generated, discharge energy concentrates locally on the target surface in a reactive gas atmosphere, which further forms an insulation or insulations and results in arcing frequently in a series.

Namely, the neutralization of potential difference on the target surface by applying a positive voltage or 0 voltage intermittently is effective only to a small insulating substance accumulated with a small amount of electric charges if the application time of positive voltage or 0 voltage is short. Accordingly, it is impossible to obtain complete neutralization of an insulating substance accumulated with a large amount of electric charges by sputtering for a long time or of an insulating substance having a large amount of electric charges produced by arcing, with use of a simple intermittent DC power.

In the sputtering method of applying an alternating current to the two closely disposed cathodes, an alternating current of several tens kHz is used. Accordingly, it can be said that this method uses the same principle as the sputtering method with use of the before-mentioned intermittent DC power, i.e. a potential difference on the target surface is neutralized. Further, in this method, the same electrode is used as a cathode and an anode. Accordingly, there is an advantage that when the electrode is used as a cathode, the surface of it is sputtered and cleaned, and when it is used as an anode, the surface is always cleaned whereby a continuous discharge can be stably carried out for a long time. However, this method requires

the two closely disposed cathodes and an AC power source of several tens kHz. Accordingly, it is impossible to suppress arcing and stabilize a normal discharge in a simple manner with use of a currently used DC sputtering apparatus.

As another cause of the occurrence of arcing, when a target material is eroded by sputtering, minute protrusions appear in the surface of the target material depending on the kind of material. An electric field concentrates to the protrusions whereby arcing occurs at a local portion. Accordingly, the composition of the target material is changed whereby a portion having a different sputtering yield may appear and uniform sputtering of target surface can not be obtained.

In particular, when an ITO (indium-tin-oxide) film is to be produced by the sputtering method, and when an ITO target or an IT (indium-tin) target is used, indium oxide which is believed to be sub oxide, or a large number of minute black protrusions (hereinbelow, referred to as nodules), are produced on the target surface during continuous sputtering, and the deposition rate of the ITO film is gradually decreased. Further, the arcing frequently occurs, whereby small pieces of the target material scattering by the arcing deposit on the substrate to reduce the quality of the ITO film.

As a common technique to remove the protrusions formed by the erosion of the target is to physically remove them by causing a discharge in an inert gas atmosphere such as Ar gas, i.e. sputter-etching.

Further, when the ITO target is used, a method of removing the nodules by a discharge in a N_2 gas atmosphere is proposed in Japanese Unexamined Patent Publication No. 293767/1992.

However, the above-mentioned methods are only effective under the condition that a vacuum chamber is maintained vacuum after the nodules have been formed, and they can not suppress the occurrence of arcing and can not realize a method of a long time stably discharge.

As another technique, there is a method of improving the surface condition of the target formed by the erosion of the target, by increasing the density of a target material of ITO in sintering. However, this method pushes up the cost of the target material and effect can not be expected.

As another technique, there is a method of increasing the density of power at the sputtering to change the erosion of the target. When the density of power is simply increased, the frequency of occurrence of arcing increases and a discharge energy of arcing also increases. So, this method increases adverse effects of the arcing.

It is an object of the present invention to provide a sputtering method, a film-deposition method by sputtering, an apparatus for obtaining sputtering and a power processing portion for sputtering whereby arcing is effectively controlled and a larger power can be supplied quickly to deposit a film of high quality with high deposition rate for a long time.

In accordance with the present invention, there is provided a sputtering method, a film-forming method by sputtering and an apparatus for sputtering and a power processing part for sputtering wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 μs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

It is possible in principle to realize the above-mentioned methods, apparatus and the power processing portion of the present invention with use of an ordinary DC power source if such a function that the arcing at the initial stage is detected to quickly stop the output and the output is again produced after the passing of the time of the extinction of arcing, is added to a DC power source. However, when a detection circuit of arcing is actually installed in the power source, it is necessary to detect through a power source cable an abnormal condition of current or voltage supplied from the positive pole to the negative pole by the power source.

Such method of detection can only detect arcing between the cathode electrode as a target material and the anode electrode disposed near the target material. However, a slight arcing at the initial stage which starts on the surface of the cathode material can not be detected because the slight arcing is filtered by the impedance of the power source cable and the circuit constant of the power source circuit. Namely, only a relatively large arcing which is produced as a result of the slight arcing at the initial stage can be detected.

Since the time of extinction of the relatively large arcing between the cathode and anode is in the order of ms, it is necessary to stop the output from the power source for more than several ms. Further, since the size of an insulation formed on the surface of the target material at the time of generation of arcing already becomes large, the arcing occurs frequently. Accordingly, an abnormal state of output is detected from the DC power source, the shut-off of several ms is repeated, and it is very difficult to continue the normal sputtering operation.

For the above-mentioned reasons, the slight arcing can not be detected in a case that the ordinary DC power source is used for sputtering, and there will be a problem such that the shutting-off of more than

BNSDOCID: <EP_______0639655A1_I_>

several ms is repeated when a large arcing occurring subsequent to the slight arcing takes place.

The inventors of this application have found through intensive observations of the waveform of arcing that the crest value (the maximum value of the waveform of current) in initial arcing before a large arcing takes place in a series and the time of extinction of the initial arcing are substantially constant when the same apparatus is used.

Therefore, they have found that the progress of arcing in a series can be prevented by minimizing the energy of arcing. Specifically, the sputtering method comprises applying a negative voltage intermittently in a constant periodic cycle to a cathode disposed in a vacuum chamber, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 μs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

The slight arcing can be seen with a waveform observing device such as an oscilloscope or the like.

Further, they have found through intensive observations of the waveform of arcing that a time from the application of a negative voltage to the generation of the initial arcing is substantially constant when the construction of the apparatus is the same.

Therefore, they have found that by using a voltage waveform wherein the time during which the negative voltage is intermittently applied is within a range of from 10 μs to 10 ms and is equal to or shorter than the period of time from the application of the negative voltage to the generation of arcing, the accumulation of electric charges on an insulation having a small surface area on the surface of a target can be minimized; the voltage is controlled to be zero volt before the arcing takes place, and the electric charges are neutralized by plasma near the target, whereby the frequency of occurrence of the initial arcing can be reduced.

As described above, it is possible to continue sputtering operations for a long time by specifying the time during which the voltage is controlled to zero volt, and this effect can be increased by specifying the time during which the negative voltage is intermittently applied.

In drawings:

Figure 1 is a diagram showing intermittent waveforms according to an embodiment of the present invention;

Figure 2 is a diagram showing intermittent waveforms in a case of applying a positive potential according to an embodiment of the present invention;

Figure 3 is a diagram showing a sputtering apparatus according to a first embodiment of the present invention;

Figure 4 is a circuit diagram showing an embodiment of an intermittent power processing portion of the present invention;

Figure 5 is a diagram showing the sputtering apparatus according to a second embodiment of the present invention;

Figure 6 is a first graph showing the effect of the present invention;

Figure 7 is a second graph showing the effect of the present invention;

Figure 8 is a diagram showing the sputtering apparatus according to a third embodiment of the present invention;

Figure 9 is a diagram showing an intermittent waveform of an embodiment of the present invention;

Figure 10 is a diagram showing an intermittent waveform according to an embodiment of the present invention; and

Figure 11 is a diagram showing an intermittent waveform according to an embodiment of the present invention.

Preferred embodiments of the present invention will be described with reference to the drawings.

Figure 1 shows waveforms according to an embodiment of the present invention wherein the upper portion shows a waveform of voltage and the lower portion shows a waveform of current. Reference numeral 1 indicates a time during which a negative voltage is intermittently applied (hereinbelow, referred to as an ON time), numeral 2 designates a time during which the voltage is controlled to be zero voltage (hereinbelow, referred to as a zero volt time) and numeral 3 shows a waveform produced when arcing takes place. In Figure 1, when the zero volt time is longer than the ON time, power efficiency becomes poor. However, the waveform is simple because the power is simply turning-on and off. Accordingly, it is advantageous in construction when the power source portion has a sufficient capacity.

On the other hand, the inventors of the present invention have found that the neutralization of charging to an insulation can be effectively done in a shorter time by using a voltage waveform wherein there is a time during which a positive voltage is applied in a range of from 1 μs to 20 μs in part of the zero volt time. By combining this waveform with the above-mentioned specified ON time, a waveform having excellent

BNSDOCID: <EP_____0639655A1_I_>

power efficiency can be obtained.

Further, they have found to suppress the occurrence of arcing for a long time and with excellent power efficiency by suitably determining the zero volt time, which is equal to or longer than the time of extinction of arcing, only just after the arcing.

Figure 2 shows the waveform obtained by the application of a positive voltage. In Figure 2, the upper portion shows the waveform of voltage and the lower portion shows the waveform of current. Reference numeral 21 indicates an ON time which is in a range of from 10 μs to 10 ms and which is equal to or shorter than the time from the rise of voltage to the generation of an arc discharge in the initial arcing.

Numeral 22 indicates a zero volt time, which is determined by a time 23 during which a positive potential is applied and a time 26 for a zero volt after the time 23.

The zero volt time just before the time 23 during which a positive potential is applied is preferably short. However, a constant time of 1 μs to 2 μs is actually set to protect the switching element.

It is not necessary that the time 23 during which a positive potential is applied is a long time, but it may be a time which is sufficient to apply the voltage to a large-sized target, and a time of about 5 μs to 20 μs is preferable. The value of a positive potential can be a potential sufficient to apply the voltage to an actual target, and may be 200 V or lower.

It is desirable that the zero volt time 22 can be adjusted depending on a situation of process by adjusting the time 26 after the application of a positive potential.

Namely, a desirable result can be obtained by adjusting the zero volt time 26 so as to form the zero volt time 22 equal to or longer than the time of extinction of a slight arcing even when a slight arcing smaller than a reference value for detection set in a detection circuit takes place.

Numeral 25 indicates the waveform of arcing. The zero volt time 24 just after the occurrence of arcing is equal to or longer than the time for extinction of the arcing.

It is preferable that the above-mentioned conditions can be changed because the optimum values are different depending on the material for sputtering and the construction of the cathode electrode.

The function of the present invention is as follows.

In the present invention, by repeating ON/OFF, a potential difference on the target surface can be eliminated to prevent the occurrence of arcing. Accordingly, a stable discharge can be maintained in comparison with a conventional DC sputtering.

If arcing takes place, the arcing can be completely distinguished by giving a sufficiently long zero volt time before the voltage is ON, whereby the magnitude of the arcing can be maintained small. Further, the initial arcing appears sometime after the rise of voltage. Accordingly, a waveform wherein a time during which the voltage is controlled to be ON is in a range of from 10 μs to 10 ms and equal to or shorter than a time of from the rise of voltage to the generation of the initial arcing is used, a potential on the surface of a target is neutralized, whereby the frequency of occurrence of arcing and the magnitude of the arcing can be reduced.

By the above-mentioned function, the frequency of occurrence of the initial arcing and the magnitude of the arcing can be kept small, and a stable sputtering can be continued for a long time even with a large power.

When the waveform shown in the upper portion of Figure 2 wherein a positive potential is added for a short time in the zero volt time is used, a potential difference on the target surface can be effectively eliminated to thereby prevent the occurrence of arcing. Accordingly, a stable discharge can be maintained for a long time in comparison with use of the ordinary DC sputtering.

Further, by determining the zero volt time 24 to be longer than the time of extinction of arcing just after the arcing 25 has been detected, the frequency of occurrence and the magnitude of the arcing at the initial stage can be kept small, and a stable sputtering can be continued for a long time even with a large power.

Even when a slight arcing whose value is smaller than a reference value of detection set in the detection circuit takes place, a further stable sputtering can be continued by adjusting the zero volt time 26 so that the zero volt time 22 is longer than the time of extinction of the slight arcing.

Figure 3 shows an embodiment of the power source device for realizing the above-mentioned sputtering method.

The power source device of the present invention preferably has a sputtering power generating portion and a power processing portion which should be separately disposed. In Figure 3, numeral 31 designates a sputtering power generating portion, numeral 32 designates a power processing portion, numeral 33 designates a vacuum chamber, numeral 34 designates a cathode electrode, numeral 35 designate anode electrodes and numeral 36 designates a substrate.

In this embodiment, the power processing portion 32 can be disposed closer to the cathode electrode 34 than the sputtering power generating portion 31, whereby the length of a power source cable between

BNSDOCID: <EP_____0639655A1_I_>

the output terminal of the power processing portion 32 and the cathode electrode 34 can be the shortest to thereby minimize the inductance of the power source cable. Accordingly, the waveform of an intermittent DC voltage can be applied to the cathode electrode 34 without any distortion.

Figure 4 shows the construction of the power processing portion 32 of the present invention.

5 The power processing portion 32 comprises a first switching circuit 41 as main circuit, a second switching circuit 42 for applying a positive potential, a control circuit (not shown) for a switching element for controlling the first and second circuits and a power measuring circuit (not shown) for measuring current, voltage, and power for sputtering.

The first switching circuit 41 is connected in series between the negative pole of the sputtering voltage 10 generating portion 31 and the cathode electrode 34. The first switching circuit 41 is composed of a semiconductor switching device and a coil for protecting the same and is operable to change a sputtering power to an intermittent power. It has a switching speed of 10 μs (100 kHz) for ON/OFF. The second switching circuit 42 is composed of a semiconductor switching device and a coil for protecting the same, and is so operable that power of DC power source 43 which supplies an optional value of positive potential 15 to the cathode electrode 34 is applied to the cathode electrode 34, beside of the sputtering power generating portions 31.

The second switching circuit 42 is operated only when the first switching circuit 41 as the main circuit is an OFF state. A time of applying a positive potential in an ON state can be about 20 μs in maximum.

It is preferable that the power source 43 for applying a positive potential is of about 200 V in maximum, 20 but it can be determined optionally.

By adjusting a turning on time of the semiconductor switching device of the second switching circuit 42 to be about 20 μs or less immediately after the semiconductor switching circuit of the first switching circuit 41 has been turning off, a positive potential of about 200 V or less can be applied to the cathode electrode 34, whereby the occurrence of arcing can be suppressed and the waveform having excellent power 25 efficiency as shown in Figure 2 can be produced.

The control circuit for the semiconductor switching device is capable of controlling the turning-on time to be 5 μs or more for the first switching circuit and the turning-off time to be 5 μs or more for the same, and capable of turning-on the second switching circuit for less than the time of turning-off the first switching circuit and within a range of from 1 μs to 20 μs when the first switching circuit is turned off.

30 It is possible that the first switching circuit is in a normally ON state while omitting the zero volt time. The adjustment allows to use the conventional DC sputtering.

The circuit for measuring current, voltage or power for sputtering has a function to measure a current value, a voltage value and a power value effective to the sputtering and a function to compare the measured values with predetermined reference values to detect arcing. In this case, it is especially effective to judge 35 whether the current value or both the current value and the voltage value are higher or lower.

The control circuit for the semiconductor switching device has a function to control the zero volt time 24 immediately after the occurrence of arcing. The zero volt time can be optionally set to be in a range of from 100 μs to 10 ms.

Further, when the arcing is detected upon the judgement as to whether or not the sputtering current 40 value or voltage value (or the impedance at the arcing) is higher or lower, the semiconductor switching device of the switching circuit 41 operates so that the zero volt time is longer than the time of extinction of arcing only immediately after the arcing, whereby the magnitude of arcing can be minimized and a stable sputtering can be continued for a long time.

Further, a smoothing circuit 44 is preferably disposed at the side of the input terminal of the power 45 processing portion, whereby the waveforms of voltage and current at the output terminal of the power generating portion 31 can be substantially in a direct current form.

The power generating portion generally has a function to feed-back the voltage, current or power at the output terminal so that it can be kept constant. The function may cause hunting on controlling.

However, since the hunting can be prevented by the smoothing circuit 44, the ordinary DC power 50 source can be used. Accordingly, the ordinary sputtering DC power source may be used for the sputtering power generating portion 31. In this case, the present invention can be practiced with a conventional sputtering apparatus with the power processing portion 32.

In the sputtering method of the present invention, it is preferable to measure and display the average value of power per period (hereinafter referred to as the effective value, see formula 1 given hereinafter). By 55 displaying the effective value, the film-deposition rate can be controlled in the same manner as use of the power for the conventional DC sputtering even when any type of waveform is used for sputtering.

Further, it is preferable that the effective value is fed-back to the sputtering power generating portion 31 for a constant voltage control, a constant current control or a constant power control.

BNSDOCID: <EP______0639655A1_I_>

When a sputtering apparatus having a plurality of cathode electrodes disposed in a vacuum chamber is used and an intermittent power waveform is supplied to each of the cathode electrode, interference such as a beat may appear. Accordingly, the power processing portion should have a function to shift the phase of waveform.

Figure 8 shows an embodiment of the sputtering apparatus of the present invention. In this embodiment, two cathode electrodes 82a, 82b and anode electrodes 83a, 83b are disposed in a vacuum chamber so that sputtering is conducted simultaneously to a substrate 85. Power generating means 81a and 81b supply power intermittently wherein the phases of voltage waveform are shifted to each other, whereby interference of plasma such as a beat or the like can be eliminated and a stable plasma 84 is produced.

Further, the waveforms shown in Figure 1 or Figure 2 can be produced by combining the apparatus with the power source as shown in Figure 3. Thus, the optimum waveform can be supplied by satisfying the conditions of process.

In the sputtering apparatus of the present invention, the frequency of occurrence of arcing can be reduced even when a reactive sputtering is conducted. Further, a larger power can be supplied to the cathode stably, and the optimum intermittent power can be expected and supplied to meet various sputtering processes. Accordingly, the sputtering apparatus of the present invention has high ability of film-deposition.

A thin film composed mainly of silicon oxide formed by the sputtering method of the present invention is of higher quality than a thin film obtained by a DC sputtering.

The thin film composed mainly of silicon oxide formed by the sputtering method and the sputtering apparatus of the present invention is of high quality since no arcing takes place during the sputtering so that attachment of particles is little. Further, it is believed that since there is no fluctuation in the sputtering condition due to arcing, a uniform film with little microscopic defects can be obtained. Further, it is believed that excellent film quality with little defects can be obtained, since sputtering is carried out intermittently with an interval of every period, whereby a very thin film is intermittently formed on the substrate with an interval of every period, and film-deposition is carried out while an oxidation reaction on the substrate is completed during every period.

Thus, it is possible to obtain an excellent thin film composed mainly of silicon oxide which has little defects macroscopically or microscopically, whereby a high alkali barrier property can be obtained even when the film is formed on a low temperature substrate.

A thin film composed mainly of silicon nitride formed by the sputtering method or the sputtering apparatus of the present invention is of higher quality than a thin film obtained by the DC sputtering.

The thin film composed mainly of silicon nitride formed by the sputtering method of the present invention is of high quality since it is unnecessary to heat the substrate, no arcing takes place during the sputtering so that attachment of particles is little. Further, it is believed that since there is no fluctuation in the sputtering condition due to arcing, a uniform film with little microscopic defects can be obtained. Further, it is believed that excellent film quality with little defects can be obtained, since sputtering is carried out intermittently with an interval of every period, whereby a very thin film is intermittently formed on the substrate with an interval of every period, and film-deposition is carried out while a nitriding reaction on the substrate is completed during every period.

Thus, it is possible to obtain an excellent thin film composed mainly of silicon nitride which has little defects macroscopically or microscopically, whereby a high alkali barrier property can be obtained even when the film is formed on a low temperature substrate.

If the concentration of nitrogen in sputtering gas is adjusted and/or power to be supplied to a silicon target is adjusted so that the composition ratio of silicon nitride (atomic molar ratio of N/Si) will be within a range of from 1.25 to 1.36, it is possible to produce silicon nitride having an excellent alkali barrier property.

In the film-deposition method of a transparent conductive film by the sputtering method of the present invention, a negative voltage is intermittently applied and power of a large power density is instantaneously supplied, and at the same time, problems of nodules of sub oxide on the target material which reduce the sputtering rate and an arcing in sputtering can be eliminated. Thus, the film-deposition method of the present invention is excellent in productivity.

As sputtering targets, there are a sputtering target composed mainly of tin or tin oxide containing metal antimony or an antimony compound, a sputtering target composed mainly of indium or indium oxide containing tin and a sputtering target composed mainly of zinc or zinc oxide containing a simple substance or a compound of at least one metal selected from the group consisting of aluminum, gallium, indium, boron and silicon.

Sputtering power used for the method and apparatus of the present invention is preferably have a voltage waveform to be applied to a target, as shown in Figure 1 wherein an application time of negative

BNSDOCID: <EP_______0639655A1_I_>

voltage is in a range of from 10 μs to 10 ms and a non-application time is in a range of from 10 μs to 100 ms, or a voltage waveform to be applied to a target as shown in Figure 2 wherein an application time of negative voltage is in a range of from 10 μs to 10 ms and an application time of negative voltage and a non-application time is in a range of from 10 μs to 100 ms.

5 Further, setting of the value of negative voltage ($-V_N$ in Figure 9) is important for suppressing formation of nodules, which is an object of the present invention. As expressed in formula 5, arcing and formation of nodules of sub oxide on the target surface can be effectively suppressed by adjusting the negative application voltage ($-V_N$) so that the average value W_A of the intermittently supplied power is from 2 to 10 times the average value W of the power per period (hereinafter referred to as the effective value W).

10 The effective value W of the power is as represented by the formula 1 where T is the period. If this is applied to the case of the waveform as shown in Figure 2, W is as shown by the formula 2.

On the other hand, the average power W_A within the time when sputtering actually takes place (when the negative voltage is applied) (a_1 in Figure 9) are as shown by the formula 3. Further, in Figure 2, the average voltage is V_A = ($-V_N$), and if this is inserted, W_a is as shown by the formula 4.

15 To effectively remove nodules, it is preferred that the average value W_A of power is from 2 to 10 times the effective value W of the power, as shown by the formula 5. If this is applied to the case of the waveform as shown in Figure 2, the formula 6 is obtained. Therefore, ($-V_N$), a_1 ($10\ \mu s \leq a_1 \leq 10$ ms), and b_1 ($10\ \mu s \leq b_1 \leq 100$ ms) should be adjusted to satisfy the formula 6.

Good results can be obtained especially when the average value of intermittent electric power density

20 ω_A (see formula 7) is within a range of from 2.5 W/cm^2 to 30 W/cm^2.

In this case, the waveform may not be necessarily be a precise rectangular waveform as shown in Figure 9, and ($-V_n$), a_1 and b_1 may be optimized depending upon the size and condition of the target and the particular apparatus.

In a case where positive voltage is applied as shown in Figure 10 or 11, application of such positive

25 voltage does not serve effectively for sputtering, and accordingly, in the calculation of the formulas 1 to 7, V_p is to be taken as 0.

The film-deposition rate of the transparent conductive film can easily be controlled by the effective value W of the intermittently supplied sputtering power. For example, in a case where by the method of the present invention, it is intended to obtain the desired film-deposition rate obtained by the conventional DC

30 sputtering method, the desired film-deposition rate can be obtained by adjusting the effective value W of the intermittently supplied power to the same level as the DC electric power value.

Namely, an equation of "the film-deposition rate by the conventional DC sputtering method/the DC power = the film-deposition rate according to the present invention/the effective value W of power" substantially holds good.

35 Thus, the film-deposition rate can be adjusted by adjusting the zero volt time so that the effective power value W corresponds to the power of the conventional DC sputtering, and the quality of a film deposited on the substrate can be kept and a stable sputtering is obtained for a long time.

40

45

50

55

BNSDOCID: <EP_______0639655A1_I_>

Formula 1

$$W = \frac{1}{T} \int_0^T V(t)\, I(t)\, dt$$

Formula 2

$$W = \frac{(-V_N)}{a_1 + b_1} \int_0^{a_1} I(t)\, dt$$

Formula 3

$$W_A = \frac{1}{a_1} \int_0^{a_1} V(t)\, I(t)\, dt$$

Formula 4

$$W_A = \frac{-V_N}{a_1} \int_0^{a_1} I(t)\, dt$$

Formula 5 $2W \leqq W_A \leqq 10W$

Formula 6

$$2 \leqq \frac{W_A}{W} = \frac{a_1 + b_1}{a_1} \leqq 10$$

Formula 7

$$\omega_A = \frac{W_A}{S} \qquad S: \text{Target surface area}$$

Now, the present invention will be described in detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples.

EXAMPLE 1

Figure 5 shows an example of the sputtering apparatus of the present invention.

In Figure 5, reference numeral 51 designates a DC power source for generating intermittently a negative DC voltage, numeral 52 designates a cathode electrode with a target material, numeral 53 designates an anode electrode, numeral 54 designates a substrate to be subjected to a film-deposition treatment, numeral 55 designates an area of glow discharge effective to sputtering, numeral 56 designates a slight arcing produced on the surface of the target and numeral 57 designates arcing produced between the cathode electrode and the anode electrode.

In the present invention, output from the DC power source generating an intermittent DC voltage may not be of a rectangular wave, but may be of a trapezoidal, a triangular or a sign waveform to obtain the same effect. Further, in construction of the power source circuit, the waveform can be produced by oscillation in the power source itself or the output of the DC power source may be processed by a semiconductor switching element to form an intermittent waveform. In either case, the effect of the present invention is the same.

BNSDOCID: <EP________0639655A1_I_>

In the apparatus having the construction shown in Figure 5, using a planar magnetron cathode having an area of 10 × 80 cm, a target material of boron-doped silicon, and a gas mixture of argon and oxygen having a ratio of 1:1, as introducing gas, a film of SiO_2 doped with boron was deposited by sputtering on a substrate under a discharging pressure of 3.0×10^{-3} Torr and an effective power value of 2 kW. When a
5 DC discharge was conducted, arcing suddenly and frequently took place after about 2 minutes and 30 seconds and the sputtering could not be continued.

Sputtering was conducted in the same manner as above except that an intermittent direct current was used wherein in the waveform shown in the upper portion of Figure 1, an ON time during which a negative voltage is applied was 100 μs and a zero volt time was 40 μs. As a result, arcing gradually increased and
10 the frequency of occurrence of the arcing after about 30 minutes was about 60 times/min.

In observing the current waveform during arcing and measuring a time of extinction of the initial arcing, there was detected 160 to 180 μs.

Sputtering was conducted in the same manner as above except that an intermittent direct current was used wherein the ON time was 100 μs and the zero volt time was 200 μs. As a result, the frequency of
15 occurrence of arcing after about 60 min was about 60 times/min. In this case, the initial arcing frequently took place after 90 μs to 100 μs of the rise of voltage.

Sputtering was conducted in the same manner as above except that an intermittent direct current was used wherein the ON time was 80 μs and the zero volt time was 200 μs. There was found that the frequency of occurrence of arcing after about 60 min was about 30 times/min. The frequency of occurrence
20 of arcing in the above-mentioned four tests is shown in Figure 6. In the measurement of arcing, a current value 10% or more than the maximum value of ordinary current waveform was used as a detection level in the oscilloscope and the number of occurrence detected was recorded.

EXAMPLE 2

25

A cathode having an area of 40 × 300 cm, aluminum-doped silicon as a target material and a gas mixture of argon and oxygen having a ratio of 2:10 as introducing gas were used in the apparatus shown in Figure 5. Sputtering was conducted under a discharge pressure of 2.0×10^{-3} Torr and at an effective power value of 13 kW to deposit a film of SiO_2 doped with aluminum on a substrate.

30 When a direct current was used for discharge, arcing suddenly took place after about 35 min and the sputtering could not be continued. In observing the waveform during the discharge, a time of extinction of the initial arcing was about 400 μs.

Sputtering was conducted in the same manner as above except that the waveform shown in the upper portion of Figure 1 was used wherein the zero volt time was 500 μs and the ON time was 500 μs. A time
35 required for the occurrence of the initial arcing was about 220 μs after the rise of voltage.

Sputtering was conducted in the same manner as above except that the ON time was 220 μs and the zero volt time was 500 μs. The frequency of occurrence of arcing was 20 times/min or lower even after the lapse of 4 hrs.

The frequency of occurrence of arcing in the case of using a direct current and the case of using the
40 intermittent waveform wherein the ON time is 220 μs and the zero volt time is 500 μs is shown in Figure 8. The condition of detecting arcing is the same as that of Example 1.

EXAMPLE 3

45 In a vacuum chamber, N-type silicon (phosphorus doped single crystal) having a specific resistance of 1.2 $\Omega \cdot$cm was placed as a target on a cathode, and on the opposite side of the target, a soda lime glass sheet was disposed as a substrate. The vacuum chamber was evacuated to 1×10^{-5} Torr. Then, a gas mixture of argon and oxygen was introduced as sputtering gas, and conductance was adjusted so that the pressure is 2×10^{-3} Torr.

50 Then, the voltage as shown in the upper portion of Figure 2 was applied to the cathode. Here, the ON time 21 was 50 μs which is the same as the time of starting the initial arcing and the zero volt time 22 was 50 μs which is the same as the time of extinction of the initial arcing in which the time 23 for applying a positive potential was about 12 μs. Here, the negative voltage was adjusted so that the application power in the application of this voltage was 500 W. The positive voltage was kept to be 100 V.

55 The substrate temperature was maintained to be at room temperature, and an electric discharge was started at an oxygen concentration in the sputtering gas of 60%. After the pre-discharge of 5 min, the shutter was opened, and the film-deposition time was adjusted so that the thickness of film was 250 Å, whereby a thin film composed mainly of silicon oxide was deposited on a soda lime glass substrate.

BNSDOCID: <EP________0639655A1_I_>

When 120 min passed after the initiation of discharge, a film was deposited on another soda lime glass substrate. However, little arcing was observed.

COMPARATIVE EXAMPLE 1

5

Sputtering was conducted to deposit a film in the same manner as Example 3 except that an intermittent DC voltage having the waveform as shown in the upper portion of Figure 1 was applied to the cathode wherein the ON time was 50 μs and the zero volt time was 25 μs.

Although little arcing was observed just after the initiation of film-deposition, occurrence of arcing was
10 observed with the lapse of time, and continuous discharge of red-hot particles was observed on the target surface at the completion of film-deposition.

When 120 min passed after the initiation of discharge, a film was deposited on another soda lime glass substrate. Arcing took place very frequently.

15 COMPARATIVE EXAMPLE 2

Sputtering was conducted in the same manner as Example 3 except that a radio frequency voltage of 13.56 MHz was applied to the cathode.

After 120 min from the initiation of discharge, a film was deposited on another soda lime glass
20 substrate. In this case, there was no arcing.

The coated side of each of the coated glass obtained in Example 3 and Comparative Examples 1 and 2 was contacted with pure water at 90 °C for 24 hours, whereupon the amount of out diffused sodium atoms (μg/cm^2) in this pure water was measured by atomic absorptiometry. Results are shown in Table 1.

25

Table 1

	Film-deposition after 5 min from initiation of discharge	Film-deposition after 120 min from initiation of discharge
Example 3	0.02	0.02
Comparative Example 1	1.3	5.6
Comparative Example 2	0.32	0.31

30

35

As is clear from the above Example and Comparative Examples, according to the present invention, it is possible to form a thin film of silicon oxide having a high alkali barrier property without heating the substrate for a long period of time and in a stable manner. Further, since the film-deposition is conducted by the DC sputtering, deposition of a film with a large area or a film-deposition at a high speed can be facilitated, whereby application to e.g. a transparent conductive substrate for liquid crystal can be made possible on an industrial production scale.

40

EXAMPLE 4

N-type silicon having a specific resistance of 1.2 Ω•cm and a surface area of 160 mm × 40 mm was
45 used as a target, and the voltage as shown in the upper portion of Figure 2 was applied to the targets. Here, the negative voltage was adjusted so that the application power in the application of this voltage was 200 W. The positive voltage was kept to be 100 V. Other conditions was the same as those of Example 3.

Discharge was started at an oxygen concentration in sputtering gas of 40%. After 5 min, the shutter was opened to deposit a film of silicon nitride having a thickness of 200 Å on a flat soda lime silicate glass at room temperature.

50

Then, when 120 min passed after the initiation of discharge, the shutter was again opened to deposit a silicon nitride film of 200 Å on another soda lime glass substrate. During the film-deposition operations, no arcing was observed.

COMPARATIVE EXAMPLE 3

55

Sputtering was conducted in the same manner as in Example 4 except for application of a DC power of 200 W. In film-deposition after 5 min from the initiation of discharge, no arcing was observed.

BNSDOCID: <EP_____0639655A1_I_>

After 120 min from the initiation of discharge, film-deposition was conducted on another soda lime glass substrate. In this case, arcing frequently took place, and discharge of red-hot particles from the target surface was observed.

5 COMPARATIVE EXAMPLE 4

Sputtering was conducted in the same manner as in Example 4 except N-type silicon having a specific resistance of 1.5 Ω•cm and a diameter of 6 inches was used as a target, the nitrogen concentration in sputtering gas was adjusted to 100%, and a radio frequency voltage of 13.56 MHz was applied so that a
10 power of 300 W was supplied.

When 120 min passed after the initiation of discharge, a film was deposited on another soda lime glass substrate. No arcing was observed.

COMPARATIVE EXAMPLE 5

15

Films of silicon nitride each having a film thickness of 200 Å were deposited on flat soda lime silicate glass substrates at a temperature of about 600 °C by CVD method in each case that the ratio of ammonia gas/silane gas in material gas was 3, 5, 10 or 15.

The coated side of each of the coated glass obtained by Example 4 and Comparative Examples 3 to 5
20 was contacted with pure water at 90 °C for 24 hours, whereupon the amount of sodium atom out diffused into the pure water from soda lime glass through silicon nitride film was measured by atomic absorptiometry. The results of Example 4 and Comparative Examples 3 and 4 are shown in Table 2 and the results of Comparative Example 5 are shown in Table 3.

25

30

35

40

45

50

55

Table 2

	Film-deposition after 5 min from initiation of discharge		Film-deposition after 120 min from initiation of discharge	
	Composition (N/Si)	Amount of out diffused Na ($\mu g/cm^2$)	Composition (N/Si)	Amount of out diffused Na ($\mu g/cm^2$)
Example 4	1.33	0.005	1.33	0.005
Comparative Example 3	1.33	0.008	1.32	0.91
Comparative Example 4	1.36	0.015	1.36	0.015

5 10 15 20 25 30 35 40 45 50 55

BNSDOCID: <EP________0639655A1_I_>

Table 3

Ratio of ammonia/silane	3	5	10	15
Composition (N/si) Amount of out diffused Na ($\mu g/cm^2$)	1.27 0.047	1.36 0.038	1.49 0.056	1.56 0.062

In comparing Examples with Comparative Examples described above, silicon nitride film deposited by the present invention shows that the amount of out diffused sodium atoms through this film is low, and there is clear superiority in the present invention.

Further, it is understood that the silicon nitride film having a high alkali barrier property can be deposited stably for a long period of time.

Further, it becomes possible to deposit a silicon nitride film having a high alkali barrier property without heating the substrate, and coating of alkali barrier on a substrate having a low heat resistance is possible.

EXAMPLE 5

By using an ordinary magnetron sputtering device as shown in Figure 5, the voltage as shown in the upper portion of Figure 1 wherein the ON time was 100 μs and the zero volt time was 400 μs, was applied to an indium oxide target 52 containing 10 wt% of tin. As a substrate 54 on which a film is to be deposited, non-alkali glass (AN glass by Asahi Glass Company Ltd.) previously heated to 200 °C was used.

A film-deposition chamber was evacuated to 1 $\times$ 10^{-5} Torr or lower. Then, argon gas containing 1 vol% of oxygen gas was introduced so that gas pressure was 3 $\times$ 10^{-3} Torr. Sputtering power was adjusted to be 1.1 kW in terms of effective value.

EXAMPLE 6

Sputtering was conducted in the same manner as in Example 5 except that the voltage as shown in Figure 2 wherein the ON time 21 was 100 μs, the application time of positive voltage 23 having an amplitude of about 10% to the power value in the application of a negative voltage was 10 μs and the zero volt time 26 was 390 μs.

COMPARATIVE EXAMPLE 6

Sputtering was conducted in the same manner as in Example 5 except that the conventional magnetron sputtering apparatus and the conventional DC sputtering power source were used.

Occurrence of nodules after continuous sputtering of 23 hours, the frequency of occurrence of arcing and the characteristic of ITO films were examined on Examples 5 and 6 and Comparative Example 6.

Table 4

	Comparative Example 6	Example 5	Example 6
Formation of nodules (after sputtering for 23 hours)	Many nodules were observed the entire erosion region except for the erosion center	Almost nil	Almost nil
Frequency of arcing (after film-sputtering for 23 hours)	15 times/min or more	3 times/min or less	Once/min or less
Specific resistance of ITO film (Ω·cm) Immediately after initiation of film-sputtering	1.9×10^{-4}	1.9×10^{-4}	1.9×10^{-4}
Specific resistance of ITO film (after film-sputtering for 23 hours)	4.0×10^{-4}	2.0×10^{-4}	1.9×10^{-4}
Change in the sputtering rate (after sputtering for 23 hours)	Decreased by about 40%	Almost nil	Almost nil

As seen in Table 4, occurrence of nodules is slight even after continuous sputtering for 23 hours (a target of a thickness of 6 mm was completely digged down) and there is no substantial reduction in sputtering rate. Further, the frequency of occurrence of arcing is reduced to about 1/5 - 1/3 in comparison with the conventional sputtering method shown in Comparative Examples. The specific resistance of ITO film is substantially the same as that of a sample by the conventional sputtering method.

BNSDOCID: <EP_______0639655A1_I_>

In Comparative Examples, the decrease of the sputtering rate was remarkable by about 40%. The specific resistance is reduced from 1.9×10^{-4} Ω•cm (at the initial stage of sputtering) to 4×10^{-4} Ω•cm due to the reduction of sputtering rate. Nodules were very rigid and it was necessary to conduct mechanical grinding for cleaning.

5 The film-deposition method for a transparent conductive film and the film-deposition apparatus of the present invention exhibit excellent effect in depositing a transparent conductive film without stopping film-deposition steps, which reduce productivity, and to suppress occurrence of nodules of sub oxide on the target surface which causes reduction in sputtering rate. Further, it provides excellent effect to suppress arcing which causes defects in the transparent conductive film. Since arcing can be suppressed, a large 10 electric power can be used and a high film-deposition rate is obtainable in comparison with the conventional DC sputtering method.

Further, use of the power processing portion of the present invention suppresses arcing without adding an arcing preventing circuit which is used for a conventional DC sputtering power source. Further, by controlling the effective value of intermittently supplied power, conditions for film-deposition can be 15 controlled in the same manner as the conventional DC sputtering method, and a transparent conductive film having the same property as the conventional film can be obtained.

In accordance with the present invention, since a potential difference on the target surface is eliminated and occurrence of arcing is prevented, a stable discharge can be maintained in comparison with a conventional DC sputtering.

20 The frequency of occurrence and the scale of initial arcing can be small, a stable sputtering can be continued for a long period of time even when a large power is used. Further, excellent efficiency of electric power is obtainable.

The sputtering apparatus of the present invention can reduce the frequency of occurrence of arcing even in a case of reactive sputtering, and a large electric power can be supplied stably to the cathode. 25 Accordingly, it has high film-deposition ability.

The power processing portion of the present invention is of a simple structure and is applicable to a conventional sputtering apparatus so that sputtering by a pulse-like intermittent DC power can be realized.

By using the power processing portion of the present invention, an intermittent voltage waveform can be easily optimized depending on the size of apparatus, material, electric power used and the scale of initial 30 arcing.

In the film-deposition method of a thin film composed mainly of silicon oxide according to the present invention, since arcing is not generated during film-deposition, a film having high quality and little attachment of particles can be obtained.

Further, in the film-deposition method of a thin film composed mainly of silicon nitride according to the 35 present invention, since arcing is not generated during film-deposition, a thin film of high quality and little attachment of particles can be obtained.

The film-deposition method for an ITO film of the present invention can provide stable operations for a long period of time because arcing can be prevented and occurrence of nodules of sub oxide formed on the target surface can be suppressed while the quality of a film and the film-deposition rate are the same as 40 those obtained by the conventional DC sputtering method.

Claims

1. A sputtering method which comprises applying a negative voltage intermittently in a constant periodic 45 cycle to a cathode disposed in a vacuum chamber, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 μs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

50 2. The sputtering method according to Claim 1, wherein the time during which the negative voltage is applied is within a range of from 10 μs to 10 ms and is equal to or shorter than the period of time from the application of the negative voltage to the generation of arcing.

3. The sputtering method according to Claim 1, wherein the time during which the voltage is controlled to 55 be zero voltage includes a period of time during which a positive voltage is applied within a range of from 1 μs to 20 μs.

BNSDOCID: <EP_____0639655A1_I_>

4. The sputtering method according to any one of Claims 1 to 3, wherein the time during which the voltage is controlled to be zero volt is immediately after arcing.

5. A sputtering apparatus comprising a cathode disposed in a vacuum chamber, a sputtering power generating portion and a power processing portion, the cathode being applied with a intermittent negative voltage, wherein the wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 µs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

6. The sputtering apparatus according to Claim 5, wherein the power processing portion is disposed closer to the cathode than the sputtering power generating portion.

7. The sputtering apparatus according to Claim 5, wherein a plurality of cathodes, sputtering power generating portions and power processing portions are provided, and the plurality of power processing portions are synchronously operated to produce waveforms having a different phase.

8. A power processing portion for a sputtering apparatus having a cathode to which a negative voltage is intermittently applied, wherein:
   the power processing portion comprises a first switching circuit, a second switching circuits, a control circuit for a switching element and a circuit for measuring current, voltage or power for sputtering
   the first and the second switching circuits are respectively formed of a semiconductor switching device and a protection circuit for protecting the device;
   the first switching circuit is connected in series between the negative pole of the sputtering power generating portion and the cathode electrode;
   the second switching circuit is connected in series between the cathode electrode and a DC power source, other than the sputtering power generating portion, for supplying a positive potential to the cathode electrode.
   the control circuit for the semiconductor switching device is capable of controlling a turning-on time of 5 µs or more for the first switching circuit and a turning-off time of 5 µs or more for the same, and capable of turning-on the second switching circuit for less than the time of turning-off the first switching circuit and within a range of from 1 µs to 20 µs when the first switching circuit is turned off; and
   the circuit for measuring current, voltage or power for sputtering has a function to measure a current value, a voltage value or a power value effective to sputtering and a function to compare the measured values with predetermined reference values to detect arcing.

9. The power processing portion according to claim 8, which further comprises a smoothing circuit to change the waveform of voltage at an output terminal of the sputtering power generating portion to be a DC voltage waveform.

10. A film-deposition method by sputtering a thin film composed mainly of silicon oxide by applying a negative voltage intermittently in a constant periodic cycle to a cathode composed mainly of silicon in a vacuum chamber and using oxygen and/or inert gas as sputtering gas, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 µs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

11. A film-deposition method by sputtering a thin film composed mainly of silicon nitride by applying a negative voltage intermittently in a constant periodic cycle to a cathode composed mainly of silicon in a vacuum chamber and using nitrogen and/or inert gas as sputtering gas, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 µs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

12. The film-deposition method according to Claim 11, wherein the composition ratio of the silicon nitride (atomic molar ratio of N/Si) is 1.25 to 1.36.

BNSDOCID: <EP_______0639655A1_I_>

13. The film-deposition method by sputtering a transparent conductive thin film composed mainly of oxide by using a sputtering target capable of forming a transparent conductive film, disposed in a vacuum chamber, applying a negative voltage intermittently and using oxygen and/or inert gas as sputtering gas, wherein the negative voltage is intermittently applied so that a time during which the negative voltage is not applied includes a time during which the voltage is controlled to be zero volt in a range of from 10 μs to 10 ms, and the zero voltage time is equal to or longer than the time required by one arcing from its generation to extinction.

14. The film-deposition method according to Claim 13, wherein the sputtering target is composed mainly of tin or tin oxide.

15. The film-deposition method according to Claim 14, wherein the sputtering target contains metal antimony or an antimony compound.

16. The film-deposition method according to Claim 13, wherein the sputtering target is composed mainly of indium or indium oxide.

17. The film-deposition method according to Claim 16, wherein the sputtering target contains tin.

18. The film-deposition method according to Claim 13, wherein the sputtering target is composed mainly of zinc or zinc oxide.

19. The film-deposition method according to Claim 18, wherein the sputtering target contains a simple substance or a compound of at least one metal selected from the group consisting of aluminum, gallium, indium, boron and silicon.

BNSDOCID: <EP_______0639655A1_I_>

FIGURE 1

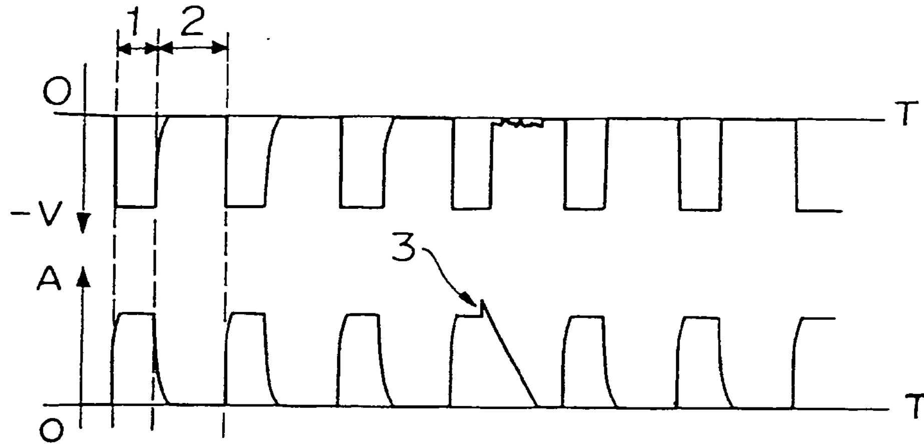


FIGURE 2

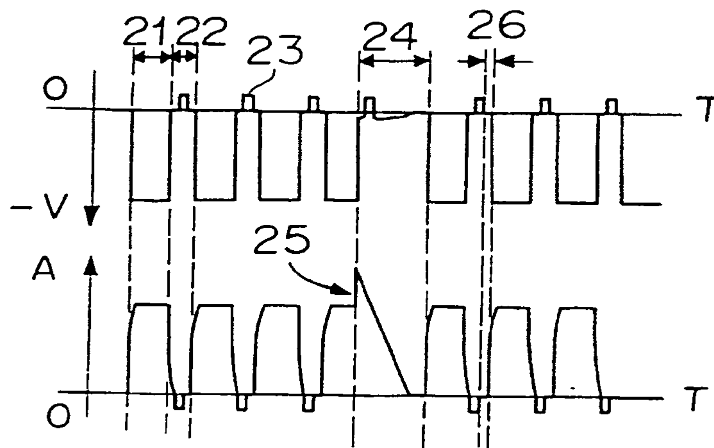
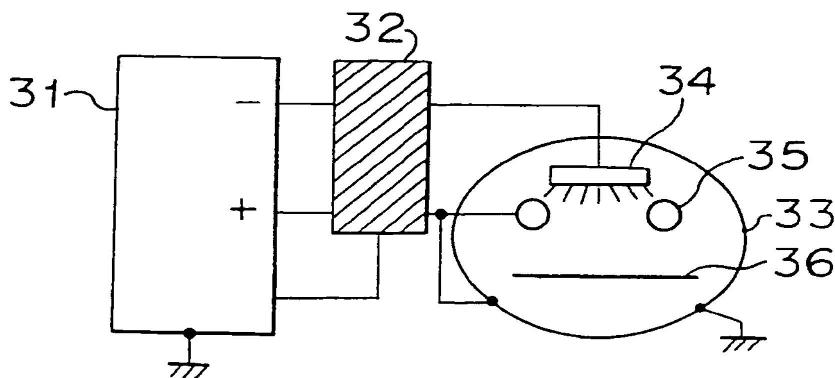


FIGURE 3



BNSDOCID: <EP________0639655A1_I_>

FIGURE 4

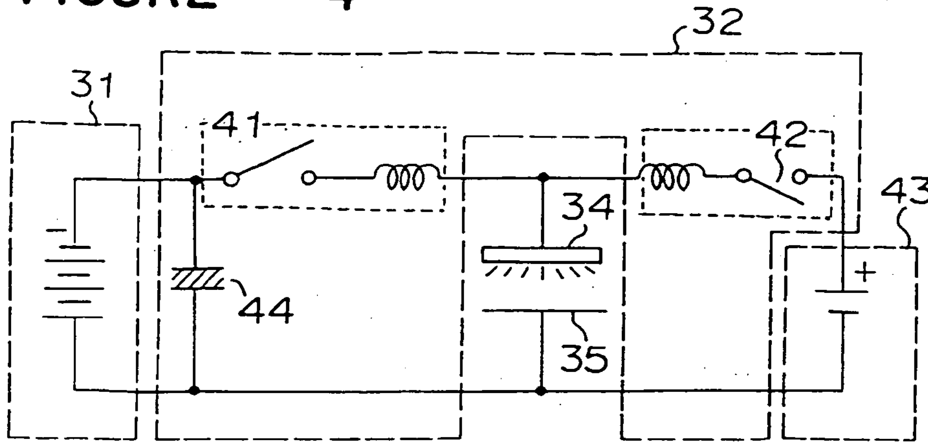


FIGURE 5

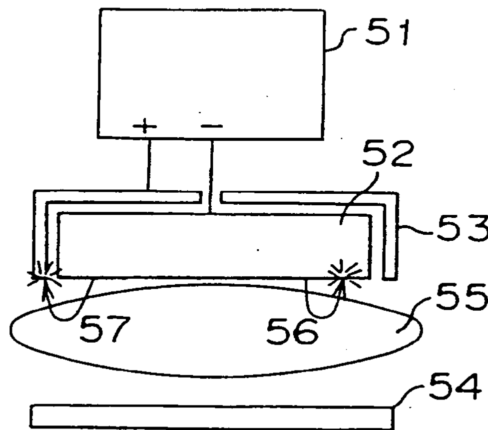


FIGURE 6

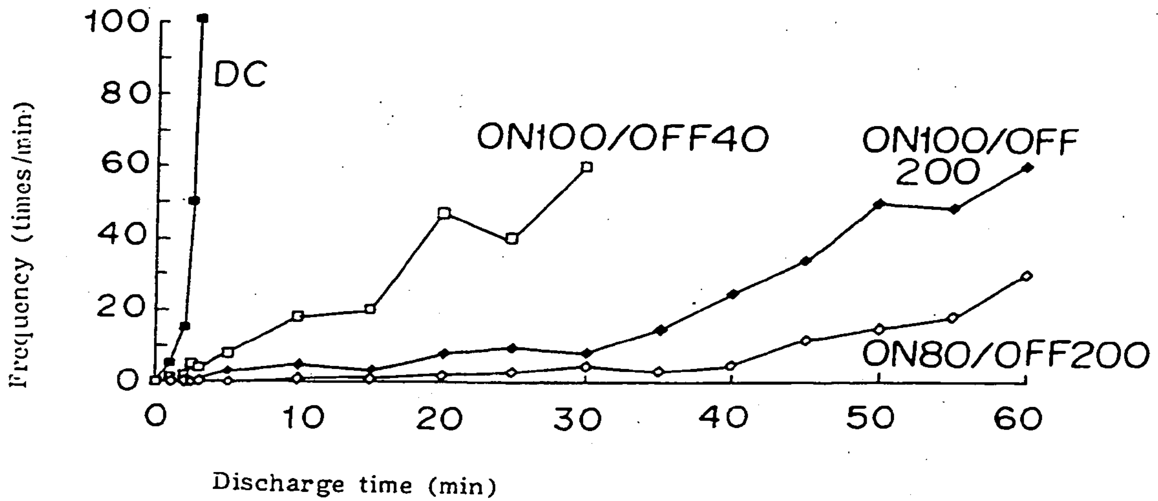


FIGURE 7

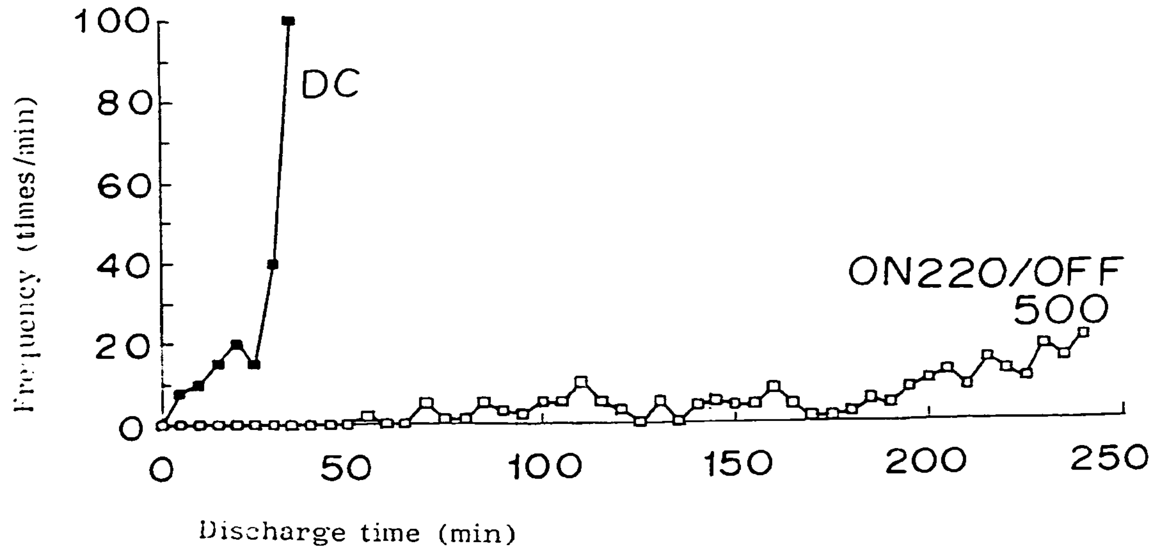
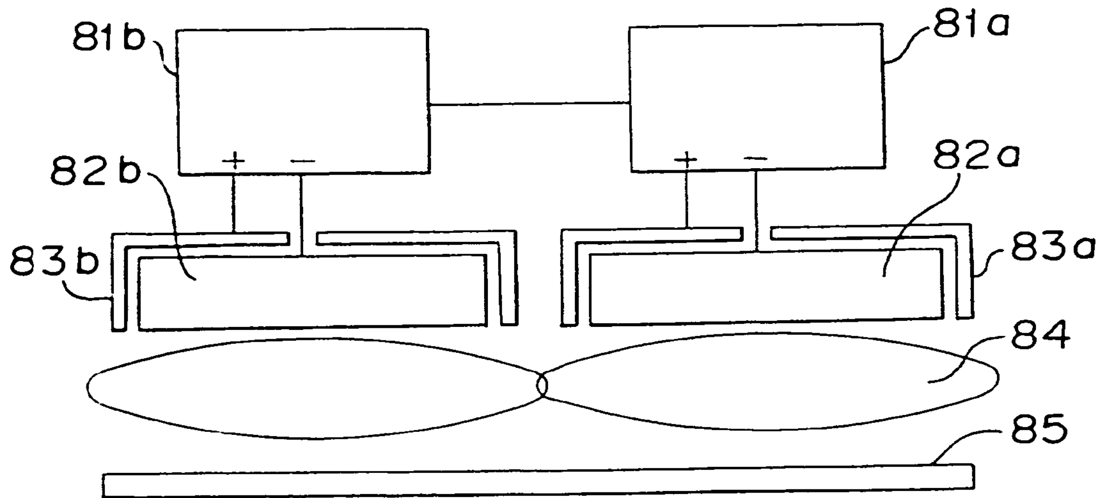


FIGURE 8



BNSDOCID: <EP_____0639655A1_I_>

FIGURE 9

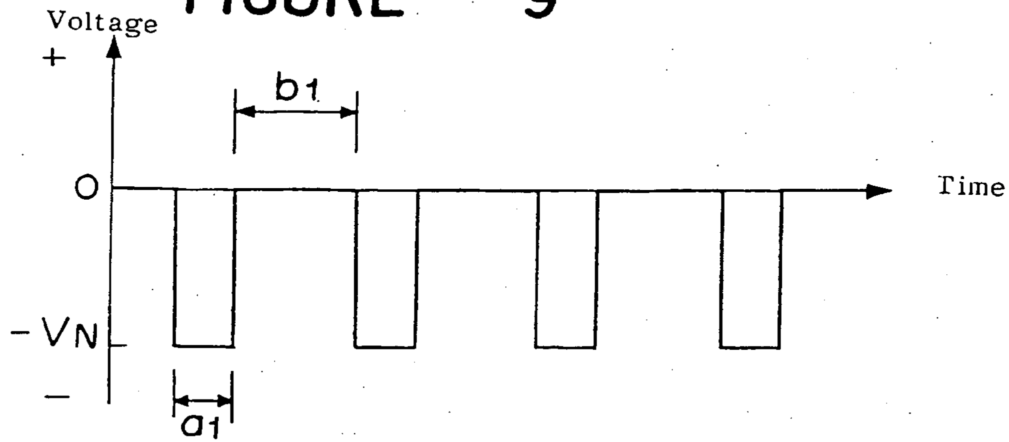


FIGURE 10

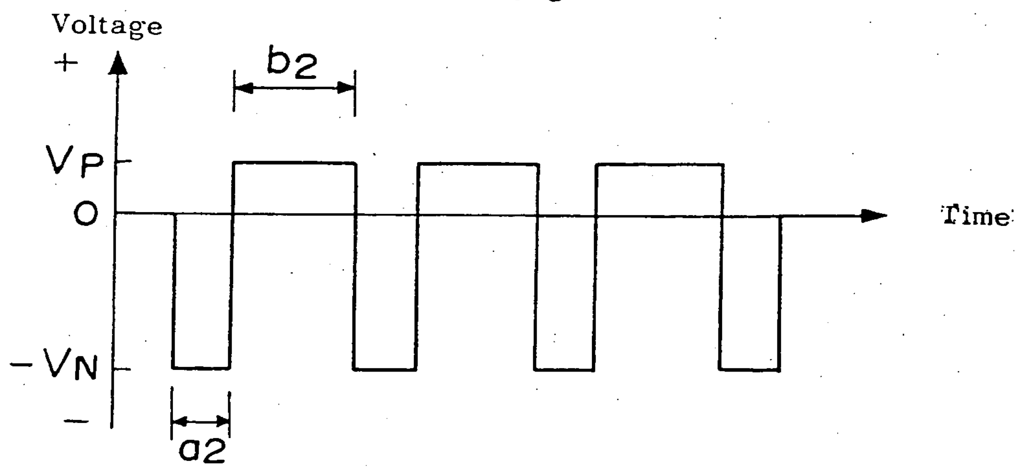
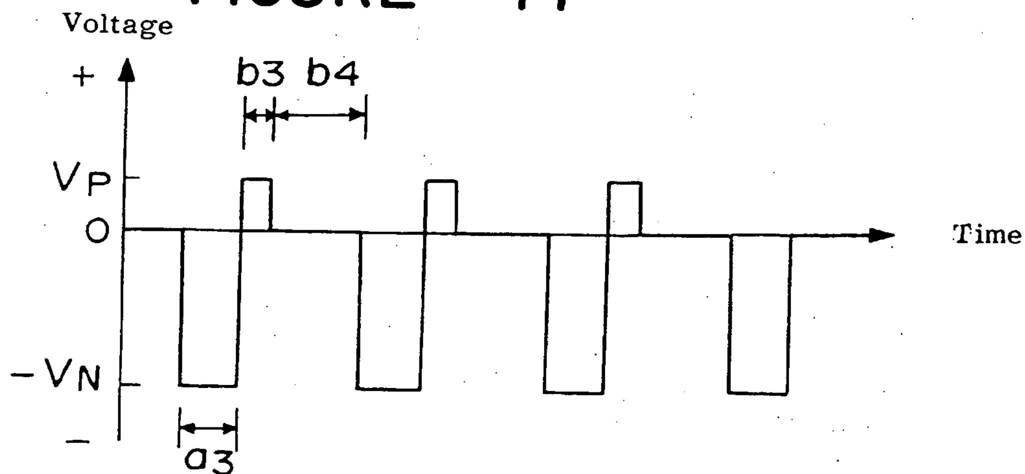


FIGURE 11



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 1669

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	THIRD INTERNATIONAL CONFERENCE ON PLASMA SURFACE ENGINEERING, GARMISCH-PARTENKIRCHEN, GERMANY, 26-29 OCT. 1992, ISSN 0257-8972, SURFACE AND COATINGS TECHNOLOGY, 1 OCT. 1993, SWITZERLAND, PAGE(S) 177 - 182 Frach P et al 'Aspects and results of long-term stable deposition of Al/sub 2/O/sub 3/ with high rate pulsed reactive magnetron sputtering' * page 180, left column, line 2 - right column, line 2 * ---	1-19	C23C14/00 C23C14/34 H01J37/32
X A	EP-A-0 275 018 (GRUN R) 20 July 1988 * column 4, line 40 - line 50; claims 1-4 * ---	5 1-4,6-19	
A	WO-A-87 05053 (QUAZI) * page 28, line 3 - line 12; claim 1 * ---	1-19	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 90 (C-0691) 20 February 1990 & JP-A-01 301 856 (SHIMADSU CORP) 6 December 1989 * abstract * ---	1-19	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C23C H01J H03J
A	CIP 93 PROCEEDINGS, 6 June 1993, FR pages 66 - 68, XP399216 B. STAUDER ET AL 'A METHOD FOR SUPRESSING THE HYSTERESIS EFFECT IN REACTIVE SPUTTERING' * page 67, line 9 - line 21 * ---	1-19	
A	WO-A-91 02103 (THE BOC GROUP INC) * claims 1,2 * -----	10-19	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 November 1994	Ekhult, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☑ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☑ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☑ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ____________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1652	band with reject with filter	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:41
L2	52349	DC and RF	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:31
L3	824596	@ad>"20020316" or @rlad>"20020316"	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:18
L4	338	1 and 2	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:18
L5	271	4 not 3	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:20
L6	1694	204/192.12.ccls.	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:21
L7	3	5 and 6	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:21
L8	180836	"438"/$.ccls or "257"/$.ccls. or 29/25.01.ccls.	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:23
L9	2	5 and 8	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:23
L12	50121	"204"/$.ccls.	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:24
L13	5	5 and 12	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:27
L14	1	("20040077161").PN.	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:28
L15	976	(pulsed with DC) and RF	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:32
L16	5	1 and 15	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:32
L17	4	16 not 3	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:36
L18	162768	notch	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:37
L19	422	1 and 18	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:37
L20	1	15 and 19	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:37
L21	1937	band with rejection with filter	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:38
L22	15	15 and 21	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:38
L23	1	22 not 3	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:38
L24	42828	band with pass with filter	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:41

L25	31	15 and 24	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:42
L26	13	25 not 3	US-PGPUB; USPAT	OR	OFF	2005/07/29 15:42

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

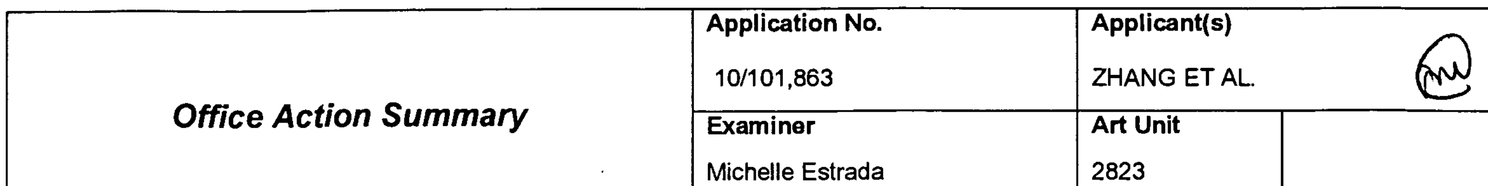
22852 7590 08/04/2005

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 08/04/2005

Please find below and/or attached an Office communication concerning this application or proceeding.



Office Action Summary	Application No.	Applicant(s)
	10/101,863	ZHANG ET AL.
	Examiner	Art Unit
	Michelle Estrada	2823

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *13 July 2005*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-14 and 20-24* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-13 and 20* is/are rejected.

7)☒ Claim(s) *14 and 21-24* is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *7/13/05*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____.

DETAILED ACTION

Continued Examination Under 37 CFR 1.114

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 7/13/05 has been entered.

Applicant's arguments with respect to claims 1 and 20 have been considered but are moot in view of the new ground(s) of rejection.

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1, 8, 10-13 and 20 are rejected under 35 U.S.C. 102(b) as being anticipated by Smolanoff et al. (6,117,279).

With respect to claim 1, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a

substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created between the target and the substrate (Col. 6, lines 8-13).

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claim 12, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claim 13, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claim 20, Smolanoff et al. disclose conditioning a target; preparing the substrate; adjusting the bias power to the substrate; setting the process gas flow; and applying pulsed DC power to the target to deposit the film (Col. 5, line 55-Col. 7, line 50).

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 2-6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Fukui et al. (5,755,938).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In

re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With respect to claim 5, Smolanoff et al. do not specifically disclose wherein the filter is a band reject filter at the frequency of the bias power.

Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter (27) at the frequency of the bias power.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fukui et al. to enable the filter type of Smolanoff et al. to be the same according to the teachings of Fukui et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable types of filters for the disclosed filter step of Smolanoff et al. and art recognized suitability for an

intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Le et al. (2003/0077914).

Smolanoff et al. do not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Leet al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Allowable Subject Matter

Claims 14 and 21-24 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

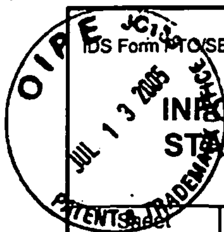
Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should

you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Patent Examiner
Art Unit 2823

ME
July 29, 2005



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	1	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
MJE		US-2004/0077161	04-22-2004	Chen et al.	
MJE		US-2003/0175142	09-18-2003	Milonopoulou et al.	
		~~US-2003/0077914~~	~~04-24-2003~~	~~Le et al.~~	
MJE		US-6,361,662	03-26-2002	Chiba et al.	
MJE		US-6,281,142	08-28-2001	Basceri et al.	
MJE		US-6,117,279	09-12-2000	Smolanoff et al.	

already cited in PTO-892 filed 2/24/04 MJE

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
MJE		Office Action dated March 25, 2005, received in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01000).	

Examiner Signature	Michelle Estrada	Date Considered	7/29/05

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 727732935 US

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

Bib Data Sheet

CONFIRMATION NO. 6938

SERIAL NUMBER 10/101,863	FILING DATE 03/16/2002 RULE	CLASS 438	GROUP ART UNIT 2823	ATTORNEY DOCKET NO. M-12245 US

APPLICANTS

Hongmei Zhang, San Jose, CA;

Mukundan Narasimhan, San Jose, CA;
Ravi B. Mullapudi, San Jose, CA;Richard E. Demaray, Portola Valley, CA;

** CONTINUING DATA ************************* none

** FOREIGN APPLICATIONS ******************** none

IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** SMALL ENTITY **
** 05/17/2002

Foreign Priority claimed ☐ yes ☑ no 35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance Verified and Acknowledged — Examiner's Signature — Initials	STATE OR COUNTRY CA	SHEETS DRAWING 27	TOTAL CLAIMS ~~39~~ 19	INDEPENDENT CLAIMS ~~3~~ 2

ADDRESS
22852
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON , DC
20001-4413

TITLE
Biased pulse DC reactive sputtering of oxide films

FILING FEE RECEIVED	FEES: Authority has been given in Paper No. ________ to charge/credit DEPOSIT ACCOUNT No. ________ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time)

690		☐ 1.18 Fees (Issue) ☐ Other ____________ ☐ Credit

ISSUE SLIP STAPLE AREA (for additional cross-references)

ISSUING CLASSIFICATION

ORIGINAL		CROSS REFERENCE(S)	
CLASS	SUBCLASS	CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)
INTERNATIONAL CLASSIFICATION			
/			
/			
/			
/			
/			

BEST AVAILABLE COPY

^ Continued on Issue Slip Inside File Jacket

INDEX OF CLAIMS

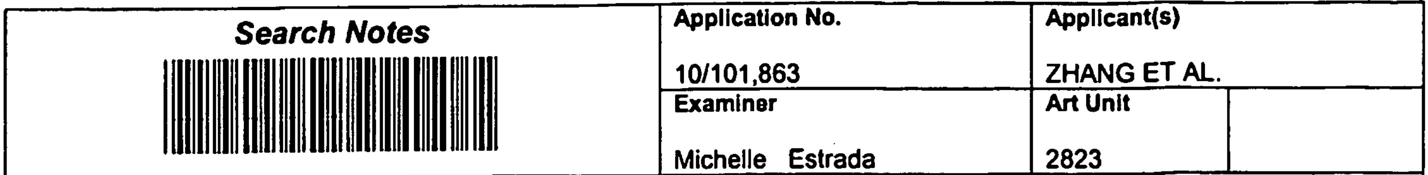
✓ .... Rejected
= .... Allowed
– (Through numeral) ... Canceled
÷ .... Restricted
N .... Non-elected
I .... Interference
A .... Appeal
O .... Objected

Claim Final	Claim Original	Date [illegible]	Date [illegible]	Date [illegible]
[illegible]	1	✓	✓	✓
	2			
	3			
	4			
	5			
	6	✓	✓	
	7	O	O	
	8	✓	✓	
	9			
	10			
	11			
	12			
	13	✓	✓	✓
	14	N	O	O
	15			
	16			
	17			
	18			
	19	N		
	20	✓	✓	✓
	21	O	O	O
	22	O	O	O
	23	O	O	O
	24	O	O	O
	25	N		
	26			
	27			
	28			
	29			
	30			
	31			
	32			
	33			
	34			
	35			
	36			
	37			
	38			
	39	N		
	40			
	41			
	42			
	43			
	44			
	45			
	46			
	47			
	48			
	49			
	50			

Claim Final	Claim Original	Date
	51	
	52	
	53	
	54	
	55	
	56	
	57	
	58	
	59	
	60	
	61	
	62	
	63	
	64	
	65	
	66	
	67	
	68	
	69	
	70	
	71	
	72	
	73	
	74	
	75	
	76	
	77	
	78	
	79	
	80	
	81	
	82	
	83	
	84	
	85	
	86	
	87	
	88	
	89	
	90	
	91	
	92	
	93	
	94	
	95	
	96	
	97	
	98	
	99	
	100	

Claim Final	Claim Original	Date
	101	
	102	
	103	
	104	
	105	
	106	
	107	
	108	
	109	
	110	
	111	
	112	
	113	
	114	
	115	
	116	
	117	
	118	
	119	
	120	
	121	
	122	
	123	
	124	
	125	
	126	
	127	
	128	
	129	
	130	
	131	
	132	
	133	
	134	
	135	
	136	
	137	
	138	
	139	
	140	
	141	
	142	
	143	
	144	
	145	
	146	
	147	
	148	
	149	
	150	

If more than 150 claims or 9 actions staple additional sheet here



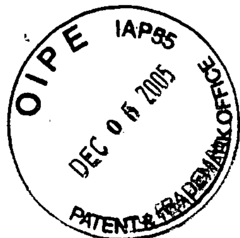
Search Notes	Application No.	Applicant(s)
	10/101,863	ZHANG ET AL.
	Examiner	**Art Unit**
	Michelle Estrada	2823

SEARCHED			
Class	Subclass	Date	Examiner
438	769	2/12/04	ME
438	770		
438	771		
438	787		
438	788		
427	533		
204	192.12		
204	192.15	2/12/2004	ME

INTERFERENCE SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES (INCLUDING SEARCH STRATEGY)	DATE	EXMR
See East search attached	2/12/2004	ME
See East search attached	7/29/05	ME

2823 IFW



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed August 4, 2005, the period for response having been extended to December 4, 2005 (a Sunday) by a request for extension of one month with authorization for the Commissioner to charge the fee of $120.00 to Deposit Account No. 06-0916, please amend the above-identified application as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 5.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Currently amended) A method of depositing a film on a substrate, comprising:
   providing pulsed DC power through a filter to a target;
   providing RF bias power to a substrate positioned opposite the target; and
   providing process gas between the target and the substrate,
   wherein the filter protects a pulsed DC power supply from the bias power, ~~and~~
   wherein a plasma is created ~~between the target and the substrate~~ by application of the pulsed DC power to the target; and
   wherein the film is deposited by exposure of the substrate to the plasma.

2. (Previously Presented): The method of Claim 1, further including holding the temperature of the substrate substantially constant.

3. (Previously Presented): The method of Claim 1, wherein providing pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously Presented): The method of Claim 1, wherein providing bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Previously Presented): The method of Claim 4, wherein the filter is a band reject filter at the frequency of the bias power.

6. (Previously Presented): The method of claim 4, wherein the bias power is zero.

7. (Previously Presented): The method of Claim 1, wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

8. (Previously Presented): The method of Claim 1, wherein the process gas includes a mixture of Oxygen and Argon.

9. (Previously Presented): The method of Claim 9, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

10. (Previously Presented): The method of Claim 8, wherein the process gas further includes nitrogen.

11. (Previously Presented): The method of Claim 1, wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously Presented): The method of Claim 1, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Currently amended): ~~The method of Claim 1, further including~~ A method of depositing a film on a substrate, comprising:

providing pulsed DC power through a filter to a target;
providing RF bias power to a substrate positioned opposite the target; and
providing process gas between the target and the substrate, and
depositing a film on the backside of the target ~~12~~,
wherein the filter protects a pulsed DC power supply from the bias power, and
wherein a plasma is created between the target and the substrate.

15.-19. (Canceled).

20. (Currently amended): A method of depositing a film on a substrate, comprising:

conditioning a target;
preparing the substrate;
adjusting a RF bias power to the substrate;
setting a process gas flow; and
applying pulsed DC power to the target through a filter to create a plasma ~~and deposit the~~

~~film,~~

wherein the substrate is exposed to the plasma to deposit the film.

21. (Currently amended): ~~The method of Claim 20,~~ A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting a RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target through a filter to create a plasma and deposit the film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. (Previously Presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

REMARKS

Claims 1-14 and 20-24 are pending in the above identified application. The Examiner has rejected claims 1-13 and 20, and objected to claims 14 and 21-24. With this paper, Applicants have amended claims 1, 14, 20, and 21. Applicants herein traverse the Examiner's rejections.[1]

Claim Rejections Under 35 U.S.C. § 102

The Examiner rejected claims 1, 8, 10-13 and 20 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 6,117,279 ("Smolanoff"). However, Smolanoff does not recite that "a plasma is created by application of the pulsed DC power to the target; and wherein the film is deposited by exposure of the substrate to the plasma," as is recited in claim 1, or "applying pulsed DC power to the target through a filter to create a plasma wherein the substrate is exposed to the plasma to deposit the film," as is recited in claim 20.

As is taught in Smolanoff,

> A further objective of the present invention is to provide a method and apparatus for ionized physical vapor deposition that utilizes a magnetron magnetic field source to provide a main plasma for sputtering coating material efficiently from a sputtering target and that employs a secondary plasma by which is produced a high ionization fraction of the material sputtered from the target. A more particular objective of the present invention is to provide such a method and apparatus in which the loss of charged particles from the secondary plasma is minimized or reduced.

(Smolanoff, col. 3, lines 1-10). Further, Smolanoff teaches that:

> According to certain principles of the present invention, an ionized physical vapor deposition (IPVD) method and apparatus are provided utilizing a target energized with a DC or pulsed DC source to energize a main plasma adjacent to a sputtering target and an RF reactively coupled source to energize a secondary

[1] The Examiner has made a number of statements that characterize the prior art or characterize the claims. Applicants do not necessarily agree or acquiesce in any of these characterizations, even if those characterizations are not specifically addressed in this paper.

> plasma in the space between the target and a substrate oriented preferably parallel to the target at the opposite end of a sputtering chamber. The space in which the secondary plasma is generated is bounded by electrically conductive structure that is electrically floating and presents a high impedance to the RF source. This structure is further connected through a low pass filter which provides a low impedance DC path to ground or to some other potential.

(Smolanoff, col. 3, lines 51-64). Therefore, Smolanoff teaches that a secondary plasma created by RF coils is created between the target and the substrate, in addition to the plasma created at the target. Deposition is performed by exposing the substrate to the secondary plasma, not the main plasma adjacent to the sputtering target. Therefore, Smolanoff fails to teach that "a plasma is created by application of the pulsed DC power to the target; and wherein the film is deposited by exposure of the substrate to the plasma," as is recited in claim 1, or "applying pulsed DC power to the target through a filter to create a plasma wherein the substrate is exposed to the plasma to deposit the film," as is recited in claim 20.

Furthermore, although Smolanoff states that the target "can be energized with a DC or pulsed DC source to energize a main plasma," (Smolanoff, col. 3, lines 53-45), Applicants contend that Smolanoff has not enabled utilization of a pulsed DC power source in an environment with RF energy. Smolanoff's may teach an RF filter between the DC source and the target, but provides no description of that filter. It is Applicants' experience that the exposure of a pulsed DC power supply to an RF environment often leads to destruction of the pulsed DC power supply. Smolanoff has enabled utilization of a DC power supply, but not a pulsed DC power supply.

As discussed above, claims 1 and 20 are allowable over Smolanoff. Claims 8 and 10-13, which depend from claim 1, are therefore allowable over Smolanoff for at least the same reasons as is claim 1.

Claim Rejections under 35 U.S.C. § 103

Claims 2-6

The Examiner has rejected claims 2-6 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of U.S. Patent No. 5,755,938 ("Fukui"). As discussed above, claim 1 is allowable over Smolanoff. Fukui does not cure the defects in the teachings of Smolanoff. Therefore, claims 2-6, which depend from claim 1, are allowable for at least the same reasons as is claim 1.

Claims 7 and 9

The Examiner has further rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Le et al. (2003/0077914) ("Le"). As discussed above, claim 1 is allowable over Smolanoff. Le does not cure the defects in the teachings of Smolanoff. Therefore, claims 7 and 9, which depend from claim 1, are allowable for at least the same reasons as is claim 1.

Allowable Subject Matter

The Examiner has indicated that claims 14 and 21-24 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. Claims 14 and 21, from which claims 22-24 depend, have been rewritten as suggested by the Examiner.

Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully request reconsideration and reexamination of this application and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: Linda J. Thayer for 45,681
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 758329165 US

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

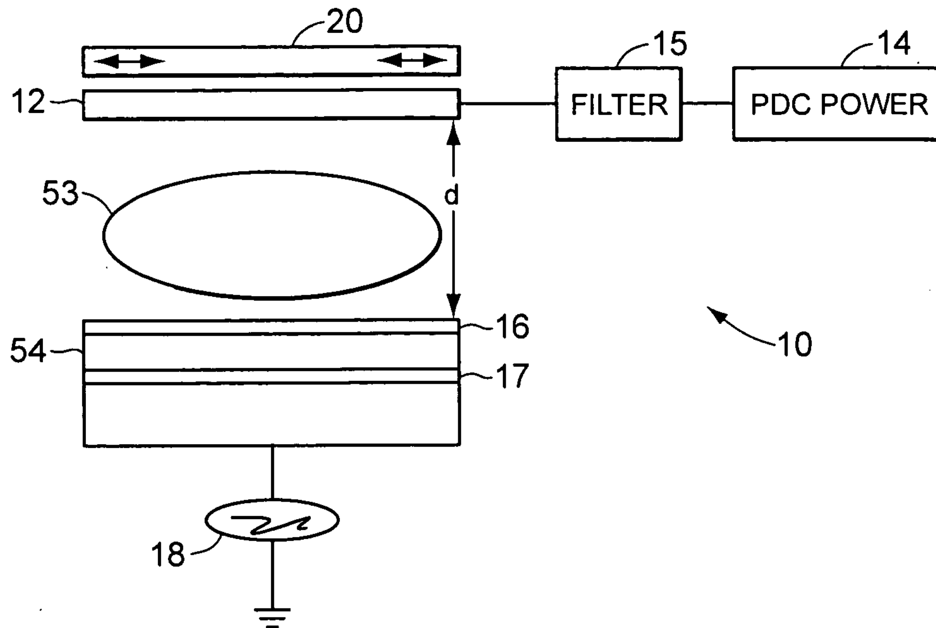


FIG. 1A

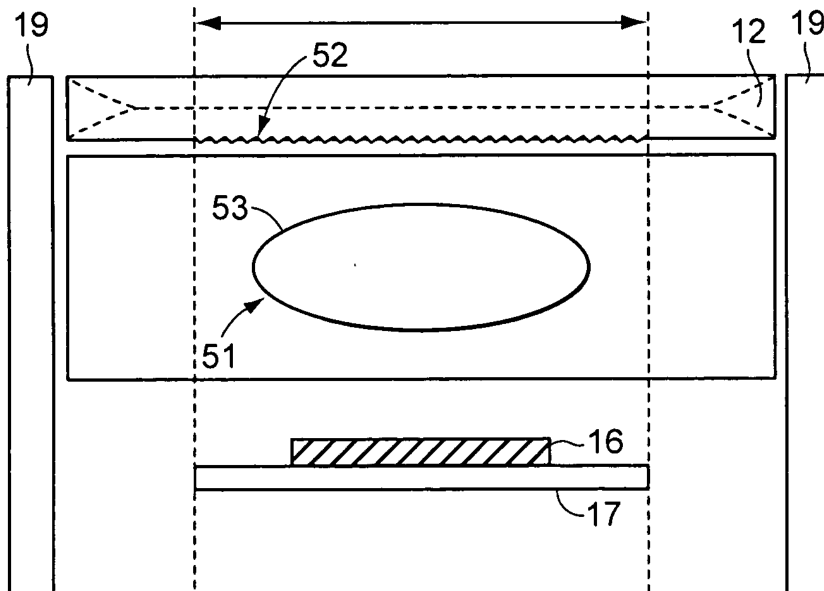
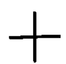
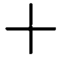


FIG. 1B



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS



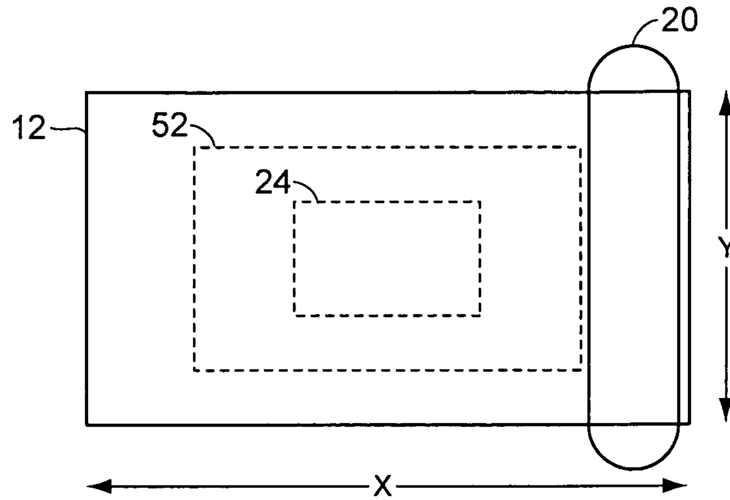


FIG. 2

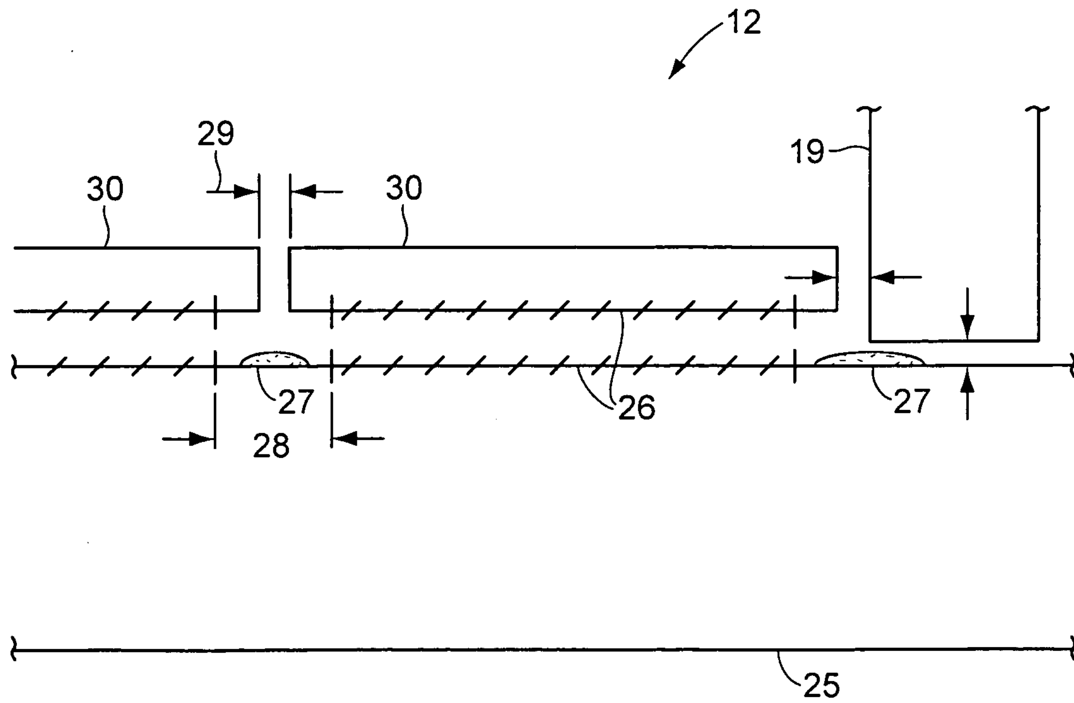


FIG. 3

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

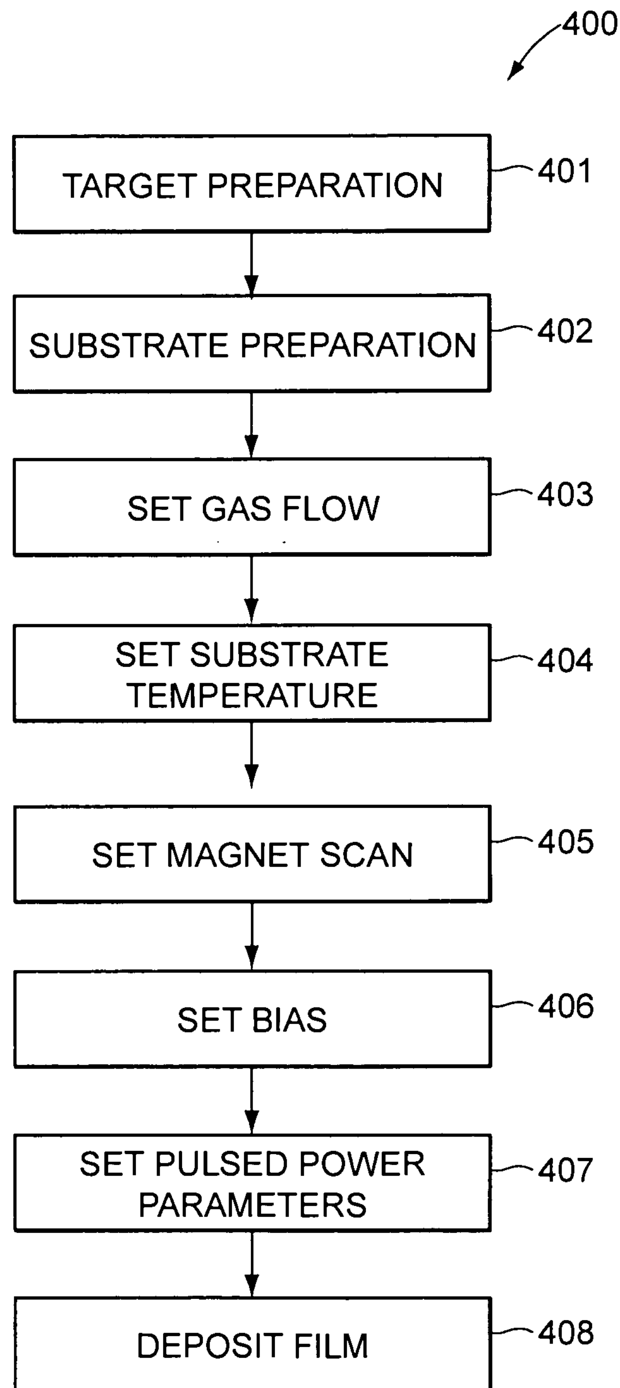
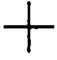


FIG. 4

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS



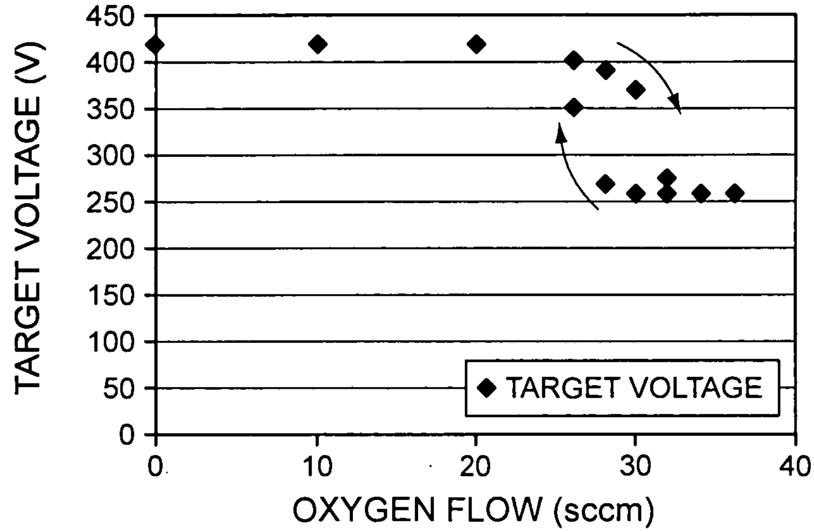


FIG. 5

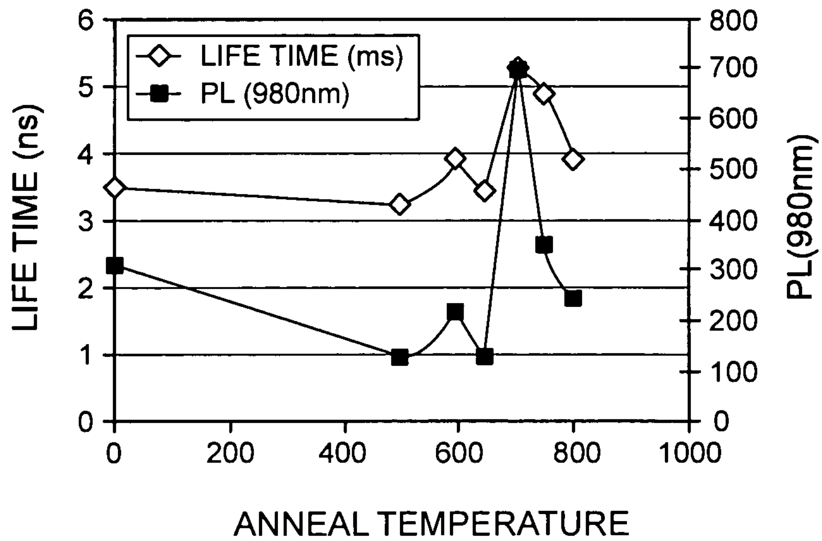
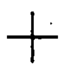


FIG. 6



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

5/27

Alumino Silicates Index Drift in Burn-in Cycle
(As Deposited from Al/Si Cast Metal Targets)

Refractive Index

1.58
1.56
1.54
1.52
1.50
1.48
1.46

0 2000 4000 6000 8000 10000 12000 14000 16000 18000 20000

Oxide Build-up After Initial Target Burn (1/2 hr Oxide) (in nm)

y=3E-06x+1.537
R^2=0.4414
35-65

y=2E-06x+1.5232
R^2=0.4009
50-50

60-40

y=1E-06x+1.4904
R^2 =0.0274

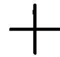
y=3E-07x+1.4735
R^2=0.9867
85-15

y=2E-07x+1.4653
R =0.9223
92-8

Si-Al CONC.
◆ 60-40 Drift
■ 50-50 Drift
□ 85-15 Drift
× 35-65 Drift
✱ 92-8 Drift
— Linear (50-50 Drift)
— Linear (60-40 Drift)
— Linear (85-15 Drift)
— Linear (35/65 Drift)
— Linear (92-8 Drift)

FIG. 7

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS



Refractive Index as a Function of Al% in Aluminosilicates

$y=1E-10x^5-3E-08x^4+3E-06x^3-8E-05x^2+0.002x+1.4583$
$R^2=0.9499$

70-30 Hipped Target
(Fe contamination)

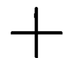
Refractive Index

1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4

0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000

◆ R.I (As Dep)
□ R.I Post Anneal
— Poly. (R.I(As Dep))

FIG. 8



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Material (Er/Yb/Al/Si)	Expected index (Post anneal)	Actual index (Post anneal)	Process Conditions (Annealed 725c 30min)
0.8/0.8/41.4/57	1.506	1.510	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.6/0.5/49/48.9	1.526	1.528	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/8/92	1.452	1.456-1.459	4.5KW, Ar-30-60,02-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/40/60	1.504	1.486-1.501	3.0-4.5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/50/50	1.520	1.491-1.503	4.0-5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/65/35	1.544	1.545-1.560	4.5-5.5KW, Ar-75-90,0285-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/30/70	1.490	1.562 (high Fe content)	5.0KW, Ar-75,02-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.5/0/48.5/50	1.523	1.509-1.513	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias

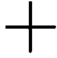
FIG. 9

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Bias Power (Watts)	DC Power (KW)	Pulsing Freq (KHz)	Reverse Time (μs)	Ar Flow (sccms)	O2 Flow (sccms)	Wafer Position	Target To Wafer Spacing (mm)	Refractive Index Avg (@1550nm)	Refractive Index STD (@1550nm)	Dep Rate (um/Hr)
150	4.5	200	2.2	100	100	1	55	1.461508	0.000535	0.957654
150	4.5	200	2.2	100	100	2	55	1.462329	0.000376	0.962581
400	4.5	200	2.2	100	100	1	55	1.462774	0.000103	0.814007
400	4.5	200	2.2	100	100	2	55	1.463583	0.000095	0.824566

FIG. 10

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS



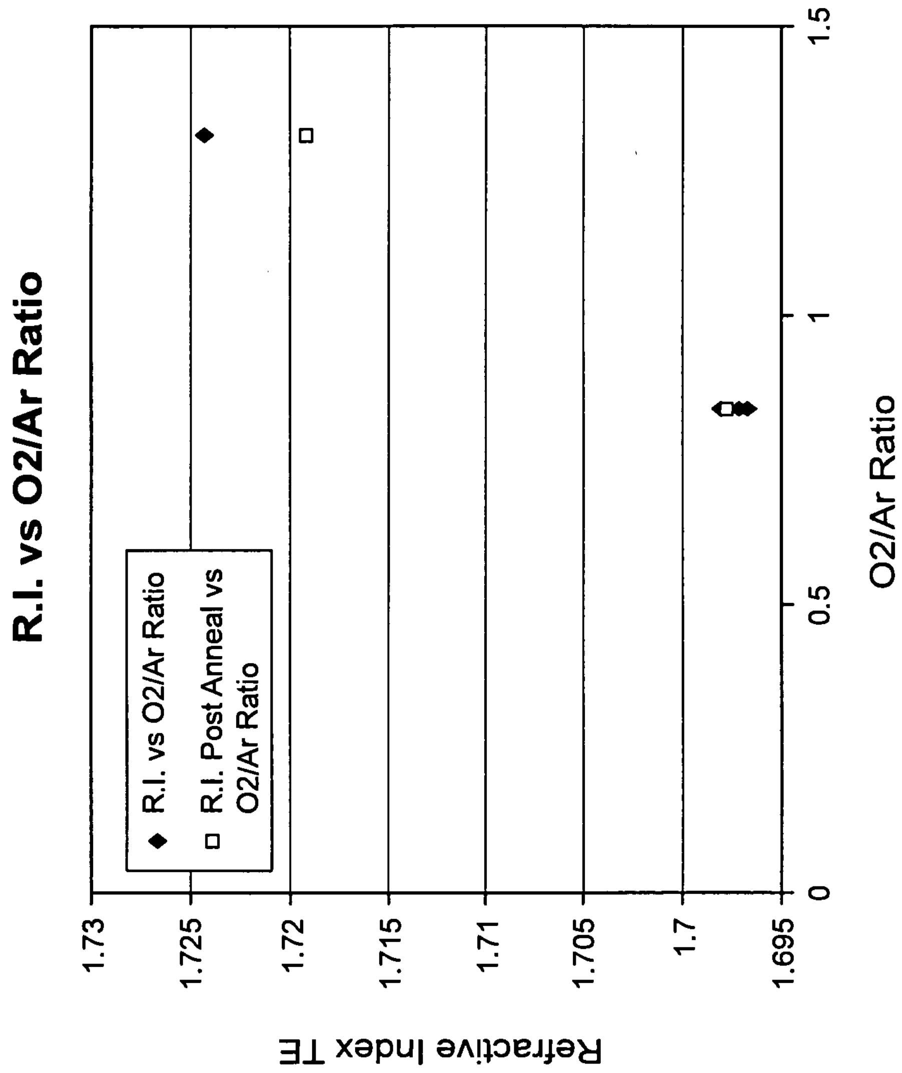
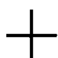


FIG. 11



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

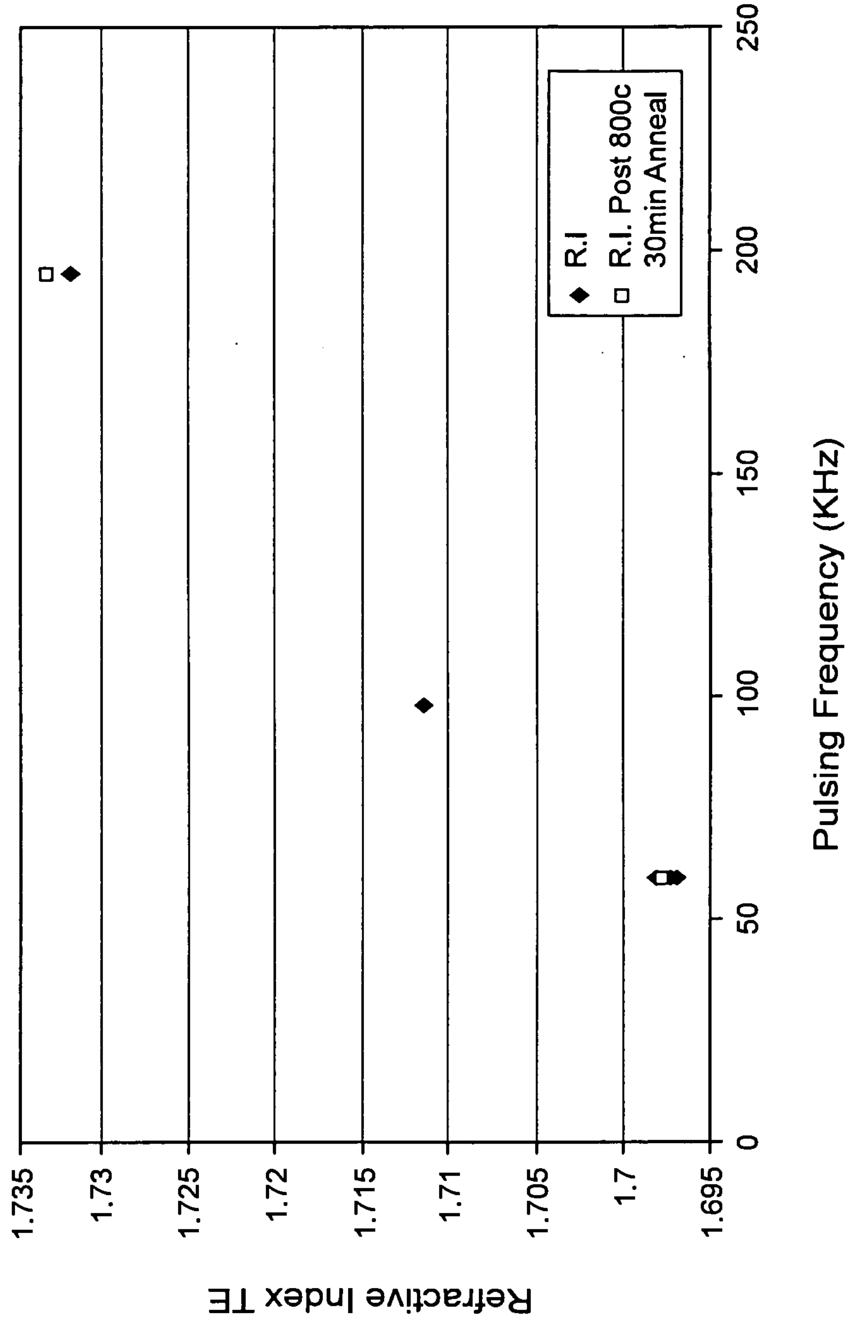


FIG. 12

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

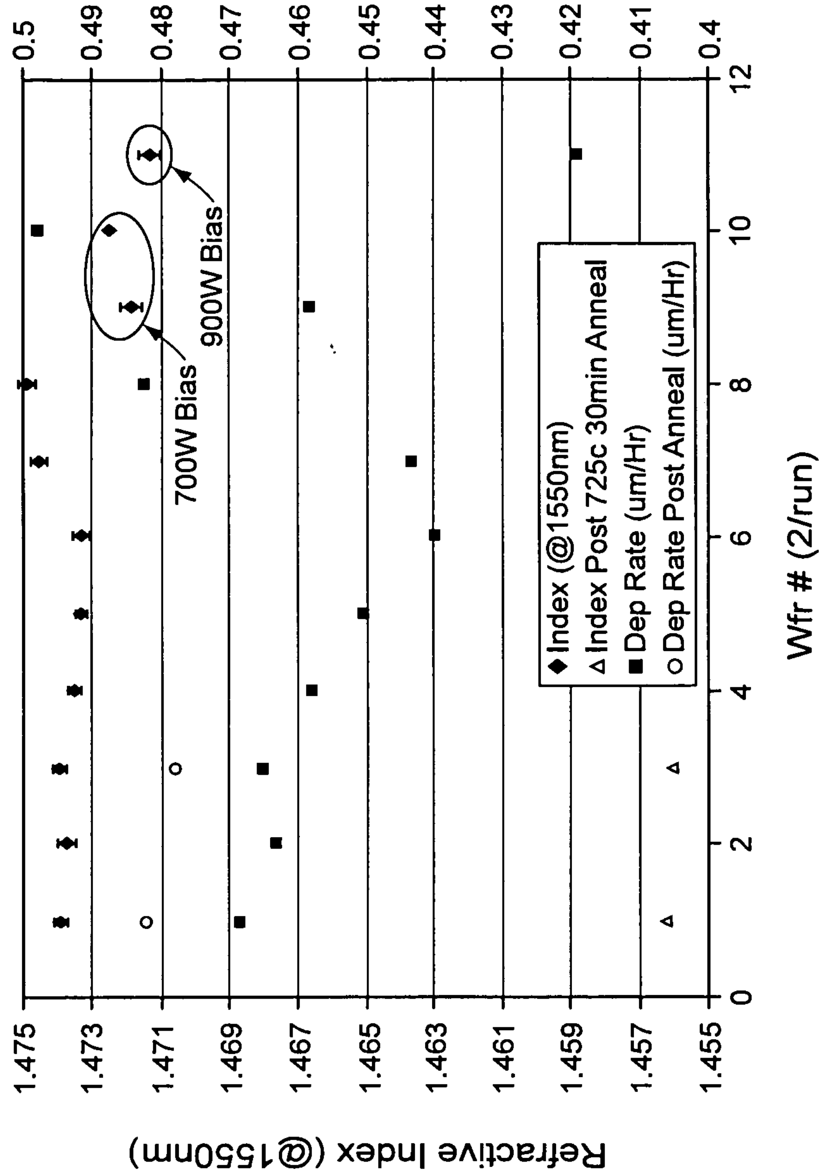


FIG. 13

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

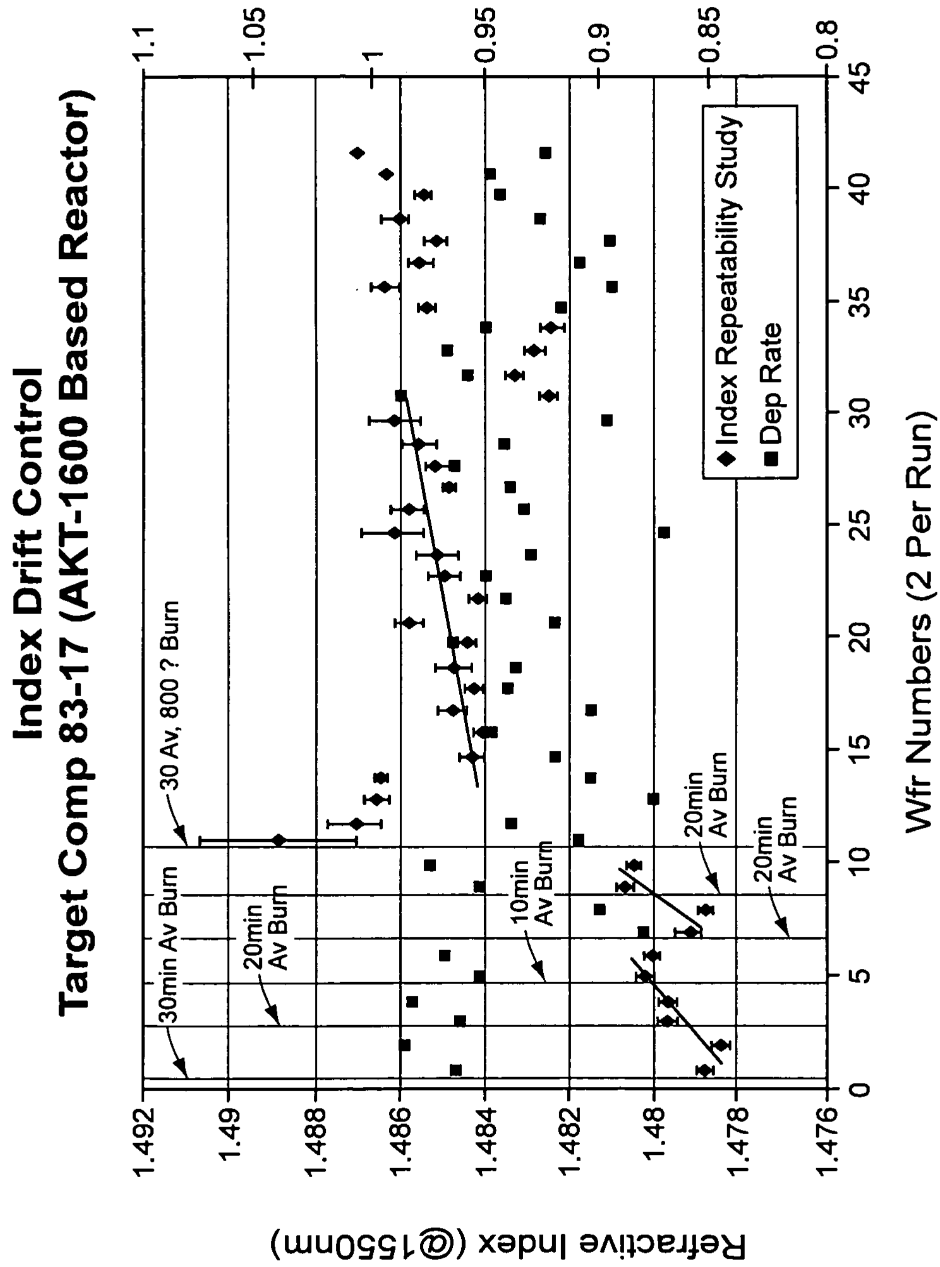


FIG. 14

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

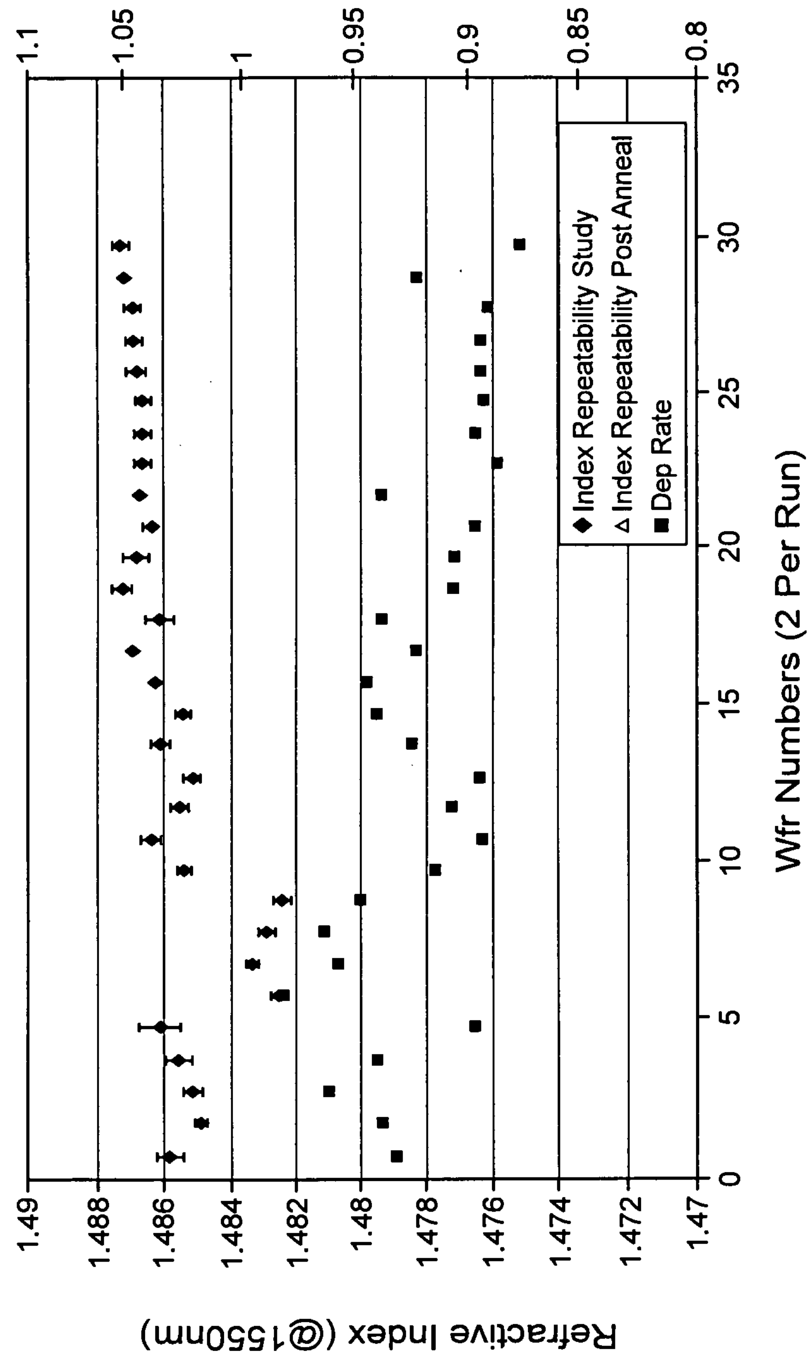
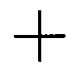


FIG. 15



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

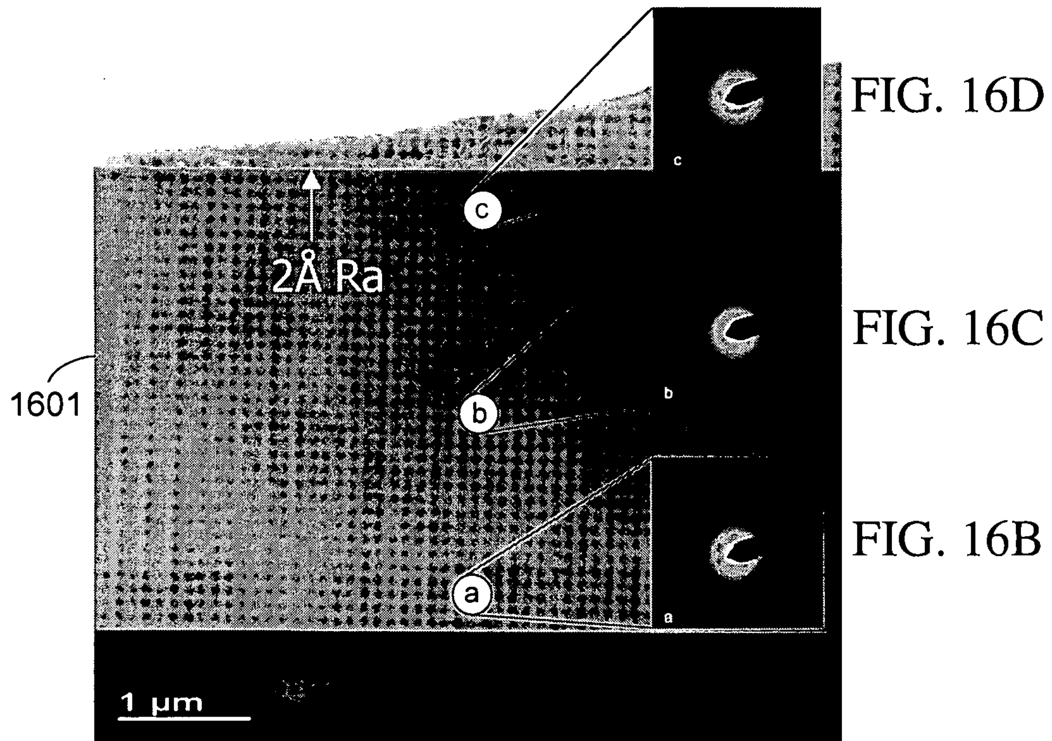
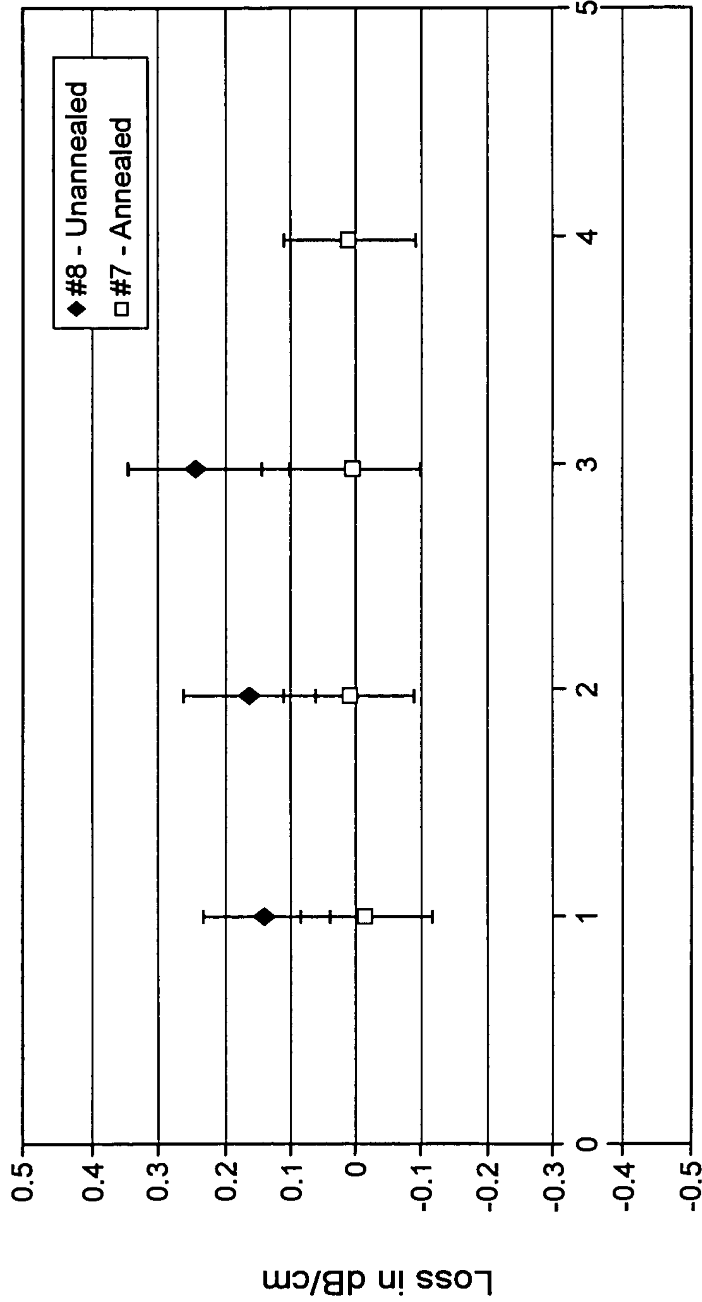


FIG. 16A

SYMMORPHIX PVD ALUMINOSILICATE

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS



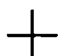
Path (cm)

FIG. 17

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

1803
11.4um
1.98um
10.0um
1802
8.33um
5.36um
5.18um
8.40um
6.08um
5.17um
5.29um
8.20um
1801
4300-92-8-650W
Mux Fill
S4700 5.0kV 10.4mm x3.00k SE(U) 3/7/02 11:05
11.4µm
8.20µm
1804

FIG. 18



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

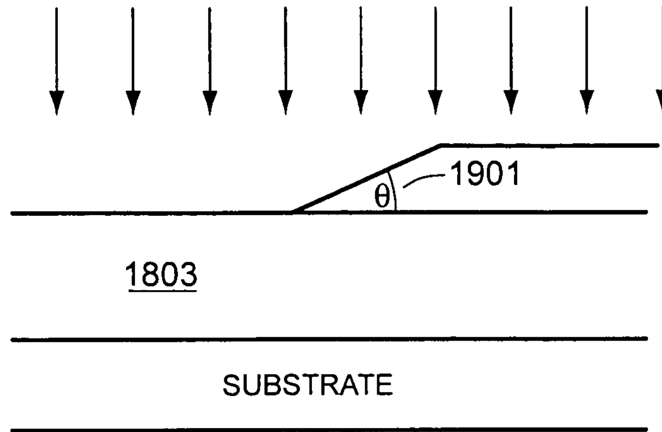


FIG. 19

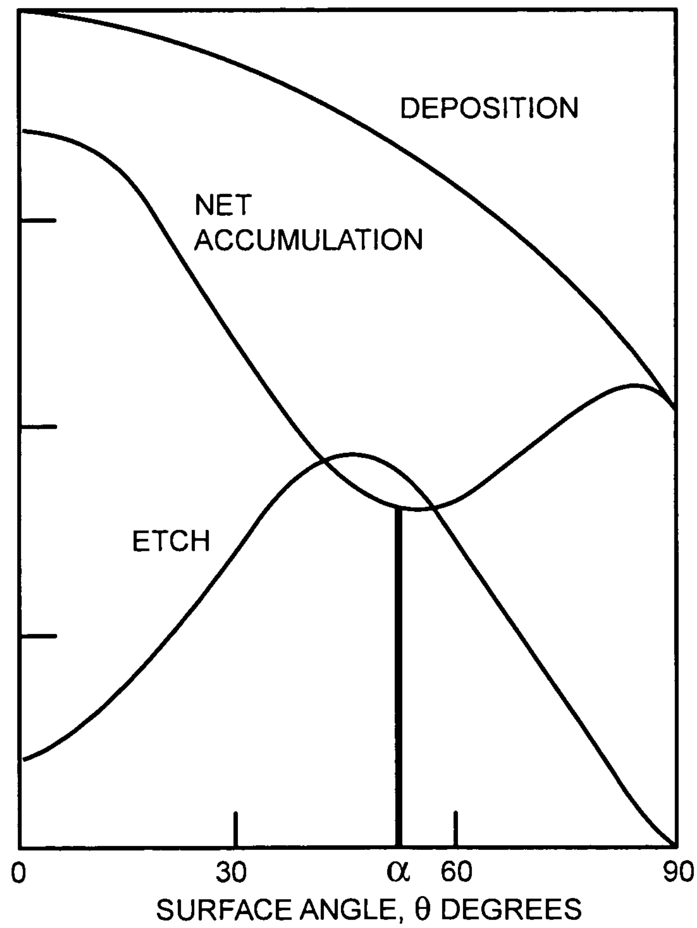


FIG. 20

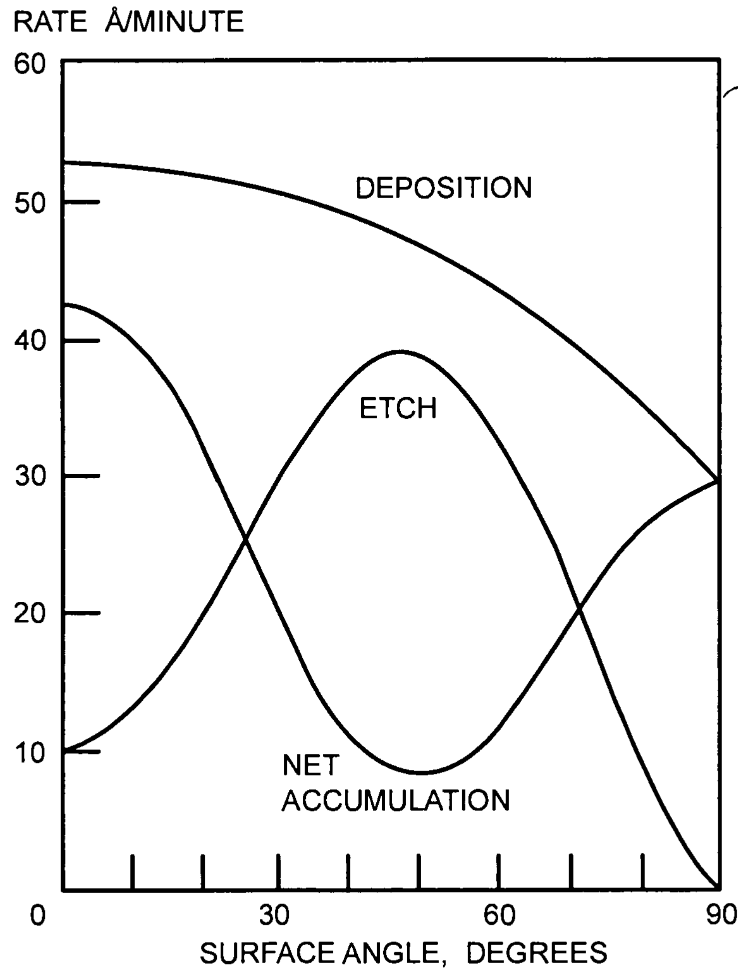


FIG. 21

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

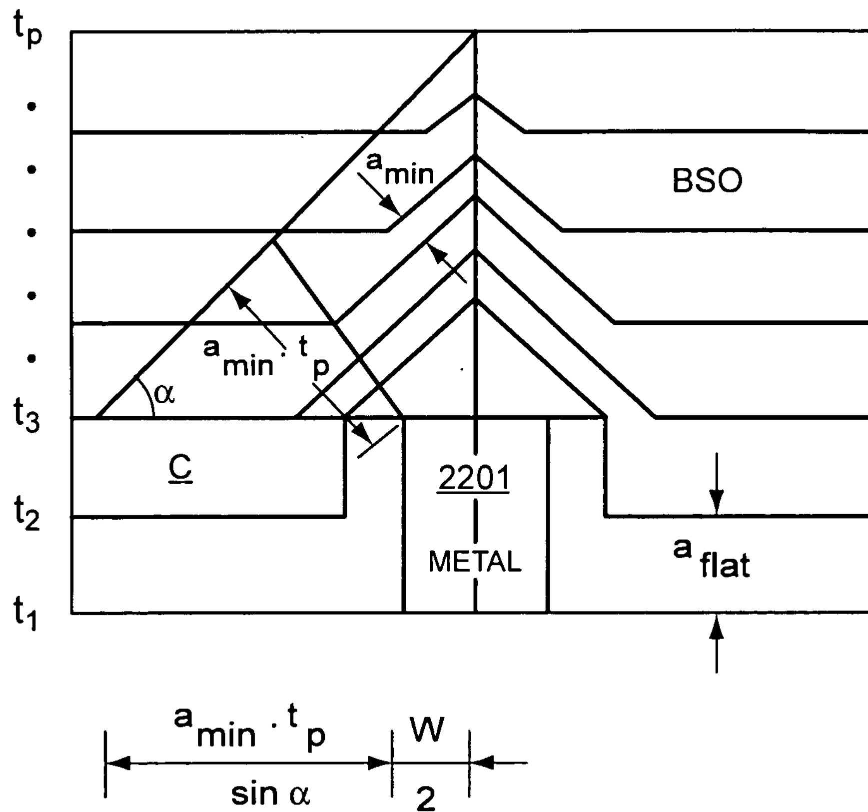


FIG. 22

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

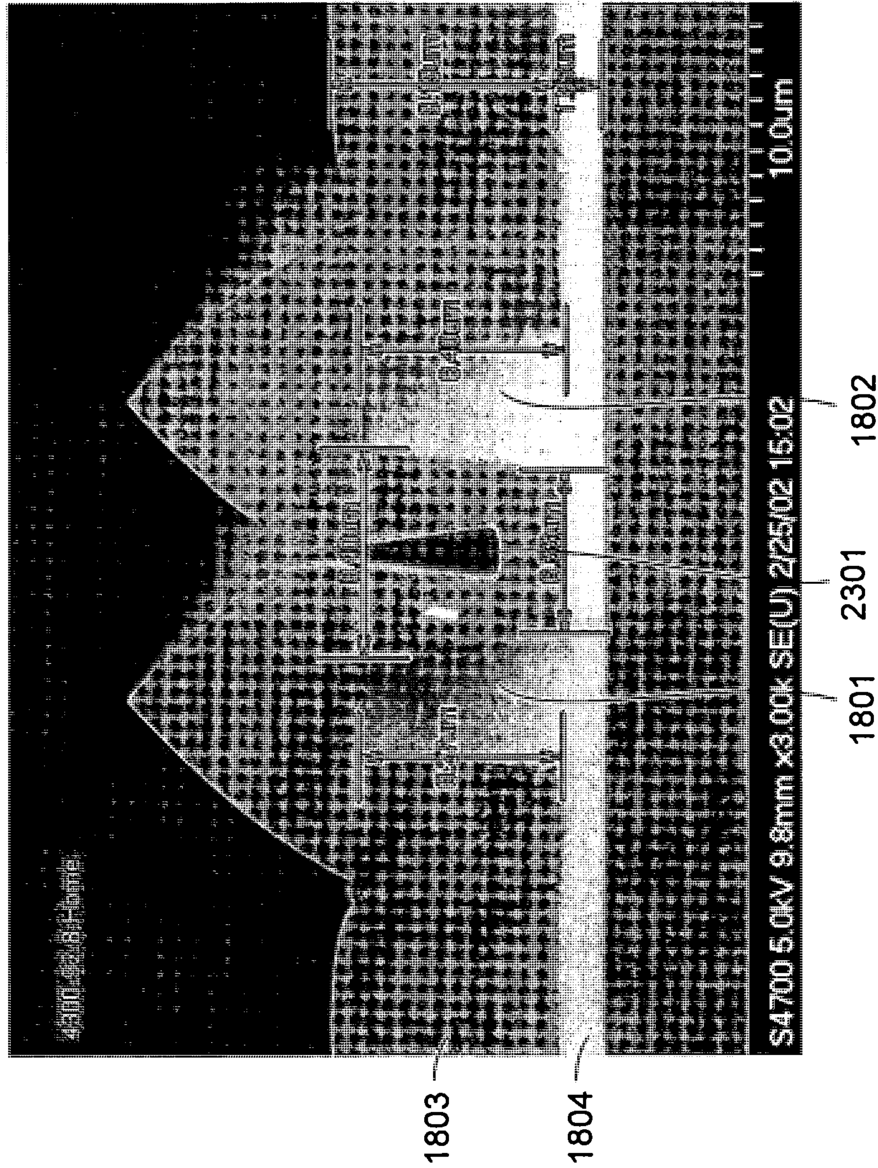


FIG. 23

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

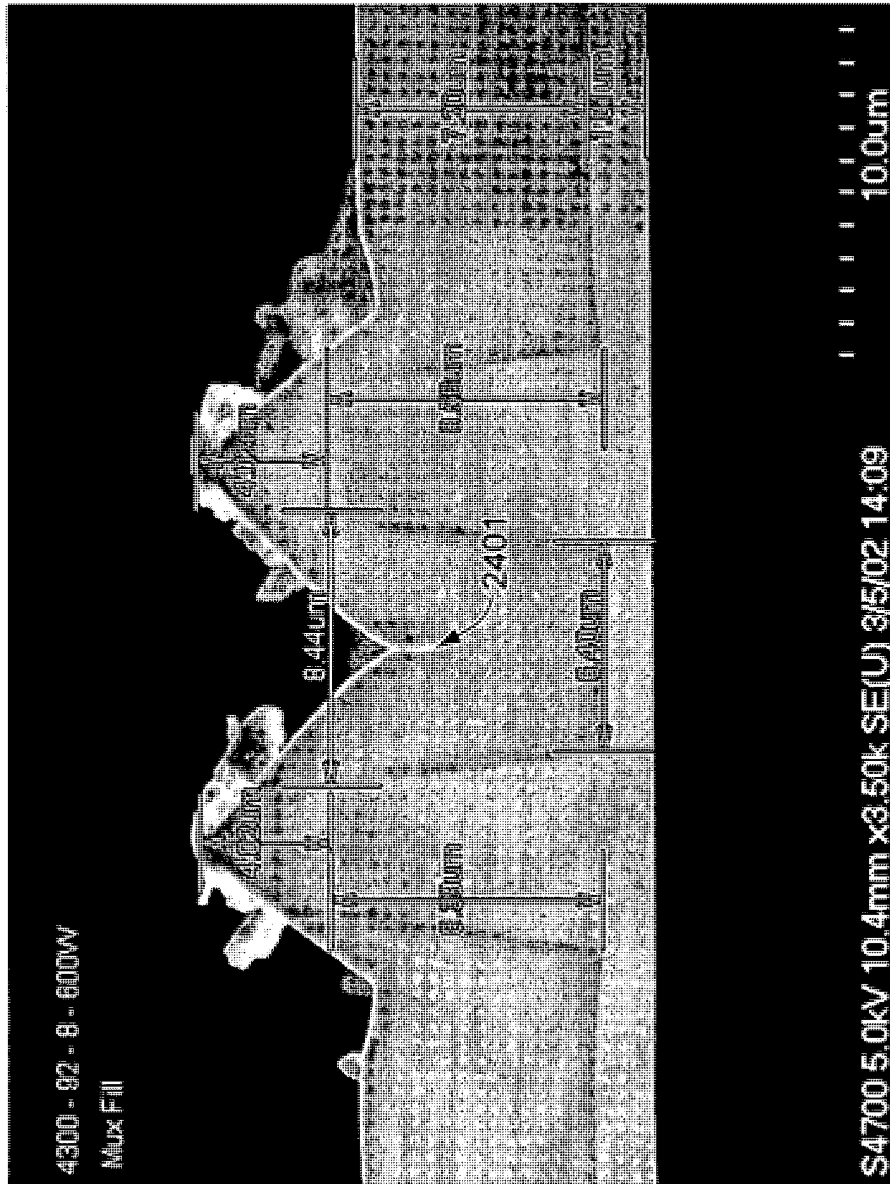


FIG. 24

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

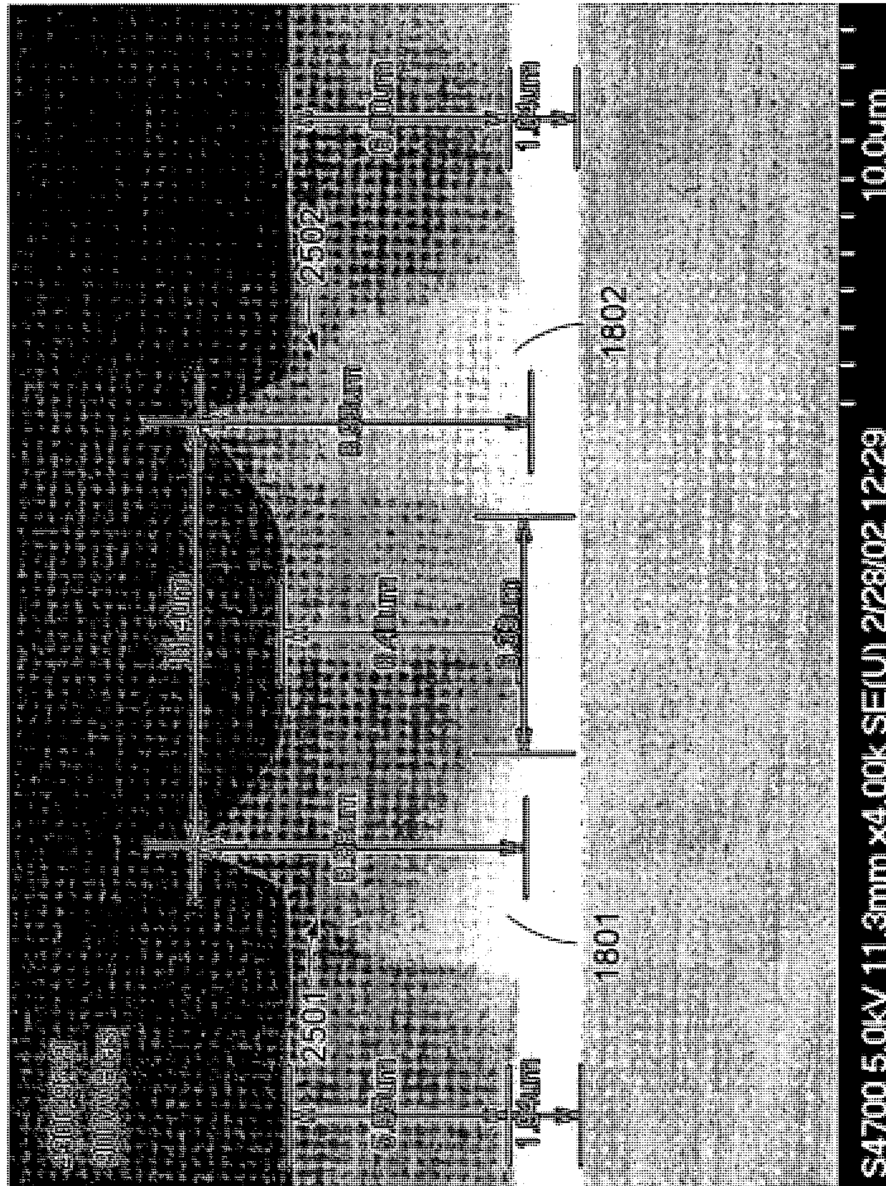


FIG. 25

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

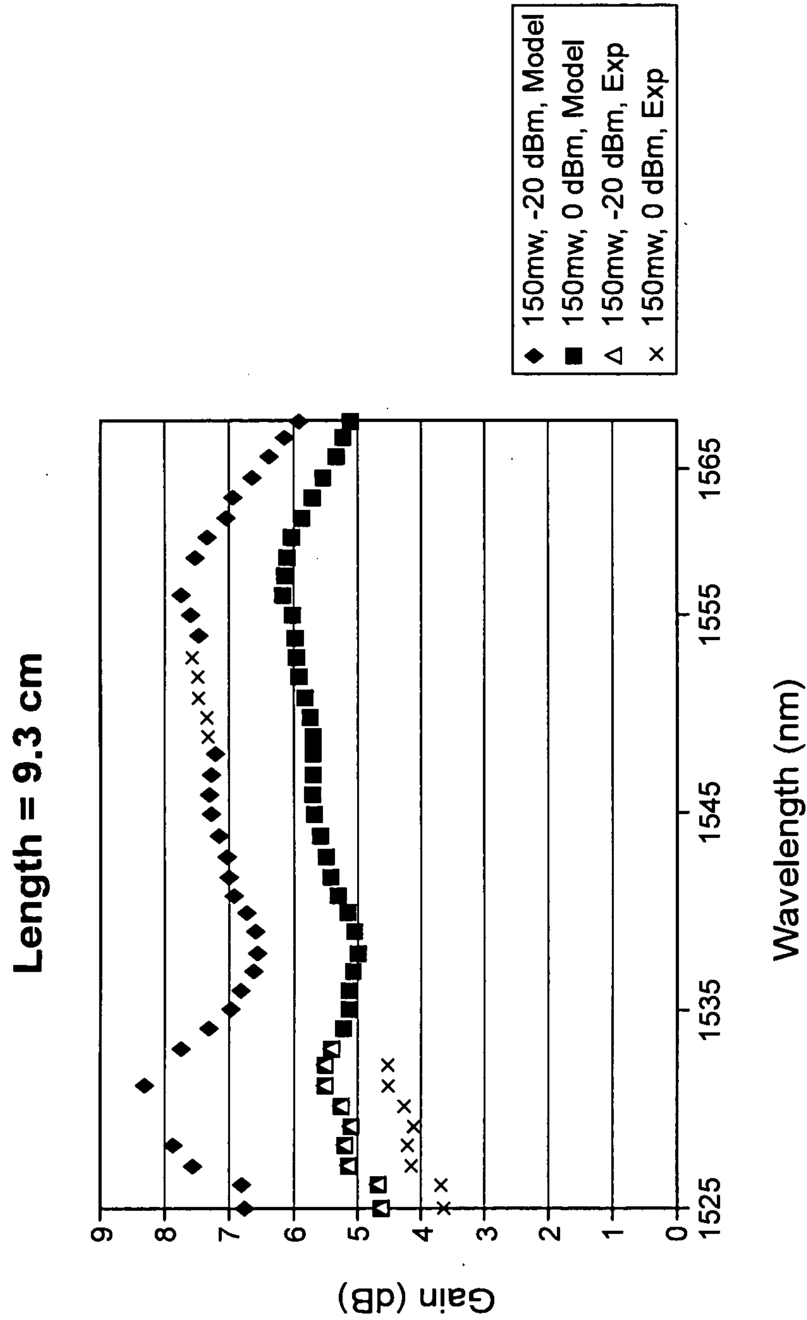
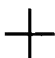


FIG. 26

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS



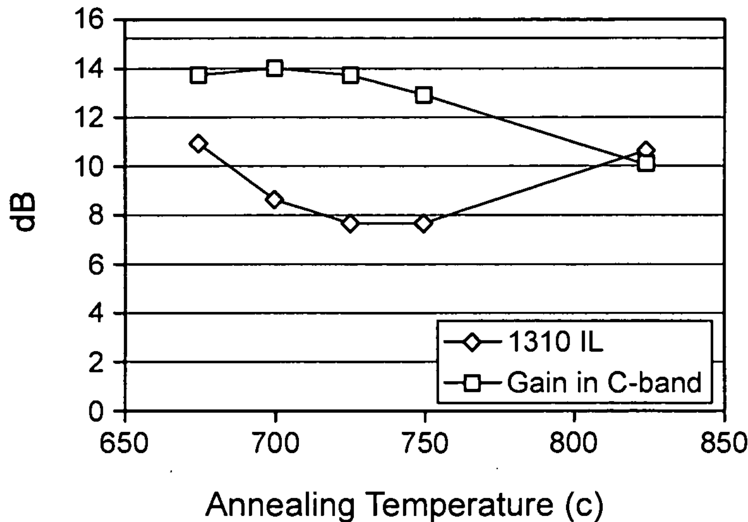


FIG. 27

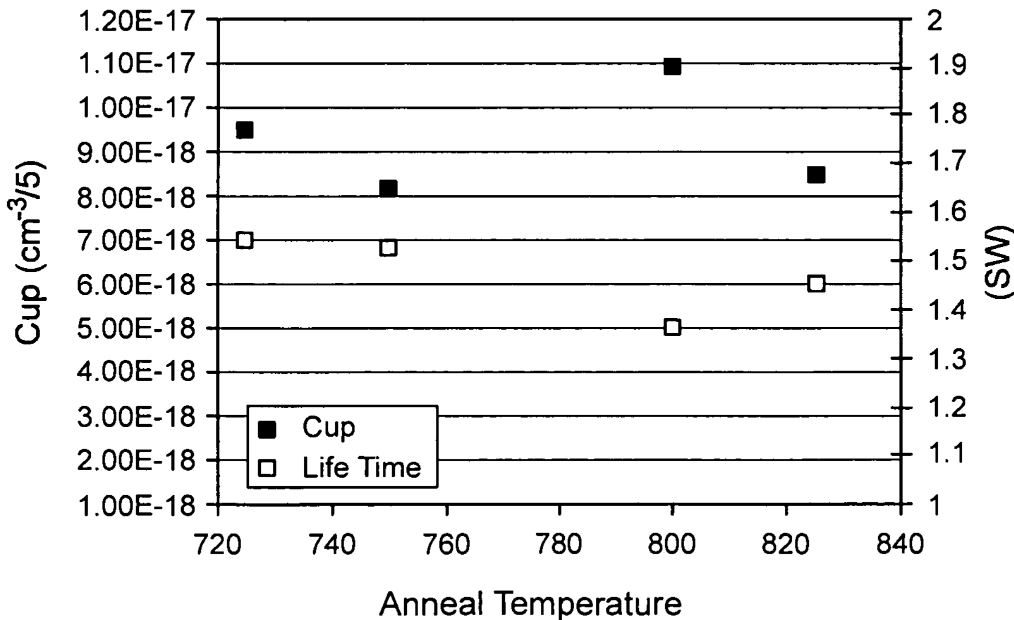
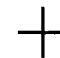


FIG. 28



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

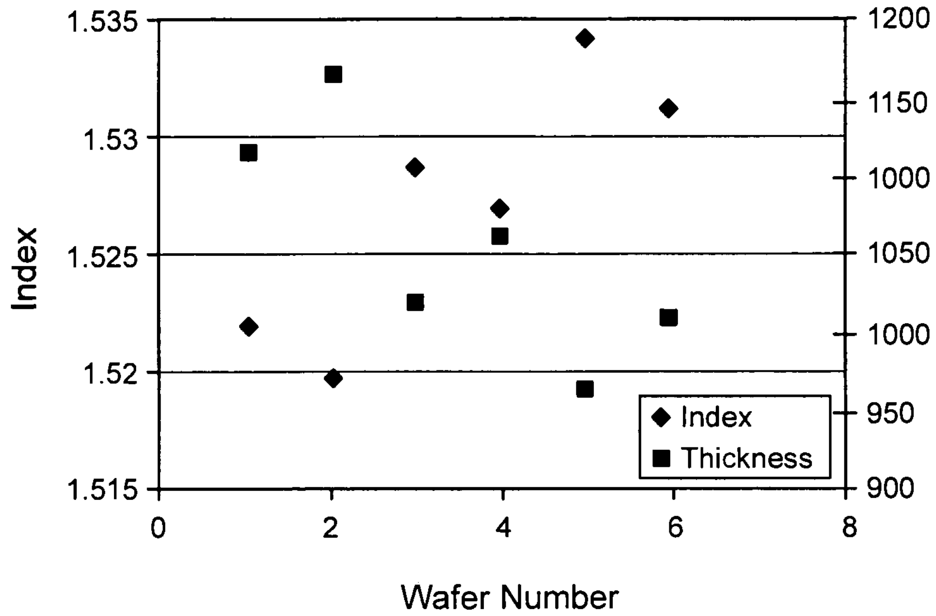


FIG. 29

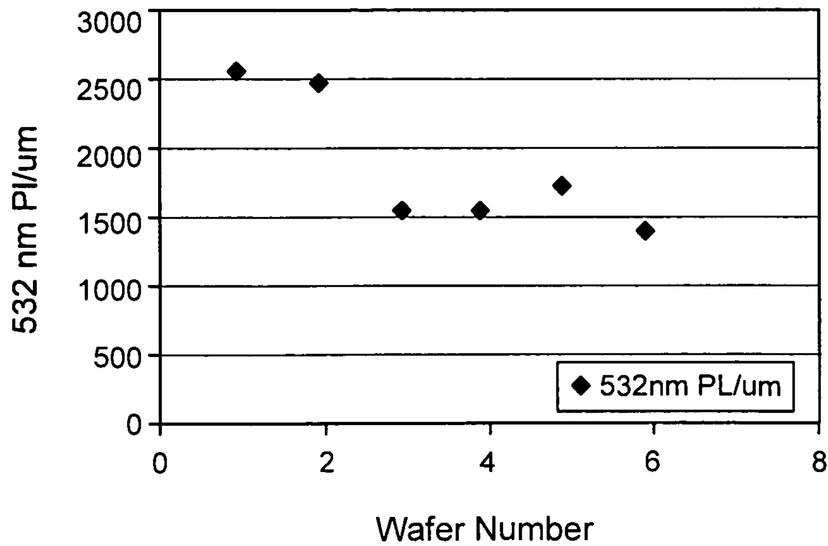


FIG. 30

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

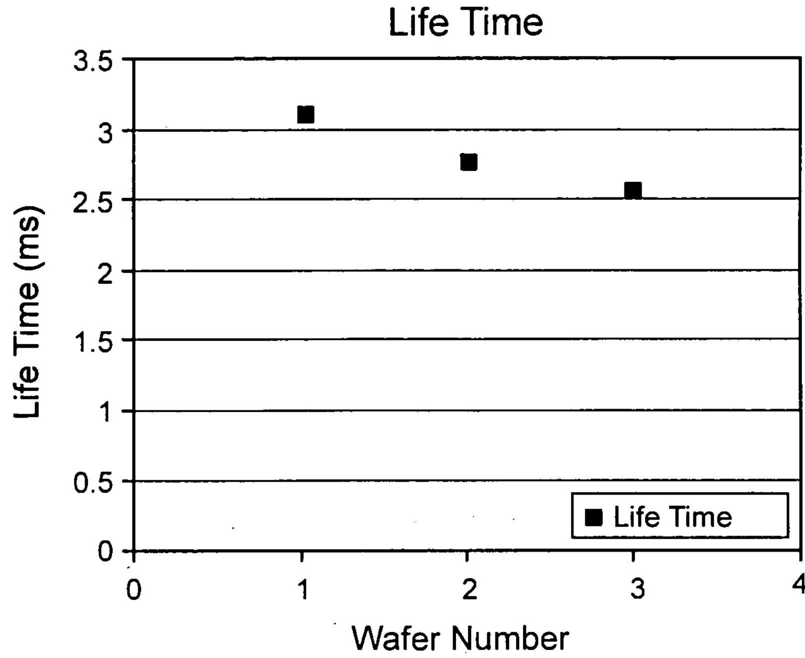


FIG. 31

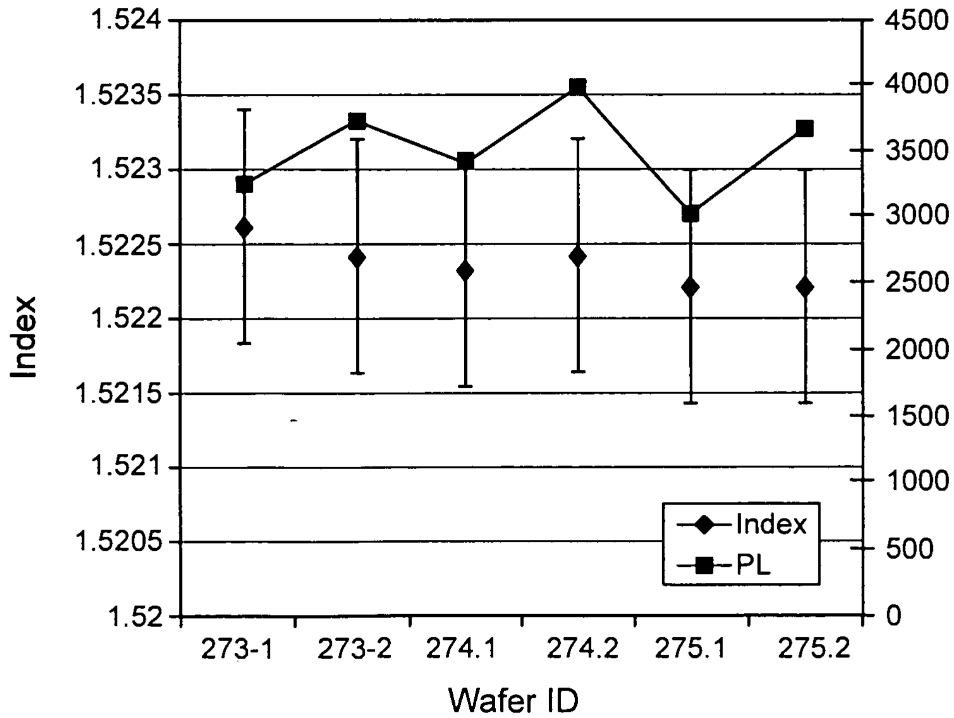
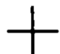


FIG. 32



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

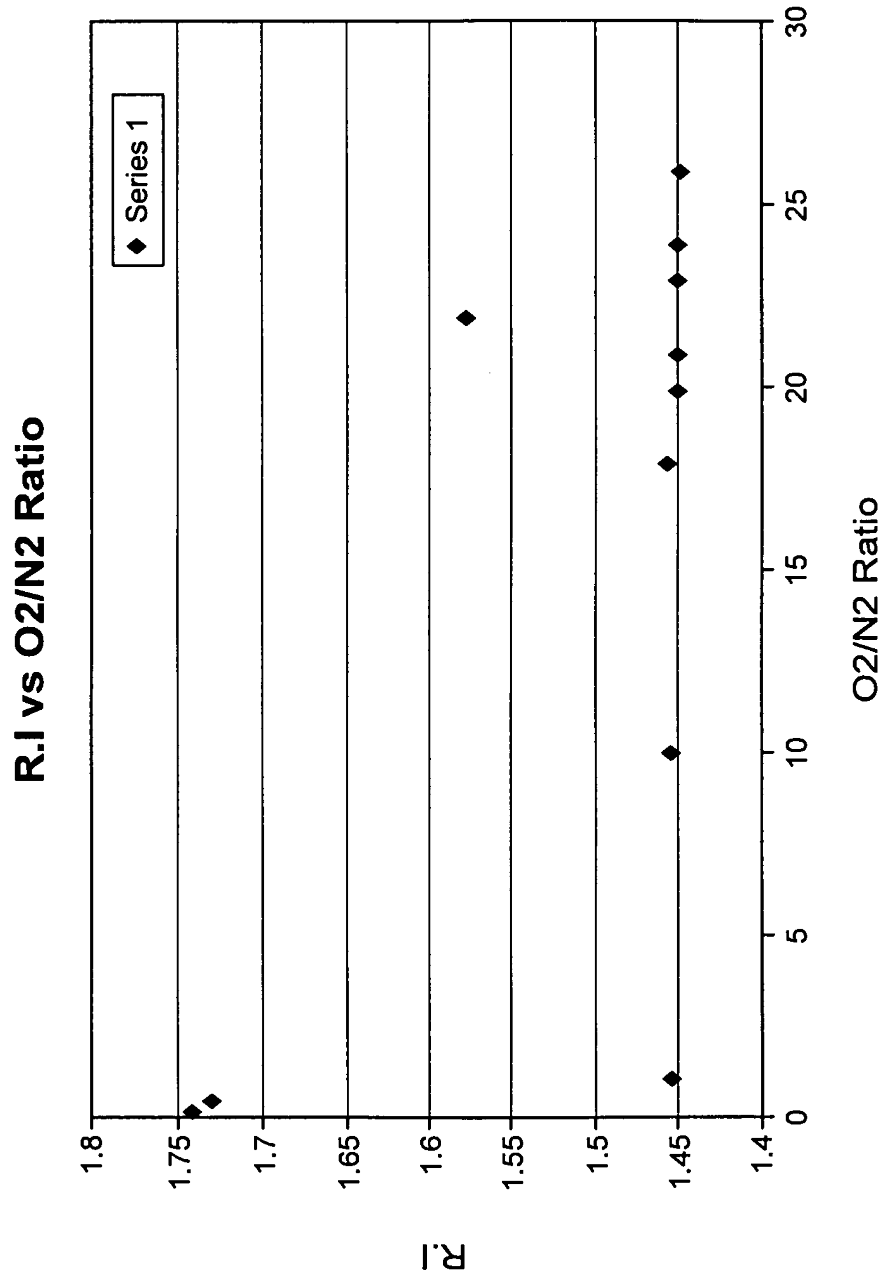


FIG. 33

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
	)
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938
	)

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

Applicants petition for a one month extension of time to reply to the Office action of August 4, 2005. The Commissioner is hereby authorized to charge the fee of $120.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

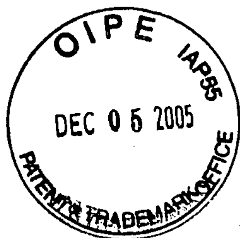
FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: [signature] 45,681
for Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 758329165 US

12/08/2005 EAREGAY1 00000041 060916 10101863
01 FC:1251 120.00 DA



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

FOURTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

12/08/2005 EAREGAY1 00000041 060916 10101863

02 FC:1806 180.00 DA

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

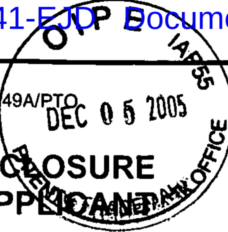
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: Linda J. Mayo 45,681
for Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 758329165 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	Hongmei ZHANG
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	1	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		5,478,456	12-26-1995	Humpal et al.	
		6,846,765 B2	1-25-2005	Imamura et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		DOREY, R.A., "Low temperature micromoulding of functional ceramic devices," Grant summary for GR/S84156/01 for the UK Engineering and Physical Sciences Research Council, 2 pages (2004).	
		HOWSON, R.P., "The reactive sputtering of oxides and nitrides," *Pure & Appl. Chem. 66*(6):1311-1318 (1994).	
		Office Action issued September 21, 2005 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01).	
		Office Action issued on August 8, 2005 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on October 3, 2005 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00).	
		Office Action issued on October 19, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

**EXPRESS MAIL LABEL NO.
EV 758329165 US**

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

PATENT APPLICATION FEE DETERMINATION RECORD

Effective December 8, 2004

10/101863

CLAIMS AS FILED - PART I

	(Column 1)	(Column 2)
TOTAL CLAIMS		
FOR	NUMBER FILED	NUMBER EXTRA
TOTAL CHARGEABLE CLAIMS	minus 20=	*
INDEPENDENT CLAIMS	minus 3 =	*
MULTIPLE DEPENDENT CLAIM PRESENT	☐	

SMALL ENTITY TYPE ☐ RATE	FEE	OR	OTHER THAN SMALL ENTITY RATE	FEE
BASIC FEE	150.00	OR	BASIC FEE	300.00
X$ 25=		OR	X$50=	
X100=		OR	X200=	
+180=		OR	+360=	
TOTAL		OR	TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2

CLAIMS AS AMENDED - PART II

AMENDMENT A

12/05/05	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	* 19	Minus	** 20	=
Independent	* 4	Minus	*** 3	= 1
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM	☐			

SMALL ENTITY RATE	ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	ADDITIONAL FEE
X$ 25=		OR	X$50=	
X100=		OR	X200=	200.00
+180=		OR	+360=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	200.00

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM	☐			

RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
X$ 25=		OR	X$50=	
X100=		OR	X200=	
+180=		OR	+360=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT C

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM	☐			

RATE	ADDITIONAL FEE	OR	RATE	ADDITIONAL FEE
X$ 25=		OR	X$50=	
X100=		OR	X200=	
+180=		OR	+360=	

UNITED STATES PATENT AND TRADEMARK OFFICE

A

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

22852 7590 02/14/2006

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	

ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 02/14/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No.	Applicant(s)
	10/101,863	ZHANG ET AL.
	Examiner	Art Unit
	Michelle Estrada	2823

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *05 December 2005*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-14 and 20-24* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☒ Claim(s) *14 and 21-24* is/are allowed.

6)☒ Claim(s) *1-13 and 20* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☒ The drawing(s) filed on *05 December 2005* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *12/5/05*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____.

DETAILED ACTION

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1, 8, 10-13 and 20 are rejected under 35 U.S.C. 102(b) as being anticipated by Smolanoff et al. (6,117,279).

With respect to claim 1, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33).

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claim 12, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claim 13, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claim 20, Smolanoff et al. disclose conditioning a target; preparing the substrate; adjusting the bias power to the substrate; setting the process gas flow; and applying pulsed DC power to the target to deposit the film (Col. 5, line 55-Col. 7, line 50).

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 2-6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Fukui et al. (5,755,938).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device

associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With respect to claim 5, Smolanoff et al. do not specifically disclose wherein the filter is a band reject filter at the frequency of the bias power.

Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter (27) at the frequency of the bias power.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fukui et al. to enable the filter type of Smolanoff et al. to be the same according to the teachings of Fukui et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable types of filters for the disclosed filter step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Le et al. (2003/0077914).

Smolanoff et al. do not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Leet al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Allowable Subject Matter

Claims 14 and 21-24 are allowed.

Response to Arguments

Applicant's arguments filed 12/5/05 have been fully considered but they are not persuasive. Applicant argues that deposition is performed by exposing the substrate to the secondary plasma, not the main plasma adjacent to the sputtering target. However, the process of Col. 5- Col. 6 of Smolanoff et al. deposits a thin film on the substrate 15 by exposure to the main plasma (Col. 6, lines 30-33). The additional teachings of the reference, like creating a secondary plasma, do not render invalid the teachings relied on.

Applicant argues that Smolanoff has enabled utilization of a DC power supply, but not a pulsed DC power supply. However, Smolanoff discloses that a pulsed DC power can be used and would work in the process described at Col. 5-Col. 6.

Conclusion

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
February 8, 2006

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

1/27

approved
2/8/06

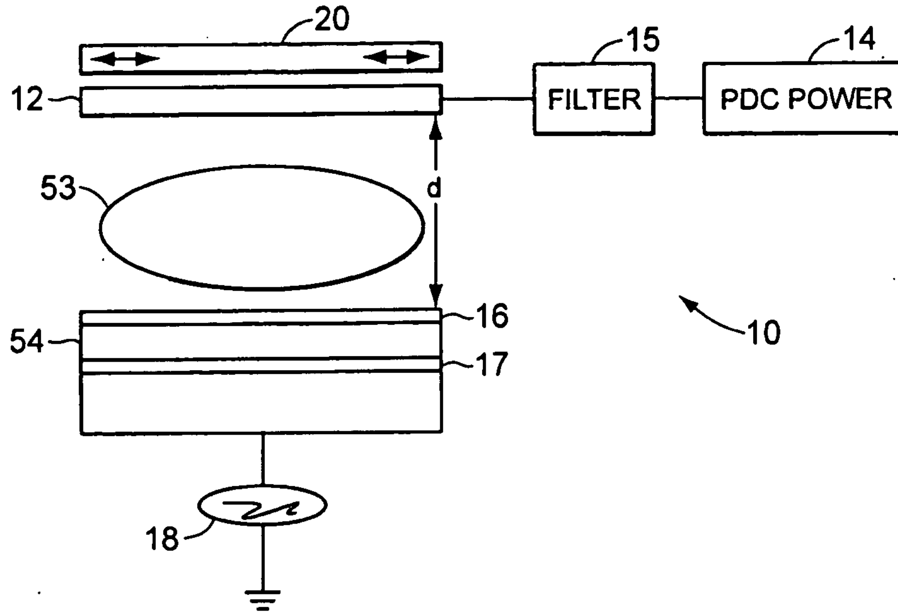


FIG. 1A

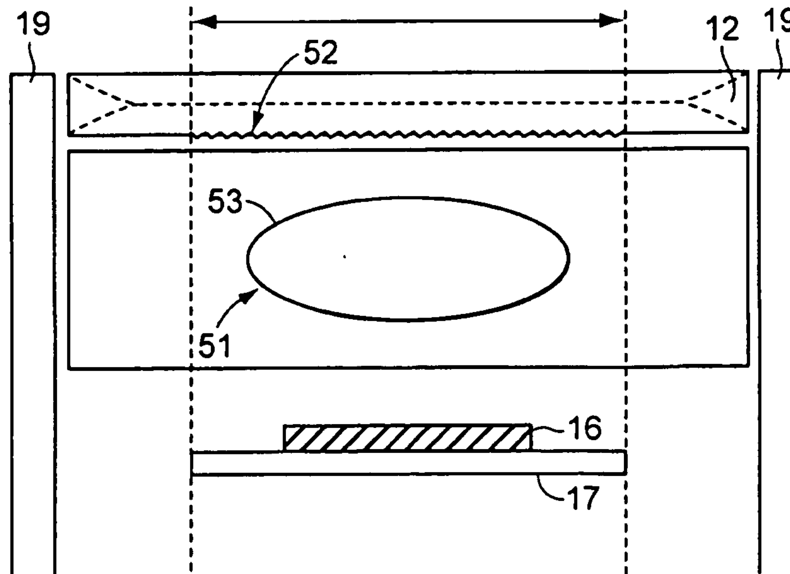


FIG. 1B

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

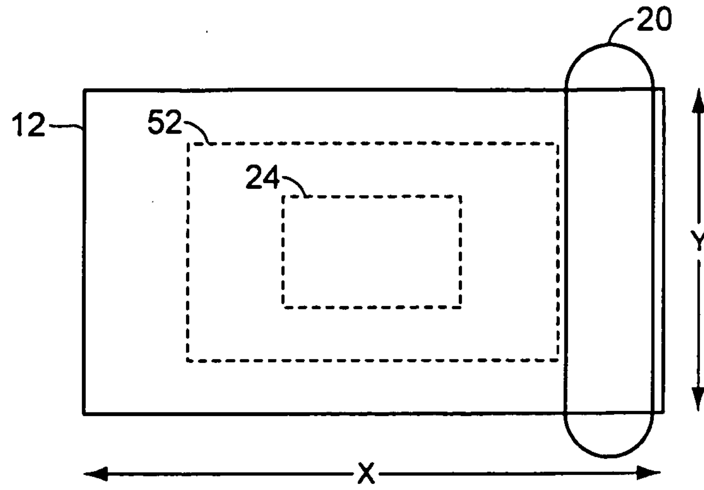


FIG. 2

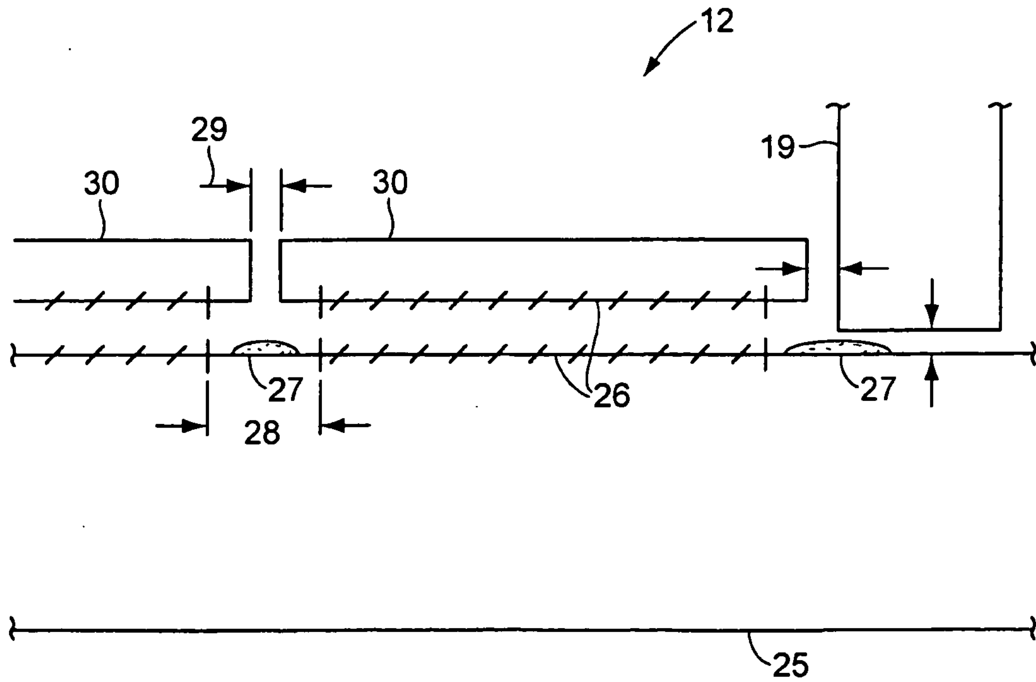


FIG. 3

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

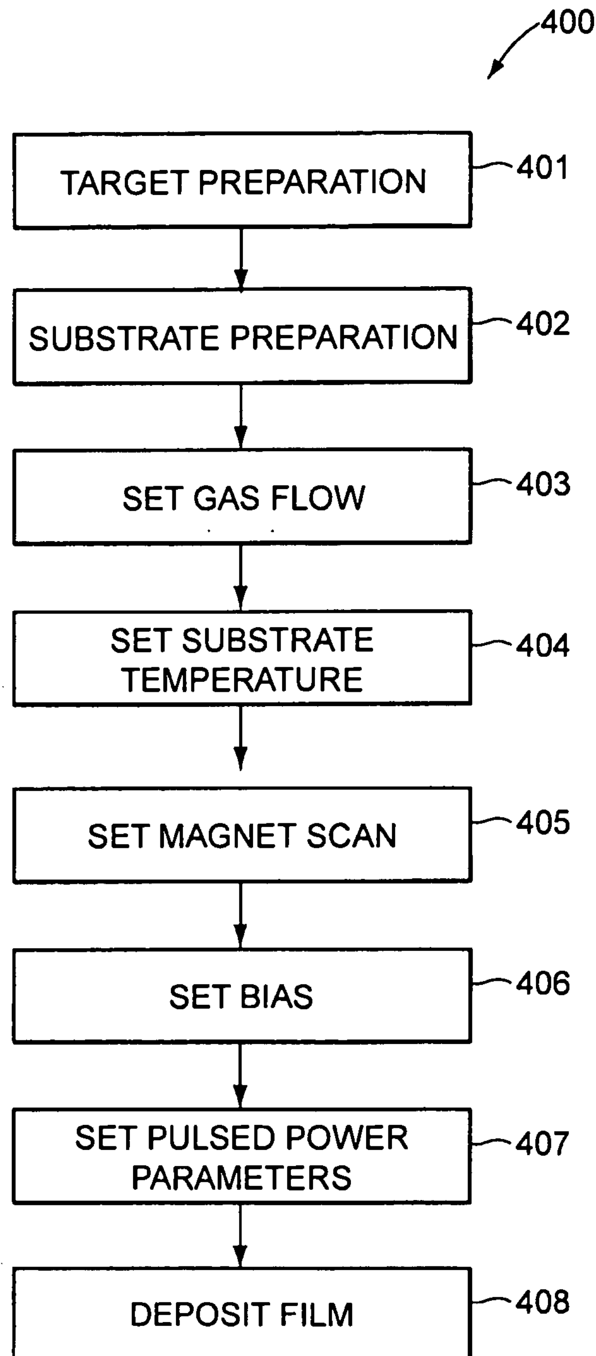


FIG. 4

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

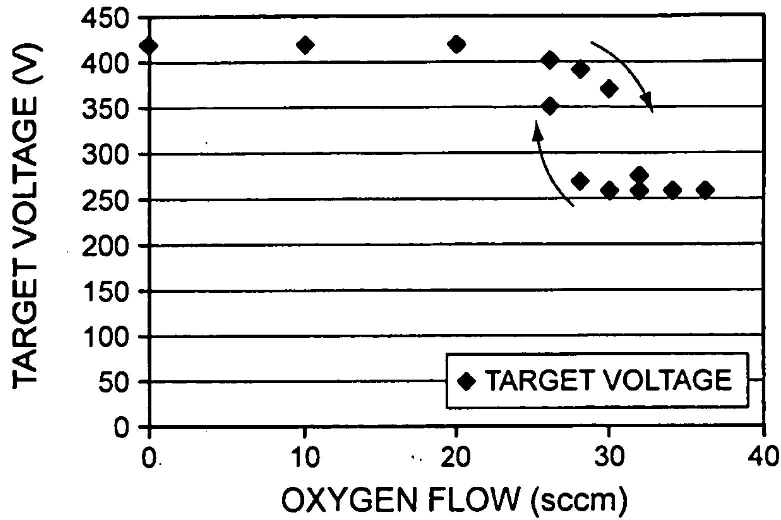


FIG. 5

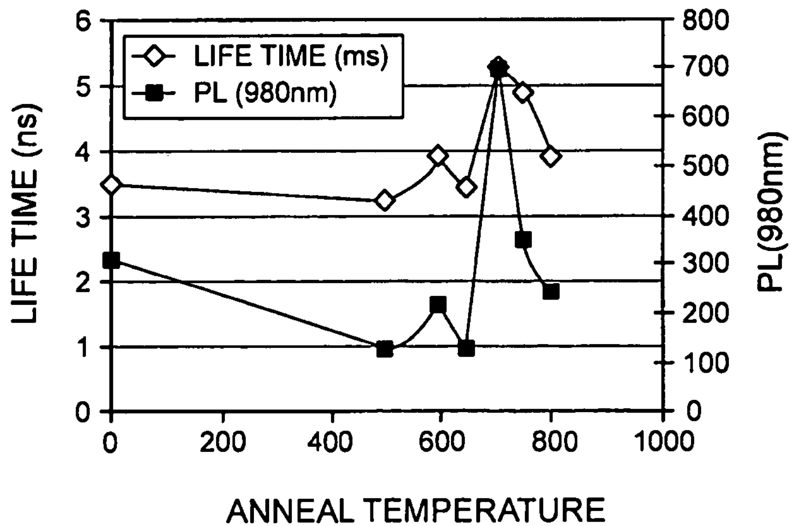
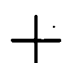


FIG. 6



REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

5/27

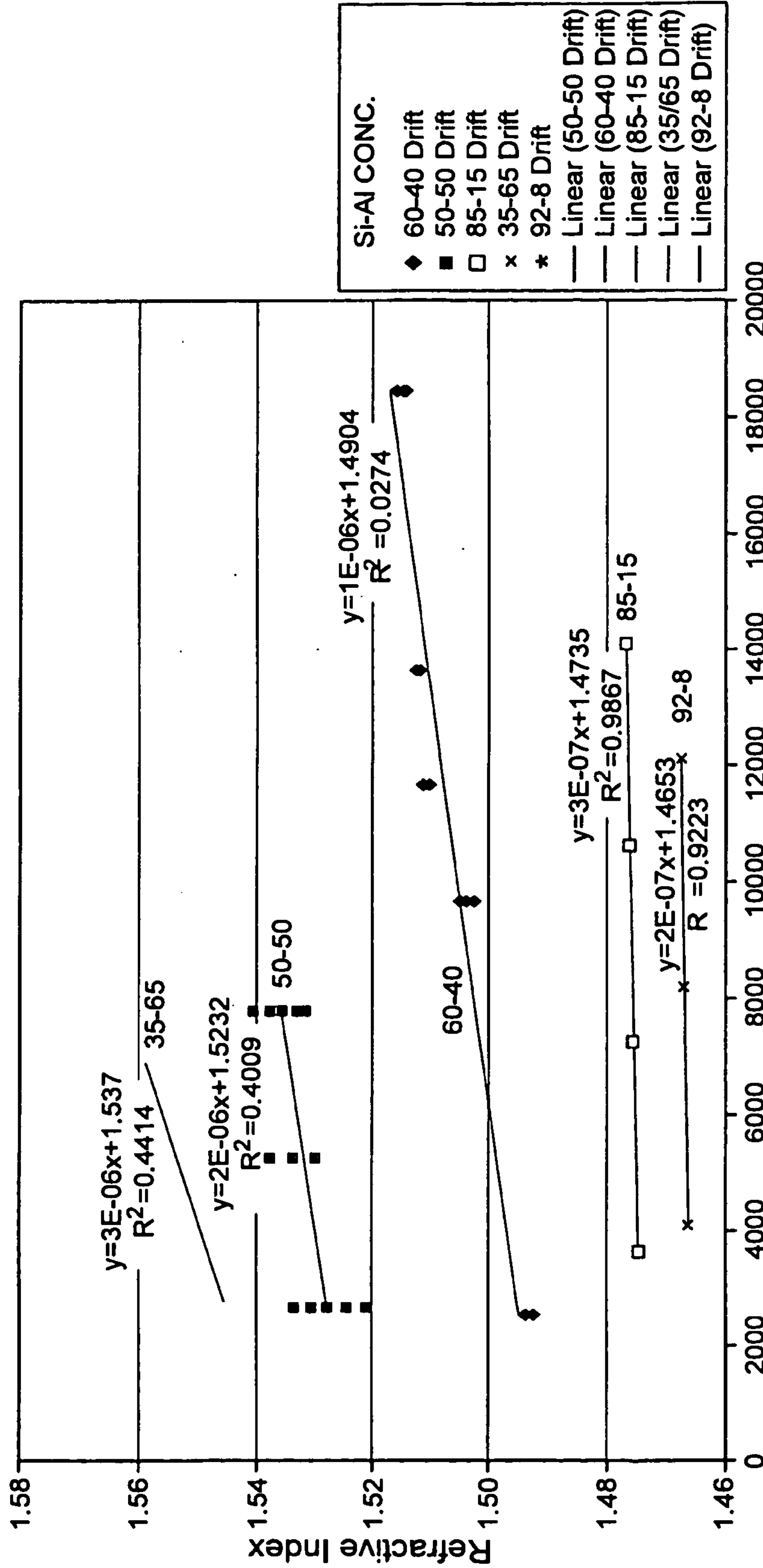


FIG. 7

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

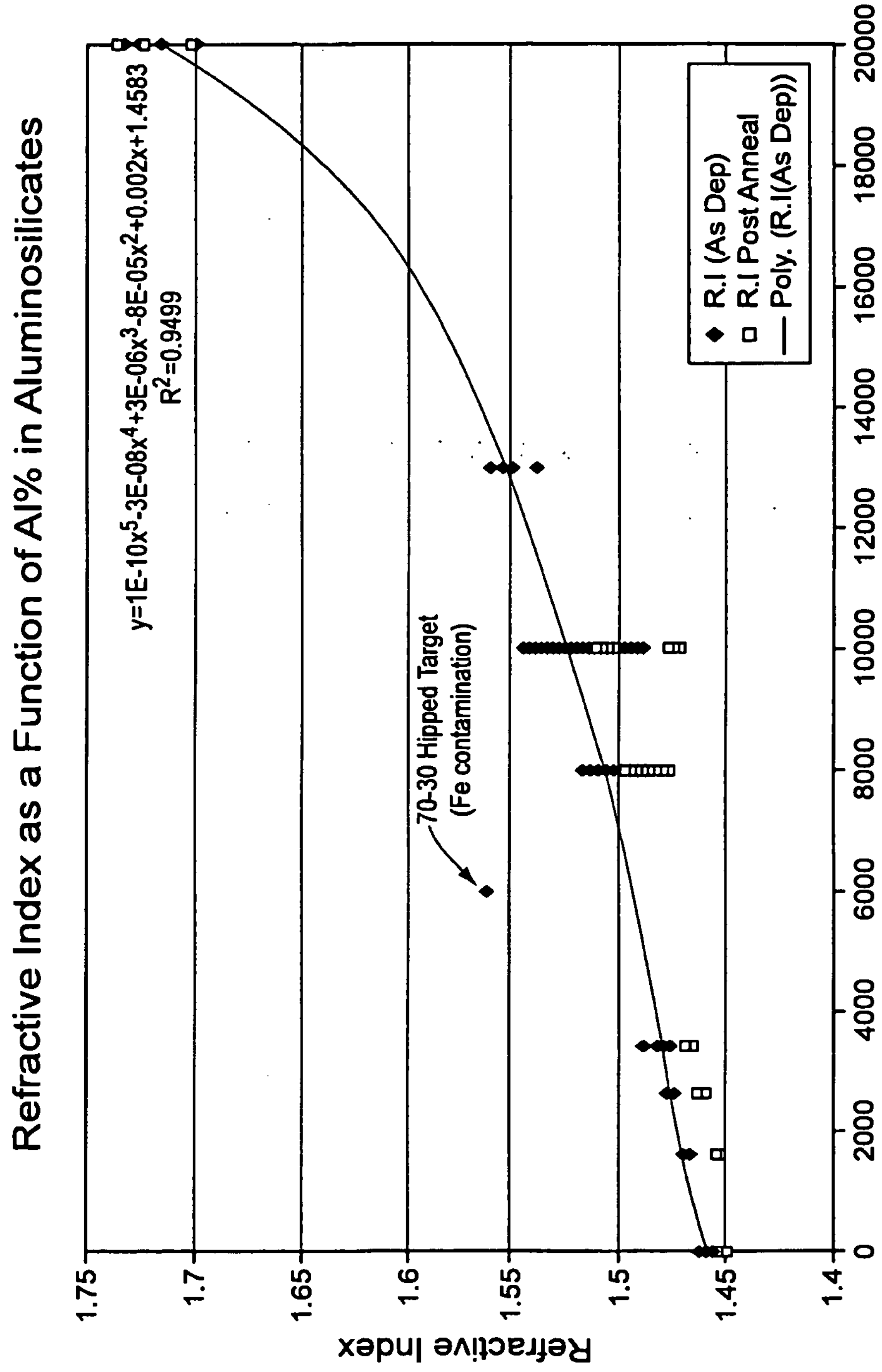


FIG. 8

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Material (Er/Yb/Al/Si)	Expected index (Post anneal)	Actual index (Post anneal)	Process Conditions (Annealed 725c 30min)
0.8/0.8/41.4/57	1.506	1.510	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.6/0.5/49/48.9	1.526	1.528	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/8/92	1.452	1.456-1.459	4.5KW, Ar-30-60,02-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/40/60	1.504	1.486-1.501	3.0-4.5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/50/50	1.520	1.491-1.503	4.0-5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/65/35	1.544	1.545-1.560	4.5-5.5KW, Ar-75-90,0285-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
0/0/30/70	1.490	1.562 (high Fe content)	5.0KW, Ar-75,02-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias
1.5/0/48.5/50	1.523	1.509-1.513	6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias

FIG. 9

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

8/27

Bias Power (Watts)	DC Power (KW)	Pulsing Freq (KHz)	Reverse Time (µs)	Ar Flow (sccms)	O2 Flow (sccms)	Wafer Position	Target To Wafer Spacing (mm)	Refractive Index Avg (@1550nm)	Refractive Index STD (@1550nm)	Dep Rate (um/Hr)
150	4.5	200	2.2	100	100	1	55	1.461508	0.000535	0.957654
150	4.5	200	2.2	100	100	2	55	1.462329	0.000376	0.962581
400	4.5	200	2.2	100	100	1	55	1.462774	0.000103	0.814007
400	4.5	200	2.2	100	100	2	55	1.463583	0.000095	0.824566

FIG. 10

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

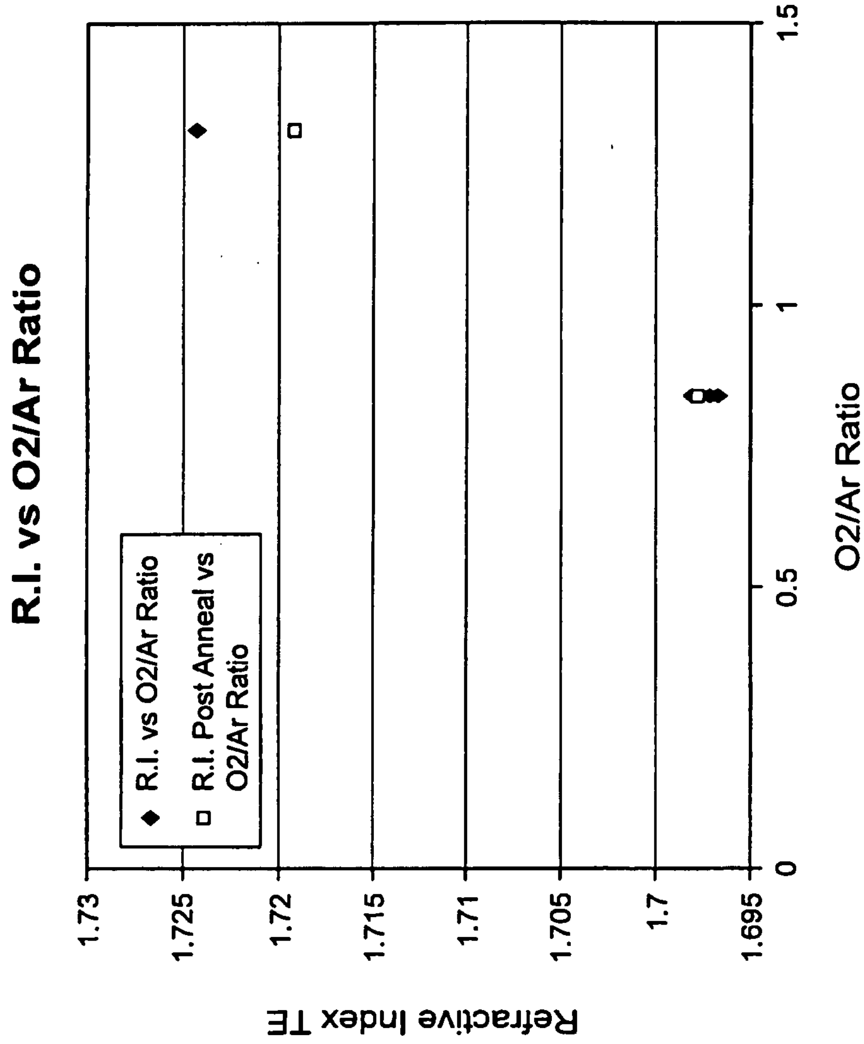


FIG. 11

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

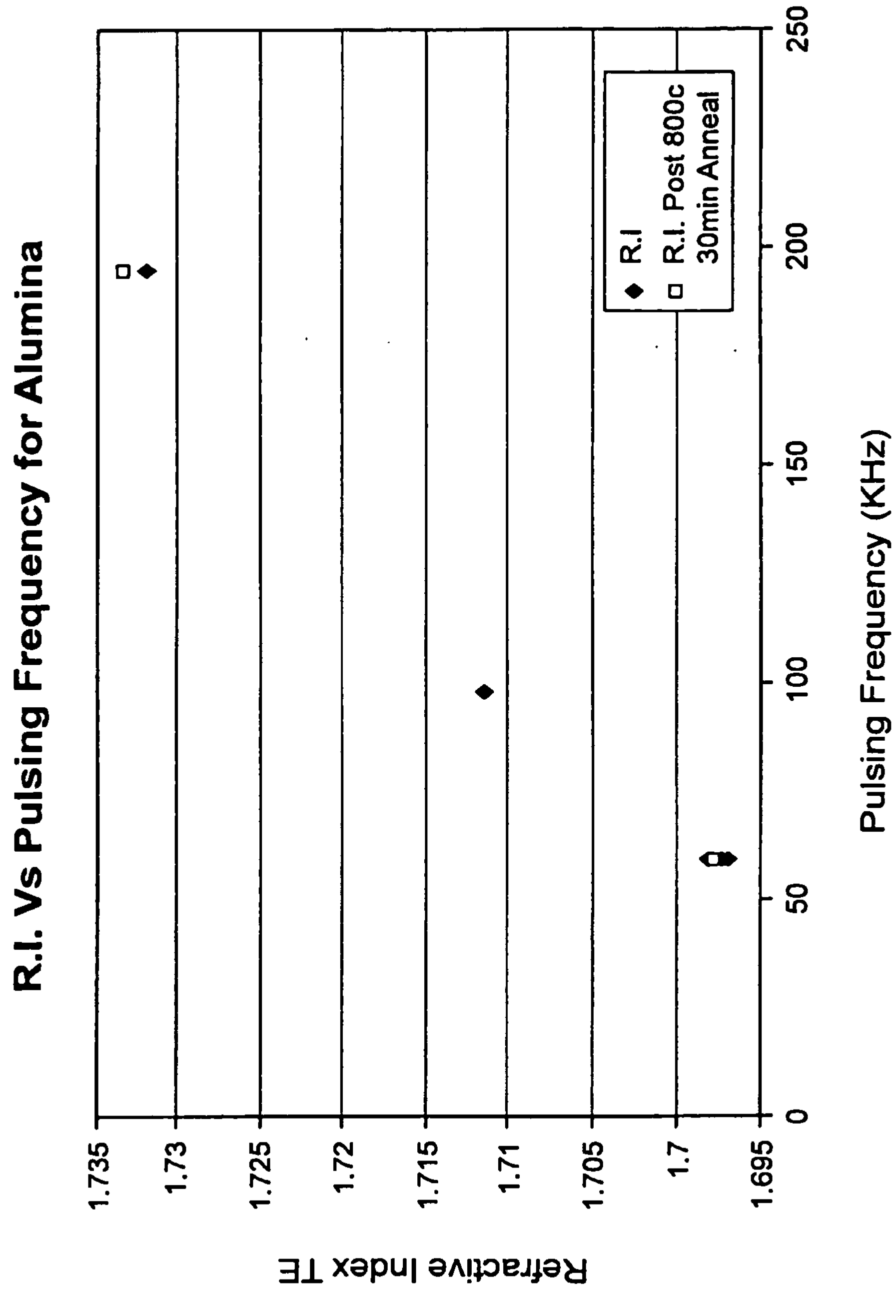


FIG. 12

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

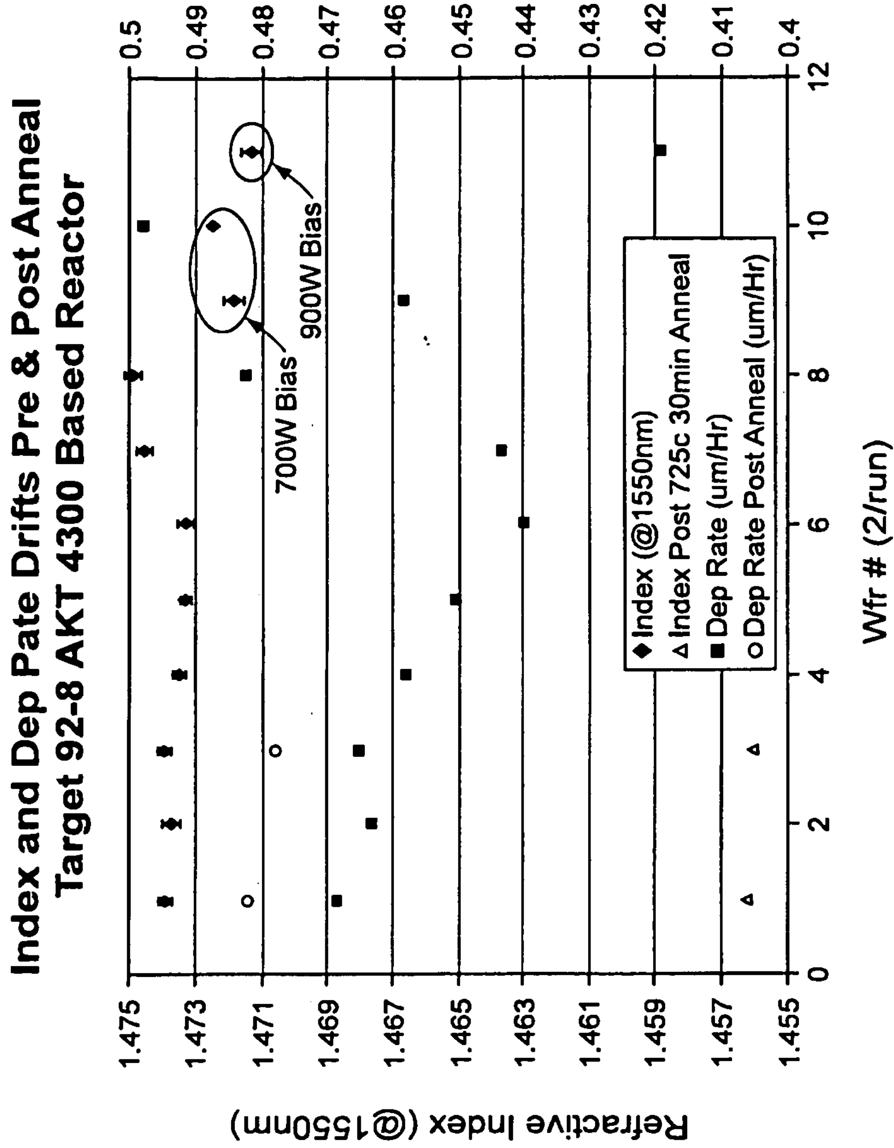


FIG. 13

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

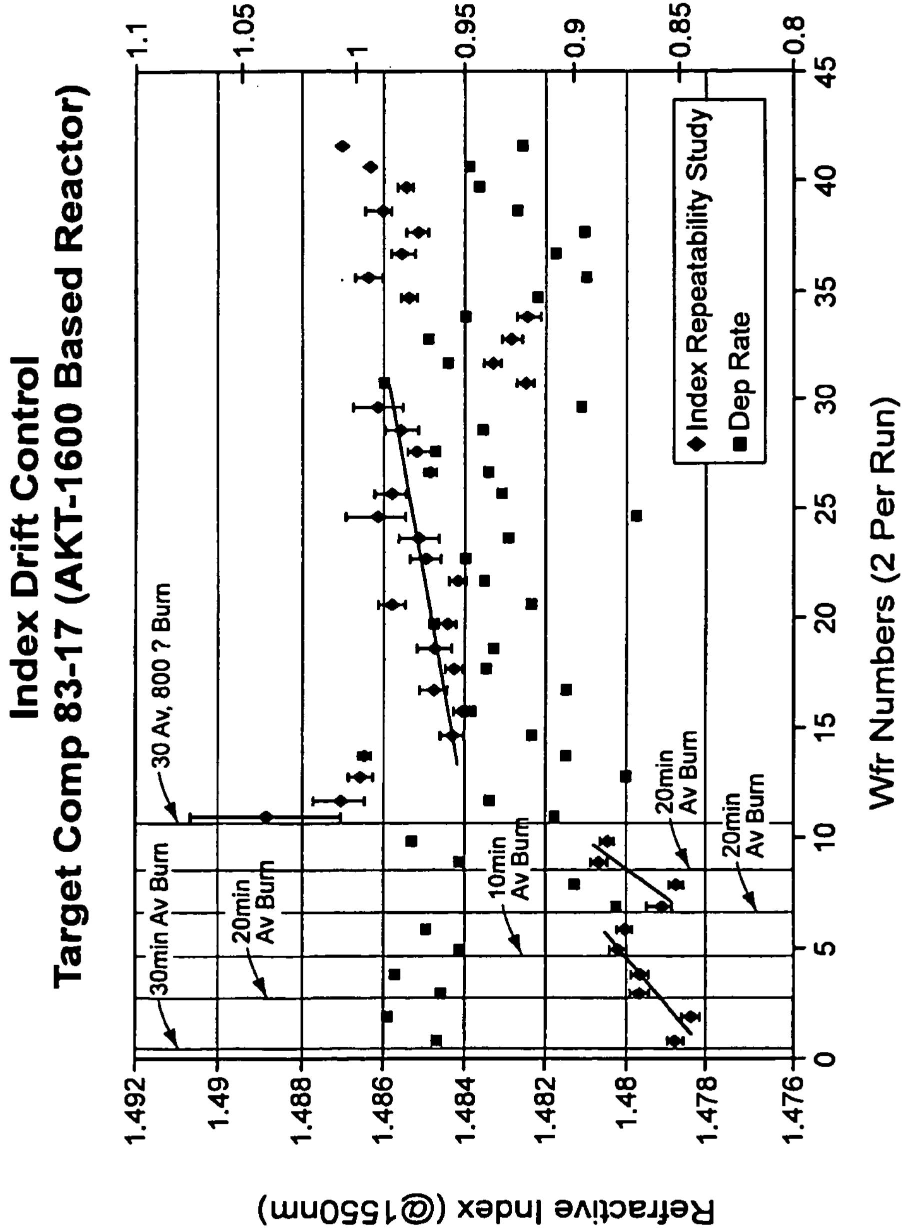


FIG. 14

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

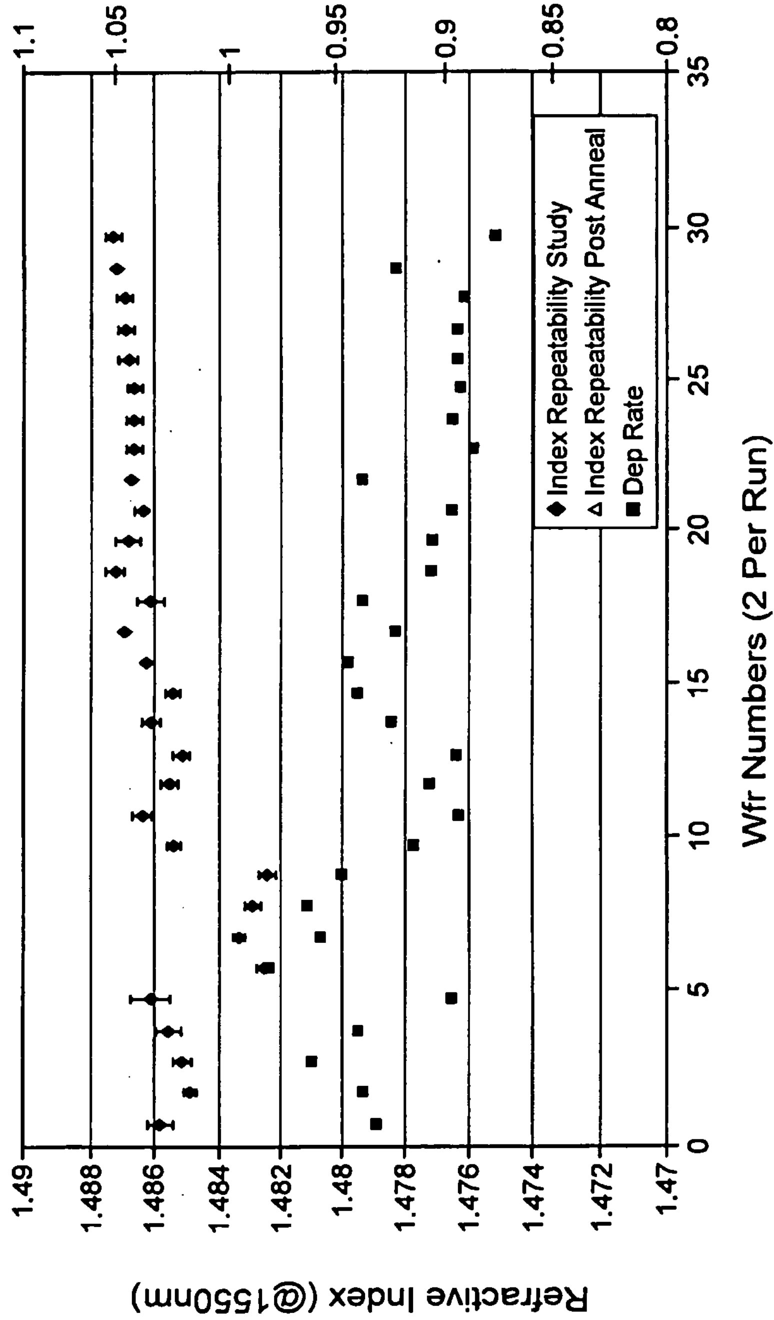


FIG. 15

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

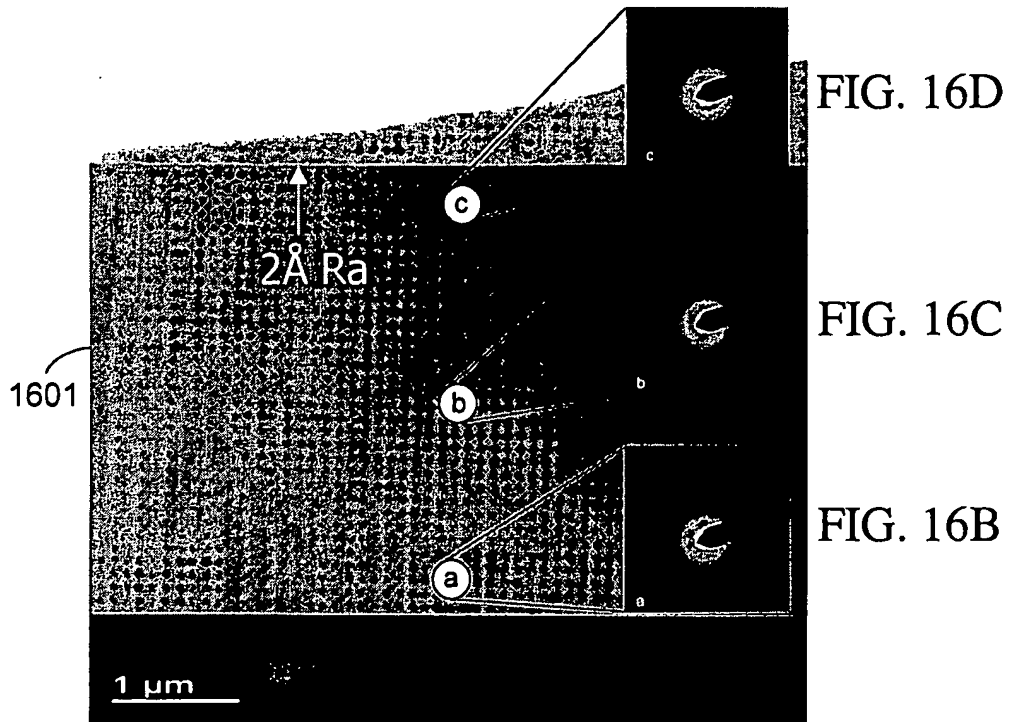


FIG. 16A

SYMMORPHIX PVD ALUMINOSILICATE

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

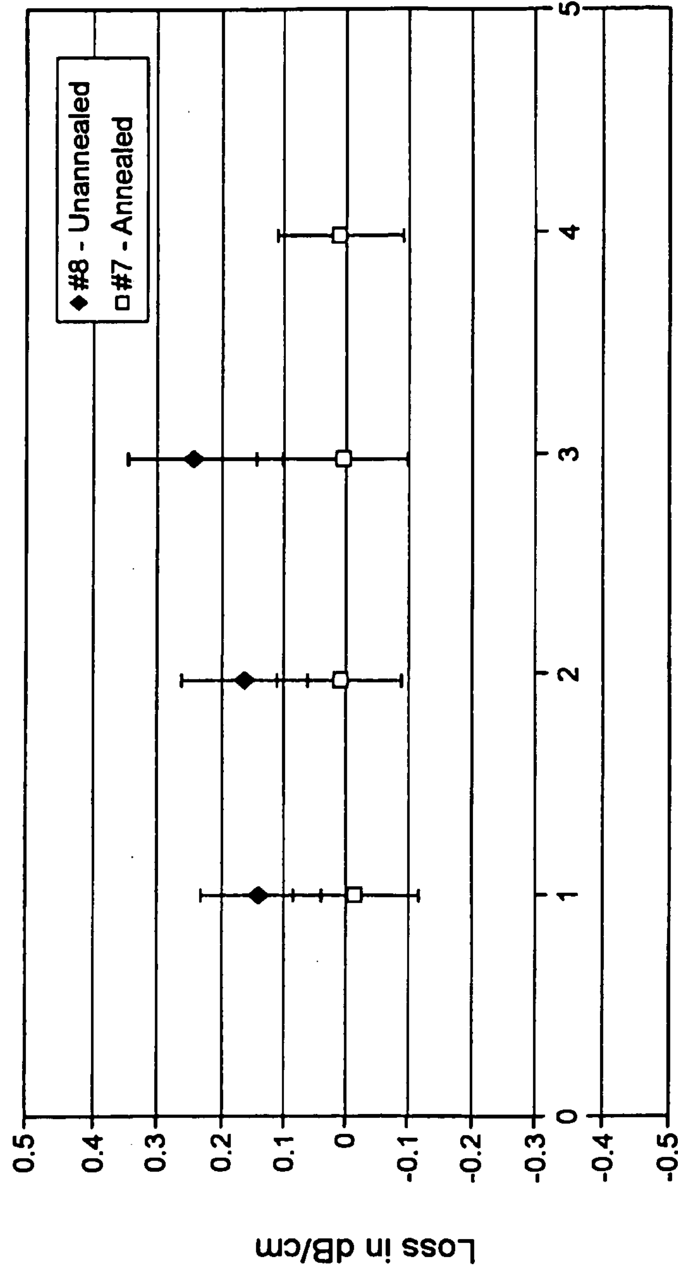


FIG. 17

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

1803

1802

1801

11.4µm

8.20µm

1804

S4700 5.0kV 10.4mm x3.00k SE(U) 3/7/02 11:05

10.0um

FIG. 18

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

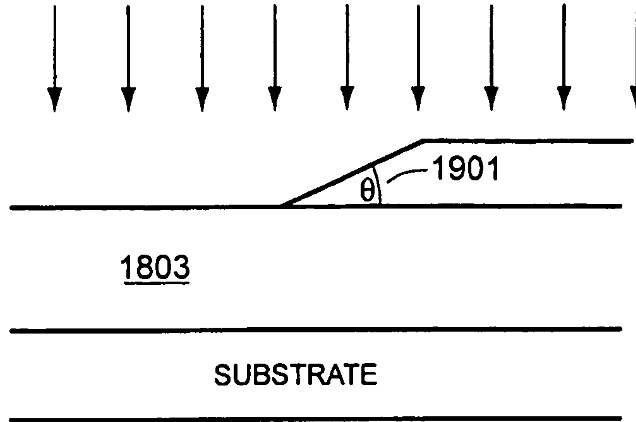


FIG. 19

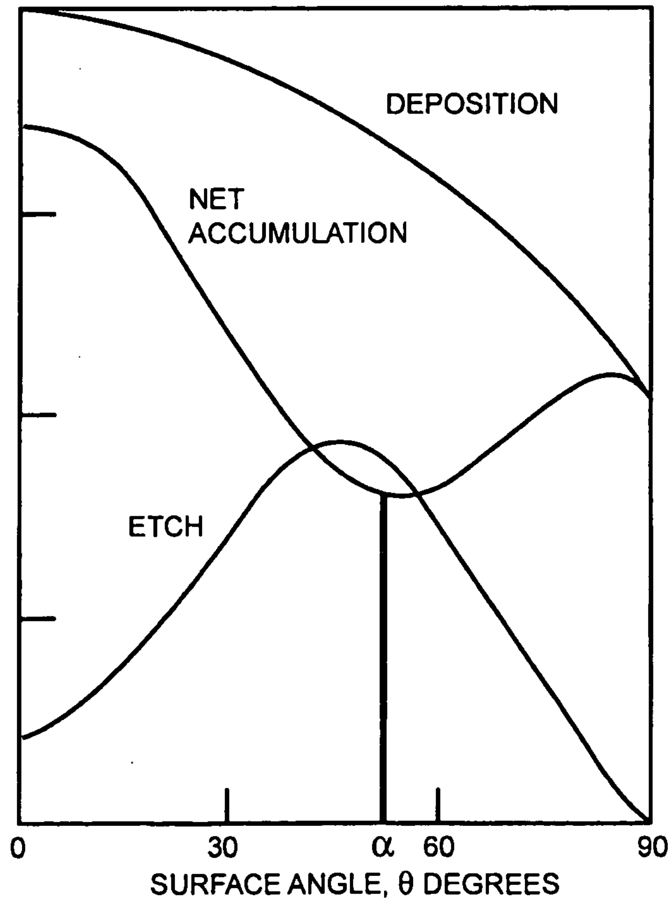


FIG. 20

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

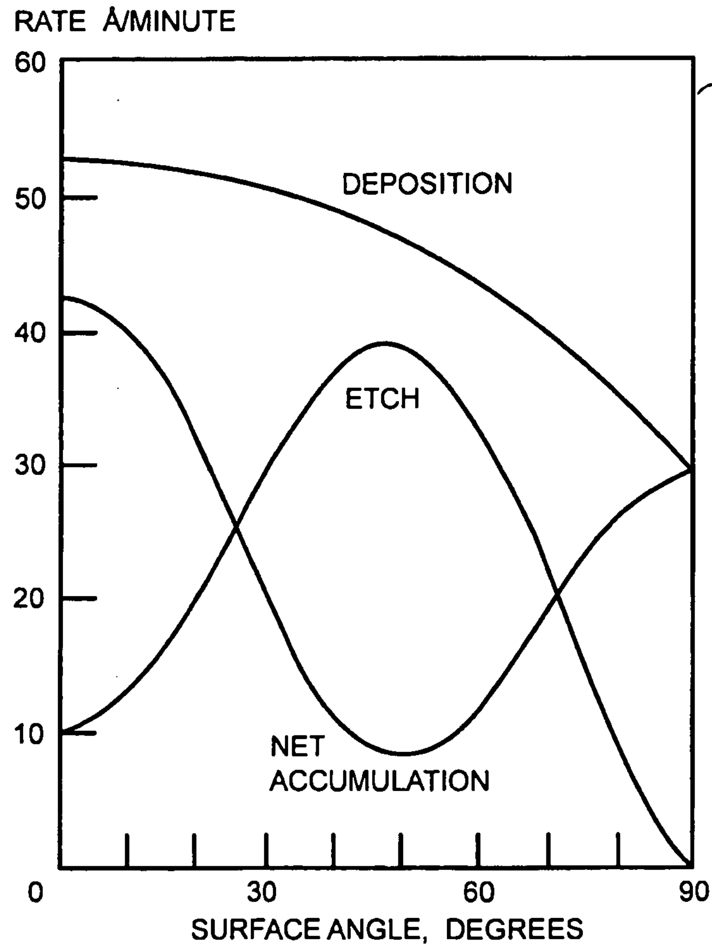


FIG. 21

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

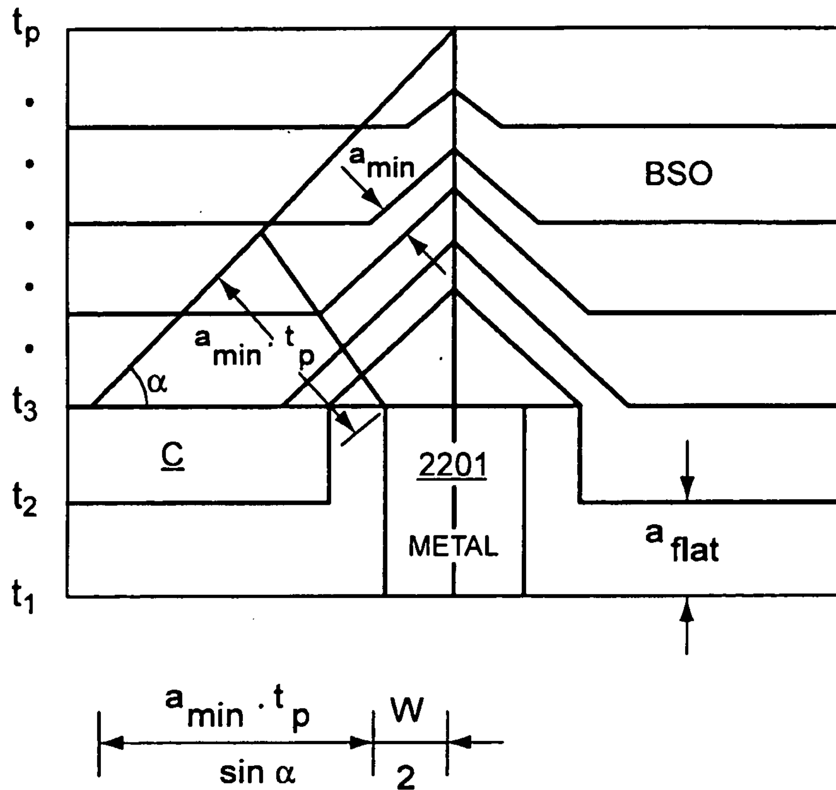


FIG. 22

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

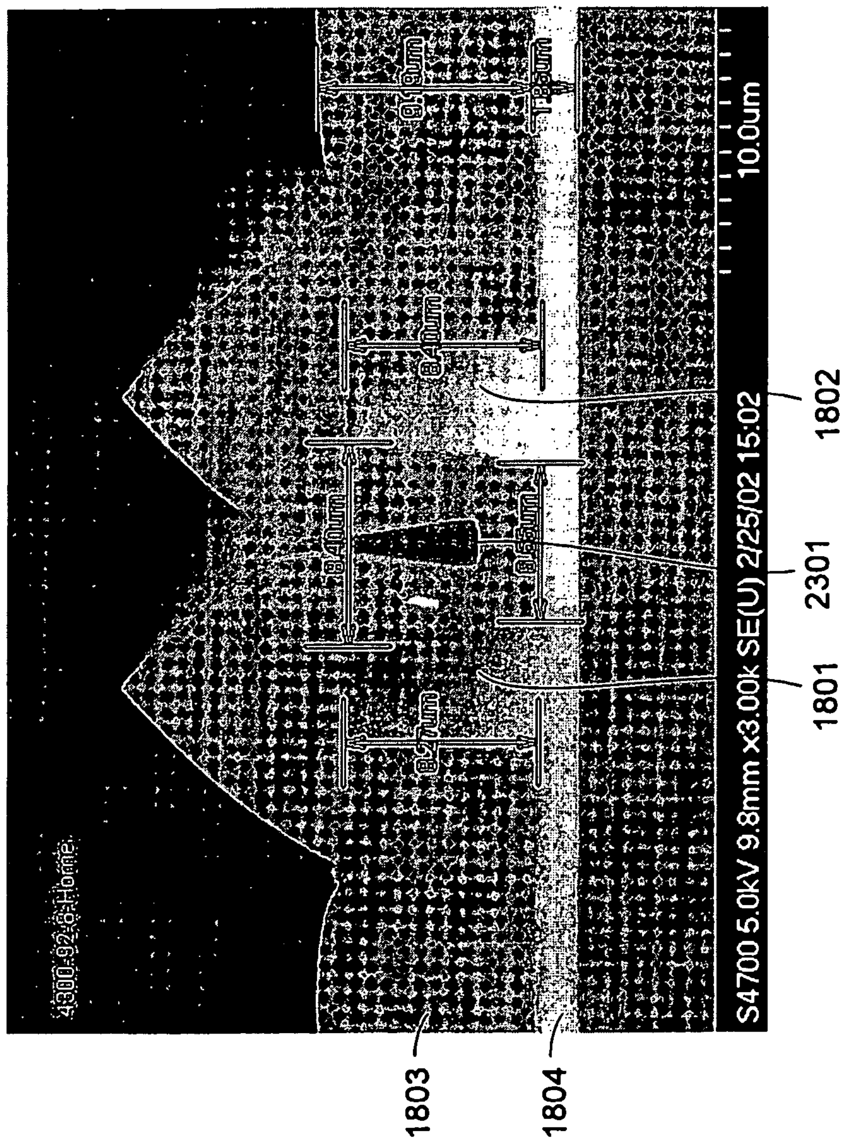


FIG. 23

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

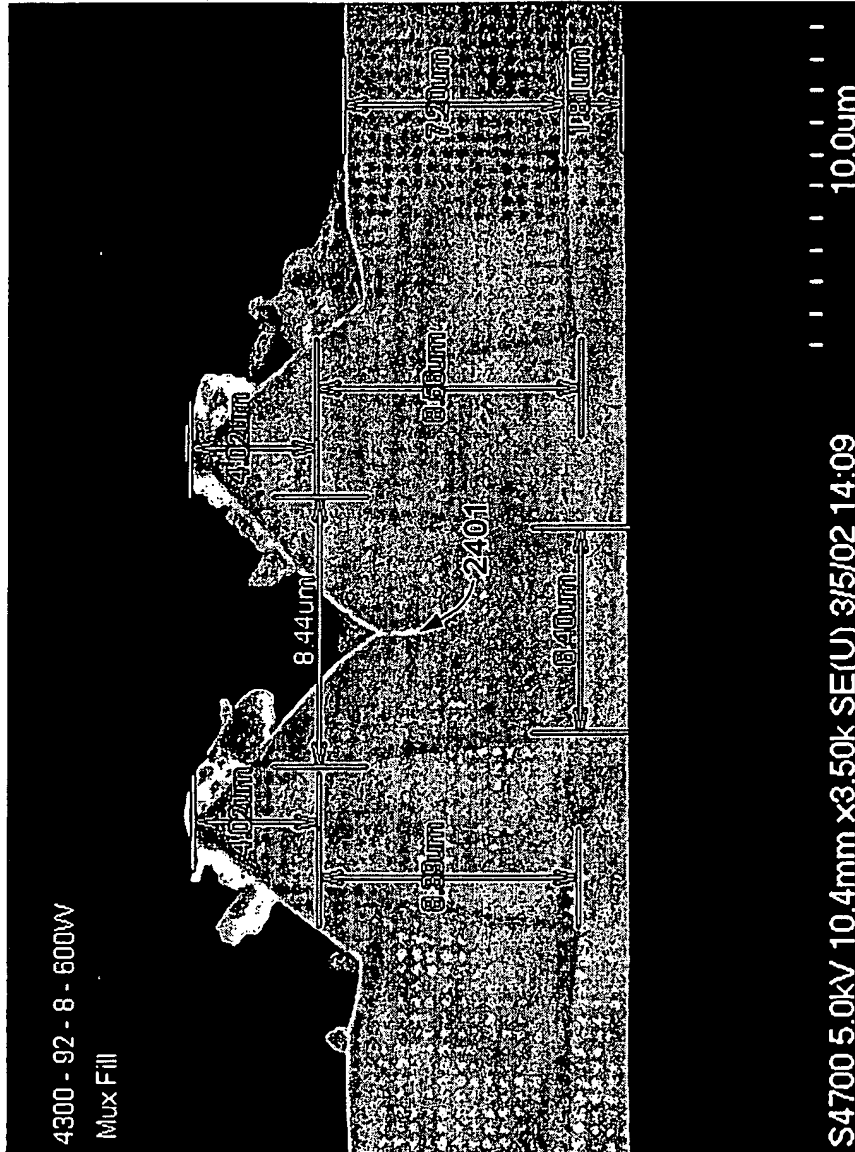


FIG. 24

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

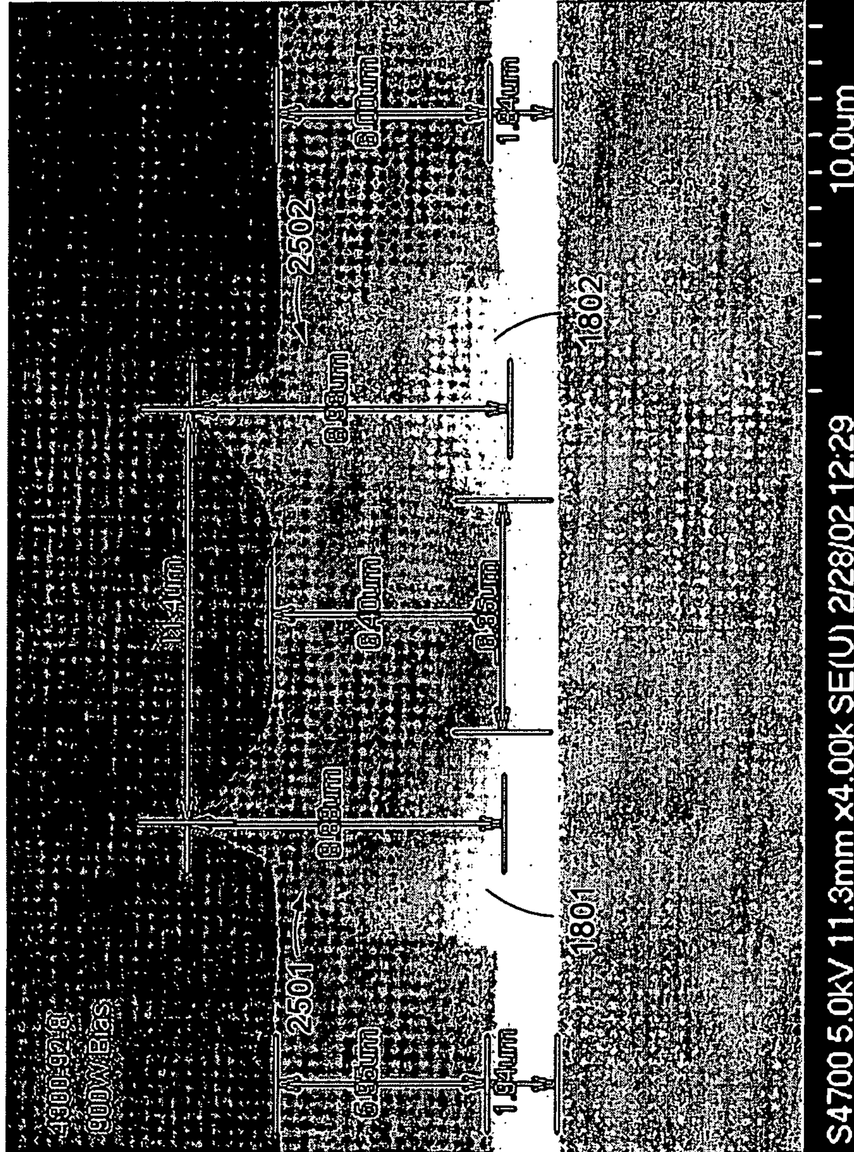


FIG. 25

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

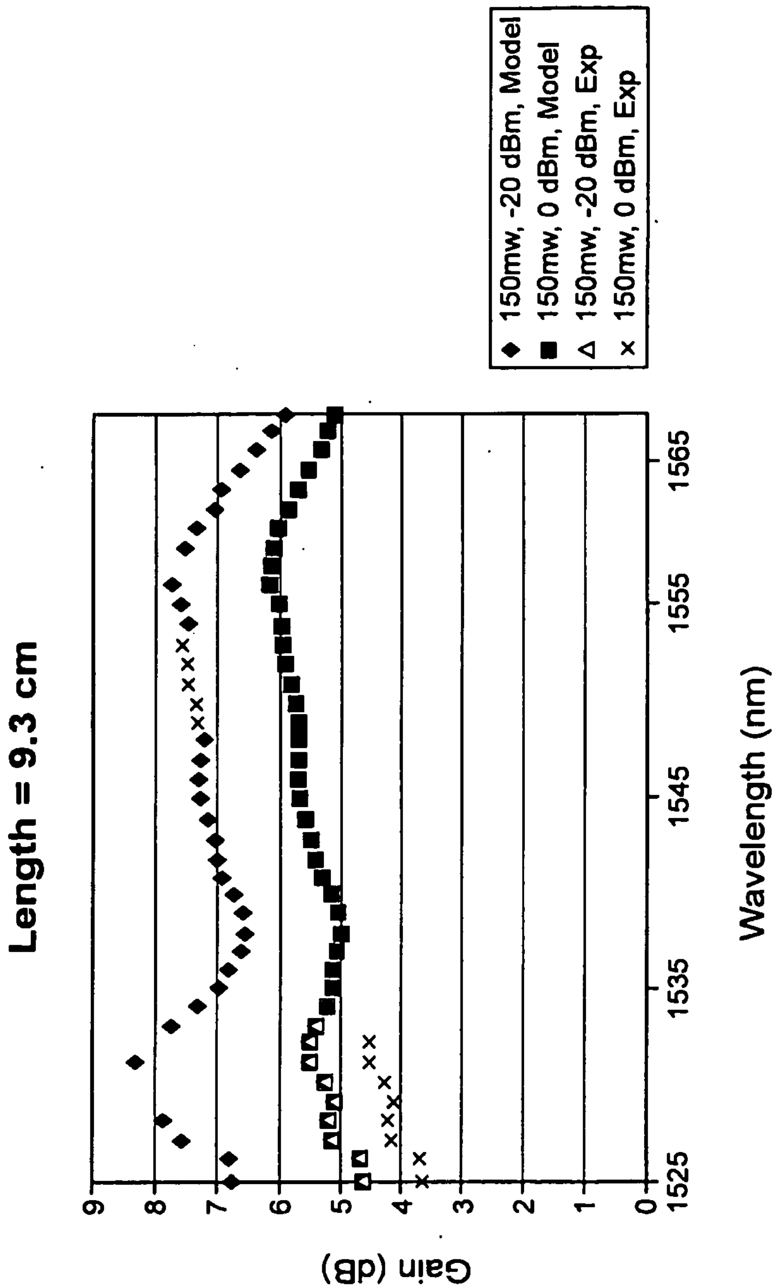


FIG. 26

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

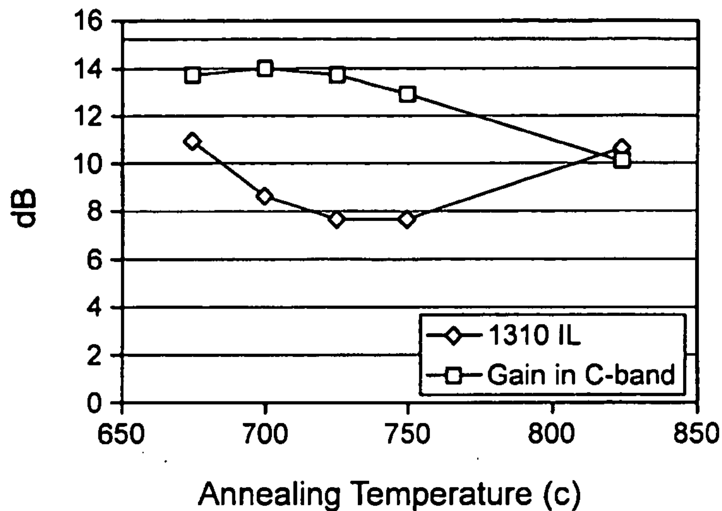


FIG. 27

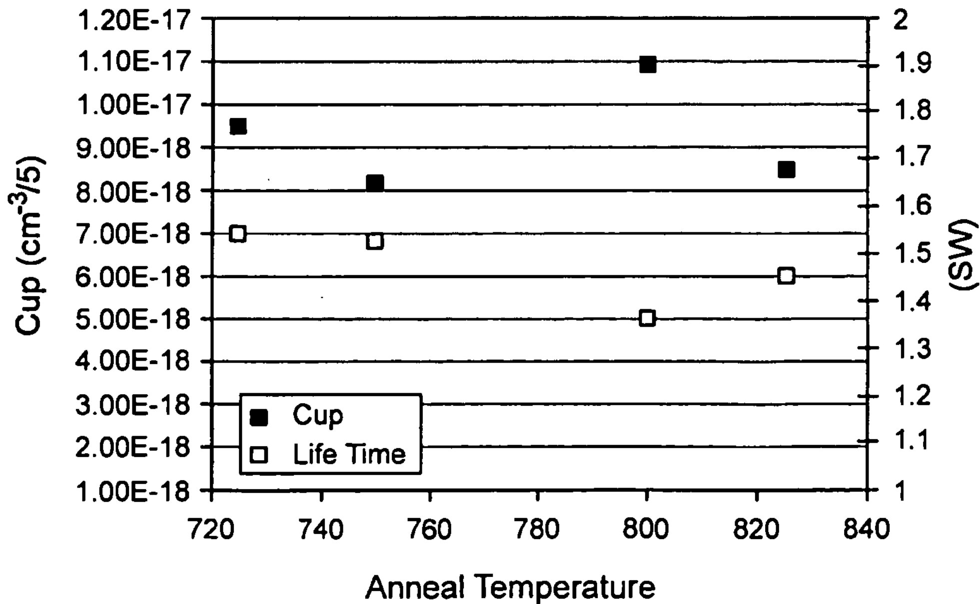


FIG. 28

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

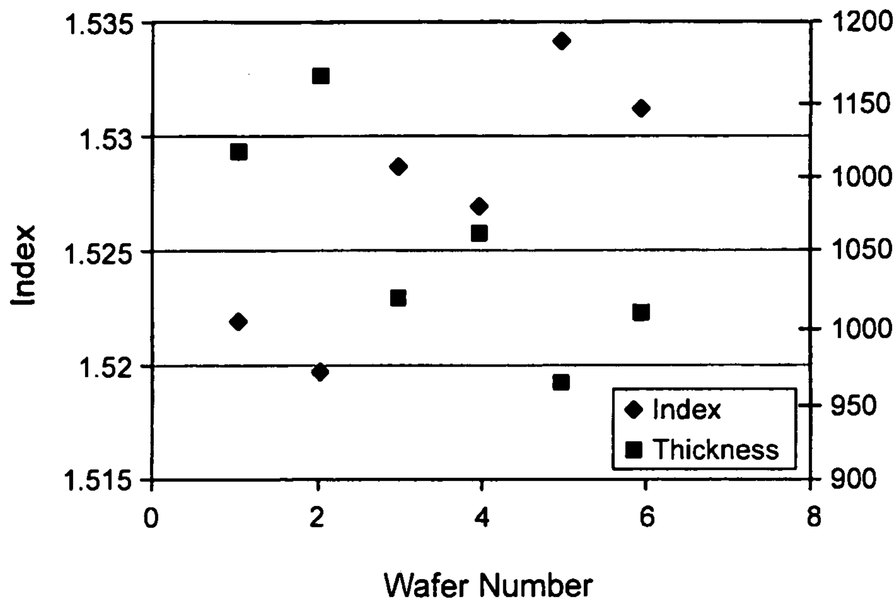


FIG. 29

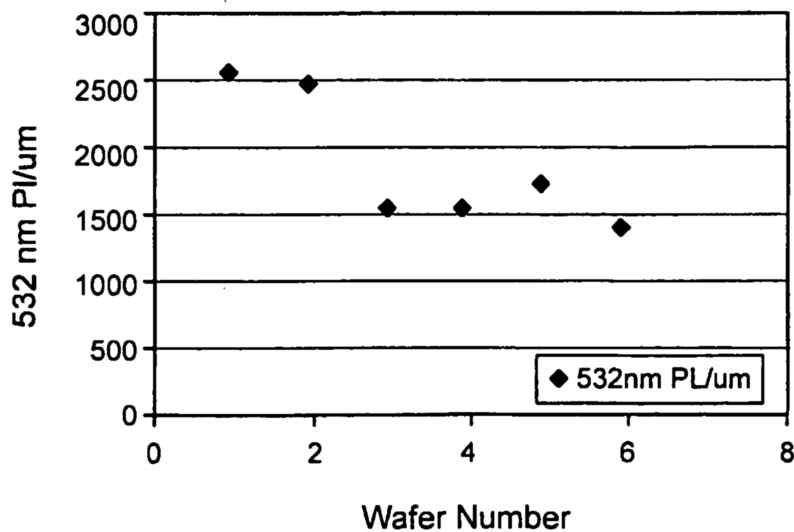


FIG. 30

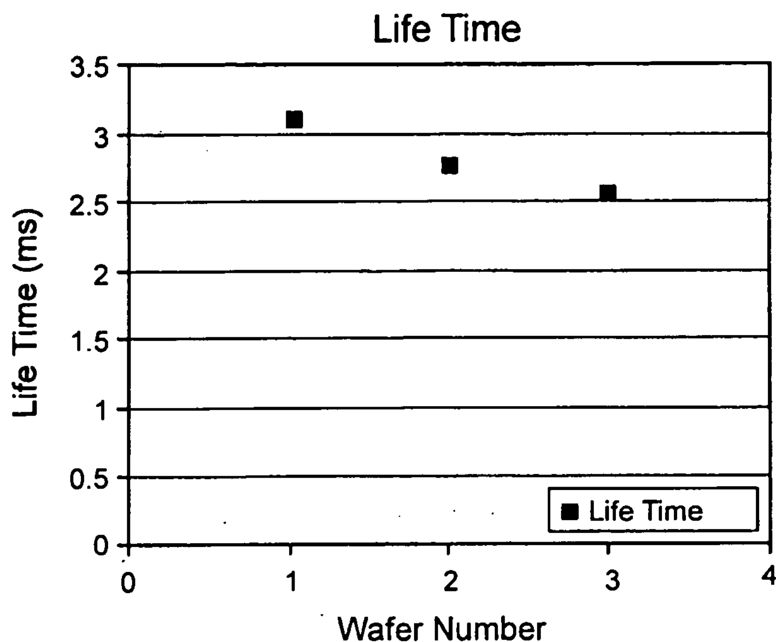


FIG. 31

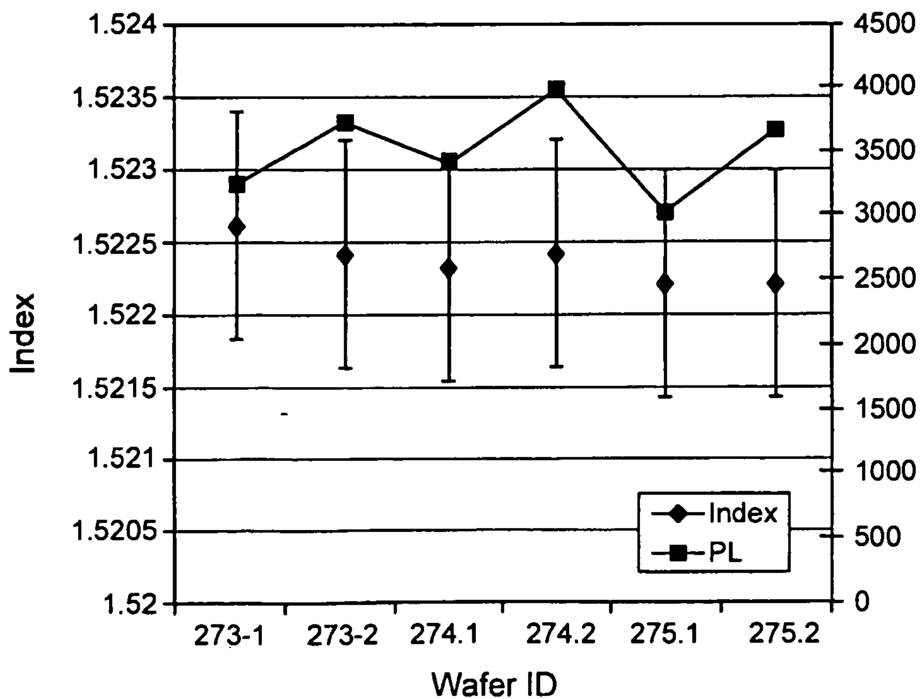


FIG. 32

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

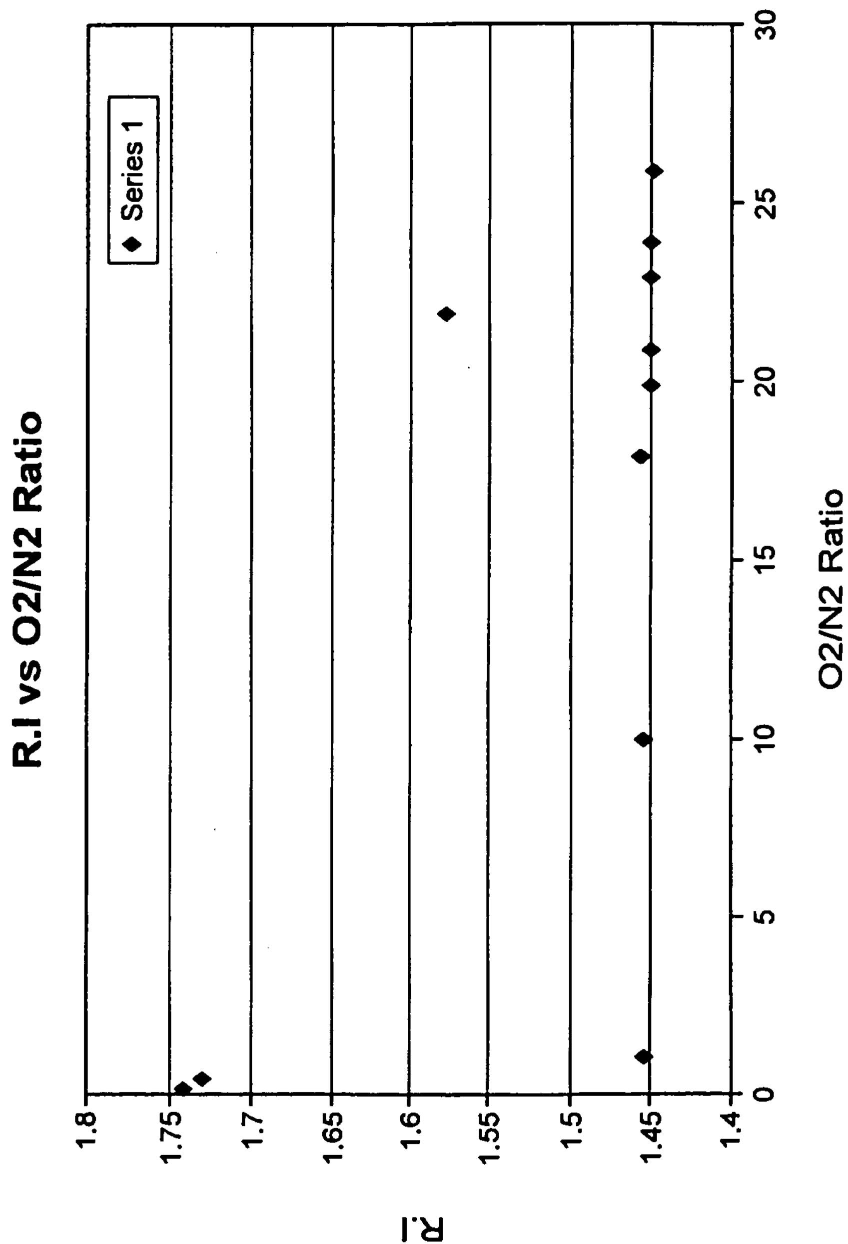
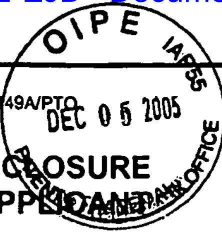


FIG. 33



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	Hongmei ZHANG
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	1	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
[initials]		5,478,456	12-26-1995	Humpal et al.	
[initials]		6,846,765 B2	1-25-2005	Imamura et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
[initials]		DOREY, R.A., "Low temperature micromoulding of functional ceramic devices," Grant summary for GR/S84156/01 for the UK Engineering and Physical Sciences Research Council, 2 pages (2004).	
[initials]		HOWSON, R.P., "The reactive sputtering of oxides and nitrides," *Pure & Appl. Chem.* *66*(6):1311-1318 (1994).	
[initials]		Office Action issued September 21, 2005 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01).	
[initials]		Office Action issued on August 8, 2005 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
[initials]		Office Action issued on October 3, 2005 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00).	
[initials]		Office Action issued on October 19, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

EXPRESS MAIL LABEL NO.
EV 758329165 US

Examiner Signature	Michelle Estrada	Date Considered	2/8/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed February 14, 2006, and filed concurrently with a Request for Continued Examination, Applicants propose that this application be amended as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 5.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Currently Amended): The method of Claim ~~1~~21, further including holding the temperature of the substrate substantially constant.

3. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Currently Amended): The method of Claim 4, wherein the filter is a band rejection filter at the frequency of the bias power.

6. (Currently Amended): The method of claim 4, wherein the RF bias power is zero.

7. (Currently Amended): The method of Claim ~~1~~21, wherein the film is an upper cladding layer of a waveguide structure and the RF bias power is optimized to provide planarization.

8. (Currently Amended): The method of Claim ~~1~~21, wherein ~~the~~a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Currently Amended): The method of Claim ~~9~~8, wherein the ~~Oxygen flow~~mixture is adjusted to adjust the index of refraction of the film.

10. (Currently Amended): The method of Claim 8, wherein the ~~process gas~~mixture further includes nitrogen.

11. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~applying pulsed DC power to ~~a~~the target includes ~~providing~~adjusting pulsed DC power to a target which has an area

larger than that of the substrate.

12. (Currently Amended): The method of Claim ~~1~~21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Previously Presented): A method of depositing a film on a substrate, comprising:
providing pulsed DC power through a filter to a target;
providing RF bias power to a substrate positioned opposite the target; and
providing process gas between the target and the substrate, and
depositing a film on the backside of the target,
wherein the filter protects a pulsed DC power supply from the bias power, and
wherein a plasma is created between the target and the substrate.

15.-20. (Cancelled).

21. (Currently Amended): A method of depositing a film on a substrate, comprising:
conditioning a target;
preparing the substrate;
adjusting an RF bias power to the substrate;
setting a process gas flow; and
applying pulsed DC power to the target through a filter to create a plasma and deposit the film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. (Previously Presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power

includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

REMARKS

Claims 1-14 and 20-24 are pending in the above identified application. The Examiner has rejected claims 1-13 and 20, and allowed claims 14 and 21-24. With this paper, Applicants have amended claims 2-12 to depend upon allowed claim 21, and amended claim 21 for a typographical error, and cancelled claims 1 and 20. Applicants reserve the right to pursue claims 1 and 20 in a separate application.

The Examiner rejected claims 1, 8, 10-13, and 20 under 35 U.S.C. § 102(b) as being anticipated by Smolanoff et al. (6,117,279). Further, the Examiner rejected claims 2-6 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. and further in view of Fukui et al. (5,755,938). Without agreeing or acquiescing with the Examiner's comments regarding the claims and the prior art, Applicants have canceled claims 1 and 20 and amended claims 8, 2-6, and 10-13 to depend from allowed claim 21. Therefore, claims 2- 6, 8, and 10-13 are allowable for at least the same reasons as is claim 21.

The Examiner has allowed claims 14 and 21-24.

Conclusion

Applicant respectfully requests that this Amendment be entered by the Examiner, placing claims 2-14 and 21-24 in condition for allowance. Applicants submit that the proposed amendments of claims 2-12 and 21 do not raise new issues or necessitate the undertaking of any additional search of the art by the Examiner, since all of the elements and their relationships claimed were either earlier claimed or inherent in the claims as examined. Therefore, this Amendment should allow for immediate action by the Examiner.

In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited

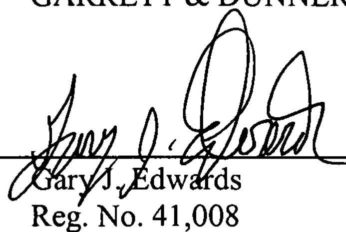
against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

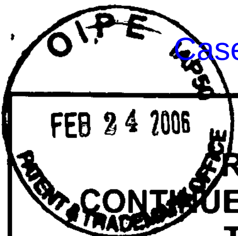
Dated: February 24, 2006

By: 

Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 746094839 US**

RCE/28823



REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL

Address to:
Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Application Number: 10/101,863	Confirmation Number: 6938
Filing Date: March 16, 2002	
First Named Inventor: ZHANG, Hongmei	
Group Art Unit: 2823	
Examiner: ESTRADA, Michelle	
Attorney Docket Number: 9140.0016-00	
Attorney Customer Number: 22,852	

This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of the above-identified application.

Request for Continued Examination (RCE) practice under 37 C.F.R. § 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application.

1. **Submission required under 37 C.F.R. § 1.114: Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment.**

   a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

      i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on ________.

      ii. ☐ Other ________________________

   b. ☐ DO NOT ENTER the amendment(s) previously filed on ________. An alternate submission is attached.

   c. ☒ Enclosed submission: .

      i. ☒ Amendment/Reply

      ii. ☐ Affidavit(s)/Declaration(s)

      iii. ☒ Information Disclosure Statement

      iv. ☐ Other ____________

2. Miscellaneous

   a. ☐ Suspension of action on the above-mentioned application is requested under 37 C.F.R. § 1.103(c) for a period of months. (Period of suspension shall not exceed 3 months; fee under 37 C.F.R. § 1.17(i) required.)

   b. ☐ Other ________________________

3. Fees

   a. ☒ The filing fee is calculated as follows:

      i. ☒ $790.00 RCE fee required under 37 C.F.R. § 1.17(e)

      ii. ☐ Petition for extension of time for (Months) $

      iii. ☐ Other ________________________

   b. ☒ The Commissioner is hereby authorized to charge the fee of $790.00 to Deposit Account No. 06-0916.

   c. ☒ The Commissioner is authorized to charge any deficiencies in the filing fees, or credit any overpayments to Deposit Account No. 06-0916.

Signature of Applicant, Attorney, or Agent Required

Name: Gary J. Edwards	Reg. No.: 41,008
Signature: [signature]	Date: February 24, 2006

EXPRESS MAIL LABEL NO.
EV 746094839 US

02/27/2006 HTECKLU1 00000098 060916 10101863

01 FC:1801 790.00 DA

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

FIFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or

constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

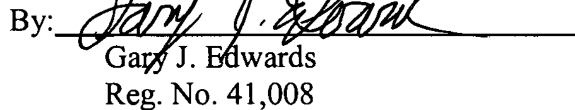
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

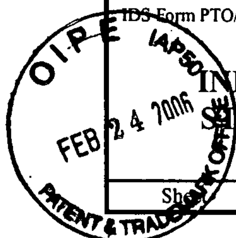
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 24, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 746094839 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
(Use as many sheets as necessary)				*Art Unit*	2823
				Examiner Name	ESTRADA, Michelle
Sheet	1	of	3	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-3,309,302	03-14-1967	Heil	
		US-5,338,625	08-16-1994	Bates et al.	
		US-5,561,004	10-01-1996	Bates et al.	
		US-5,930,046	07-27-1999	Solberg et al.	
		US-6,242,129 B1	06-05-2001	Johnson	
		US-6,280,875 B1	08-28-2001	Kwak et al.	
		US-6,376,027 B1	04-23-2002	Lee et al.	
		US-6,632,563 B1	10-14-2003	Krasnov et al.	
		US-6,683,244 B2	01-27-2004	Fujimori et al.	
		US 2002/0001746 A1	01-03-2002	Jenson	
		US 2002/0076133 A1	06-20-2002	Li et al.	
		US 2002/0140103 A1	10-03-2002	Kloster et al.	
		US 2003/0178637 A1	09-25-2003	Chen et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		WO 2004/106581 A2	12-09-2004	Symmorphix, Inc.		
		WO 2004/106582 A2	12-09-2004	Symmorphix, Inc.		

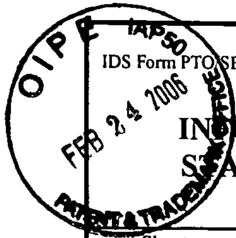
NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		KIM, H-K. and YOON, Y., "Characteristics of rapid-thermal-annealed $LiCoO_2$ cathode film for an all-solid-state thin film microbattery," *J. Vac. Sci. Technol. A 22*(4):1182-1187 (2004).	
		Response to Office Action filed on October 17, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US



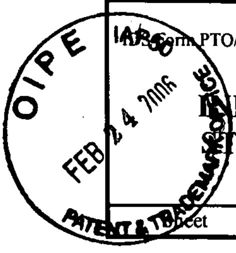
IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	2	of	3	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		Final Office Action issued on December 14, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		PCT Invitation to Pay Additional Fees for PCT/US01/22750, dated March 13, 2002 (Attorney Docket No. 09140.0002-00304).	
		PCT International Search Report for PCT/US01/22750, dated July 19, 2002 (Attorney Docket No. 09140.0002-00304).	
		PCT Written Opinion for PCT/US01/22750, dated July 23, 2002 (Attorney Docket No. 09140.0002-00304).	
		PCT International Preliminary Examination Report for PCT/US01/22750, dated October 8, 2002 (Attorney Docket No. 09140.0002-00304).	
		Office Action issued on November 28, 2005 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed on December 21, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01).	
		Response to Office Action filed on July 25, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01).	
		Office Action issued on October 25, 2005, in U.S. Appl. No. 10/954,182 (Attorney Docket No. 09140-0016-01000).	
		Response to Office Action filed on November 8, 2005, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on February 13, 2006, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Response to Office Action filed on January 3, 2006 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00).	
		PCT International Preliminary Examination Report mailed April 15, 2004 in PCT/US03/24809 (Attorney Docket No. 09140-0025-00304).	
		Office Action issued on December 2, 2005 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	
		Specification and Preliminary Amendment as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0030-01).	
		Office Action issued on March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	
		Response to Office Action dated July 25, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00).	
		Response to Office Action filed January 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US



Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	3	of	3

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		PCT International Search Report and Written Opinion for Application No. PCT/US2004/014524 dated March 2, 2005 (Attorney Docket No. 09140.0033-00304).	
		PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014524, dated December 8, 2005 (Attorney Docket No. 09140.0033-00304).	
		PCT International Search Report for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304).	
		PCT Written Opinion for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304).	
		PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014523, dated December 8, 2005 (Attorney Docket No. 09140.0034-00304).	
		Specification as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0042-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 December 2004 (09.12.2004)

PCT

(10) International Publication Number
WO 2004/106581 A2

(51) International Patent Classification[7]: C23C 14/08, 14/34

(21) International Application Number: PCT/US2004/014523

(22) International Filing Date: 21 May 2004 (21.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/473,379 23 May 2003 (23.05.2003) US

(71) Applicant (*for all designated States except US*): SYMMORPHIX, INC. [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): DEMARAY, Richard, Ernest [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). NARASIMHAN, Mukundan [IN/US]; 293 Bluefield Drive, San Jose, CA 91536 (US).

(74) Agent: GARRETT, Arthur, S.; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street N.W., Washinton, D.C. 20005-3315 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/106581 A2

(54) Title: TRANSPARENT CONDUCTIVE OXIDES

(57) Abstract: A method of deposition of a transparent conductive film from a metallic target is presented. A method of forming a transparent conductive oxide film according to embodiments of the present invention include depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias, and controlling at least one process parameter to affect at least one characteristic of the conductive oxide film. The resulting transparent oxide film, which in some embodiments can be an indium-tin oxide film, can exhibit a wide range of material properties depending on variations in process parameters. For example, varying the process parameters can result in a film with a wide range of resistive properties and surface smoothness of the film.

BEST AVAILABLE COPY

Transparent Conductive Oxides

Related Applications

[0001] The present application claims priority to U.S. Provisional Application 60/473,379, "Transparent Conductive Oxides from a Metallic Target," by R. Ernest Demaray and Mukundan Narasimhan, filed on May 23, 2003, herein incorporated by reference in its entirety.

Background

1. Field of the Invention

[0002] The present invention is related to deposition of oxides on a substrate and, in particular, deposition of transparent conductive oxides.

2. Discussion of Related Art

[0003] Transparent conductive oxides have a wide variety of uses, including applications to solar cells, organic light emitting diodes (OLEDs), electric field devices, current devices (i.e. touch screens), energy efficient windows, conductive anti-reflective devices, electromagnetic interference shields, heaters, transparent electrodes, coatings for cathode ray tube (CRT) displays, to name only a few. Another important application is for touch sensitive MEMS devices, such as those used, for example, in fingerprint sensors and such. In many cases, the electrical properties of the conducting film is of great importance.

[0004] Specifically, for OLED applications, films deposited with current technologies are generally rough, resulting in stress risers and field concentration issues, that can cause leakage. Further, asperities in the resulting film can induce lifetime dependent defects in nearest neighbor films that can shorten device lifetimes. Additionally, the brightness of the emergent light from the OLED can be reduced.

[0005] Transparent conductive oxides have been deposited from ceramic targets by RF magnetron sputtering. However, the surface of properties of the resulting films often include nodules or asperites which can cause arcing, defects, surface roughness, and other deleterious effects in the resulting film. Additionally, ceramic targets tend to be more expensive to produce than metallic targets.

[0006] Previous attempts at deposition of transparent conductive oxides, for example indium tin oxide (ITO), with metallic targets have presented numerous

problems, including small process windows, problems in process controllability, a disappearing anode effect, and particle deposition on the film. Such attempts have been abandoned. Deposition with ceramic targets has also been difficult, including problems with particles, nodule formation, and arching during deposition. In both cases, film smoothness has presented major difficulties. Additionally, control of film parameters such as, for example, resistivity and transparency has been difficult.

[0007] Therefore, there is need for cost effective deposition of smoother layers of transparent conductive oxides with greater control over layer properties such as resistivity and transparency.

Summary

[0008] In accordance with the present invention, a method of depositing of a transparent conductive film from a metallic target is presented. A method of forming a transparent conductive oxide film according to embodiments of the present invention includes depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias, and controlling at least one process parameter to provide at least one characteristic of the conductive oxide film at a particular value.

[0009] A method of depositing a transparent conductive oxide film on a substrate according to some embodiments of the invention, then, includes placing the substrate in a reaction chamber, adjusting power to a pulsed DC power supply coupled to a target in the reaction chamber, adjusting an RF bias power coupled to the substrate, adjusting gas flow into the reaction chamber, and providing a magnetic field at the target in order to direct deposition of the transparent conductive oxide film on the substrate in a pulsed-dc biased reactive-ion deposition process, wherein the transparent conductive oxide film has a particular characteristic.

[0010] The resulting transparent oxide film, which can be deposited according to some embodiments of the present invention, can be an indium-tin oxide (ITO) film. An ITO film can have a wide range of material properties depending on variations in process parameters. For example, varying the process parameters according to some embodiments of the present invention can result in a wide range of resistive properties and surface smoothness of the film.

[0011] These and other embodiments of the invention are further discussed below

with reference to the following figures.

Short Description of the Figures

[0012] Figures 1A and 1B illustrate a pulsed-DC biased reactive ion deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[0013] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B

[0014] Figure 3A shows an Atomic Force Microscopy (AFM) image of an indium-tin-oxide (ITO) process according to some embodiments of the present invention.

[0015] Figure 3B shows an Atomic Force Microscopy (AFM) image of another ITO process deposited using a process according to some embodiments of the present invention.

[0016] Figure 4 shows the variation of bulk resistivity of an ITO layer according to some embodiments of the present invention as a function of the oxygen flow for two different target powers before and after a 250 °C anneal in vacuum.

[0017] Figure 5 shows the variation of the sheet resistance of an ITO layer according to some embodiments of the present invention as a function of the oxygen flow used for two different target powers before and after a 250 °C anneal in vacuum.

[0018] Figure 6 shows the target current and voltage (min and max) as a function of oxygen flow.

[0019] Figure 7 shows the thickness change in layers of ITO according to embodiments of the present invention as a function of oxygen flow.

[0020] Figure 8 illustrates the relationship between oxygen flow and oxygen partial pressure for a metallic target.

[0021] Figures 9A-9D illustrate the smoothness of transparent conductive oxides deposited with ceramic targets according to the present invention.

[0022] In the figures, elements having the same designation have the same or similar function.

Detailed Description

[0023] Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films are deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101863.

[0024] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These Komatsu reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[0025] Apparatus 10 includes target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[0026] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10,

the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[0027] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[0028] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[0029] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[0030] However, both RF and pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications. By applying a RF bias on wafer 16 during deposition, the deposited film can be densified by energetic ion bombardment and the columnar structure can be substantially eliminated.

[0031] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between -50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of

apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 600 mm.

[0032] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

[0033] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[0034] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction,

density, transmission or absorptivity.

[0035] Target 12 can be formed of any materials. Typically metallic materials, for example, include combinations of In and Sn. Therefore, in some embodiments, target 12 includes a metallic target material formed from intermetallic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetallics. *See* U.S. Application Serial No. 10/101,341. Typical ceramic target materials include alumina, silica, alumina silicates, and other such materials.

[0036] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 to 20 individual tiles. Tiles can be finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[0037] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as

chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0038] Reactive gases that provide a constant supply of ionic oxygen to keep the target surface oxidized can be provided to expand the process window. Some examples of the gases that can be utilized for controlling surface oxidation are CO_2, water vapor, hydrogen, N_2O, fluorine, helium, and cesium. Additionally, a feedback control system can be incorporated to control the oxygen partial pressure in the reactive chamber. Therefore, a wide range of oxygen flow rates can be controlled to keep a steady oxygen partial pressure in the resulting plasma. Other types of control systems such as target voltage control and optical plasma emission control systems can also be utilized to control the surface oxidation of the target. As shown in Figure 1A, power to target 12 can be controlled in a feedback loop at supply 14. Further, oxygen partial pressure controller 20 can control either oxygen or argon partial pressures in plasma 53.

[0039] In some embodiments, transparent conductive oxides can be deposited on various substrates utilizing an inidium-tin (In/Sn) metallic target. A series of depositions on glass in accordance with the present invention is illustrated in Table I. The parameters in the process column of Table I are in the format (pulsed DC power/RF bias power/pulsing frequency/reverse time/deposition time/Ar flow (sccms)/O_2 flow (sccms)). An indium-tin (In/Sn: 90%/10% by weight) target using a reactive-pulsed DC (RPDC) process such as that described in U.S. Application Serial No. 10/101,863 was utilized. A power supply with 2MHz RF bias applied to substrate 16 was utilized in the process. Along with the process parameters for each of the separate depositions, each defined by a "Slot" number in the first column, the target voltage, and target current ranges for each of the depositions is also listed.

[0040] Table 2 shows the results obtained by using the process parameters in Table 1. The results include the sheet resistance, thickness, bulk resistivity, and refractive indices of the resulting films. Again, the first column indicates the slot

number of the deposition. The process for each slot number is reiterated in column 2 of Table 2. The sheet resistance of selected ones of the films resulting from the deposition is listed in the third column and the uniformity of the sheet resistance is indicated in the fourth column. The thickness of the film and its uniformity of each of the films deposited by the indicated process is indicated in the fifth and sixth columns. The bulk resistance of selected ones of the films, ρ, is also indicated. Additionally, the refractive index taken at 632 nm is indicated along with the film uniformity of that index. The comments section of Table 2 indicates whether the resulting film is transparent, translucent, or metallic in character.

[0041] Figure 3A shows the Atomic Force Microscopy (AFM) image of an ITO film produced by the process identified in slot #5 in tables 1 and 2. That process, with particularly low oxygen flow rates (24 sccm), produced a rough film with an Ra of about 70 Å and an Rms of about 90 Å. The film also appears to be metallic with this particular oxygen flow and the film roughness is high. Such a film could be applicable to large surface area requirements, for example solar cell applications. Wile not being limited by any particular theory, it is suspected that the roughness of this film reflects the sub-stoichiometric nature of the film caused by insufficient oxygen flow in the plasma. As can be seen in Figure 3B, where the oxygen flow during deposition has been significantly increased to about 36 sccm, the film is smooth.

[0042] Figure 3B shows an Atomic Force Microscopy (AFM) image of an ITO film deposited using the process described in slot #19 of Tables 1 and 2. In that process, the oxygen flow rate is increased to 36 sccm. The film appears to be transparent and conductive and the surface roughness is ~6Å Ra and Rms of about 13 Å, which is acceptable for OLED requirements. As can be seen from Figures 3A and 3B, variation in oxygen partial pressure (as indicated by increased flow rate) has a large influence on the characteristics of the resulting deposited film.

[0043] The resistivity of the film layer and the smoothness of the film layer can be related. In general, the higher the resistivity of the film layer, the smoother the film layer. Figure 4 shows the variation of bulk resistivity of the ITO as a function of the oxygen flow rate used for two different target powers before and after a 250 °C anneal

in vacuum. The bulk resistivity of the film exhibits a sudden transition downward as the oxygen flow rate is lowered. This transition occurs when the target surface becomes metallic from being poisoned with oxygen. The data utilized to form the graph shown in Figure 4 has been taken from Tables 1 and 2.

[0044] Figure 5 shows the variation of the sheet resistance of an ITO film as function of the O_2 flow used for two different target powers before and after a 250C anneal in vacuum. As shown in Figure 5, the sheet resistance follows similar trends as the bulk resistivity of the film.

[0045] Figure 6 shows the target current and voltage (min and max) as a function of the oxygen flow rate. The target voltage increases as the oxygen flow rate is lowered. It could be seen here that at a 40 sccm oxygen flow rate through repeated depositions, the target voltage is not constant. This illustrates the utility of a target voltage feedback control system that adjusts the power supplied to target 12 to hold the target voltage constant. Therefore, as shown in Figure 1A, PDC power 14 can include feedack loop to control the voltage on target 12.

[0046] Figure 7 shows the thickness change of a resulting film as a function of oxygen flow rate in sccm. The thickness of the film increases as the oxygen flow decreases but this could make opaque metallic films and so choosing the correct oxygen flow and utilizing an oxygen flow feedback control system to control material characteristics such as, for example, transparency or conductivity can be desirable.

[0047] In some embodiments, instead of oxygen flow rate, oxygen partial pressure can be controlled with a feedback system 20 (see Figure 1A). Controlling the oxygen partial pressure can provide better control over the oxygen content of the plasma, and therefore the oxygen content of the resulting films, and allows better control over the film characteristics. Figure 8 illustrates the relationship between the flow rate and partial pressure. As can be seen from Figure 8, in order to reach the saturated region (e.g., when target 12 is completely poisoned with oxygen), no increase in flow rate is required. In some embodiments, reactor 10 can include a partial pressure feedback loop controller 20 that controls the oxygen flow in order to maintain a desired partial pressure of oxygen in the plasma. Such a controller can be the IRESS system, that can be purchased from Advanced Energy, Inc., Ft. Collins, Colorado. It has been

found that film parameters such as resistivity, smoothness, and transparency can be highly dependent on oxygen partial pressures, and therefore these characteristics of the resulting deposited layer can be controlled by adjusting the oxygen partial pressures.

[0048] Some embodiments of the present invention can be deposited with ceramic targets. An example target is an ITO (In/Sn 90/10) ceramic target can be utilized. Table 3 illustrates some example processes for deposition of ITO utilizing a ceramic target according to the present invention. Bulk resistivity, sheet resistance, resistance, thicknesses, deposition rates, and index of refraction of the resulting films are shown along with the process parameters utilized in the deposition. Figure 9A shows an AFM depiction of a transparent conductive oxide film corresponding to run #10 in Table 3. Figure 9B shows an AFM depiction of a transparent conductive oxide film corresponding to run #14 in Table 3. Figure 9C shows an AFM depiction of a transparent conductive oxide film corresponding to run #16 in Table 3. Figure 9D shows an AFM depiction of a transparent conductive oxide film layer corresponding to run #6 in Table 3.

[0049] Figures 9A through 9D illustrate the roughnesses of selective depositions of ITO deposited utilizing the ceramic target. In Figure 9A, the roughest surface shown, the film was deposited using 3kW RF power, 100W bias, 3 sccm O_2 and 60 sccm Ar at a temperature of 280 °C. The layer grew to a thickness of 1200 Å in 100 seconds of deposition time and exhibited a sheet resistance of 51 ohms/sq. The roughness illustrated in Figure 9A is characterized by an Ra=2.3 nm and R_{MS} of 21 nm.

[0050] The ITO film shown in Figure 9B was deposited using 3 kW RF power, 300 W bias, 3 sccm O_2 and 60 sccm Ar at a temperature of 280 °C. The layer illustrated in Figure 9B grew to a thickness of 1199 Å in 100 sec. The layer in Figure 9B exhibited a sheet resistance of 39 ohms/sq. The roughness illustrated in Figure 9B is characterized by an Ra=1.1 nm and Rmax of 13 nm.

[0051] The ITO film shown in Figure 9C was deposited using 3 kW RF power, 300 W bias, 3 sccm O_2, 30 sccm Ar at a temperature of 280 °C. The layer grew to a thickness of 1227 Å in 100 seconds of deposition time and exhibited a sheet resistance

of 57 ohms/sq. The roughness illustrated in Figure 9C can be characterized by an Ra=0.88 nm and a Rmax of 19.8 nm.

[0052] Figure 9D was deposited using 1.5 kW RF power, 300 W bias, 0 sccm O_2, 30 sccm Ar at a temperature of 280 C. The layer grew to a thickness of 580 Å in 100 seconds of deposition time and exhibited a sheet resistance of 106 ohms/sq. The roughness illustrated in Figure 9C can be characterized by an Ra=0.45 nm and an Rmax of 4.6 nm.

[0053] Utilizing the example depositions described herein, the roughness and resistivity of a transparent oxide film can be tuned to particular applications. In general, particularly high resistivities can be obtained, which are useful for touch sensitive devices. As shown in Table 3, the sheet resistance ranged from about 39 Ω/sq for trial # 14 to a high of 12,284 Ω/sq for trial #1. Careful variation of the process parameters, therefore, allow control of sheet resistance over an extremely broad range. Low resistivities can be obtained by adjusting the process parameters for uses in devices such as OLEDS and MEMS display devices. As is illustrated in Table 3, the bulk resistivity can be controlled to be between about 2E-4 micro-ohms-cm to about 0.1 micro-ohms-cm. Additionally, other parameters such as refractive index and transparency of the film can be controlled.

[0054] Further, deposition of transparent conductive oxide layers, for example ITO, can be doped with rare-earth ions, for example erbium or cerium, can be utilized to form color-conversion layers and light-emission sources. In some embodiments, a rare-earth doped target can be made in a single piece to insure uniformity of doping. Co-doping can be accomplished in the target.

[0055] Similar processes for other metallic conductive oxides can also be developed. For example, deposition of zinc oxide films. Further, as can be seen in the examples shown in Table 3, low temperature depositions can be performed. For example, transparent conductive oxides according to the present invention can be deposited at temperatures as low as about 100 °C. Such low temperature depositions can be important for depositions on temperature sensitive materials such as plastics.

[0056] Other thin film layers according to the present invention include deposition of other metal oxides to form conducting and semi-conducting films. Thin films

formed according to the present invention can be utilized in many devices, including, but not limited to, displays, photovoltaics, photosensors, touchscreens, and EMI shielding.

[0057] Embodiments of the invention disclosed here are examples only and are not intended to be limiting. Further, one skilled in the art will recognize variations in the embodiments of the invention described herein which are intended to be included within the scope and spirit of the present disclosure. As such, the invention is limited only by the following claims.

Table I

Slot #	Process	Target Voltage (V)		Target Current (Amps)	
		Min	Max	Mix	Max
14	1.5kw/100w/200khz/2.2μs/300s/20Ar/80O_2	244	252	5.94	6.14
15	1.5kw/100w/200khz/2.2μs/300s/20Ar/40O_2	254	263	5.7	5.9
17	1.5kw/100w/200khz/2.2μs/300s/20Ar/40O_2	252	260	5.76	5.96
19	1.5kw/100w/200khz/2.2μs/300s/20Ar/36O_2	254	263	5.72	5.92
21	1.5kw/100w/200khz/2.2μs/300s/20Ar/30O_2	255	268	5.76	5.9
1	1kw/100w/200khz/2.2μs/300s/20Ar/ 80O_2	224	233	4.32	4.5
2	1kw/100w/200khz/2.2μs/300s/20Ar/ 36O_2	231	243	4.12	4.3
3	1kw/100w/200khz/2.2μs/300s/20Ar/ 32O_2	232	242	4.12	4.28
4	1kw/100w/200khz/2.2μs/300s/20Ar/ 28O_2	237	243	4.1	4.22
5	1kw/100w/200khz/2.2μs/300s/20Ar/ 24O_2	233	243	4.1	4.34
6	1kw/100w/200khz/2.2μs/300s/20Ar/ 28O_2	231	245	4.12	4.3

Table II

Slot #	Process	Rs (Ohms/ Sq)	Rs unif %	Th (nm)	Th std 1sig	Bulk Rho (μOhm-cm)	R.I (@632nm)	R.I Unif (%)	Comments
14	1.5kw/100w/200khz/2.2μs/ 300s/20Ar/80O2			38.59	0.16		1.980758	0.000005	transparent
15	1.5kw/100w/200khz/2.2μs/ 300s/20Ar/40O2	94112	2	57.28	0.51	539073.5	1.951452	0.029342	translucent
17	1.5kw/100w/200khz/2.2μs/ 300s/20Ar/40O2	33927	60.282	58.48	1.37	198405.1	1.936166	0.040957	translucent
19	1.5kw/100w/200khz/2.2μs/ 300s/20Ar/36O2	7335.32	72.49	67.75	1.03	49696.8	1.980746	0.000018	translucent
21	1.5kw/100w/200khz/2.2μs/ 300s/20Ar/30O2	22.3507	2.995	80		178.8			metallic
1	1kw/100w/200khz/2.2μs/ 300s/20Ar/80O2			26.69	0.32		1.980326	0.00096	transparent
2	1kw/100w/200khz/2.2μs/ 300s/20Ar/36O2			36.4	0.13		1.980756	0.000003	transparent
3	1kw/100w/200khz/2.2μs/ 300s/20Ar/32O2			39.3	0.15		1.980761	0	transparent
4	1kw/100w/200khz/2.2μs/ 300s/20Ar/28O2			44.02	0.24		1.98076	0.000001	transparent
5	1kw/100w/200khz/2.2μs/ 300s/20Ar/24O2	58.1031	7.467	50		290.5			metallic
6	1kw/100w/200khz/2.2μs/ 300s/20Ar/28O2	58.0992	10.566	45		261.4			metallic

Table III

Trial	Run (sec)	Target Power (kW)	Bias/ W	O2	Ar	T (oC)	Rs (Ohms/Sq)	Rs (non-unif)	Bulk Rho (uOhmcm)	Thickness (Å)	n	DepRate (A/sec)	Target /V	Target/I
14	100	3	300	3	60	280	38.69	4.07%	4.64E-04	1200	1.864	12		
16	100	3	300	3	30	280	56.90	7.94%	6.98E-04	1227	1.888	12.27	288-308	9.86-10.42
10	100	3	100	3	60	280	50.98	11.89%	6.25E-04	1225	1.933	12.25	265-275	10.92-11.36
4	100	1.5	100	3	30	280	383.62	21.72%	2.09E-03	543.9	2.016	5.439	238-251	5.98-6.32
8	100	1.5	300	3	30	280	504.02	7.23%	2.44E-03	483.5	2.082	4.835	239-250	5.98-6.33
2	100	1.5	100	3	30	280	402.52	26.80%	2.10E-03	520.7	2.056	5.207	225-239	6.46-6.68
6	100	1.5	300	0	30	280	106.21	6.12%	6.17E-04	580.5	1.945	5.805	237-250	5.98-6.38
12	100	3	100	4	30	280	374.34	19.43%	4.18E-03	1116	1.917	11.16	285-300	9.98-10.52
15	100	3	300	4	30	100	6264.69	58.18%	6.81E-02	1087	1.897	10.87	282-304	10.00-10.62
7	100	1.5	200	4	30	100	7509.45	44.14%	2.95E-02	392.3	2.149	3.923	237-250	6.02-632
1	100	1.5	100	4	30	100	12284.82	112.55%	4.78E-02	389.1	2.236	3.891	238-250	6.04-632

Table III (Cont.)

11	100	3	100	3	60	100	631.77	49.40%	7.30E-03	1155	1.958	11.55	266-273	10.96-11.38
9	100	3	100	0	30	100	43.78	7.47%	5.55E-04	1268	1.945	12.68	288-307	9.78-10.42
5	100	1.5	200	3	60	100	1293.53	14.82%	5.88E-03	454.8	2.149	4.548	225-235	6.46-6.68
3	100	1.5	100	4	60	100	4154.43	28.25%	1.78E-02	428.8	2.211	4.288	226-235	6.44-6.64
13	100	3	200	0	60	100	49.05	7.24%	6.16E-04	1256	1.913	12.56	264-275	10.96-11.38
18	100	2.25	100	3	30	100	1476.79	21.54%	1.10E-02	744.5	2.044	7.445	263-277	8.08-8.56
17	100	1.5	150	0	60	100	157.23	8.83%	9.91E-04	630.5	1.931	6.305	225-231	6.48-6.74
19	100	2.25	150	3	60	100	526.72	13.01%	4.29E-03	814.2	2.021	8.142	247-255	8.78-9.14

Claims

We claim:

1. A method of forming a transparent conductive oxide film, comprising:

depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias; and

controlling at least one process parameter to provide at least one characteristic of the conductive oxide film at a particular value.

2. The method of claim 1, wherein controlling at least one process parameter includes controlling the oxygen partial pressure.

3. The method of claim 1, wherein the transparent conductive oxide film includes indiuim-tin oxide.

4. The method of claim 1, wherein the at least one characteristic includes sheet resistance.

5. The method of claim 1, wherein the at least one characteristic includes film roughness.

6. The method of claim 5, wherein the transparent conductive oxide film includes an indium-tin oxide film and the film roughness is characterized by R_a less than about 10 nm with Rms of less than about 20 nm.

7. The method of claim 4, wherein the bulk resistance can be varied between about $2x10^{-4}$ micro-ohms-cm to about 0.1 micro-ohms-cm.

8. The method of claim 1, wherein the at least one process parameter includes a power supplied to a target.

9. The method of claim 1, wherein the at least one process parameter includes an oxygen partial pressure.

10. The method of claim 1, wherein the at least one process parameter includes bias power.

11. The method of claim 1, wherein the at least one process parameter includes deposition temperature.

12. The method of claim 1, wherein the at least one process parameter includes an argon partial pressure.

13. The method of claim 1, further including supplying a metallic target.

14. The method of claim 1, further including supplying a ceramic target.

15. The method of claim 1, wherein the transparent conductive oxide film is doped with at least one rare-earth ions.

16. The method of claim 15, wherein the at least one rare-earth ions includes erbium.

17. The method of claim 15, wherein the at least one rare-earth ions includes cerium.

18. A method of depositing a transparent conductive oxide film on a substrate, comprising:

placing the substrate in a reaction chamber;

adjusting power to a pulsed DC power supply coupled to a target in the reaction chamber;

adjusting an RF bias power coupled to the substrate;

adjusting gas flow into the reaction chamber; and

providing a magnetic field at the target in order to direct deposition of the transparent conductive oxide film on the substrate in a pulsed-dc biased reactive-ion deposition process, wherein the transparent conductive oxide film exhibits at least one particular property.

19. The method of claim 18, wherein at least one particular property of the transparent conductive oxide film is determined by parameters of the pulsed-dc biased reactive ion deposition process.

20. The method of claim 19, wherein the at least one particular property includes resistivity of the transparent conductive oxide film.

21. The method of claim 19, wherein the transparent conductive oxide film includes an indium-tin oxide film.

22. The method of claim 19, wherein the parameters include oxygen partial pressure.

23. The method of claim 19, wherein the parameters include bias power.

24. The method of claim 18, wherein the target can include at least one rare-earth ions.

25. The method of claim 24, wherein the at least one rare-earth ions includes erbium.

26. The method of claim 24, wherein the at least one rare-earth ion includes cerbium.

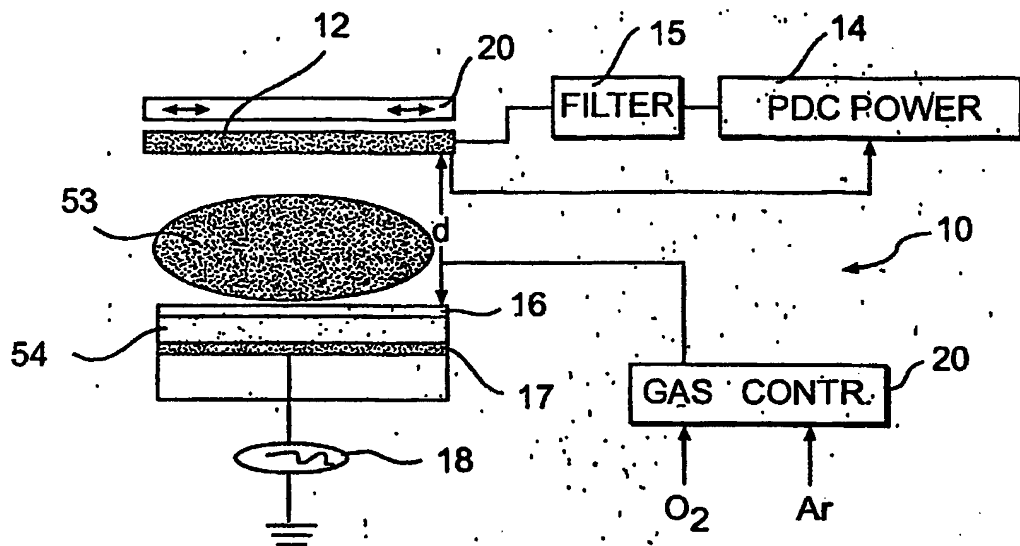


FIG. 1A

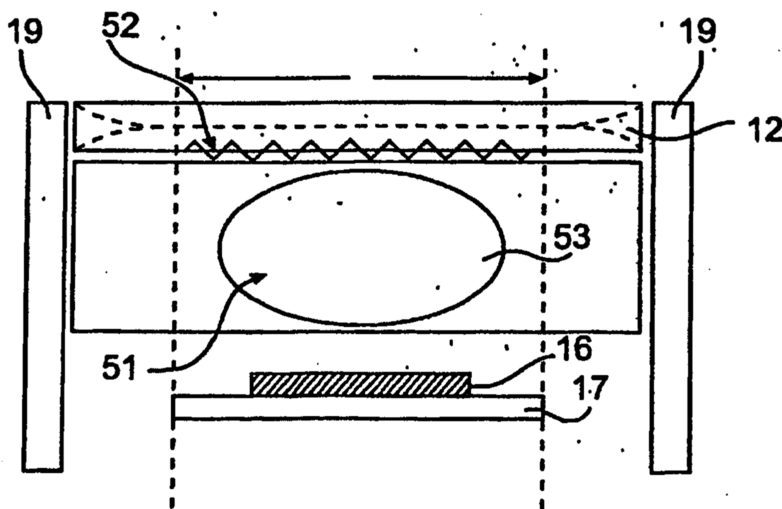


FIG. 1B

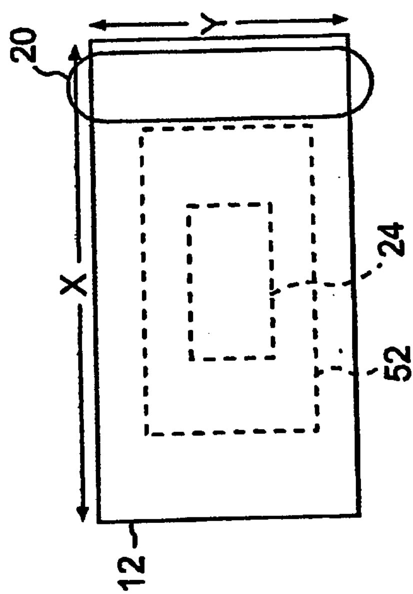


FIG. 2

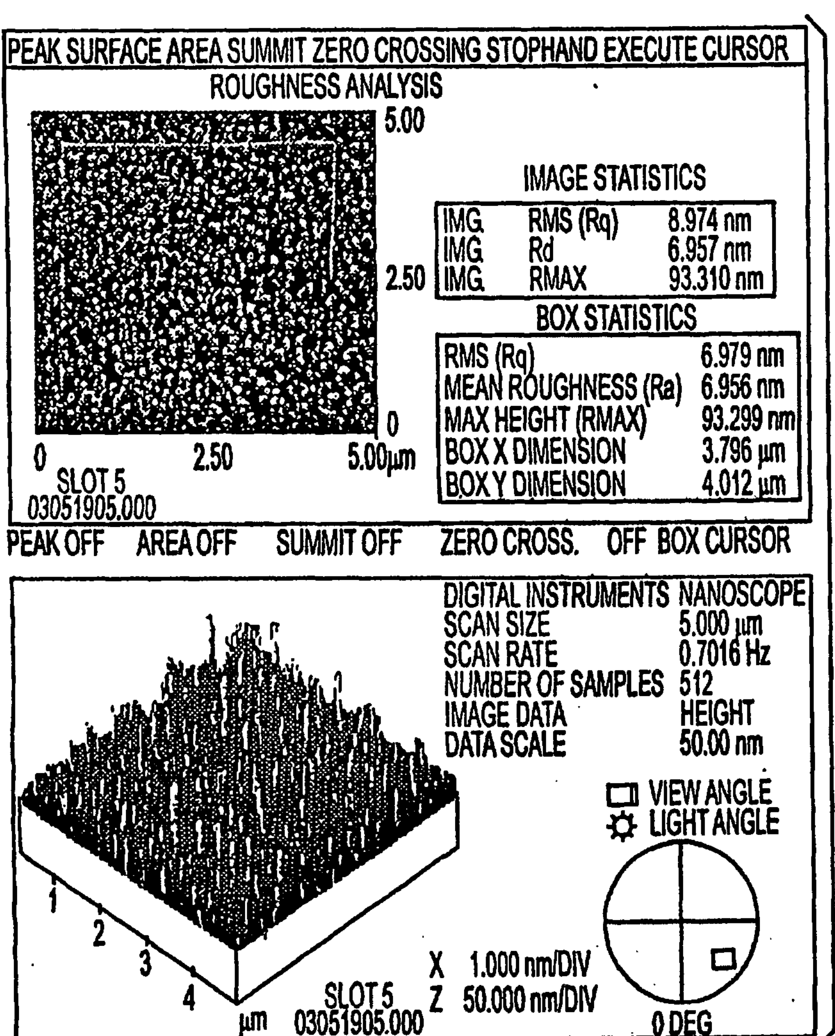


FIG. 3A

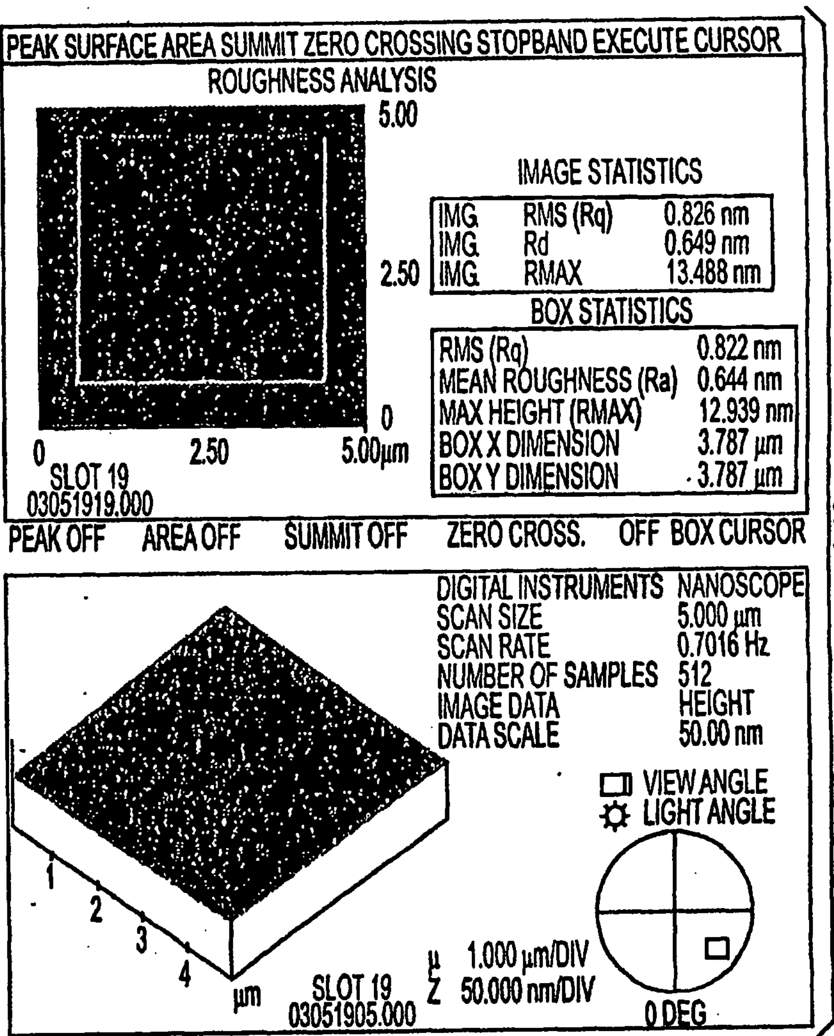


FIG. 3B

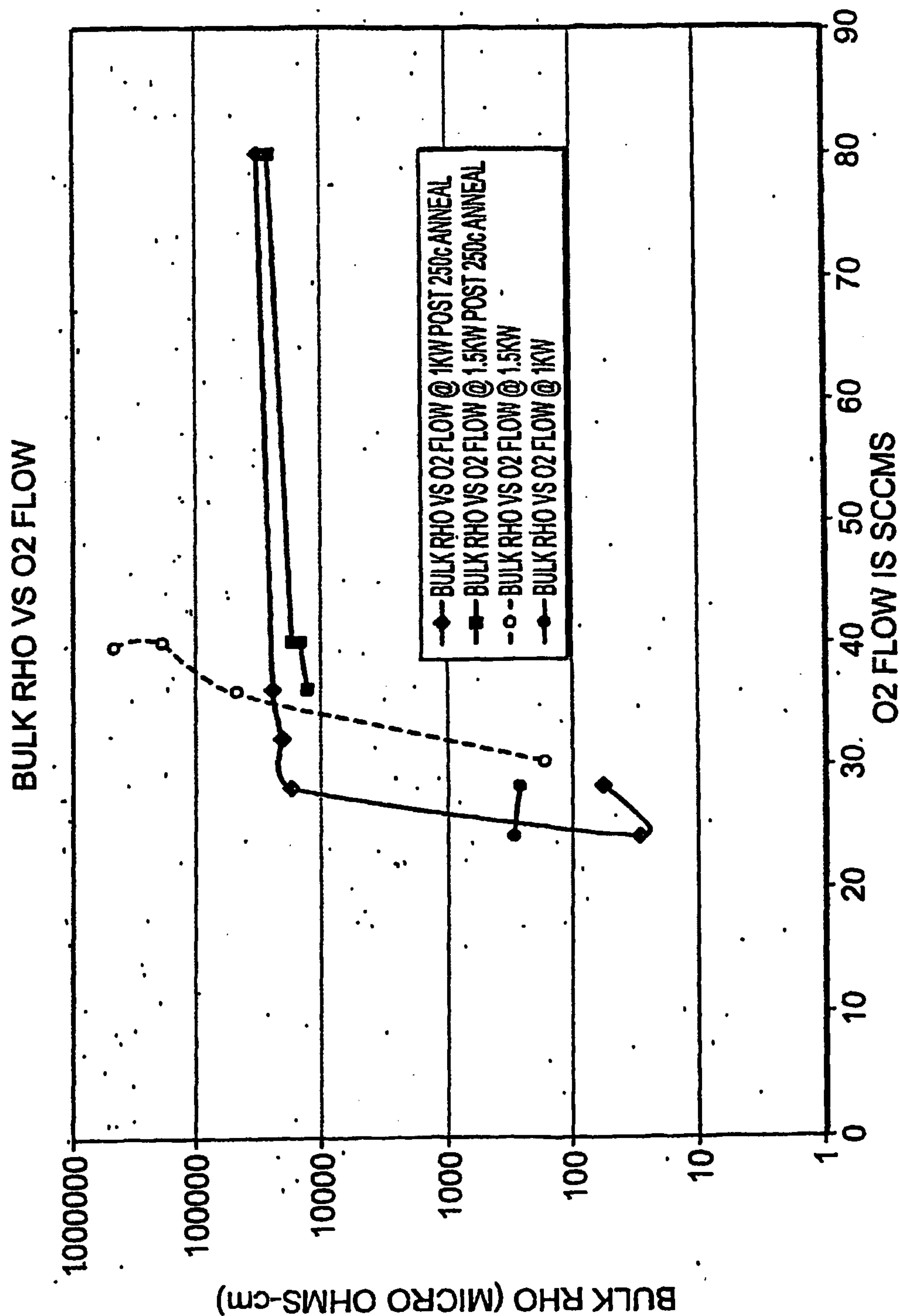


FIG. 4

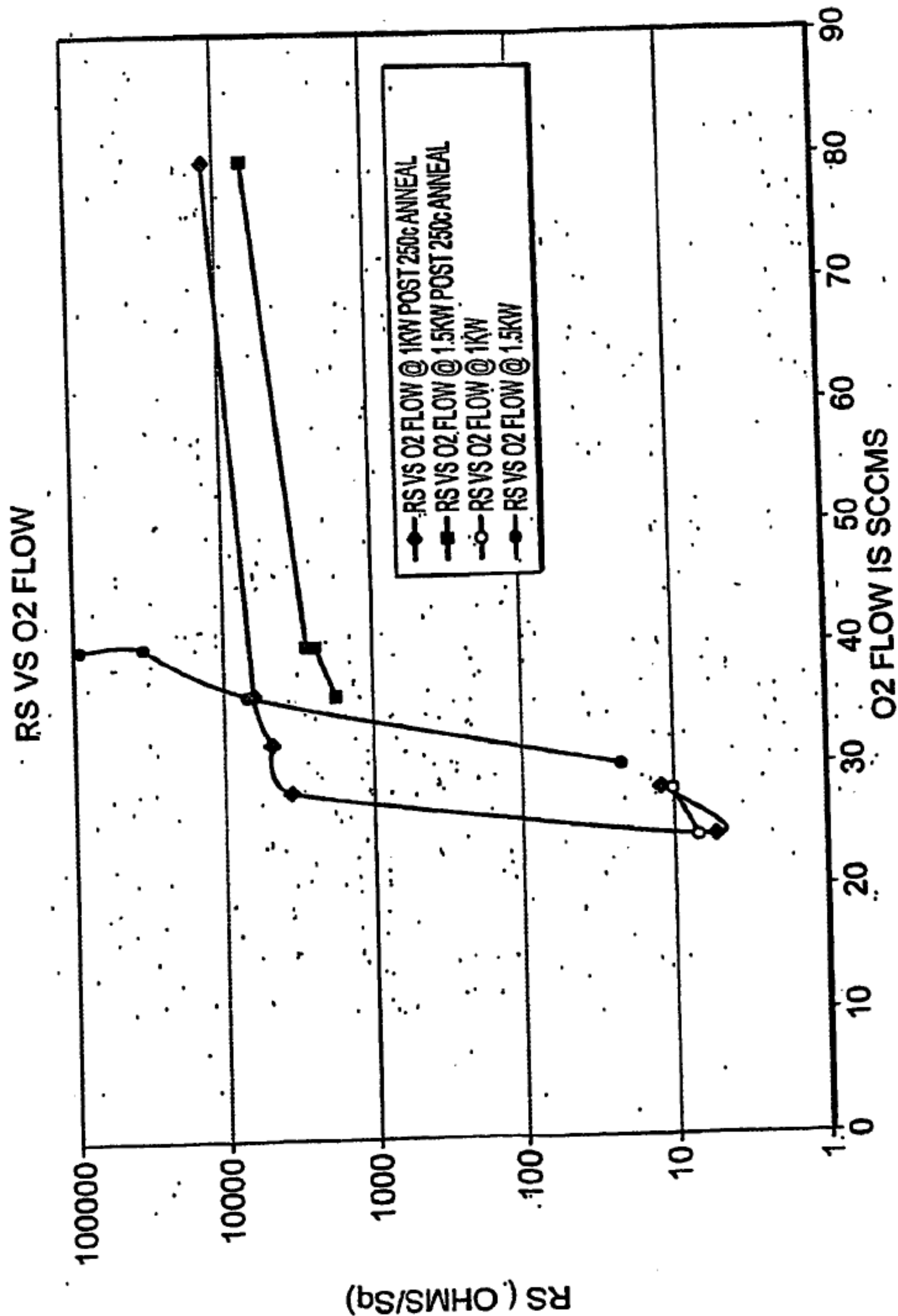


FIG. 5

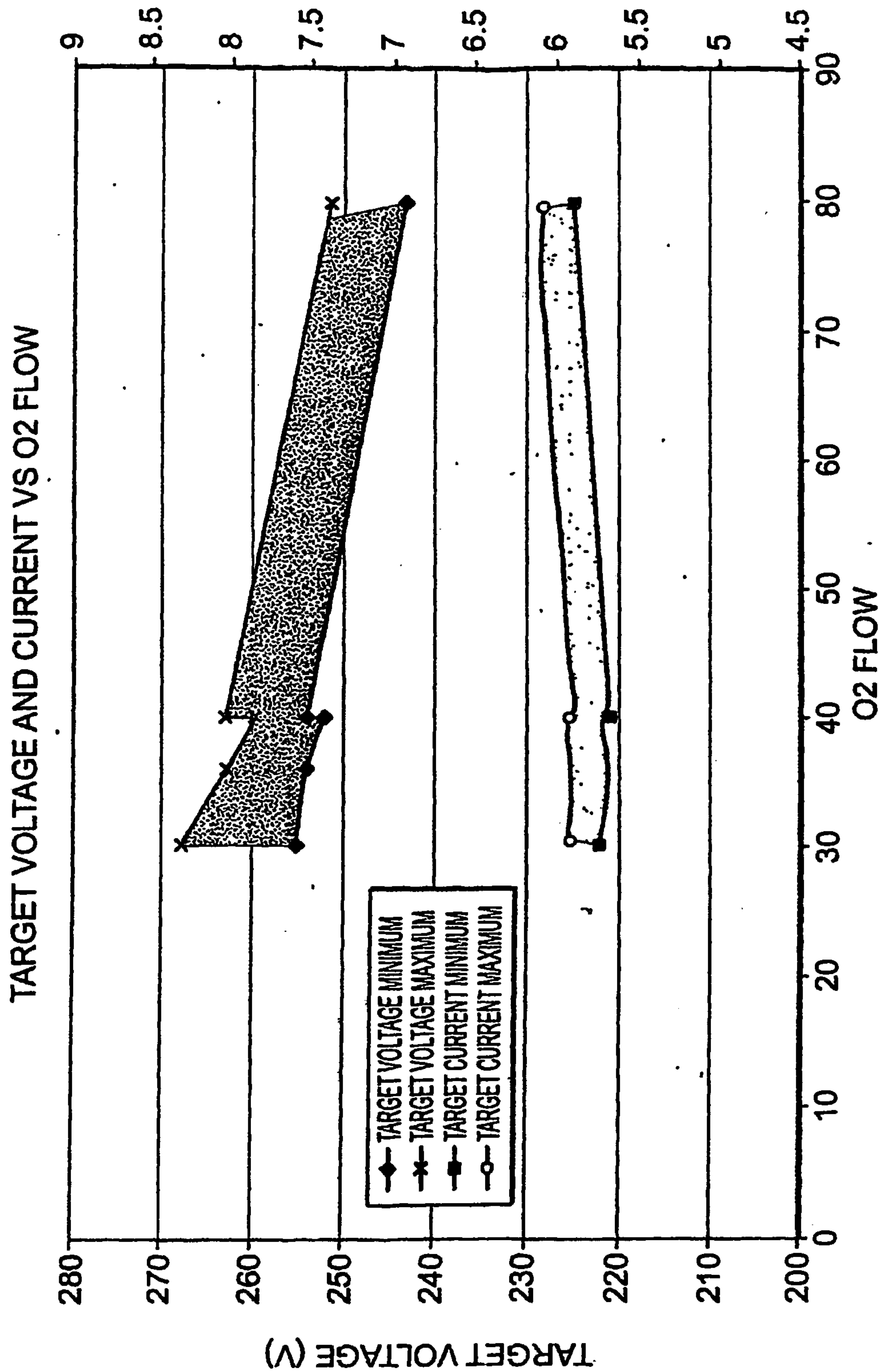


FIG. 6

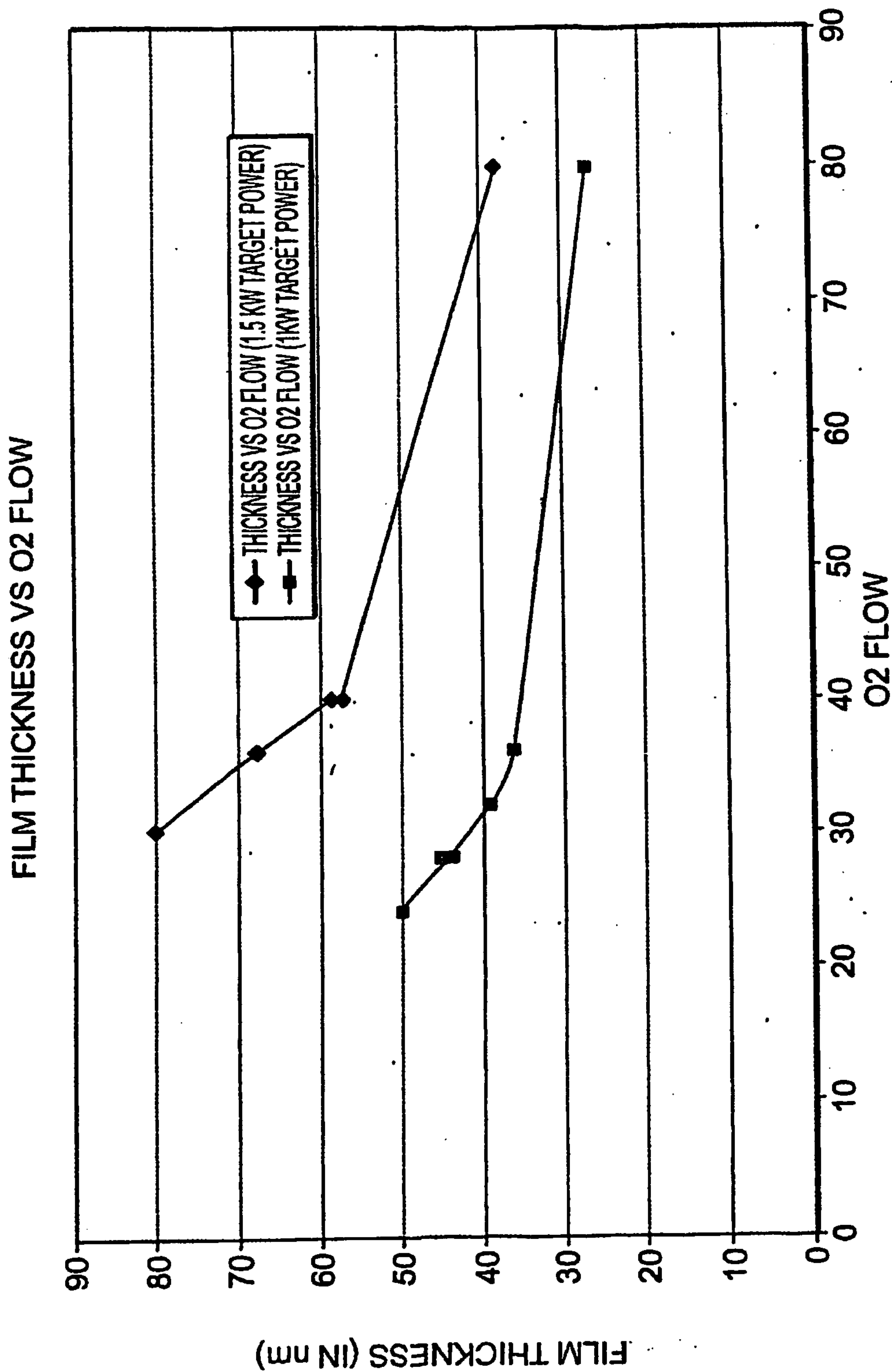


FIG. 7

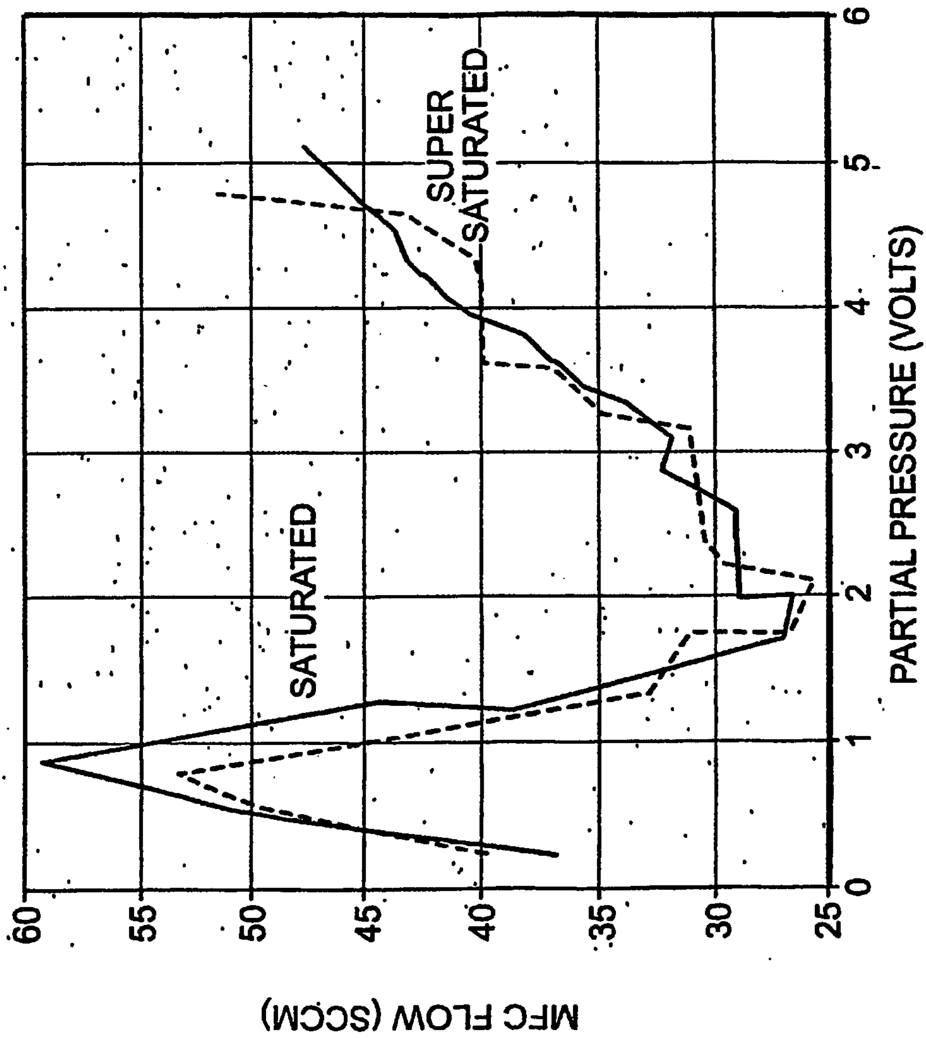


FIG. 8

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 1049 of 1543

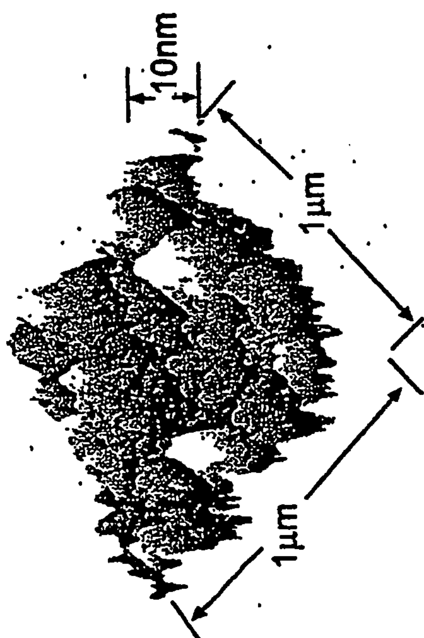


FIG. 9A

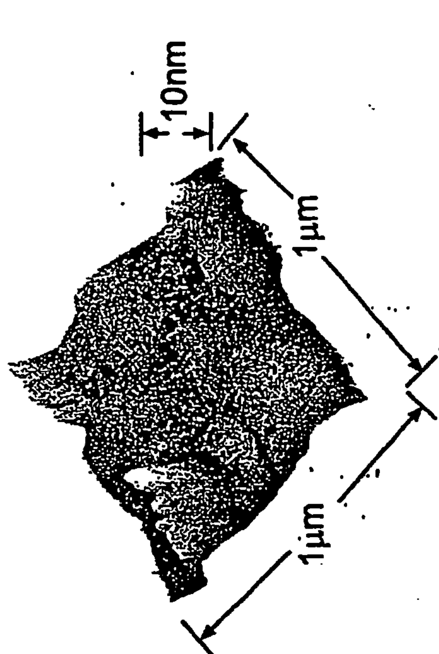


FIG. 9B

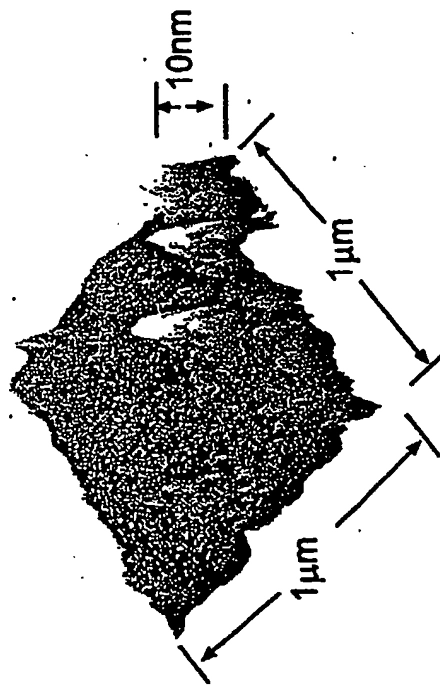


FIG. 9C

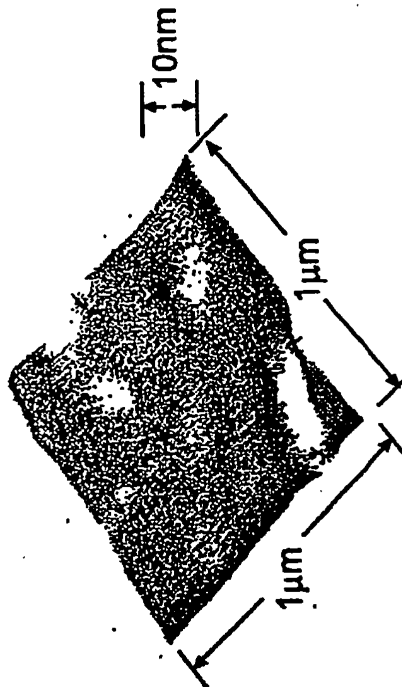


FIG. 9D

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☑ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 December 2004 (09.12.2004)

PCT

(10) International Publication Number
WO 2004/106582 A2

(51) International Patent Classification[7]: C23C 14/14, 14/08, 14/34, H01L 21/316

(21) International Application Number: PCT/US2004/014524

(22) International Filing Date: 21 May 2004 (21.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/473,375 23 May 2003 (23.05.2003) US

(71) Applicant *(for all designated States except US)*: **SYMMORPHIX, INC.** [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **DEMARAY, Richard, Ernest** [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). **ZHANG, Hongmei** [US/US]; 1330 Rodney Drive, San Jose, CA 95118 (US). **NARASIMHAN, Mukundan** [IN/US]; 293 Bluefield Drive, San Jose, CA 95136 (US). **MILONOPOULOU, Vassiliki** [GR/US]; 6160 Paseo Pueblo Drive, San Jose, CA 95120 (US).

(74) Agent: **GARRETT, Arthur, S.**; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street N.W., Washinton, D.C. 20005-3315 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/106582 A2

(54) **Title:** ENERGY CONVERSION AND STORAGE FILMS AND DEVICES BY PHYSICAL VAPOR DEPOSITION OF TITANIUM AND TITANIUM OXIDES AND SUB-OXIDES

(57) **Abstract:** High density oxide films are deposited by a pulsed-DC, biased reactive sputtering process from a titanium containing target to form high quality titanium containing oxide films. A method of forming a titanium based layer or film according to the present invention includes depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate. In some embodiments, the layer is TiO_2. In some embodiments, the layer is a sub-oxide of Titanium. In some embodiments, the layer is Ti_xO_y wherein x is between about 1 and about 4 and y is between about 1 and about 7. In some embodiments, the layer can be doped with one or more rare-earth ions. Such layers are useful in energy and charge storage, and energy conversion technologies.

BEST AVAILABLE COPY

Energy Conversion and Storage Films and Devices by Physical Vapor Deposition of Titanium and Titanium Oxides and sub-Oxides

Related Applications

The present invention claims priority to U.S. Provisional Application Serial No. 60/473,375, "Energy Conversion and Storage Devices by Physical Vapor Deposition of Titanium Oxides and Sub-Oxides," by Richard E. Demaray and Hong Mei Zhang, filed on May 23, 2003, herein incorporated by reference in its entirety.

Background

1. Field of the Invention

[0001] The present invention is related to fabrication of thin films for planar energy and charge storage and energy conversion and, in particular, thin films deposited of titanium and titanium oxides, sub oxides, and rare earth doped titanium oxides and sub oxides for planar energy and charge storage and energy conversion.

2. Discussion of Related Art

[0002] Currently, titanium oxide layers are not utilized commercially in energy storage, charge storage, or energy conversion systems because such layers are difficult to deposit, difficult to etch, are known to have large concentrations of defects, and have poor insulation properties due to a propensity for oxygen deficiency and the diffusion of oxygen defects in the layers. Additionally, amorphous titania is difficult to deposit due to its low recrystalization temperature (about 250 °C), above which the deposited layer is often a mixture of crystalline anatase and rutile structures.

[0003] However, such amorphous titania layers, if they can be deposited in sufficient quality, have potential due to their high optical index, n~2.7, and their high dielectric constant, k less than or equal to about 100. Further, they have substantial chemical stability. There are no known volatile halides and titania is uniquely resistant to mineral acids. Amorphous titania is thought to have the further advantage that there are no grain boundary mechanisms for electrical breakdown, chemical corrosion, or optical scattering. It is also well known that the sub oxides of titanium have unique and useful properties. *See, e.g.*, Hayfield, P.C.S., "Development of a

New Material- Monolithic Ti_4O_7 Ebonix Ceramic", Royal Society Chemistry, ISBN 0-85405-984-3, 2002. Titanium monoxide, for example, is a conductor with a uniquely stable resistivity with varying temperature. Additionally, Ti_2O_3, which can be pinkish in color, is known to have semiconductor type properties. However, these materials have not found utilization because of their difficult manufacture in films and their susceptibility to oxidation. Further, Ti_4O_7 demonstrates both useful electrical conductivity and unusual resistance to oxidation. Ti_4O_7, however, is also difficult to fabricate, especially in thin film form.

[0004] Additional to the difficulty of fabricating titanium oxide or sub oxide materials in useful thin film form, it also has proven difficult to dope these materials with, for example, rare earth ions, in useful or uniform concentration.

[0005] Therefore, utilization of titanium oxide and suboxide films, with or without rare earth doping, has been significantly limited by previously available thin film processes. If such films could be deposited, their usefulness in capacitor, battery, and energy conversion and storage technologies would provide for many value-added applications.

[0006] Current practice for construction of capacitor and resistor arrays and for thin film energy storage devices is to utilize a conductive substrate or to deposit the metal conductor or electrode , the resistor layer, and the dielectric capacitor films from various material systems. Such material systems for vacuum thin films, for example, include copper, aluminum, nickel, platinum, chrome, or gold depositions, as well as conductive oxides such as ITO, doped zinc oxide, or other conducting materials.

[0007] Materials such as chrome-silicon monoxide or tantalum nitride are known to provide resistive layers with 100 parts per million or less resistivity change per degree Centigrade for operation within typical operating parameters. A wide range of dielectric materials such as silica, silicon nitride, alumina, or tantalum pentoxide can be utilized for the capacitor layer. These materials typically have dielectric constants k of less than about twenty four (24). In contrast, TiO_2 either in the pure rutile phase or in the pure amorphous state can demonstrate a dielectric constant as high as 100. *See, e.g.*, R. B. van Dover, "Amorphous Lanthanide-Doped TiO_2 Dielectric Films,"

Appl. Phys Lett., Vol. 74, no. 20, p. 3041-43 (May 17, 1999).

[0008] It is well known that the dielectric strength of a material decreases with increasing value of dielectric constant k for all dielectric films. A 'figure of merit' (FM) is therefore obtained by the product of the dielectric constant k and the dielectric strength measured in Volts per cm of dielectric thickness. Capacitive density of 10,000 to 12,000 pico Farads /mm^2 is very difficult to achieve with present conductors and dielectrics. Current practice for reactive deposition of titanium oxide has achieved a figure-of-merit, FM, of about 50 (k MV/cm). *See* J.-Y. Kim et al., "Frequency-Dependent Pulsed Direct Current Magnetron Sputtering of Titanium Oxide Films," J. Vac. Sci. Technol. A 19(2), Mar/Apr 2001.

[0009] Therefore, there is an ongoing need for titanium oxide and titanium sub-oxide layers, and rare-earth doped titanium oxide and titanium sub-oxide layers, for various applications.

Summary

[0010] In accordance with the present invention, high density oxide films are deposited by a pulsed-DC, biased, reactive sputtering process from a titanium containing target. A method of forming a titanium based layer or film according to the present invention includes depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate. In some embodiments, the layer is TiO_2. In some embodiments, the layer is a sub-oxide of Titanium. In some embodiments, the layer is Ti_xO_y wherein x is between about 1 and about 4 and y is between about 1 and about 7.

[0011] In some embodiments of the invention, the figure of merit of the layer is greater than 50. In some embodiments of the invention, the layer can be deposited between conducting layers to form a capacitor. In some embodiments of the invention, the layer includes at least one rare-earth ion. In some embodiments of the invention, the at least one rare-earth ion includes erbium. In some embodiments of the invention, the erbium doped layer can be deposited between conducting layers to form a light-emitting device. In some embodiments of the invention, the erbium doped layer can be an optically active layer deposited on a light-emitting device. In some embodiments of the invention, the layer can be a protective layer. In some

embodiments, the protective layer can be a catalytic layer.

[0012] In some embodiments of the invention, the layer and a TiO_2 layer can be deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the TiO_2 layer. In some embodiments, the TiO_2 layer can be a layer deposited according to some embodiments of the present invention.

[0013] These and other embodiments of the present invention are further discussed below with reference to the following figures.

Short Description of the Figures

[0014] Figures 1A and 1B illustrate a pulsed-DC biased reactive ion deposition apparatus that can be utilized in the deposition according to the present invention.

[0015] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B.

[0016] Figures 3A and 3B illustrate various configurations of layers according to embodiments of the present invention.

[0017] Figures 4A and 4B illustrate further various configurations of layers according to embodiments of the present invention.

[0018] Figure 5 shows another layer structure involving one or more layers according to the present invention.

[0019] Figure 6 shows a transistor gate with a TiOy layer according to the present invention.

[0020] Figure 7 illustrates the roll-off of the dielectric constant with decreasing film thickness.

[0021] Figure 8 illustrates data points from a bottom electrode that helps reduce or eliminate the roll-off illustrated in Figure 7.

[0022] Figures 9A and 9B illustrate an SEM cross-section of a Ti_4O_7 target obtained from Ebonex™ and an SEM cross section of the $Ti_4O_{6.8}$ film deposited from the Ebonex™ target according to the present invention.

[0023] Figure 10 shows the industry standard of thin-film capacitor performance in comparison with layers according to some embodiments of the present invention.

[0024] Figure 11 shows the performance of various thin films deposited according

to the present invention in a capacitor structure.

[0025] Figure 12 shows a cross-section TEM and diffraction pattern amorphous and crystalline layers of TiO_2 on n++ wafers.

[0026] Figure 13 shows a comparison of the leakage current for TiO_2 films according to embodiments of the present invention with and without erbium ion doping.

[0027] Figures 14A and 14B show a photoluminescence signal measured from a 5000 Å layer of 10% erbium containing TiO_2 deposited from a 10% erbium doped TiO conductive target and a photoluminescence signal measured from the same layer after a 30 minute 250 °C anneal.

[0028] In the figures, elements having the same designation have the same or similar functions.

Detailed Description

[0029] Miniaturization is driving the form factor of portable electronic components. Thin film dielectrics with high dielectric constants and breakdown strengths allow production of high density capacitor arrays for mobile communications devices and on-chip high-dielectric capacitors for advanced CMOS processes. Thick film dielectrics for high energy storage capacitors allow production of portable power devices.

[0030] Some embodiments of films deposited according to the present invention have a combination of high dielectric and high breakdown voltages. Newly developed electrode materials allow the production of very thin films with high capacitance density. The combination of high dielectric and high breakdown voltages produce thick films with new levels of available energy storage according to $E=1/2CV^2$.

[0031] Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent

Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Additionally, deposition of materials is further described in U.S. Patent 6,506,289, which is also herein incorporated by reference in its entirety.

[0032] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering of material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC (PDC) power is supplied to the target and RF power is supplied to the substrate during deposition of a material film. The PDC power supply 14 can be protected from RF bias power 18 by use of a filter 15 coupled between PDC power supply 14 and target 12.

[0033] Apparatus 10 includes a target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. Magnet 20 is scanned across the top of target 12.

[0034] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that depends on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulsed DC magnetron sputtering in apparatus 10.

[0035] Pulsed DC power supply 14 can be any pulsed DC power supply, for example

an AE Pinnacle plus 10K by Advanced Energy, Inc. With this example supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. In some embodiments, the reverse voltage is 10% of the negative target voltage. Utilization of other power supplies will lead to different power characteristics, frequency characteristics, and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted to between 0 and 5 μs.

[0036] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[0037] Therefore, filter 15 can be a 2 MHz band sinusoidal rejection filter. In some embodiments, the bandwidth of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[0038] However, both RF sputtered and pulsed DC sputtered films are not fully dense and may typically have columnar structures. These columnar structures are detrimental to thin film applications. By applying a RF bias on wafer 16 during deposition, the deposited film can be densified by energetic ion bombardment and the columnar structure can be substantially eliminated or completely eliminated.

[0039] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C by introduction of back-side gas in a physical or electrostatic clamping of the substrate, thermo-electric cooling, electrical heating, or other methods of active temperature control. In Figure 1A, a temperature controller 22 is shown to control the temperature of substrate 16. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed

in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimension about 150 mm by 600 mm.

[0040] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, where physical and chemical uniformity provide refractive index uniformity, for example. Figure 2 indicates that region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

[0041] In some embodiments, magnet 20 extends beyond area 52 in one direction, the Y direction in Figure 2, so that scanning is necessary in only one direction, the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[0042] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the surface of target 12, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission, or absorptivity.

[0043] Target 12 can be formed of any materials, but is typically metallic materials such as, for example, combinations of In and Sn. Therefore, in some embodiments,

target 12 includes a metallic target material formed from intermetallic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetallics. *See* U.S. Application Serial No. 10/101,341.

[0044] In several embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 to 20 individual tiles. Tiles are finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of the tiles. The distance between the tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or provide for thermal expansion tolerance during processing, chamber conditioning, or operation.

[0045] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12, can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0046] Figure 3A illustrates deposition of a layer 102 according to the present invention deposited on a substrate 101. In some embodiments, layer 102 can be a conducting protective layer of TiO_y. Figure 3B shows a first layer 102 according to the present invention deposited over a second layer 103, which can also be a layer according to some embodiments of the present invention. In some embodiments, first layer 102 can be a conducting protective layer and second layer 103 can be a titanium or other conducting layer. Layer 103 is deposited on substrate 101.

[0047] The fabrication of high density capacitor and resistor arrays as well as high energy storage solid state devices can be accomplished with embodiments of processes according to the present invention on a wide variety of substrates such as silicon wafers or glass or plastic sheets at low temperature and over wide area. With reference to Figure 3B, layer 102 can be an amorphous film of TiO_2, which is deposited by a process such as that described in U.S. Application Serial No. 10/101,341. Utilization or formation of a conducting layer 103 such as TiO or Ti_4O_7 between a conducting layer of titanium, which is substrate 101, and the dielectric TiO_2 layer 102 is shown in the present invention to substantially reduce or eliminate the 'roll off' of the dielectric constant k with decreasing film thickness below about 1000 Angstroms. Consequently, capacitors fabricated from titanium on low temperature substrates result in high value planar capacitors and capacitor arrays with very high capacitive density and low electrical leakage. Such electrical arrays are useful for shielding and filtering and buffering high frequency and may be used in stationary as well as in portable electronic devices.

[0048] In particular, the low temperature deposition of amorphous titania capacitors provides for the fabrication of integrated passive electronic circuits on plastic and glass. It also provides for the integration of such devices on other electronic devices and arrays at low temperature.

[0049] Similarly, a conducting layer of TiO or Ti_4O_7 as layer 103 in Figure 3B, deposited between a conducting layer of titanium as layer 101 and a layer of titania as layer 102 of Figure 3B can be deposited so as to provide an increase in the surface smoothness by planarization of the titanium in layer 101 or other metallurgical conductive substrate layer 101 of Figure 3B. Consequently, roughness or asperity

based defects can be minimized or eliminated. As an example, charge injection from a metallurgical electrode can be decreased at the interface with a dielectric. The titanium based dielectric layer can be formed on a smooth conducting oxide layer, which according to some theories can prevent charge depletion of the high k dielectric layer, decrease point charge accumulation and support dipole formation at the conductor-dielectric interface, sometimes referred to as dipole coupling. These features are important to prevent the roll-off of the dielectric strength of the dielectric layer as the layer thickness is decreased below about 1000 Å. It is consequently useful in the formation of thin layers having high capacitive value.

[0050] A thick film of dielectric material may be deposited having a high dielectric strength for the storage of electrical energy. Such energy is well known to increases with the square of the applied Voltage. For example, in Figure 3B layer 102 can be a thick layer of dielectric according to the present invention. Layer 104 in Figure 3B, then, can be a conducting layer deposited on layer 102 while layer 103 is a conducting layer deposited between a substrate 101 and layer 102 to form a capacitor. As the dielectric strength of the amorphous dielectric layer of layer 102 increases in proportion to it's thickness, the energy storage also increases effectively as the square of the thickness. It is shown that both record capacitance density and electrical energy storage density result for films according to the present invention. For thick film applications, smoothing of the metallurgical electrode by a conductive sub-oxide can decrease leakage at the interface in high voltage applications.

[0051] Protective conductive sub-oxide films of titanium can also be deposited on conductive and insulating substrates to protect them from harmful chemical attack while acting as conducting layers. For example, as illustrated in Figure 3A layer 102 can be a protective conductive sub-oxide film deposited on substrate 101. These layers can be used to protect an electrode, which can be substrate 101, from oxidation in the gas phase and in the liquid phase as well as the solid phase. Examples of such applications include electrolytic energy storage or as an active electrode surface for catalytic reactions and energy conversion such as in the oxygen-hydrogen fuel cell. Transparent oxides and semi-transparent sub-oxides can be deposited sequentially so that the conducting sub-oxides are protected by the transparent non-conducting oxides

for purposes of photovoltaic or electrochromic energy conversion devices. It is well known that organic based photovoltaic cells are enhanced by the presence of titania in the organic absorbing layer. Layers according to the present invention can be utilized both for the conductivity of electricity, the enhancement of the organic absorber, as well as the overall protection of the device.

[0052] TiO_2 layers, for example, can photocatylitically produce ozone in the presence of sunlight. However, in the course of such activity, the TiO_2 layer can build up a fixed charge. Absent a metallurgical conductor, as shown in Figure 3B layer 102 can be a catalytic oxide while layer 103 can be a conducting suboxide while substrate 101 is a dielectric substrate such as glass or plastic and layer 104 is absent. In such a two-layer device, where the oxide is provided on the surface of the sub-oxide, the sub-oxide can form an electrode so that electric charge can be conducted to the oxide layer for enhanced photochemical photalysis such as in an AC device, or for the purpose of charge dissipation.

[0053] Protective conductive sub-oxide films of titanium can also be deposited on conductive and insulating substrates to protect them from harmful chemical attack while acting as conducting layers for electrolytic energy storage or as an active electrode for catalytic energy conversion. Transparent and semi-transparent oxides can be deposited sequentially so that the conducting suboxides are protected by the transparent non-conducting oxide for purposes of protecting layered devices. Alternatively, it is well known that certain crystalline suboxides of titania, collectively referred to as Magnelli phases, posses unusual levels of durability to mineral acid solutions and other corrosive gassious or liquid environments. Hayfield, P.C.S., "Development of a New Material- Monolithic Ti_4O_7 Ebonix Ceramic", Royal Society Chemistry, ISBN 0-85405-984-3, 2002 describes these in detail and discusses many applications of the monolithic suboxides. Hayfield also explains that the basis of conductivity of sub-oxides is due to the presence of the Ti^{+2} cation in layers having the stoichometry TiO. Of the several compositions, Ti_4O_7 in particular is known to posses both useful conductivity and also chemical resistance to both anodization, which would decrease it's conductivity, as well as reduction, which would decrease it's chemical durability. Therefore, as shown in Figure 3A, substrate 101 can be a

metallurgical substrate such as aluminum or titanium and layer 102 can be Ti_4O_7. An example is the catalytic of H_2 and O_2 to make water and electricity.

[0054] In this disclosure, an amorphous coating layer according to embodiments of the present invention, derived from a crystalline target of Ti_4O_7, can obtain a similar composition as described above, measured as $Ti_4O_{6.8}$. Similar useful levels of chemical conductivity can be obtained. The sputtered film was dense, adherent, and also displayed robust durability to immersion in concentrated mineral acid and oxidizing solution. A similar material was deposited directly from a titanium target using the subject reactive sputtering process.

[0055] The increased density of the amorphous sputtered film according to embodiments of the present invention such as film 102 shown in Figure 3A can provide high levels of impermeability. Planarization can also be achieved by layer 102 over structures on substrate 101. Layer 102 can therefore achieve 'atomic' smooth surfaces on otherwise rough substrates. The sputtering process according to the present invention also allows the formation of a continuous range of stoicheometry between what are, in their crystalline environment, 'line compounds' with whole number integer ratios of titanium cations to oxygen atoms. In the present amorphous films, as long as one Ti^{+2} has a nearest neighbor cation in the amorphous glass matrix with the Ti^{+2} valence, conductive paths will be available in the sputtered film.

[0056] The sputtered sub-oxides also have the advantage that they can be layered, without removal from the vacuum system, with metallic titanium, other sub-oxides, as well as TiO_2 for connection to electrical conduction and insulation. This feature provides the utility of multiplayer depositions by integrated processes in one vacuum chamber. Where thick films of a particular sub-oxide are desired, a target 12 (Figure 1) fabricated of the desired sub-oxide can be utilized. TiO is particularly a good conductor and possesses very stable resistivity with temperature variation. Ti_2O_3 is a semiconductor. The higher oxygen-containing Magnelli compositions obtain higher resistivity as well as increased chemical stability and robustness and can be utilized as a resistive layer or as a protective, conductive layer.

[0057] Erbium doped TiO_2 is known to display useful levels of

photoluminescence. And rare earth doped titanium oxide is known to display decreased levels of electrical leakage current under conditions of high electrical field. Layer 102 of Figure 3B, deposited according to some embodiments of the present invention, then can be erbium doped TiO_2 and therefore displays very high level of breakdown and very low leakage under electrical stress. Additionally, a capacitor can be formed by deposition of conductors as layers 103 and 104 on a substrate 101. Consequently, capacitive and energy storage devices formed from rare earth doped layers formed according to the present invention are extremely useful for very high field applications such as capacitors, high voltage dielectric batteries, and electro luminescent devices and also for low-leakage devices.

[0058] A TiO or erebium-doped TiO target, target 12 of Figure 1A, can be formed by mixing of TiO powder or TiO powder and Erbium or Erbium-Oxide powder. TiO powder can be formed from the partial oxygenation in a controlled furnace. The mixed powder is then hipped under a controlled environment (for example hydrogen or CO_2) to a high density to form tiles. As discussed above, such tiles can be mounted to form target 12. Additionally, other rare-earth doped titanium containing targets can be formed in the same fashion.

[0059] As an example, a layer of erbium doped titania or titania containing alloy deposited by means of the present invention, could be coupled as a continuous oxide layer to a photo diode constructed proximate to dielectric layer 102 of Figure 3A. Such an arrangement could provide an optical means for the measurement of the applied electrical field or the leakage current.

[0060] Alternatively, such a rare earth doped dielectric layer 102 might be coupled to conducting transparent oxides so that a light wave device might be provided for the conversion of electrical energy to light energy. In another embodiment, a titanium oxide containing a rare earth ion can be deposited directly on a light emitting diode device so that the rare earth ion can absorb some or all of the light emitted by the diode and re-fluoresce that light at another wavelength. In this embodiment, layer 102 can be a rare earth containing titanium oxide or sub oxide and substrate 101 includes a light emitting diode. An example of this may be the conversion of blue light from a LED to yellow-green light by layer 102. In that case,

layer 102 may be cerium doped titanium oxide or sub-oxide. Partial absorption of the blue light by layer 102 with conversion to yellow-green light by layer 102 would result in a white light source. Other colors of light can be obtained by doping the titanium oxide or sub-oxide with other rare earth ions.

[0061] Figures 4A and 4B illustrate further stackings of layers according to embodiments of the present invention. For example, layer 201 can be a TiO_2 dielectric protective deposited over a conducting layer 103 on substrate 101. Figure 4B can show dielectric protective layer 201 deposited over conducting protective layer 102 of TiO_y, which is deposited on a metal conducting layer 103 on substrate 101. The TiO_y conducting protective layer can act as a smoothing layer, resulting in a better barrier layer in dielectric 201. The end result is a better roll-off characteristic than has previously been obtained.

[0062] In general, layer 102 can be formed of any Ti_xO_y layer or rare earth doped Ti_xO_y layer according to the present invention. As illustrated here, layers of various compositions of Ti_xO_y, with or without rare-earth doping, have various properties. In some embodiments of the invention, x can be between about 1 and about 4 and y can be between about 1 and about 7.

[0063] Figure 5 shows an example of a capacitor stack according to the present invention. A metal conducting layer 103 is deposited on substrate 101. A conducting protective layer 102 is deposited over conducting layer 103 and a TiO_2 dielectric protective layer is deposited over the protective conducting layer 102. Another protective conducting layer 102 can be deposited over the TiO_2 dielectric layer and a metal layer can be deposited over the protective conducting layer 102. The resulting capacitor stack has upper and lower smoothing due to the two TiO_y layers and results in improved roll-off characteristics in the dielectric constant. Such capacitor stacks can be very useful in energy storage devices.

[0064] Figure 6 shows a transistor structure according to the present invention. A source 401, drain 402 and gate structure 404 are deposited on a semiconducting substrate 403. An intermediate dielectric 400 can then be deposited over the source, drain and gate structure. A protective conducting layer 102, which can be formed of TiO_y, can then be deposited over an opening in the intermediate dielectric layer 400

followed by a conducting layer 103. The protective conducting layer 102 prevents roll-off of the gate dielectric 404.

Example 1. Deposition of Ti_4O_7 film

[0065] In this example, Ti_4O_7 films were deposited using a Pulse DC scanning magnetron PVD process as was previously described in U.S. Application Serial No. 10/101,341. The target was a about 1mm thick, about 16.5x12.5 mm^2 tiles of titanium oxide target obtained from a sheet of Ebonex™ which compounded of bulk Ti_4O_7 was bonded onto a backing plate. Ebonex™ can be obtained from Atraverda Ltd., Oakham Business Park, Mansfield, UK. A pulsed DC generator from Advanced Energy (Pinnacle Plus) was used as the target power supply. The pulsing frequency can be varied from 0-350 KHz. Reversed duty cycle can be varied from 1.3μs to 5μs depending on the pulsing frequency. Target power was fixed at 2 KW and pulsing frequency was 200KHz during deposition, Ar flow rate is 100sccm. The deposition rate at this condition is 14Å/sec over a 40 by 50 cm substrate 101. A 100 W at 2 MHz bias was supplied to the substrate. The bias power supply can be an RF supply produced by ENI.

[0066] Utilizing the above parameters, a layer 102 of Figure 3A was deposited on a substrate 101 of 150mm p-type Si wafer. The sheet resistance was measured using 4 point probe to be 140 ohms/sq, with film thickness of 1.68μm. The resistivity of the resulting film is measured to be 0.023 ohms-cm. The composition of film was determined using EDX to be $Ti_4O_{6.8}$.

Example 2. Deposition of TiO2 on Ti-Ti4O7 film Stack

[0067] In this example, TiO_2 films were deposited using a 2MHz RF biased, Pulse DC scanning magnetron PVD process as was previously described in U.S. Application Serial No. 10/101,341. The substrate size can be up to 600x720mm^2. The target was a ~7mm thick, ~630x750 mm^2 Ti plate of 99.9% purity. A pulsed DC generator, or PDC power supply from Advanced Energy (Pinnacle Plus) was used as the target power supply. The pulsing frequency can be varied from 0-350 KHz. Reversed duty cycle can be varied from 1.3μs to 5μs depending on the pulsing

frequency. An ENI RF generator and ENI Impedance matching unit were used for the substrate bias. A 100 W with a 2 MHz RF generator, which can be an EFI supply, was utilized. The chamber base pressure was kept below $2x10^{-7}$ Torr. The substrate temperature was below 200°C during deposition.

[0068] A systematic DOE (design of experiments) were carried out on both n++ type bare Si wafers and Al metallized wafers. All n++ wafers were HF cleaned just before loading into the chamber for deposition. A series of 150nm thick, Al films were deposited onto the bare Si wafers using the same PVD system at low temperature (<100°C).

[0069] The total PDC target power, pulsing frequency, oxygen partial pressure, and substrate bias power were variables in the DOE. Total gas flow of Ar and O_2 were kept constant at 100 sccm. The PDC target power was between 4 and 7 kW with a pulsing frequency of between 100 and 250 kHz. The oxygen flow rate ranged from 30 to 60%. The bias power ranged from 0 to 300 W at 2 Mhz. Both dielectric strength and breakdown voltage were measured using a mercury probe. Film thickness in this DOE range from 100nm to 270nm.

[0070] Therefore, with reference to Figure 3B, layer 101 is the Si wafer substrate, layer 103 is the 150 nm thick Al layer, layer 102 is the Ti_4O_7 layer, and layer 104 is TiO_2. Figure 7 shows the thickness dependence of the dielectric constant of layer 102, showing the roll off effect. The capacitance of the layer stack 101, 103, 102, and 104 was measured with a mercury electrode impressed upon layer 104 and coupled to layer 103. The precise thickness of dielectric layer 104 was measured optically. The dielectric constant of layer 104 was then calculated from the measured capacitance. As shown in Figure 7, the TiO_2 film thickness decreases, so does the dielectric constant of the TiO_2 film.

[0071] However, this roll-off effect can be greatly reduced or eliminated in certain embodiments of the present invention. Figure 8 shows two additional data points shown as circles which represent the dielectric constant of thin TiO_2 layers for layer 104 with Ti-Ti_4O_7 deposited as layer 102 of Figure 3B.

Example 3. Deposition of TiO_2 on Ti-TiO_x (x<2) film Stack

[0072] A layer of TiO_2 was deposited on a titanium coated substrate. About 2000 Å of Ti metal was deposited at 7KW of PDC target power, with Ar flow of 100 sccm and bias power of 200W. After Ti deposition, TiO_2 was deposited in the same chamber without oxide burn in. This process resulted in a Ti-TiO_y –TiO_2 (y<2) film stack. The k value of a 200Å film was as high as 60.

[0073] Figures 9A and 9B illustrate an SEM cross-section of a Ti_4O_7 Ebonex™ target (Figure 9A) and an SEM cross section of the $Ti_4O_{6.8}$ layer (Figure 9B) deposited from the Ebonex™ target according to the present invention. The deposited film shows smooth deposition of the layer. The Ebonex™ target shown in Figure 9A shows an open porousity material with high roughness. The deposited layer shown in Figure 9B, however, shows a highly dense layer with a smooth surface condition.

[0074] Table I shows the effects of the dielectric properties of TiO_2 deposited according the present invention in comparison with previously obtained values. The values for the previously obtained reactive sputtering was taken from the paper "Frequency-Dependent Pulsed Direct Current magnetron Sputtering of Titanium Oxide Films," by J. Y. Kim et al., J. Vac. Sci. Techn., A 19(2), Mar/Apr. 2001. The values for PDC PVD with bias was experimentally obtained from layers deposited as described in Example 2 above.

Table I

Process	V_{bd} (Mv/cm)	K	FM
Reactive Sputtering	0.46 ~ 1.35	34 ~ 65.9	19 ~ 50
PDC physical Vapor Deposition with Bias	3.48	83	288

[0075] As can be seen from Table I, the breakdown voltage V_{bd} is significantly improved in layers according to the present invention. Further, the dielectric constant of the resulting layer is also higher. The figure of merit (FM) then for the deposited

layer was 288, very much higher than that report by Kim et al. The reference Kim et al. was the reference reporting the best quality TiO_2 films available at the time of filing of the prior application to which this disclosure claims priority.

[0076] Figure 10 shows data of capacitance made with layers according to the present invention in processes as described in Example 2 above are shown in comparison with available industry values. As is observed in Figure 10, layers of TiO_2 deposited according to the present invention have higher dielectric breakdown voltages than other dielectric films utilized in industry, which is represented by the solid line. However, due to the roll-off in dielectric constant K in films below about 1000 Å in thickness (as is indicated in the top two points in Figure 10), a capacitance density above about 5000 or 6000 pF/mm2 could not be achieved using thinner films. This is also shown in Figure 7.

[0077] However, combined with the use of a conductive sub-oxide and the higher dielectric constant of thinner films as shown in Figure 11, a capacitance density of 12000 pF/mm2 can be achieved with a 500 Å thickness film and a capacitance density of greater than 24000 pF/mm2 can be achieved with a 220 Å film, as is shown in Figure 11. These film stacks were deposited as described in Example 3 above.

[0078] Figure 12 shows a deposited layer 102 on a substrate 101 formed of n++ silicon wafer. Layer 102 is formed of TiO_2 deposited according to the present invention. As shown in the SEM cross-section, the TiO_2 layer shows several layers. A layer 1201 is formed of SiO_2 formed on substrate 101 and is formed about 20 Å thick. An amorphous layer 1202 of thickness about 250 Å is then formed above layer 1201. Finally, a crystalling TiO_2 layer 1203 is formed about 4000 Å thick. In some embodiments of the present invention, a continuous deposition on a substrate results in a first amorphous layer deposited at initially cooler temperature followed by a further crystalline layer deposited during the increased temperature of the process. A diffraction pattern inset in Figure 12 illustrates the crystalline nature of layer 1203.

[0079] Table II tabulates data taken from a number of bi-layer film such as that shown in Figure 12 and completely amorphous films formed by repeated initial deposition layers at cool deposition conditions. Films near 1000 Å of thickness are compared and display similar values for the dielectric constant. However, the

amorphous film exhibits much higher dielectric breakdown strengths. Due to the similar thickness and values of the dielectric constant, the two films exhibit similar values for capacitance. However, the amorphous film illustrates superior breakdown voltage and therefore has a higher figure of merit (FM). These trends are more pronounced in the thicker films with thicknesses close to 2000 Å. In this case, the values of the dielectric constant and capacitance are nearly identical but again there is a significantly higher breakdown voltage in the amorphous film, which results in a significant improvement in the figure of merit for the amorphous films.

Table II

Film Thickness (nm)	k	V_{bd} (MV/cm)	FM	C (pF/mm2)	Breakdown Voltage (V)	Film Morphology
969	63	3.6	227	540	348	Bi-layer
1036	62	6.4	396	538	660	Amorphous
2020	98	3.5	335	429	705	Bi-Layer
2322	98	5.5	539	429	1110	Amorphous

[0080] Therefore, it is clear that amorphous TiO_2 films have much better performance. As discussed above, those layers are the result of low temperature depositions. Therefore, as was demonstrated with the data shown in Table II, one method of producing thick amorphous TiO_2 layers is to simply utilize a sequence of low temperature depositions, halting the deposition prior to thermal heating of the depositing film. However, this method can take a significant amount of production time for thick films. Another embodiment of obtaining thick TiO_2 amorphous films is to apply active cooling to the substrate in an amount sufficient to provide continuously amorphous TiO_2 films.

[0081] Figure 13 shows a comparison of the leakage current for TiO_2 films according to embodiments of the present invention with and without erbium ion doping. The lower data points in Figure 13 are from capacitors formed from films deposited from a 10 at. % Er doped TiO target. The target was electrically

conductive. One example of the 10% doped film of 1000 Å thickness was formed with 60 sccm Ar, 6 sccm O_2, with a target power of 3 kW, bias power of 100 W, with a deposition time of 200 sec on a metal coated glass wafer. With the metal coating forming a copper titanium lower electrode and a titanium copper gold upper electrode patterned as 1X1 mm, discreet capacitors was then formed. The layers corresponding to the upper data points were deposited from a pure titanium target with no erbium doping on a TaN substrate with a evaporated platinum upper electrode. This structure of the bottom data is illustrated in Figure 4B where, for example, layer 101 is a glass substrate, layer 103 is a copper titanium layer, layer 102 is the erbium doped TiO_2 layer, and layer 201 is a titanium copper gold layer.

[0082] As can be seen in Figure 13, the leakage current density is reduced by many orders of magnitude by addition of erbium.

[0083] Figures 14A and 14B show a photoluminescence signal with excitation at 580 nm and measurement at 1.53 µm, measured from a 5000 Å layer of 10% erbium containing TiO_2 deposited from a 10% erbium doped TiO conductive target and a photoluminescence signal measured from the same layer after a 30 minute 250 °C anneal, respectively. Table III shows similar data for several layers deposited from the erbium-doped TiO conductive target.

Table III

Thickness	Before Anneal	Anneal (°C)	After Anneal
5000 Å	6704	150	5809
5000 Å	6493	200	4042
5000 Å	6669	250	2736
5000 Å	6493	300	3983
1 µm	6884	150	6743
1 µm	5197	200	3685
1 µm	6253	250	3612
1 µm	5324	300	3381

[0084] According to some explanations of the reduction of leakage current in layers as illustrated by Figure 13, fast electrons that have sufficient energy to excite

the erbium ion would cause the rare earth ion to undergo excitation upon electron impact or passage within a distance sufficient for energy exchange. Consequently, the leakage current electrons capable of causing ionization within the dielectric oxide would be reduced by electron collisions with erbium ions. Excited state ions have at least two relaxation mechanisms for disposal of the energy: radiative and non-radiative. In radiative relaxation, the excited ion emits light. In non-radiative relaxation, the excited ion undergoes a cooperative process with vibrational modes of it's host dielectric oxide and produces a vibration which is the elemental form of heat. In the data illustrated in Figure 13, it was not possible to observe light in the leakage test, but photoluminescence was observed from optical excitation of the similar 10% Er doped TiO_2 deposited from the 10% Er doped TiO conductive target, as shown in Table III.

[0085] As can be seen from the data in Table III, an erbium doped layer of titanium oxide was shown to fluoresce strongly under optical excitation by light of a wavelength 580 nm, using a Phillips PhotoLuminescence Microscope, model no. PLM-100. The target was electrically conductive and sputtered at a higher rate and a lower oxygen partial pressure than characteristic of a metallic titanium target. One example of the 10% doped film of 2,032 angstroms was 60 sccm Ar, 6 sccm O_2, with a target power of 3 kW, bias power of 100 W, with a deposition time of 300 sec.

[0086] The level of photoluminescence observed from the layer was similar to that obtained in as-deposited and annealed films providing commercial levels of optical absorption and fluorescence for applications to planar waveguide amplifiers having at least 15 dB gain for signals as weak as -40dB at the 1.5 micron wavelength utilized for photonic C band communications.

[0087] Such a device can be illustrated with Figure 3B, where layer 103 can be a conductive layer deposited on substrate 101, layer 102 can be a rare-earth doped TiO_2 layer deposited according to embodiments of the present invention, and layer 104 can be a further conductive layer or a conductive transparent layer to form an metal-insulating-metal (MIM) capacitor structure. Such a structure could function as a light emitting layer under either DC or AC electrical excitation. In another embodiment, layer 103 can be a lift-off layer such as CaF_2 or other organic material, layer 102 is

the rare-earth doped TiO_2 layer, and layer 104 is absent, then upon lift-off or upon transfer of layer 102, a free standing or applied layer having electroluminescent or photoluminescent applications can be provided over a selected device.

[0088] Thin films according to the present invention can be utilized in advanced display devices, electrical energy storage and conversion, and to form optical and electronic films with scratch resistance and barrier properties. Advanced display product applications include OLED encapsulation, barriers for flexible polymer substrates, outcoupling mirrors and anti-reflection coatings, transparent conducting oxides, and semiconducting materials for active matrix displays. Electrical energy storage and conversion applications include high density capacitor arrays for mobile communication devices, on-chip high "K" capacitors for advanced CMOS, and high voltage energy storage for portable power devices. Other applications include touch-sensitive devices and durable bar code scanners and see-through sensors as well as implantable biometric devices.

[0089] The embodiments described in this disclosure are examples only and are not intended to be limiting. Further, the present invention is not intended to be limited by any particular theory or explanation presented to explain experimental results. As such, examples of titanium oxide and titanium sub-oxide films illustrated herein and their applications are not intended to be limiting. One skilled in the art may contemplate further applications or films that are intended to be within the spirit and scope of the present invention. As such, the invention is limited only by the following claims.

Claims

We claim:

1. A method of forming a titanium based layer, comprising:

depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate.

2. The method of claim 1, wherein the layer is TiO_2.

3. The method of claim 2, wherein the figure of merit of the layer is greater than 50.

4. The method of claim 2, wherein the layer is deposited between conducting layers to form a capacitor.

5. The method of claim 2, wherein the layer includes at least one rare-earth ion.

6. The method of claim 5, wherein the layer is deposited between conducting layers to form a capacitor.

7. The method of claim 5, wherein the at least one rare-earth ion includes erbium.

8. The method of claim 5, wherein the layer is deposited between conducting layers to form a light-emitting device.

9. The method of claim 5, wherein the layer is an optically active layer deposited on a light-emitting device.

10. The method of claim 5, wherein the layer is an optically active layer applied to a light-emitting device.

11. The method of claim 1, wherein the layer is a sub-oxide of Titanium.

12. The method of claim 11, wherein the figure of merit of the layer is greater than 50.

13. The method of claim 11, wherein the layer is deposited between conducting layers to form a capacitor.

14. The method of claim 11, wherein the layer includes at least one rare-earth ion.

15. The method of claim 14, wherein the layer is deposited between conducting layers to form a capacitor.

16. The method of claim 14, wherein the at least one rare-earth ion includes erbium.

17. The method of claim 14, wherein the layer is deposited between conducting layers to form a light-emitting device.

18. The method of claim 14, wherein the layer is an optically active layer deposited on a light-emitting device.
19. The method of claim 14, wherein the layer is an optically active layer applied to a light-emitting device.
20. The method of claim 2, wherein the layer is a protective layer.
21. The method of claim 20, wherein the protective layer is a catalytic layer.
22. The method of claim 20, wherein the protective layer includes at least one rare-earth ion.
23. The method of claim 1, wherein the layer is Ti_xO_y wherein x is between about 1 and about 4 and y is between about 1 and about 7.
24. The method of claim 23, wherein the figure of merit of the layer is greater than 50.
25. The method of claim 23, further including depositing an TiO_2 layer on the layer wherein the layer and the TiO_2 layers are deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the TiO_2 layer.
26. The method of claim 23, wherein the TiO_2 layer is an amorphous layer deposited by a pulsed DC, biased, reactive ion process.
27. The method of claim 23, wherein the layer includes at least one rare-earth ion.
28. The method of claim 27, wherein the at least one rare-earth ion includes erbium.
29. The method of claim 27, wherein the layer is deposited between conducting layers to form a light-emitting device.
30. The method of claim 27, wherein the layer is an optically active layer deposited on a light-emitting device.
31. The method of claim 27, wherein the layer is an optically active layer applied to a light-emitting device.
32. The method of claim 23, wherein the layer is a conducting oxide.
33. The method of claim 32, wherein the substrate is a conducting electrode and the layer is a protective layer.
34. The method of claim 33, wherein the protective layer is a catalytic layer.

35. The method of claim 33, wherein the protective layer includes at least one rare-earth ion.

36. The method of claim 32, wherein the substrate is a dielectric and the layer is a protective layer.

37. The method of claim 36, wherein the protective layer is a catalytic layer.

38. The method of claim 1, further including

controlling the temperature of the substrate during deposition.

39. The method of claim 38, wherein controlling the temperature includes active temperature control.

40. The method of claim 1, wherein the layer is an amorphous layer.

41. The method of claim 1, wherein the substrate includes a transistor structure.

42. A titanium based layer, comprising:

a layer compounded from titanium and oxygen deposited by pulsed-DC, biased reactive sputtering process on a substrate.

43. The layer of claim 42, wherein the layer is TiO_2.

44. The layer of claim 43, wherein the figure of merit of the layer is greater than 50.

45. The layer of claim 43, wherein the layer is deposited between conducting layers to form a capacitor.

46. The layer of claim 43, wherein the layer includes at least one rare-earth ion.

47. The layer of claim 46, wherein the layer is deposited between conducting layers to form a capacitor.

48. The layer of claim 46, wherein the at least one rare-earth ion includes erbium.

49. The layer of claim 46, wherein the layer is deposited between conducting layers to form a light-emitting device.

50. The layer of claim 46, wherein the layer is an optically active layer deposited on a light-emitting device.

51. The layer of claim 46, wherein the layer is an optically active layer applied to a light-emitting device.

52. The layer of claim 42, wherein the layer is sub-oxide of Titanium.

53. The layer of claim 52, wherein the figure of merit is greater than 50.

54. The layer of claim 52, wherein the layer is deposited between conducting layers to form a capacitor.

55. The layer of claim 52, wherein the layer includes at least one rare-earth ion.

56. The layer of claim 55, wherein the layer is deposited between conducting layers to form a capacitor.

57. The layer of claim 55, wherein the at least one rare-earth ion includes erbium.

58. The layer of claim 55, wherein the layer is deposited between conducting layers to form a light-emitting device.

59. The layer of claim 55, wherein the layer is an optically active layer deposited on a light-emitting device.

60. The layer of claim 55, wherein the layer is an optically active layer applied to a light-emitting device.

61. The layer of claim 43, wherein the layer is a protective layer.

62. The layer of claim 61, wherein the protective layer is a catalytic layer.

63. The layer of claim 61, wherein the protective layer includes at least one rare-earth ion.

64. The layer of claim 42, wherein the layer is Ti_xO_y wherein x is between about 1 and about 4 and y is between about 1 and about 7.

65. The layer of claim 64, wherein the figure of merit is greater than 50.

66. The layer of claim 64, further including depositing an TiO_2 layer on the layer wherein the layer and the TiO_2 layers are deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the TiO_2 layer.

67. The layer of claim 64, wherein the TiO_2 layer is an amorphous layer deposited by a pulsed DC, biased, reactive ion process.

68. The layer of claim 64, wherein the layer includes at least one rare-earth ion.

69. The layer of claim 68, wherein the at least one rare-earth ion includes erbium.

70. The layer of claim 68, wherein the layer is deposited between conducting layers to form a light-emitting device.

71. The layer of claim 68, wherein the layer is an optically active layer deposited on a light-emitting device.

72. The layer of claim 68, wherein the layer is an optically active layer applied to a light-emitting device.

73. The layer of claim 64, wherein the layer is a conducting oxide.

74. The layer of claim 73, wherein the substrate is a conducting electrode and the layer is a protective layer.

75. The layer of claim 74, wherein the protective layer is a catalytic layer.

76. The layer of claim 74, wherein the protective layer includes at least one rare-earth ion.

77. The layer of claim 73, wherein the substrate is a dielectric and the layer is a protective layer.

78. The layer of claim 77, wherein the protective layer is a catalytic layer.

79. The layer of claim 42, further including

controlling the temperature of the substrate during deposition.

80. The layer of claim 79, wherein controlling the temperature includes active temperature control.

81. The layer of claim 42, wherein the substrate includes a transistor structure.

82. The layer of claim 42, wherein the layer is an amorphous layer.

83. A target, comprising:

hipped TiO having composition TiO.

84. The target of claim 83, further including at least one rare-earth dopant.

85. A method of forming a target, comprising:

forming a TiO powder;

mixing the TiO powder to form a mix;

hipping the mix under a controlled atmosphere to form tiles; and

forming a target from the tiles.

86. The method of claim 85, further including mixing at least one rare-earth oxide powder with the mix.

87. The method of claim 86, wherein the at least one rare-earth oxide includes erbium oxide.

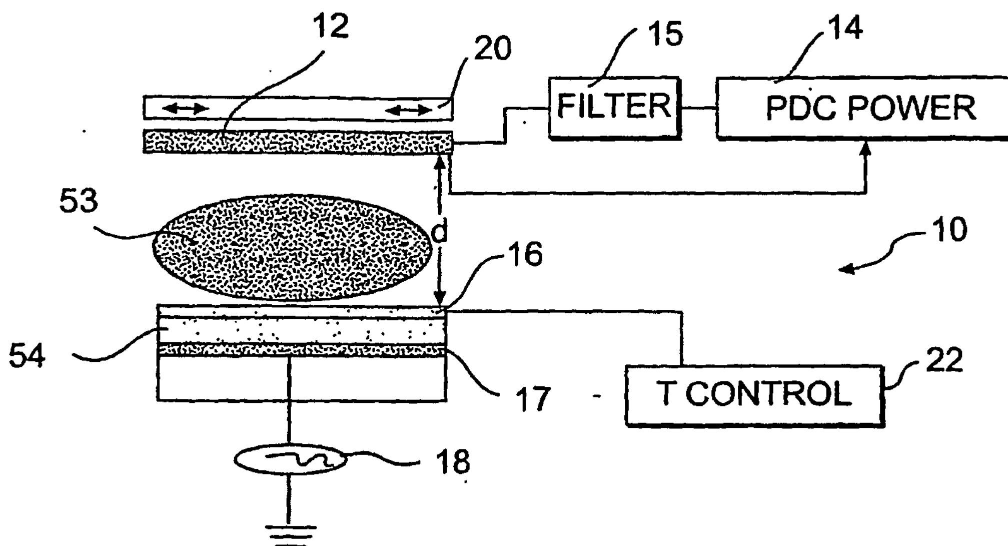


FIG. 1A

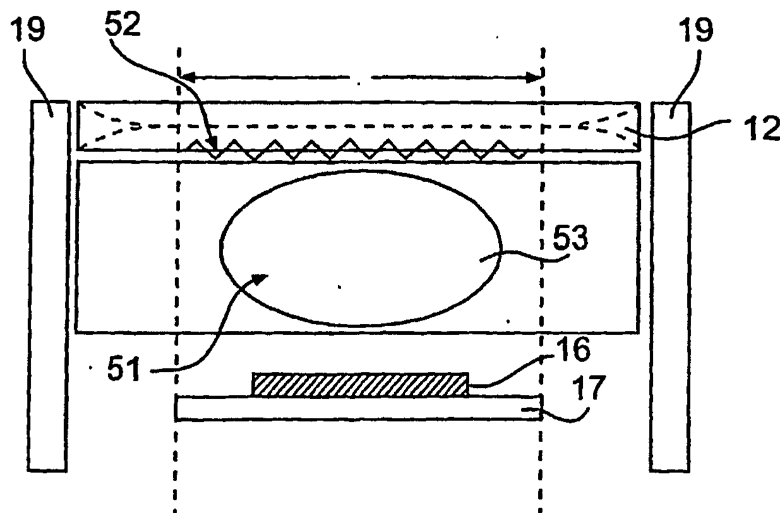


FIG. 1B

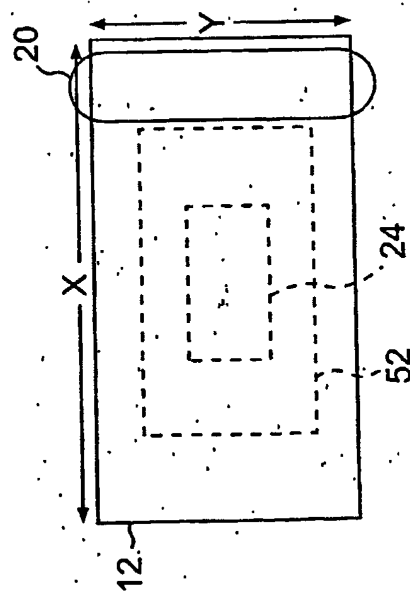


FIG. 2

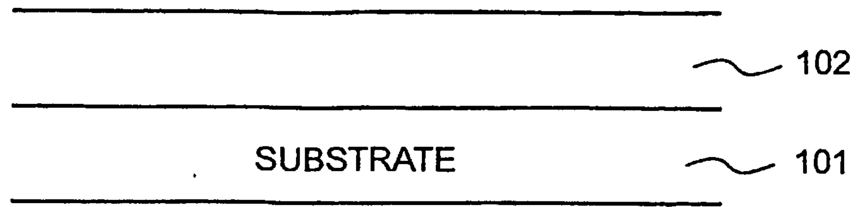


FIG. 3A

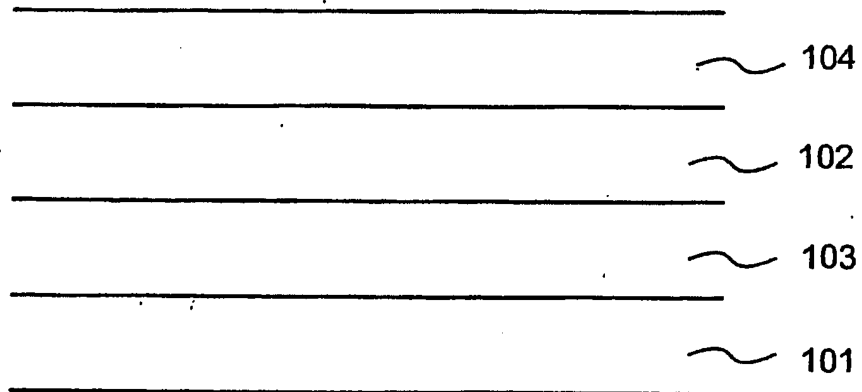


FIG. 3B

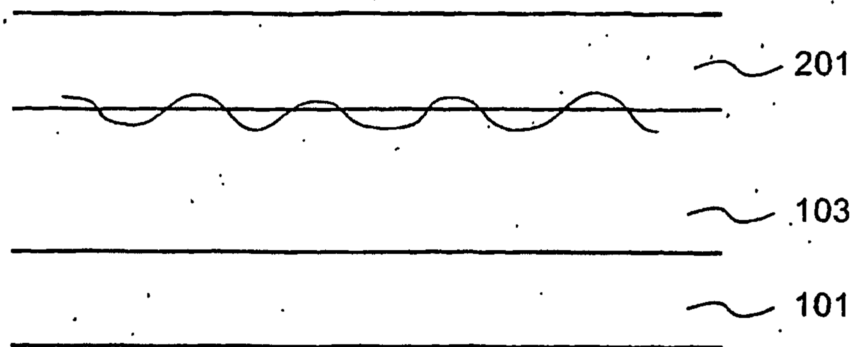


FIG. 4A

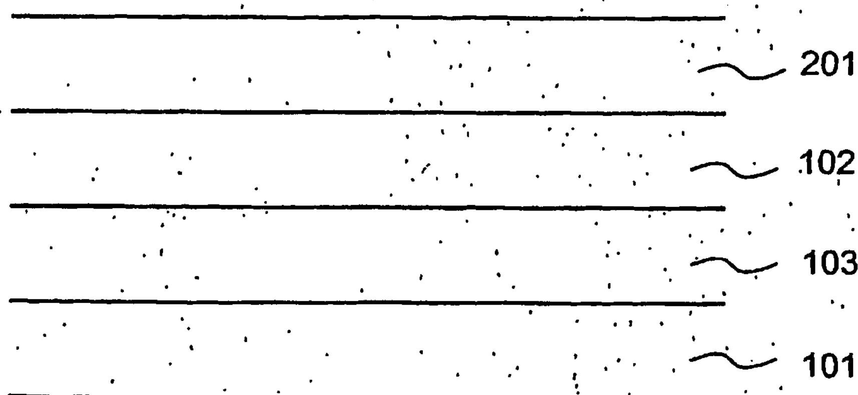


FIG. 4B

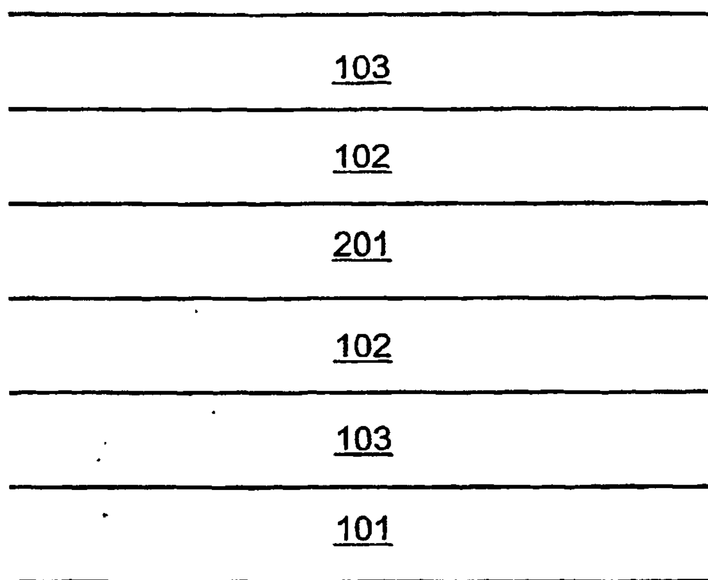


FIG. 5

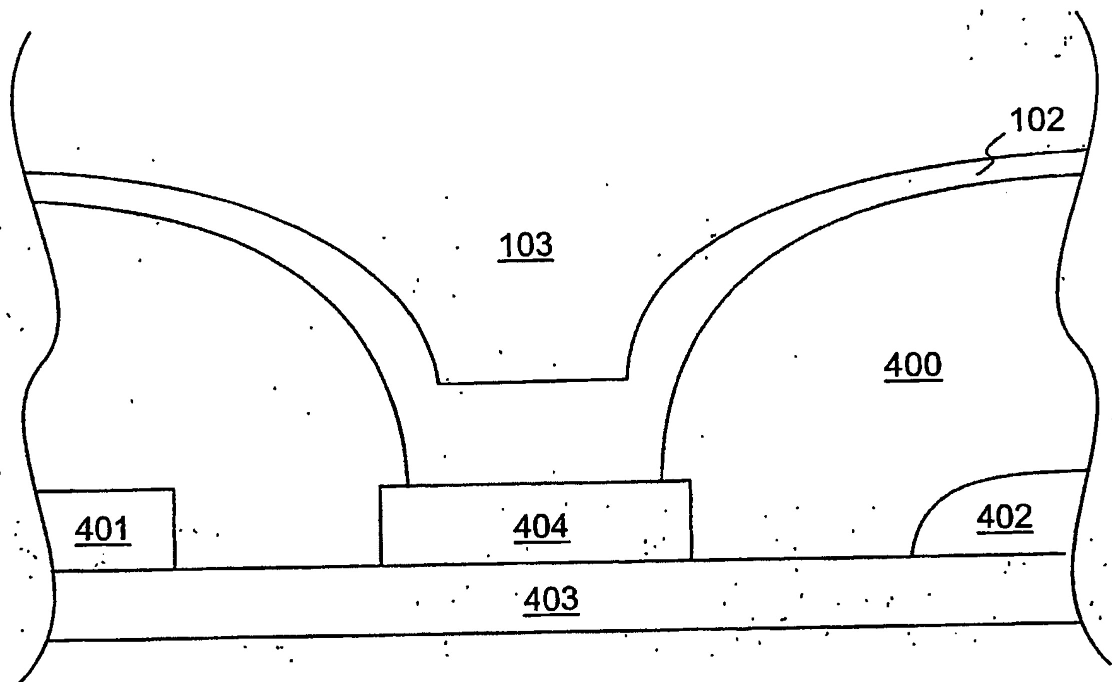


FIG. 6

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 1086 of 1543

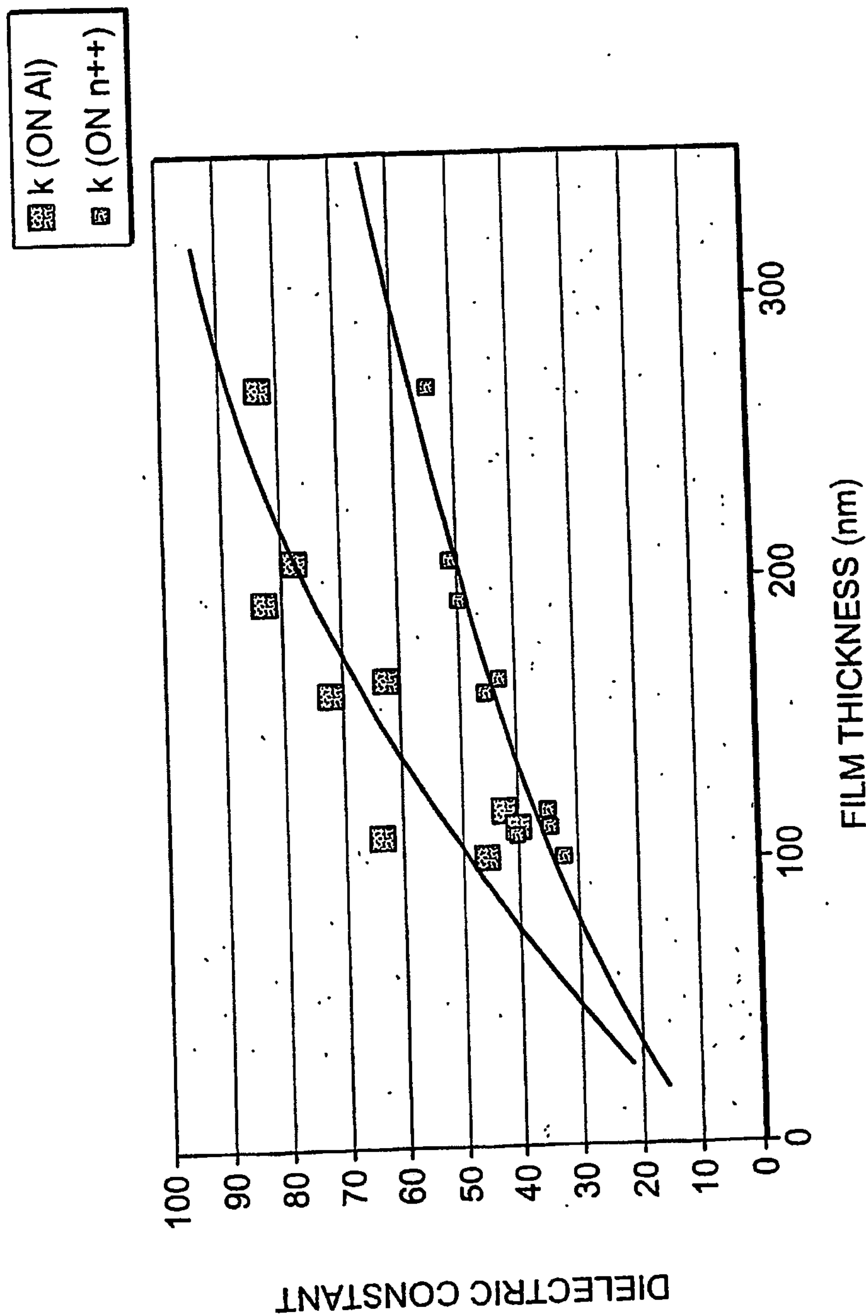


FIG. 7

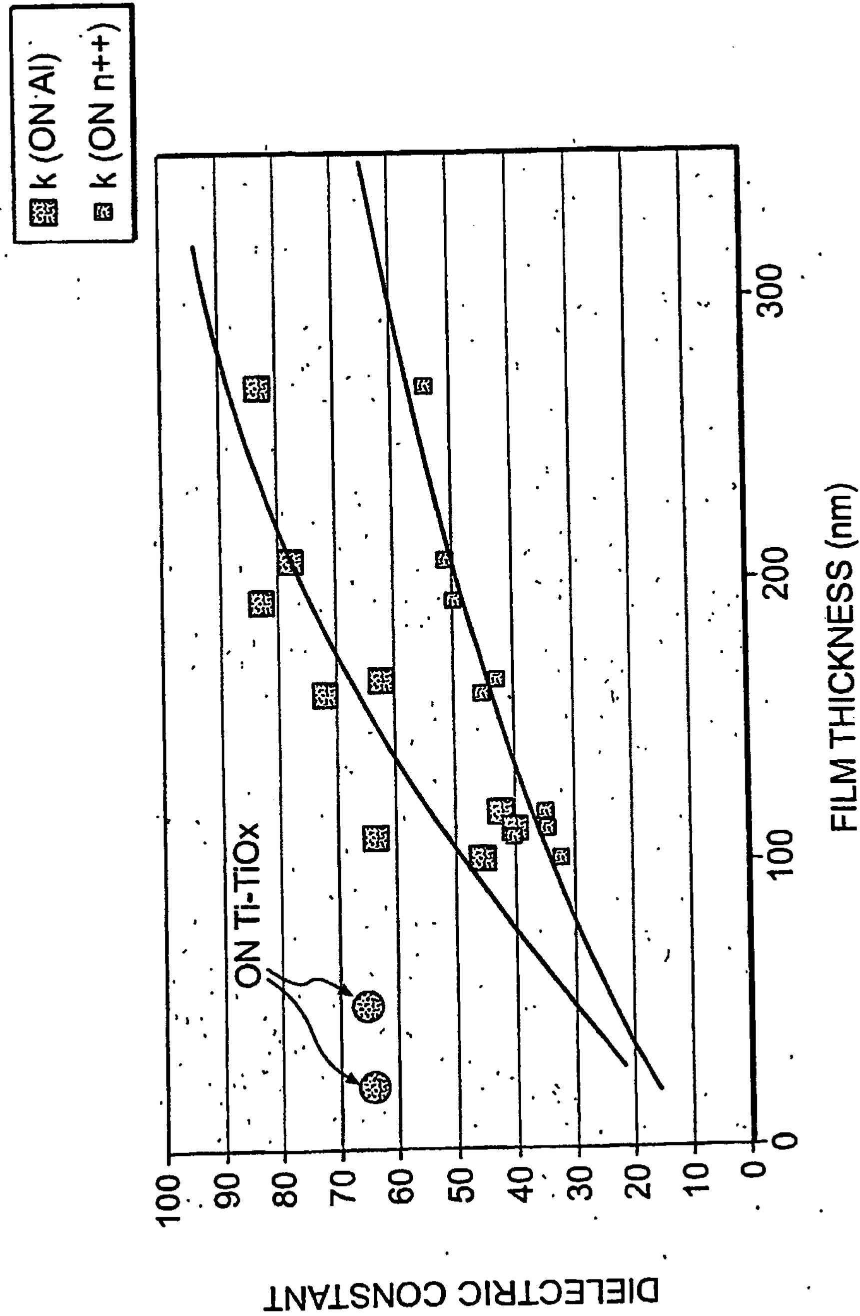


FIG. 8

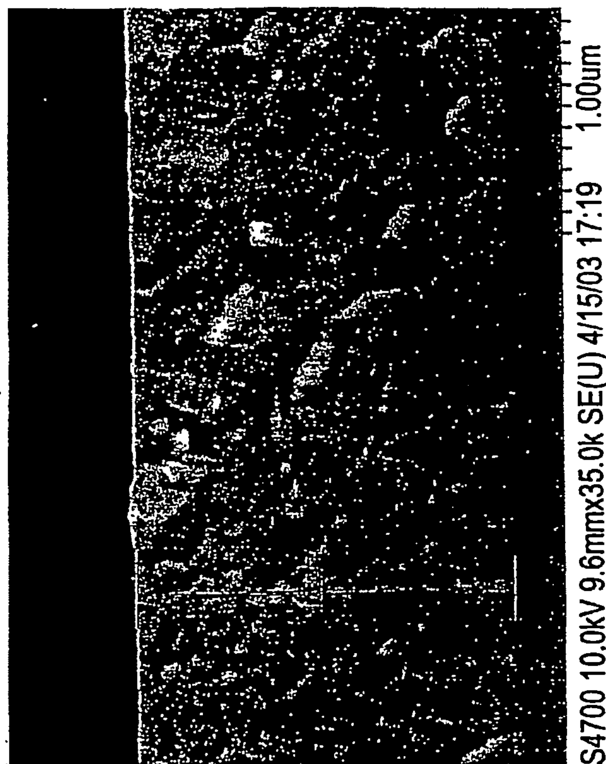


FIG. 9B

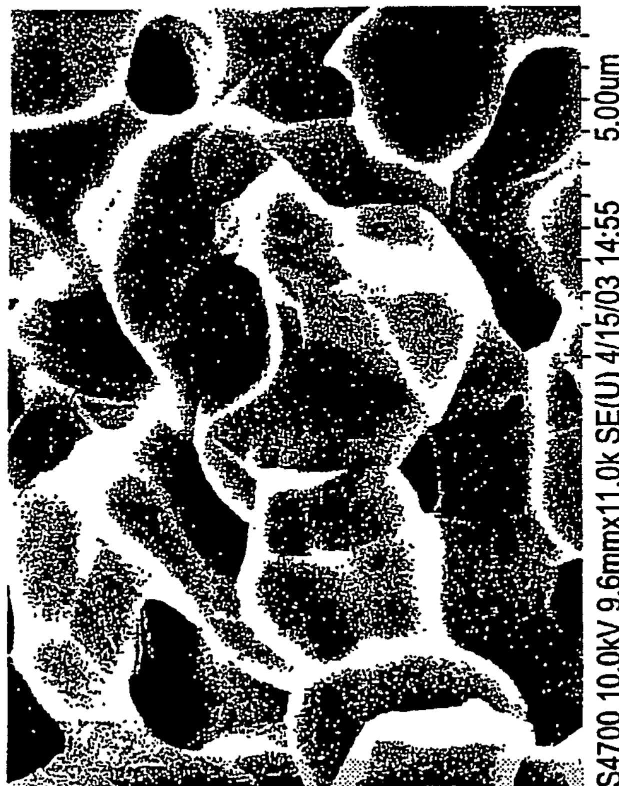


FIG. 9A

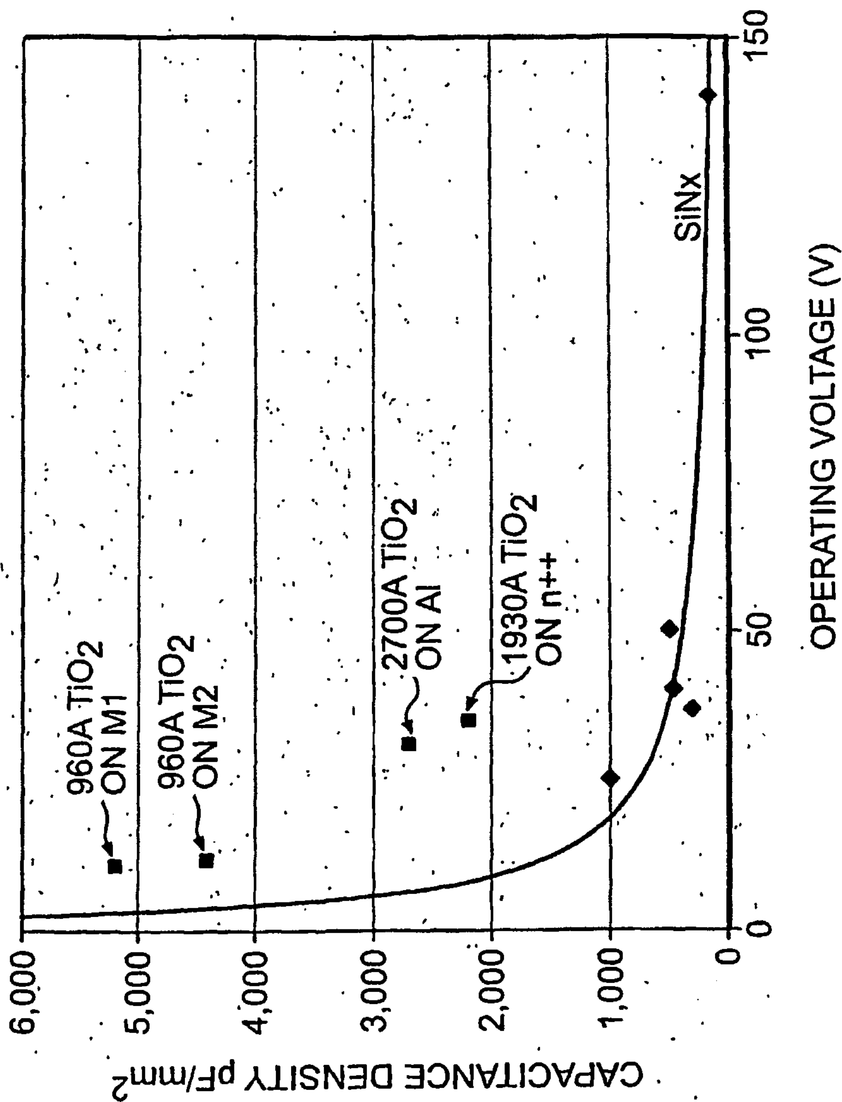


FIG. 10

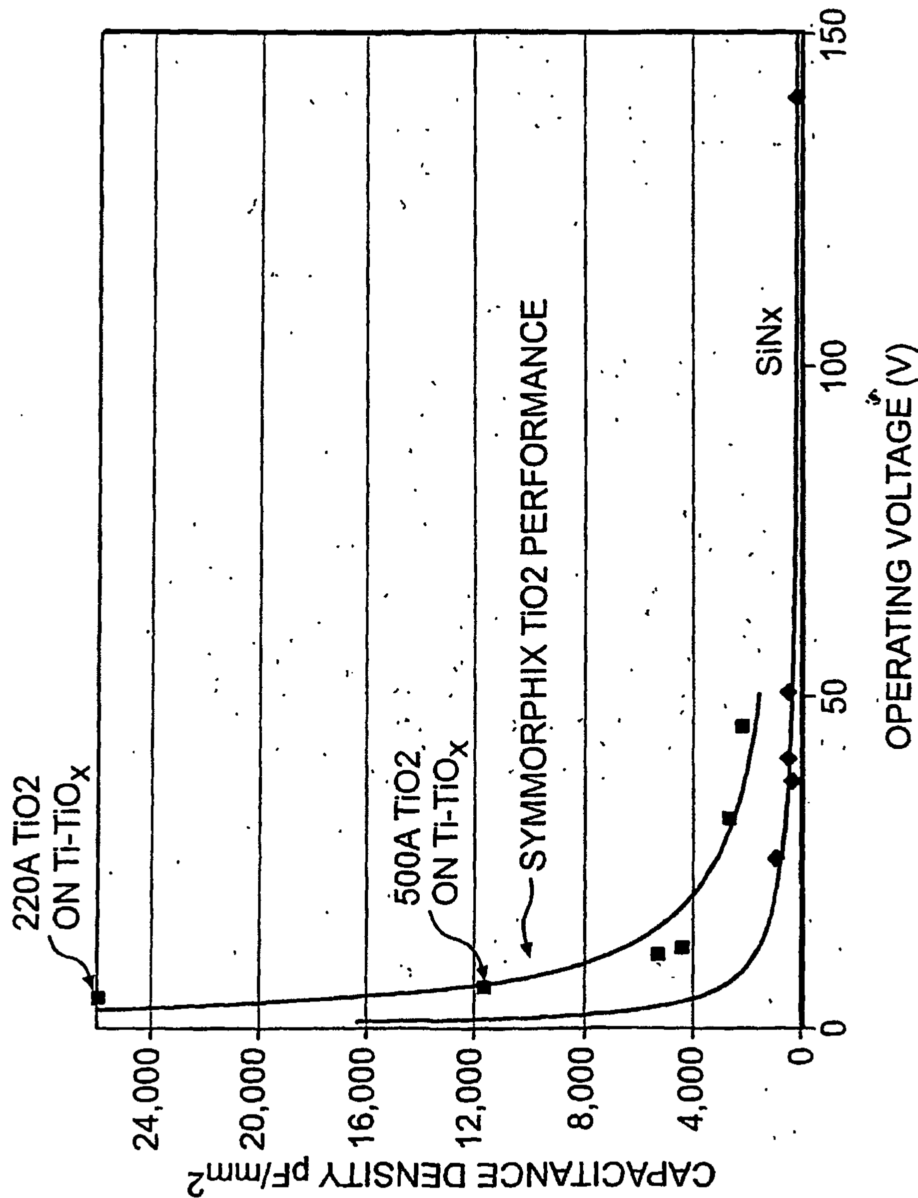


FIG. 11

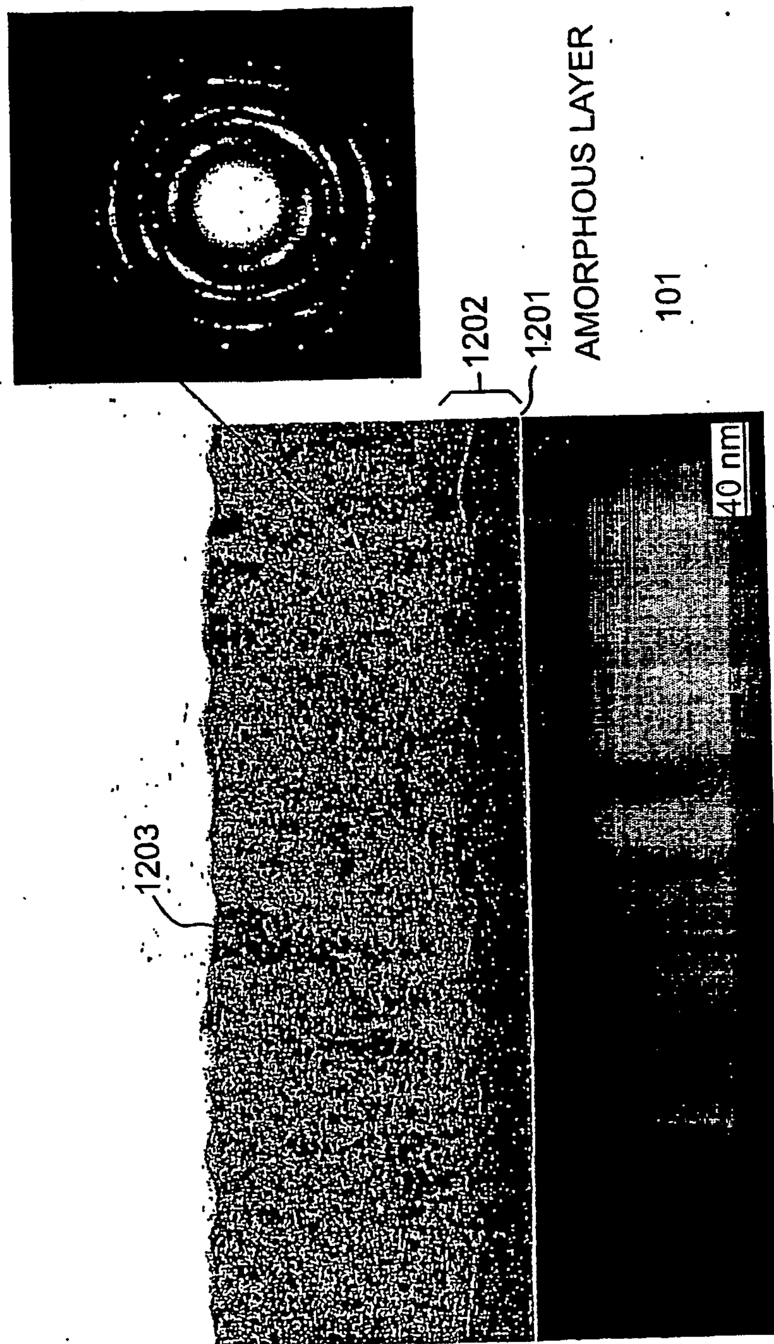


FIG. 12

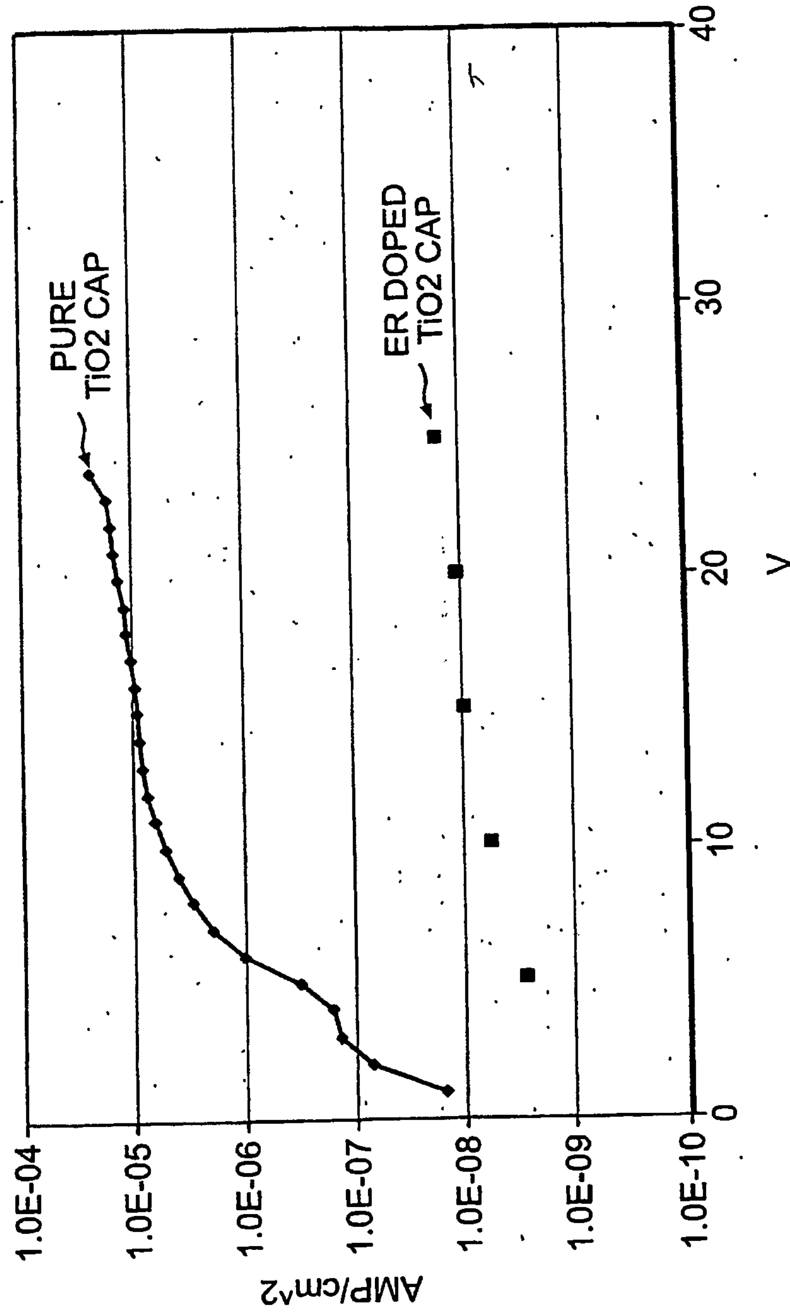


FIG. 13

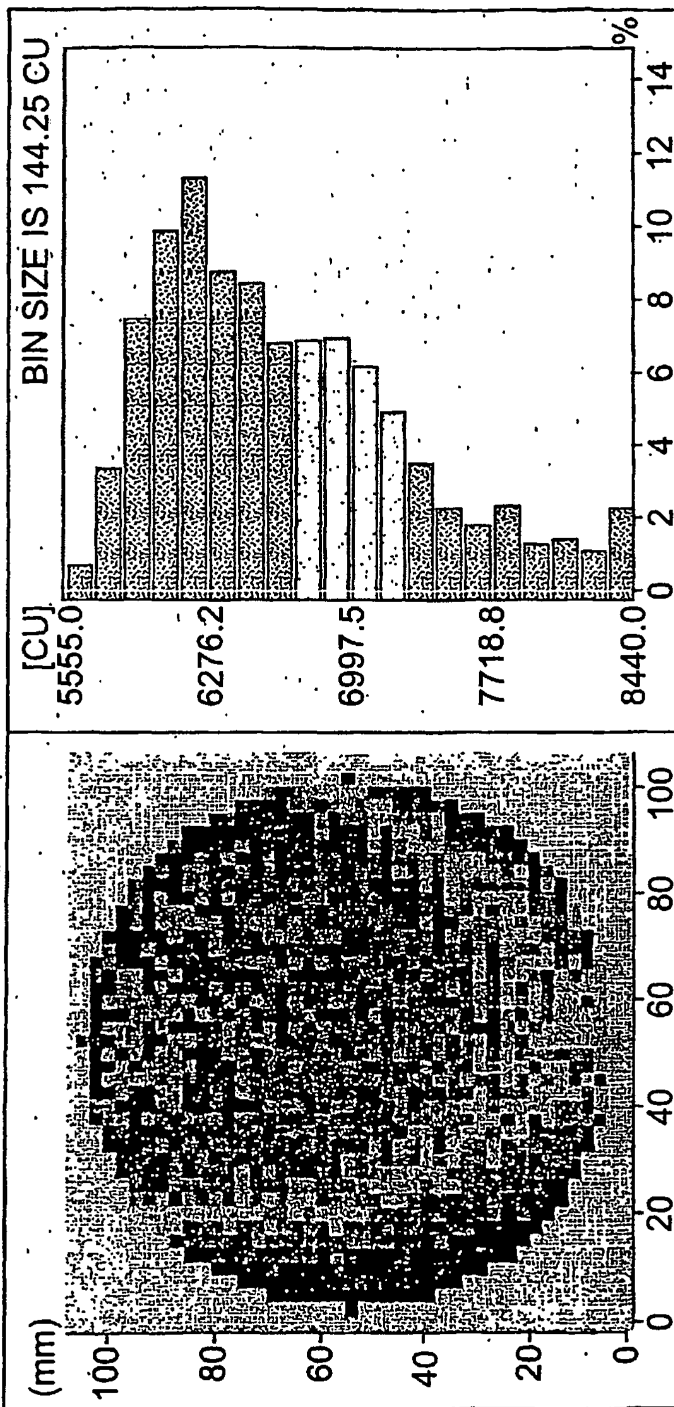


FIG. 14A

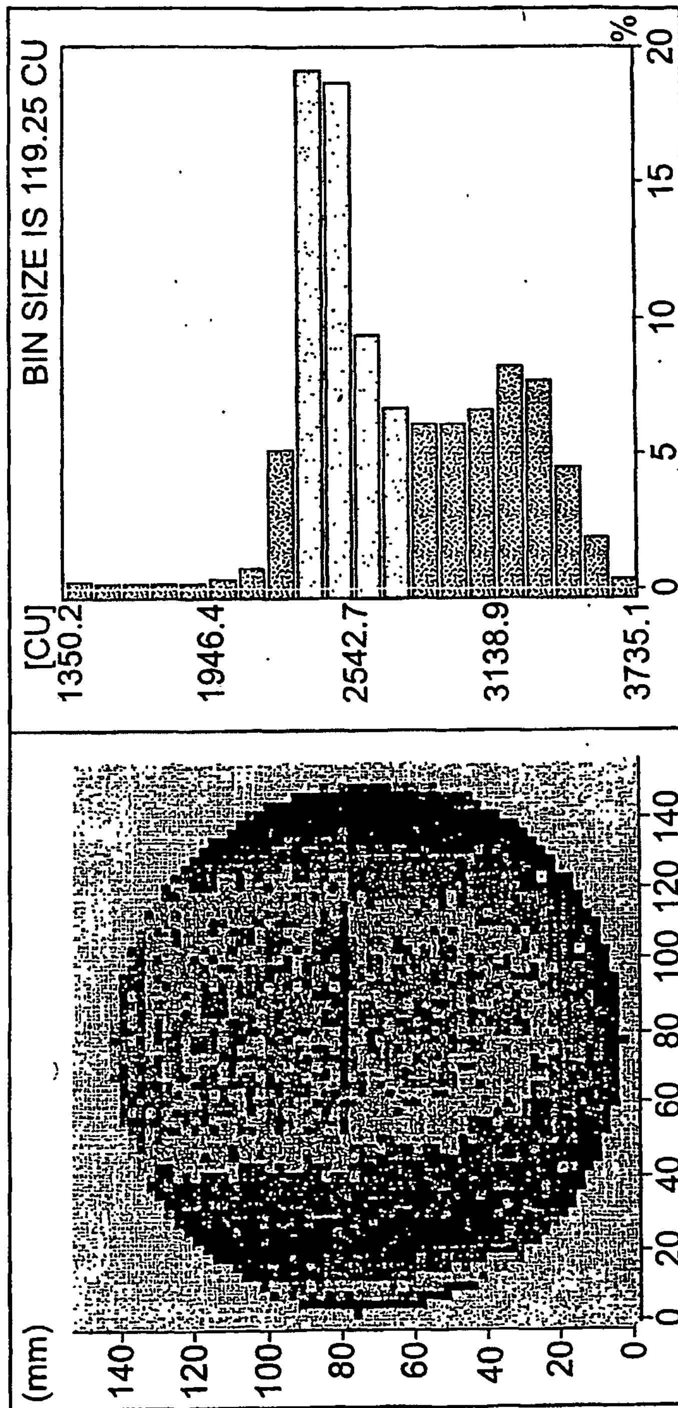


FIG. 14B

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

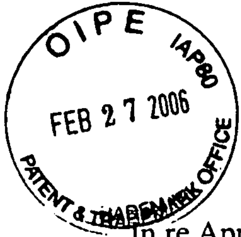
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☑ **SKEWED/SLANTED IMAGES**
- ☑ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

3-01-06 2823



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
Filed: March 16, 2002	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SIXTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the U.S. patents and patent publications cited are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

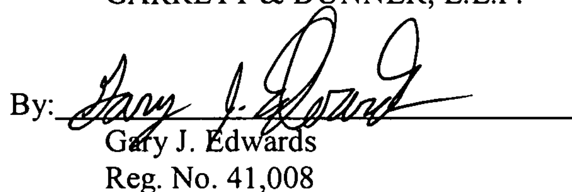
claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

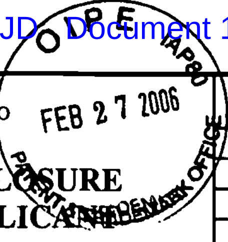
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.



Dated: February 27, 2006

By: Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 860819704 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	1	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 5,909,346	06-01-1999	Malhotra et al.	
		US 6,000,603	12-14-1999	Koskenmaki et al.	
		US 6,133,670	10-17-2000	Rodgers et al.	
		US 6,356,694 B1	03-12-2002	Weber	
		US 6,768,855 B1	07-27-2004	Bakke et al.	
		US 6,683,749 B2	01-27-2004	Daby et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819704 US

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SEVENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

A copy of the document cited is enclosed.

Applicants respectfully request that the Examiner consider the listed document and indicate that it was considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

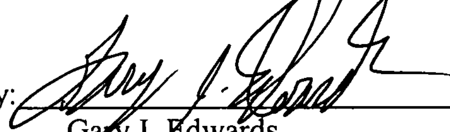
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed document, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

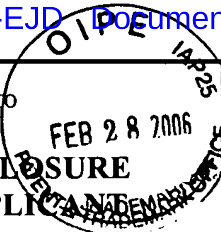
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 28, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 860819602 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	1	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819602 US

RCE filed 2-24-06

PTO/SB/06 (12-04)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875 Effective December 8, 2004

Application or Docket Number: 10/101,863

APPLICATION AS FILED – PART I

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	SMALL ENTITY RATE ($)	SMALL ENTITY FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY FEE ($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	150.00		N/A	300.00
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	$250		N/A	$500
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	$100		N/A	$200
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X$ 25 =		OR	X$50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X100 =			X200 =	
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))			+180=			+360=	
			TOTAL			TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

AMENDMENT A — 2-24-06

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 17	Minus	** 39	=	X$ 25 =		OR	X$50 =	
Independent (37 CFR 1.16(h))	* 2	Minus	*** 5	=	X100 =		OR	X200 =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					+180=		OR	+360=	
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X$ 25 =		OR	X$50 =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X100 =		OR	X200 =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					+180=		OR	+360=	
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

CLAIMS ONLY

2-24-06

Application Number: 10/101,863

Filing Date:

Applicant(s):

CLAIMS	AS FILED Indep	AS FILED Depend	AFTER FIRST AMENDMENT Indep	AFTER FIRST AMENDMENT Depend	AFTER SECOND AMENDMENT Indep	AFTER SECOND AMENDMENT Depend
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
43						
44						
45						
46						
47						
48						
49						
50						
Total Indep			2			
Total Depend			15			
Total Claims			17			

* May be used for additional claims or amendments

CLAIMS	* Indep	* Depend	* Indep	* Depend	* Indep	* Depend
51						
52						
53						
54						
55						
56						
57						
58						
59						
60						
61						
62						
63						
64						
65						
66						
67						
68						
69						
70						
71						
72						
73						
74						
75						
76						
77						
78						
79						
80						
81						
82						
83						
84						
85						
86						
87						
88						
89						
90						
91						
92						
93						
94						
95						
96						
97						
98						
99						
100						
Total Indep						
Total Depend						
Total Claims						

03-06-06

TFW 2823

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

EIGHTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

A copy of the document cited is enclosed.

Applicants respectfully request that the Examiner consider the listed document and indicate that it was considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

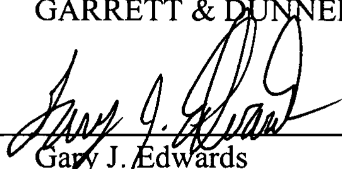
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed document, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

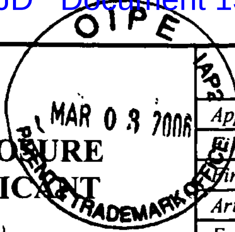
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 3, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 860819633 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

Sheet	1	of	1

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 6,290,821 B1	09-18-2001	McLeod	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action filed February 20, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01).	
		Response to Office Action filed July 17, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01).	
		Response to Office Action filed February 28, 2006 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed March 2, 2006 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819633 US

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	14	sputter$3 with metallic with (poison or poisonous)	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:23
L2	1083543	@ad>"20020316" or @rlad>"20020316"	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:22
L3	8	1 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:22
L4	5	sputter$3 with metallic with (poison or poisonous) with target	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:24
L5	1	4 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:23
L6	14	(sputter$3 with metallic with (poison or poisonous)) same target	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:24
L7	8	6 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:25
L8	8	3 and 7	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:28
L9	458	backside with target	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:28
L10	19	"pulsed DC" and "RF bias" and plasma and filter	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:30
L11	4	10 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:30
L12	1	11 and 9	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:30
L13	79	"pulsed DC" and "RF bias"	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:31
L14	5	9 and 13	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:30
L15	1	14 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:30
L16	4869	"pulsed DC" or "RF bias"	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:31
L17	50	9 and 16	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:31
L18	27	17 not 2	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:35
L19	1	("6290821").PN.	US-PGPUB; USPAT	OR	OFF	2006/03/16 16:36
L20	6	(("5909346") or ("6000603") or ("6133670") or ("6356694") or ("6768855") or ("6683749")).PN.	US-PGPUB; USPAT	OR	OFF	2006/03/16 17:07

EAST Search History

L21	13	("20020001746"|"20020076133"|"20020140103"|"20030178637"|"3309302"|"5338625"|"5561004"|"5930046"|"6242129"|"6280875"|"6376027"|"6632563"|"6683244").PN.	US-PGPUB; USPAT	OR	OFF	2006/03/16 17:07

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

22852 7590 03/22/2006

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 03/22/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No.	Applicant(s)
	10/101,863	ZHANG ET AL.
	Examiner	Art Unit
	Michelle Estrada	2823

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on 24 February 2006.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) 2-14 and 21-24 is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☒ Claim(s) 14 is/are allowed.

6)☒ Claim(s) 2-14 and 21-24 is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date 2/24/06, 2/27/06, 2/28/06, 3/3/06

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____.

DETAILED ACTION

Continued Examination Under 37 CFR 1.114

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 2/24/06 has been entered.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13 and 21 rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claim 21, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created

by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33).

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claim 12, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claim 13, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

Claims 2-6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Fukui et al. (5,755,938).

With respect to claims 2-4, 6 and 22-24, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art

ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With respect to claim 5, Smolanoff et al. do not specifically disclose wherein the filter is a band reject filter at the frequency of the bias power.

Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter (27) at the frequency of the bias power.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fukui et al. to enable the filter type of Smolanoff et al. to be the same according to the teachings of Fukui et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable types of filters

for the disclosed filter step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Allowable Subject Matter

Claim 14 is allowed.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

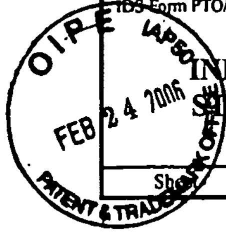
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
March 16, 2006



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 3

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number: Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
MAE		US-3,309,302	03-14-1967	Heil	
		US-5,338,625	08-16-1994	Bates et al.	
		US-5,561,004	10-01-1996	Bates et al.	
		US-5,930,046	07-27-1999	Solberg et al.	
		US-6,242,129 B1	06-05-2001	Johnson	
		US-6,280,875 B1	08-28-2001	Kwak et al.	
		US-6,376,027 B1	04-23-2002	Lee et al.	
		US-6,632,563 B1	10-14-2003	Krasnov et al.	
		US-6,683,244 B2	01-27-2004	Fujimori et al.	
		US 2002/0001746 A1	01-03-2002	Jenson	
		US 2002/0076133 A1	06-20-2002	Li et al.	
		US 2002/0140103 A1	10-03-2002	Kloster et al.	
MAE		US 2003/0178637 A1	09-25-2003	Chen et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document: Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
MAE		WO 2004/106581 A2	12-09-2004	Symmorphix, Inc.		
MAE		WO 2004/106582 A2	12-09-2004	Symmorphix, Inc.		

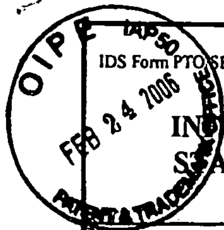
NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
MAE		KIM, H-K. and YOON, Y., "Characteristics of rapid-thermal-annealed $LiCoO_2$ cathode film for an all-solid-state thin film microbattery," *J. Vac. Sci. Technol. A 22*(4):1182-1187 (2004).	
MAE		Response to Office Action filed on October 17, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00).	

Examiner Signature	Michelle Estrada	Date Considered	3/16/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	3

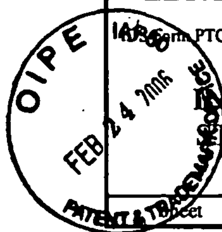
Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
ME		Final Office Action issued on December 14, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
ME		PCT Invitation to Pay Additional Fees for PCT/US01/22750, dated March 13, 2002 (Attorney Docket No. 09140.0002-00304).	
ME		PCT International Search Report for PCT/US01/22750, dated July 19, 2002 (Attorney Docket No. 09140.0002-00304).	
ME		PCT Written Opinion for PCT/US01/22750, dated July 23, 2002 (Attorney Docket No. 09140.0002-00304).	
ME		PCT International Preliminary Examination Report for PCT/US01/22750, dated October 8, 2002 (Attorney Docket No. 09140.0002-00304).	
ME		Office Action issued on November 28, 2005 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
ME		Response to Office Action filed on December 21, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01).	
ME		Response to Office Action filed on July 25, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01).	
ME		Office Action issued on October 25, 2005, in U.S. Appl. No. 10/954,182 (Attorney Docket No. 09140-0016-01000).	
ME		Response to Office Action filed on November 8, 2005, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
ME		Office Action issued on February 13, 2006, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
ME		Response to Office Action filed on January 3, 2006 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00).	
ME		PCT International Preliminary Examination Report mailed April 15, 2004 in PCT/US03/24809 (Attorney Docket No. 09140-0025-00304).	
ME		Office Action issued on December 2, 2005 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	
ME		Specification and Preliminary Amendment as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0030-01).	
ME		Office Action issued on March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	
ME		Response to Office Action dated July 25, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00).	
ME		Response to Office Action filed January 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature	Michelle Estrada	Date Considered	3/16/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US



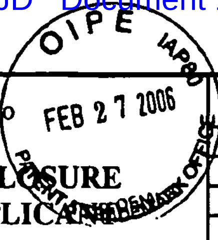
Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	3	of	3	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
MIE		PCT International Search Report and Written Opinion for Application No. PCT/US2004/014524 dated March 2, 2005 (Attorney Docket No. 09140.0033-00304).	
MIE		PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014524, dated December 8, 2005 (Attorney Docket No. 09140.0033-00304).	
MIE		PCT International Search Report for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304).	
MIE		PCT Written Opinion for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304).	
MIE		PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014523, dated December 8, 2005 (Attorney Docket No. 09140.0034-00304).	
MIE		Specification as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0042-00).	

Examiner Signature	Michelle Estrada	Date Considered	3/16/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746094839 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	1	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
MK		US 5,909,346	06-01-1999	Malhotra et al.	
MK		US 6,000,603	12-14-1999	Koskenmaki et al.	
MK		US 6,133,670	10-17-2000	Rodgers et al.	
MK		US 6,356,694 B1	03-12-2002	Weber	
MK		US 6,768,855 B1	07-27-2004	Bakke et al.	
		US 6,683,749 B2	01-27-2004	Daby et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

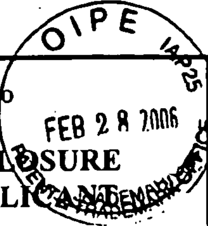
NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]

Examiner Signature	Michelle Estrada	Date Considered	3/16/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819704 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

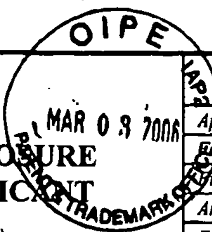
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		~~Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856~~ (Attorney Docket No. 09140.0015-01).	

copy missing

Examiner Signature	*Michelle Estrada*	Date Considered	3/6/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819602 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
ME		US 6,290,821 B1	09-18-2001	McLeod	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
ME		Response to Office Action filed February 20, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01).	
ME		Response to Office Action filed July 17, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01).	
ME		Response to Office Action filed February 28, 2006 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
ME		Response to Office Action filed March 2, 2006 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	

Examiner Signature	Michelle Estrada	Date Considered	3/16/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860819633 US

Notice of References Cited	Application/Control No. 10/101,863	Applicant(s)/Patent Under Reexamination ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,306,265 B1	10-2001	Fu et al.	204/192.12
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

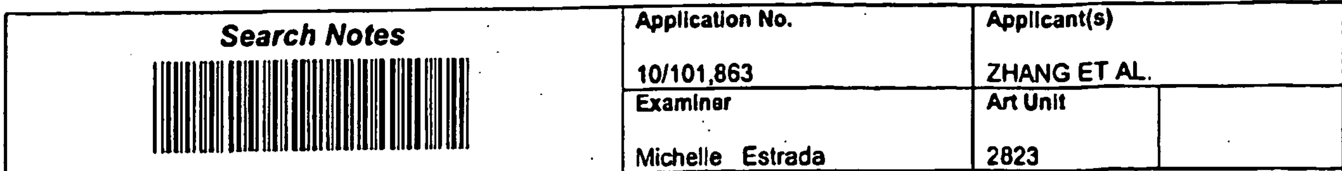
FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.



Search Notes	Application No. 10/101,863	Applicant(s) ZHANG ET AL.
	Examiner Michelle Estrada	Art Unit 2823

SEARCHED

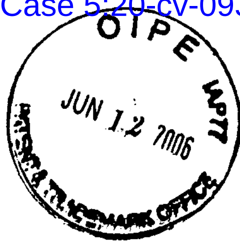
Class	Subclass	Date	Examiner
438	769	2/12/04	ME
438	770	↓	↓
438	771	↓	↓
438	787	↓	↓
438	788	↓	↓
427	533	↓	↓
204	192.12	↓	↓
204	192.15	2/12/2004	ME

INTERFERENCE SEARCHED

Class	Subclass	Date	Examiner

SEARCH NOTES (INCLUDING SEARCH STRATEGY)

	DATE	EXMR
See East search attached	2/12/2004	ME
See East search attached	7/29/05	ME
See East search attached	3/16/06	ME



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	
ZHANG, Hongmei et al.	Group Art Unit: 2823
Application No.: 10/101,863	Examiner: ESTRADA, Michelle
Filed: March 16, 2002	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed March 22, 2006, Applicants propose that this application be amended as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 6.

Attachment to this amendment include Declaration of R. E. Demaray under 37 C.F.R. §1.132.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the film is an upper cladding layer of a waveguide structure and the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Previously Presented): A method of depositing a film on a substrate, comprising:

providing pulsed DC power through a filter to a target;

providing RF bias power to a substrate positioned opposite the target; and

providing process gas between the target and the substrate, and

depositing a film on the backside of the target,

wherein the filter protects a pulsed DC power supply from the bias power, and

wherein a plasma is created between the target and the substrate.

15.-20. (Cancelled).

21. (Currently amended): A method of depositing a film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target through a filter to create a plasma and deposit the film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface, and

wherein the filter is a band rejection filter at a frequency of the bias power.

22. (Previously Presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power

includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (New): The method of claim 21, wherein the band rejection filter is a narrow band-pass filter.

41. (New): The method of claim 21, wherein a bandwidth of the band rejection filter is about 100 kHz.

42. (New): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (New): A method of depositing a film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power.

44. (New): The method of claim 43, wherein a bandwidth of the band rejection filter is about 100 kHz.

45. (New): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (New): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (New): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (New): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (New): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (New): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

REMARKS

Claims 2-14 and 21-24 are pending in this application. The Examiner has allowed claim 14 and rejected claims 2-14 and 21-24. Applicants have amended claim 21, canceled claim 5, and added new claims 40-50. Applicants traverse the Examiner's rejection and request reconsideration of the pending claims.

Information Disclosure Statement

One of the references cited in the Seventh Supplemental Information Disclosure Statement submitted on February 27, 2006, was not initialed by the Examiner. Therefore, Applicants have listed such reference for the Examiner to initial in the enclosed Ninth Supplemental Information Disclosure Statement.

Additionally, the Examiner states the Dayco reference "Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01)" was not attached with the Eighth Supplemental Information Disclosure Statement filed on February 28, 2006. Therefore, Applicants have provided a copy and re-listed such Dayco reference on the attached Ninth Supplemental Information Disclosure Statement for the Examiner's initials.

Claim Rejections under 35 U.S.C. § 103

The Examiner has rejected claims 2-13 and 21-24 under 35 U.S.C. § 103 over various combinations of Smolanoff et al. (U.S. Patent No. 6,117,279), Fu et al. (U.S. Patent No. 6,3065,265), Fukui et al. (U.S. Patent No. 5,755,938), and Le et al. (U.S. Application No. 2003/0077914). Specific rejections are further discussed below.

In making a rejection under 35 U.S.C. § 103(a), the Examiner must establish the three elements of a *prima facie* case of obviousness. MPEP § 2142. First, the Examiner must show that the prior art references teach all elements of the claims. Second, the Examiner must show

that the prior art provides the reason or motivation to make the claimed combination. The mere fact that references can be combined does not create a *prima facie* case of obviousness. Moreover, the motivation to combine cannot come from the applicant's own disclosure but must come from the prior art itself. Additionally, no motivation to combine references exists where doing so would render one of the prior art references unsatisfactory for its intended purpose. Third , the Examiner must prove that there is a reasonable expectation of success in combining the prior art references. As further discussed below, the Examiner has not met this burden.

I. Claims 2-4, 6-13, and 21-24 are allowable because the cited prior art does not collectively teach all of the elements of the claims.

Claims 2-6, 8, 10-13, and 21-24

The Examiner has rejected claims 8, 10-13, and 21 under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265). Claims 2-6 and 22-24 are rejected over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21 and further in view of Fukui et al. (5,755,938). Claim 21 has been amended to recite "a band rejection filter at a frequency of the bias power," which is substantially the limitation of claim 5. Claim 5 has been canceled.

As the Examiner states, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claim 21. (*See*, Office Action, page 5). As stated in the Declaration of Ernest Demeray filed with this amendment under 37 C.F.R. §1.132, the filter protecting the pulsed DC power supply from the RF power of the bias is an aspect of the claimed invention. The filter must pass the pulsed DC signal without unduly affecting the shape of that signal while rejecting the RF power. Therefore, the filter passes all frequencies except for the

frequency of the bias power itself. As stated in the Declaration of Ernest Demeray, other filter designs resulted in a distortion of the pulsed DC signal or in leakage of RF power back to the pulsed DC power supply -- resulting in the catastrophic failure of the power supply.

The Examiner relies on Fukui for this element. However, Fukui does not teach a "band rejection filter at a frequency of the bias power." As stated in Fukui,

> [a]lso connected to the first electrode 20 is a dc power supply 28 through a band-pass filter 27 such as a low-pass filter for adjustment of impedance. The band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a dc power from the dc power supply 28.

(Fukui, col. 6, lines 31-36). Fukui teaches a band pass filter, specifically a low-pass filter, which would not protect the DC power supply from RF and which would unreasonably distort the pulsed-dc shape. Further, there is no indication that the band-pass filter of Fukui is related to the frequency of the bias power supply. A band pass filter, below at or above the frequency of the RF bias, will not protect the pulsed DC power supply from catastrophic failure as a result of the RF power. Further, a band pass filter does not allow the broad frequency range required for the square wave of the pulsed-DC supply to reach the substrate.

Therefore, as discussed above, claim 21 is allowable over Smollanoff, Fu, and Fukui. Claims 2-4, 6-13, 22-24, and new claims 40-41 depend from claim 21 and are therefore allowable for at least the same reasons as is claim 21.

Claims 7 and 9

The Examiner rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of Le et al. (2003/0077914). Claims 7 and 9 depend from claim 21. Le does not cure the defects in the teachings of Smolanoff , Fu, or Fukui.

New Claims

Claims 42-50 have been added to this application. Claim 42 is similar in scope to claim 21 except for the limitation regarding conditioning the target. Claims 43-50 are similar to dependent claims from claim 21. Therefore, claims 42-50 are allowable over the cited art.

Conclusion

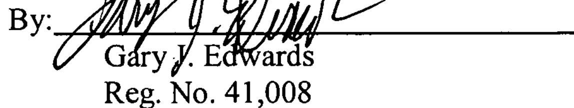
In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 12, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

Attachment: Declaration of Dr. R.E. Demaray under 37 C.F.R. §1.132

EXPRESS MAIL LABEL NO.
EV 860818108 US

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
Filed: March 16, 2002	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Declaration of Dr. R. E. Demaray under 37 C.F.R. §1.132

I, Dr. R. Ernest Demaray, declare as follows:

1. I am currently the President and Chief Technology Officer of Symmorphix, Inc., and have served as the Chairman of the Board, the Chief Executive Officer, and the Chief Technology Officer during the history of Symmorphix, Inc. I have been with Symmorphix for the past eight years. I was previously employed at Applied Materials, Inc., of Santa Clara as General Manager and Managing Director of the PVD division of Applied Komatsu. Since receiving my B.S. in Physical Chemistry in 1972, I have worked in the semiconductor equipment field for more than 34 years. I received a Ph.D. in Chemical Physics from the University of California at Santa Cruz in 1977.

2. I am an inventor of U.S. Application Serial No. 10/101, 863. At Symmorphix, my co-inventors and I developed a pulsed-DC, RF-biased deposition apparatus and various deposition methods utilized in that apparatus for deposition of thin film oxides and dielectrics. To my knowledge, the combination of pulsed-DC with RF bias applied to the substrate of an RF power

applied to the deposition chamber had not been disclosed or demonstrated previous to my invention.

3. During development of the deposition chambers and methods claimed in this application, we damaged a number (more than six units) of pulsed-DC power supplies due to RF bias power coupling through the plasma into the pulsed-dc power supply. We utilized the Advanced Energy Pinacle Plus power supply, which produced a 10 kW square wave at a frequency of from 180 kHz to 300 KHz together with a pulse reverse time from 1.3 to 5.0 μsec. Utilizing a band-pass filter between the pulsed-DC power supply and the plasma, however, will not protect the pulsed-DC power supply from the RF bias and will also unduly distort the square-wave of the pulsed-DC power signal applied to the target, which detrimentally affects the deposition conditions.

4. My co-inventors and I developed the band-rejection filter described in the specification and claimed in U.S. Application Serial No. 10/101, 863 to overcome the problem of catastrophic failure of the pulsed-DC power supply output electrometer circuit during operation. We discovered that a band-rejection filter, which is a filter that passes all of the frequencies of the square wave power supply except within a narrow band centered on the RF frequency of the RF bias, protected the pulsed-DC power supply from the RF energy while not distorting the pulses generated by the pulsed-DC power supply applied to the target.

5. I have further studied the art cited by the Examiner, namely Smolanoff et al. (U.S. Patent No. 6,117,279) (Smolanoff), Fu et al. (U.S. Patent No. 6,306,265) (Fu), Fukui et al. (U.S. Patent No. 5,755,938) (Fukui), and Le et al. (U.S. Publication No. 2003/0077914) (Le). None of these references teach a pulsed-DC system that allows an RF bias in a fashion that would not damage the pulsed-DC power supply if actually implemented as shown and described. None of these references describe a band-rejection filter at a frequency of the bias power.

6. Smolanoff discloses a reactor where the target is coupled through a filter to a DC source. No description of the filter is provided. However, in the chamber described in Smolanoff, RF power can be supplied to the target, to a secondary plasma generated below the target, and to the

substrate itself. A pulsed-DC power supply without the protection disclosed in the present application would catastrophically fail under these conditions. .

7. Fu describes a PVD sputtering chamber with no pulsed-dc and no filter to protect a pulsed-dc power supply. Therefore, Fu also does not describe a band rejection filter centered at the frequency of an RF bias.

8. Fukui describes a band-pass filter (specifically a low pass filter) coupled between the pulsed-dc power supply and the filter. Again, a band-pass filter does not protect the pulsed-DC power supply, as is required, and will distort the pulsed-DC square wave. Further, Fukui indicates that "[t]he band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a dc power from the dc power supply 28." (Fukui, col. 6, lines 33-36). This is quite the opposite of what occurs in our applications, where the RF signal is superimposed on the pulsed DC power signal in the plasma, to which the substrate is exposed. Therefore, Fukui does not teach a band-rejection filter at the frequency of the RF bias.

9. Le describes neither a biased power nor a filter and simply teaches an un-biased deposition process. Therefore, Le does not teach a band rejection filter.

10. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: June 7 2006

By: [signature]
R. Ernest Demaray

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
	)
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938
	)

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

NINTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Ninth Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

06/15/2006 MAHMED1 00000056 060916 10101863
01 FC:1806 180.00 DA

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

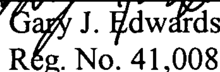
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

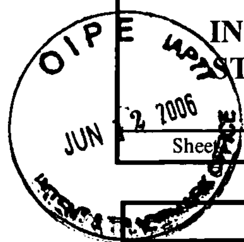
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 12, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 860818108 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 4,082,569	04-04-1978	Evans, Jr.	
		US 5,472,795	12-05-1995	Atita	
		US 5,645,626	07-08-1997	Edlund et al.	
		US 5,702,829	12-30-1997	Paidassi et al.	
		US 6,045,626	04-04-2000	Yano et al.	
		US 6,673,716 B1	01-06-2004	D'Couto et al.	
		US 6,683,749 B2	01-27-2004	Daby et al.	
		US 6,884,327 B2	04-26-2005	Pan et al.	
		US 2002/0115252 A1	08-22-2002	Haukka et al.	
		US 2003/0035906 A1	02-20-2003	Memarian et al.	
		US 2004/0043557 A1	03-04-2004	Haukka et al.	
		US 2005/0048802 A1	03-03-2005	Zhang et al.	
		US 2005/0183946 A1	08-25-2005	Pan et al.	
		US 2006/0054496 A1	03-16-2006	Zhang et al.	
		US 2006/0057283 A1	03-16-2006	Zhang et al.	
		US 2006/0057304 A1	03-16-2006	Zhang et al.	
		US 2006/0071592 A1	04-06-2006	Narasimhan et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		JP 7-224379 A	08-22-1995	Ulvac Japan Ltd		Abstract

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818108 US

IDS Form PTO/SB/08: Substitute for form 1449A/PTO	*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	*Application Number*	10/101,863
	Filing Date	March 16, 2002
	First Named Inventor	ZHANG, Hongmei
	Art Unit	2823
(Use as many sheets as necessary)	*Examiner Name*	ESTRADA, Michelle
Sheet 2 of 2	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		BARBIER, D., "Performances and potential applications of erbium doped planar waveguide amplifiers and lasers," *Proc. OAA*, Victoria, BC, Canada, pp. 58-63 (July 21-23, 1997).	
		KELLY, P.J. et al., "A novel technique for the deposition of aluminum-doped zinc oxide films," *Thin Solid Films 426*(1-2):111-116 (2003).	
		TOMASZEWSKI, H. et al., "Yttria-stabilized zirconia thin films grown by reactive r.f. magnetron sputtering," *Thin Solid Films 287*:104-109 (1996).	
		Response to Final Office Action filed April 14, 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
		Office Action mailed April 27, 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
		Final Office Action mailed May 8, 2006 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01).	
		Office Action issued on March 9, 2006, in U.S. Appl. No. 10/954,182 (Attorney Docket No. 09140-0016-01000).	
		Response to Office Action filed on May 15, 2006, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Final Office Action issued on May 19, 2006 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	
		Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated March 20, 2006 (Atty. Docket No. 9140.0030-00256).	
		Office Action mailed April 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818108 US

(19) JAPANESE PATENT OFFICE

COPY

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **07224379 A**

(43) Date of publication of application: **22.08.95**

(51) Int. Cl **C23C 14/34**

(21) Application number: **06017653**

(22) Date of filing: **14.02.94**

(71) Applicant: **ULVAC JAPAN LTD**

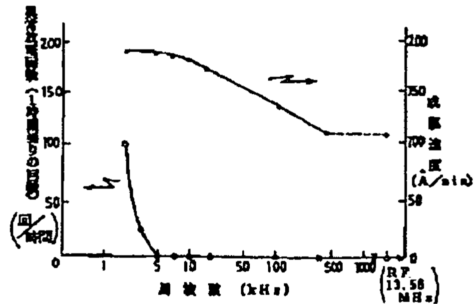
(72) Inventor: **OTA ATSUSHI**
HAGA HIDEAKI
TANI NORIAKI
SUU KOUKOU
KOMATSU TAKASHI
NAKAMURA KYUZO
MOMONO TAKESHI
KAWAMURA HIROAKI
SUZUKI IKUO
IKEDA SATOSHI
ISHIKAWA MICHIO
OTA YOSHIFUMI
MATSUMOTO MASAHIRO

(54) **SPUTTERING METHOD AND DEVICE THEREFOR**

(57) Abstract

PURPOSE: To form a film at a high rate without generating an abnormal discharge for a long time at the time of sputtering a conductive target in a gaseous reactant atmosphere by DC sputtering by applying a positive potential on a negative-potential target in the form of a pulse.

CONSTITUTION: A substrate and a conductive target are opposed in a vacuum treating chamber, and the target is sputtered in a gaseous reactant atmosphere by DC sputtering to form a thin film on the substrate. In this case, a device with a power source to apply a positive potential on a negative potential connected to the target is used, and a positive potential is applied on the negative-potential target in the form of a pulse at the frequency of 5-400kHz to conduct sputtering. The electron in the plasma is attracted by the positive potential to neutralize the plus ion accumulated on the insulator and high-resistance film, and the abnormal discharge due to an arc discharge is not generated.



COPYRIGHT: (C)1995,JPO

(19)日本国特許庁（JP）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平7－224379

(43)公開日　平成7年(1995)8月22日

(51)Int.Cl.⁶	識別記号	庁内整理番号	F I	技術表示箇所
C23C　14/34	R	8414－4K		
	A	8414－4K		
	M	8414－4K		

審査請求　未請求　請求項の数4　OL　（全 5 頁）

(21)出願番号　特願平6－17653

(22)出願日　平成6年(1994)2月14日

(71)出願人　000231464
日本真空技術株式会社
神奈川県茅ヶ崎市萩園2500番地

(72)発明者　太田　淳
千葉県山武郡山武町横田523　日本真空技術株式会社千葉超材料研究所内

(72)発明者　羽賀　日出明
千葉県山武郡山武町横田523　日本真空技術株式会社千葉超材料研究所内

(72)発明者　谷　典明
千葉県山武郡山武町横田523　日本真空技術株式会社千葉超材料研究所内

(74)代理人　弁理士　北村　欣一　（外2名）

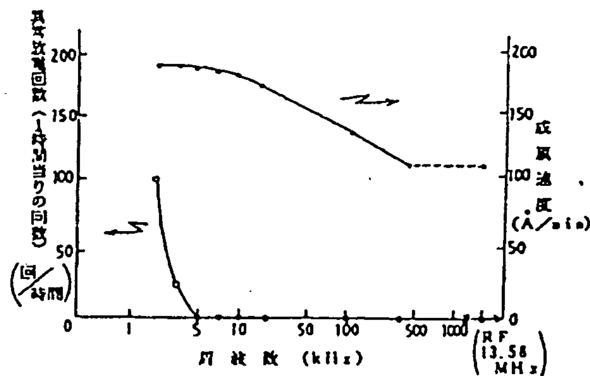
最終頁に続く

(54)【発明の名称】　スパッタ方法およびそのスパッタ装置

(57)【要約】

【目的】　反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行っても高速成膜が可能であり、かつ、長時間スパッタリングを行っても異常放電のないスパッタ成膜が出来るスパッタ方法。

【構成】　反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を一定の周波数でパルス状に印加しながらスパッタリングする。



PTO 99-4732
S.T.I.C. Translations Branch

監修　日本国特許庁

【特許請求の範囲】
【請求項1】 反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を周波数5～400kHzでパルス状に印加しながらスパッタリングすることを特徴とするスパッタ方法。
【請求項2】 前記導電性ターゲットはSi、Al、Ta、Ti、C、ITO、ZnO、SnO_2またはこれらの合金であり、また、反応ガスはN_2、O_2、H_2、NH_3、CO、CO_2、CH_4、C_2H_2、H_2Oのいずれか1つまたは2つ以上の混合ガスであることを特徴とする請求項第1項に記載のスパッタ方法。
【請求項3】 真空処理室内に基板と導電性ターゲットを対向させて設け、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ装置において、負電位に正電位を周波数5～400kHzでパルス状に印加する電源を導電性ターゲットに接続したことを特徴とするスパッタ装置。
【請求項4】 前記導電性ターゲットはSi、Al、Ta、Ti、C、ITO、ZnO、SnO_2またはこれらの合金であり、また、反応ガスはN_2、O_2、H_2、NH_3、CO、CO_2、CH_4、C_2H_2、H_2Oのいずれか1つまたは2つ以上の混合ガスであることを特徴とする請求項第3項に記載のスパッタ装置。
【発明の詳細な説明】
【0001】
【産業上の利用分野】本発明はスパッタ方法およびそのスパッタ装置に関し、更に詳しくは、反応ガス雰囲気中で導電性ターゲットにスパッタリングを行うスパッタ方法およびそのスパッタ装置に関する。
【0002】
【従来の技術】従来から、反応ガス雰囲気中で導電性ターゲットにスパッタリングを行って基板上に誘電体膜、光学膜、保護膜等の膜を成膜するスパッタ方法に用いられるスパッタ装置としては、真空処理室内に基板とターゲットカソードを対向して設け、該ターゲットカソードに導電性ターゲットを装着し、真空処理室内を所定の雰囲気とした状態でターゲットに所定電圧を印加してターゲットにスパッタリングを行う装置が知られている。
【0003】そして、スパッタリング時の電源としては直流電源、または例えば13.56MHzの高周波電源を用いている。
【0004】
【発明が解決しようとする課題】前記従来のスパッタ装置を用いて基板上に誘電体膜、光学膜、保護膜等の膜を成膜する際、高周波電源を用いるRFスパッタリングは長時間異常放電なしに成膜することが可能であるが、成膜速度が遅いという問題がある。
【0005】また、前記従来のスパッタ装置を用いて基板上に誘電体膜、光学膜、保護膜等の膜を成膜する際、直流電源を用いるDCスパッタリングは成膜速度は速いが、スパッタリングの経時と共に、ターゲット表面に絶縁物や高抵抗膜が堆積するため、異常放電を起こすという問題がある。
【0006】スパッタリング中に異常放電が発生すると欠陥のない均質な膜を成膜する上で致命的な悪影響を及ぼす。
【0007】従って、従来のスパッタ装置では通常RFスパッタリングを行っているが、高速成膜を必要とする場合は、DCスパッタリングを行い、ターゲット表面に絶縁物や高抵抗膜が堆積しないようにターゲット全面に亘ってエロージョン化するようにしているが、異常放電を十分に除去することが出来ない。
【0008】本発明はかかる問題点を解消し、反応ガス雰囲気中でスパッタリングを行っても高速成膜が可能であり、かつ、長時間スパッタリングを行っても異常放電のないスパッタ成膜の可能なスパッタ方法およびそれに用いるスパッタ装置を提供することを目的とする。
【0009】
【課題を解決するための手段】本発明のスパッタ方法は、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を周波数5～400kHzでパルス状に印加しながらスパッタリングすることを特徴とする。
【0010】また、前記導電性ターゲットはSi、Al、Ta、Ti、C、ITO、ZnO、SnO_2またはこれらの合金とし、また、反応ガスはN_2、O_2、H_2、NH_3、CO、CO_2、CH_4、C_2H_2、H_2Oのいずれか1つまたは2つ以上の混合ガスとしてもよい。
【0011】本発明のスパッタ装置は、真空処理室内に基板と導電性ターゲットを対向させて設け、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ装置において、負電位に正電位を周波数5～400kHzでパルス状に印加する電源を導電性ターゲットに接続したことを特徴とする。
【0012】また、前記導電性ターゲットはSi、Al、Ta、Ti、C、ITO、ZnO、SnO_2またはこれらの合金とし、また、反応ガスはN_2、O_2、H_2、NH_3、CO、CO_2、CH_4、C_2H_2、H_2Oのいずれか1つまたは2つ以上の混合ガスとしてもよい。
【0013】
【作用】反応ガス雰囲気中で導電性ターゲットに直流電源より直流電圧を印加し、スパッタリングを行うとターゲットはスパッタされて基板上に薄膜が形成される。

【0014】長時間連続してスパッタリングを行うと、ターゲット上に堆積した絶縁物や高抵抗膜上に不活性ガスまたは反応ガスのプラス（＋）イオンが蓄積される。このプラス（＋）イオンの電荷がターゲット間、エロージョン部、アース電極等とアーク放電を引き起こして異常放電の原因となる。

【0015】この異常放電でターゲット材、絶縁物、高抵抗膜が粒子状となって飛散し、基板上に付着し、成膜された薄膜の欠陥となる。

【0016】ターゲットに直流電圧を印加してＤＣスパッタリングを行う際、負電位のターゲットに正電位を一定の周波数でパルス状に印加すると、正電位によりプラズマ中の電子を引き寄せ、ターゲット上に堆積した絶縁物、高抵抗膜上に蓄積するプラス（＋）イオンの電荷を中和し、アーク放電による異常放電を防止する。

【0017】その際、ターゲットに印加する正電位の印加時間は負電位の時間に比べて極めて短くとも効果があるため、成膜速度は直流電流のみによる成膜速度より数％の減少となる程度であり、この成膜速度は高周波１３．５６ＭＨｚスパッタ時の成膜速度よりも高い。

【0018】

【実施例】以下添付図面に従って本発明の実施例について説明する。

【0019】図１は、スパッタ装置の１例を示すもので、図中、１は真空処理室を示す。

【0020】真空処理室１を外部のクライオポンプのような真空ポンプ等の真空排気系２にバルブ３を介して接続し、該真空処理室１内の真空度を調節自在とすると共に、真空処理室１内に基板４とターゲットカソード５とを対向に配置し、該ターゲットカソード５の前面に導電性ターゲット６をロウ材でボンデングするようにしたまた、該真空処理室１内にガス導入管７を介してガスボンベ等のガス供給源８よりスパッタガスを導入するようにした。図示例ではガス導入管７を分岐し、一方の分岐管９ａにガス圧調節弁１０ａを介して不活性ガス（例えばアルゴンガス）のガス供給源８ａを接続し、他方の分岐管９ｂにガス圧調節弁１０ｂを介して反応ガス（例えば窒素ガス）のガス供給源８ｂを接続した。

【0021】また、ターゲットカソード５に直流電源１１をパルスユニット１２を介して接続し、パルスユニット１２を調節して導電性ターゲット６に負電位と正電位を所定の周波数でパルス状に印加するようにした。

【0022】また、ターゲットカソード５の背面側にマグネトロンスパッタのためのマグネット１３を配設して、ターゲットカソード５に取り付けられた導電性ターゲット６の表面にマグネトロンスパッタに必要な磁場を与えるようにした。

【0023】次に、図１装置を用いて本発明のスパッタ方法の具体的実施例について説明する。

【0024】実施例１

先ず、真空処理室１内に基板４と、ターゲットカソード５に導電性ターゲット６としてケイ素（Ｓｉ）製ターゲットを装着した。

【0025】続いて、真空処理室１内を真空排気系２により 6.7×10^{-4}Pa（ 5×10^{-7}Torr）に排気した後、真空処理室１内にガス供給源８ａからのアルゴン（Ａｒ）ガスと、ガス供給源８ｂからの窒素（N_2）ガスとから成る反応ガスをガス導入管７を介して導入して、該真空処理室１内のスパッタ圧が 6.7×10^{-1}Pa（ 5×10^{-3} Ｔｏｒｒ）となるようにした。次に基板４上に形成される窒化ケイ素（ＳｉＮｘ ）の屈折率が2.03となるようにＡｒガスとN_2 ガスの流量をそれぞれ 100sccmと50sccmに調整した後、ＤＣマグネトロンスパッタ法により導電性ターゲット６に直流電源１１より直流電力３ｋＷを印加し、負電位のターゲット６に正電位をパルスユニット１２より周波数を2kHzから400kHzに変化させながらパルス状（図２参照）に印加し、スパッタリングを行って基板４上に膜厚 900Åの窒化ケイ素（ＳｉＮｘ ）膜を形成した。尚、負電位のターゲットにパルス状に印加する正電位の印加時間は周波数 10kHzまでの場合は10μsecとし、周波数 10kHzを超えて100kHzまでの場合は 5μsecとし、周波数100kHzを超えた場合は1μsec とした。また、ＤＣマグネトロンスパッタ時の磁場強度を 250Ｏｅとした。

【0026】そして異常放電回数と成膜速度を負電位の導電性ターゲット６に印加する正電位の周波数毎に測定した。得られた測定結果を図３に示す。

【0027】図３から明らかなように負電位に印加する正電位の周波数の増加に伴い、異常放電回数は減少し、周波数が5kHz以上ではその回数はほとんど０になり、これ以上の周波数で正電位を負電位のターゲットに印加すれば異常放電が発生しないことが分かる。また、負電位に印加する正電位の周波数が400kHz（時間1μsec ）の場合は、通常の高周波電源（13.56MHz）とほぼ同じ成膜速度となり、400kHz以上の周波数では正電位の印加は意味がない。従って、負電位のターゲットに印加する正電位の周波数範囲は 5～400kHzであることが確認された。

【0028】また、周波数範囲 5～400kHzでの成膜速度は高周波電源（13.56MHz）よりも高い成膜速度である。

【0029】反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行うと、ターゲット上の非エロージョン部分に絶縁物または高抵抗膜が堆積し、従来の直流電源でターゲットに負の電位を放電し続けると、絶縁物上にプラス（＋）の電荷が蓄積し、ターゲット、エロージョン部、アース電極との間でアーク放電を起こし、電荷を放出する。その結果異常放電が発生することになるが、本発明では図２に示すように負電位に正電位を周期的に、即ち一定の周波数で印加することにより前記の電荷を補償して異常放電の発生を防止するようにしている。

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 1145 of 1543

【0030】実施例2
反応ガスとして酸素（O_2）ガスを用い、スパッタ圧を6.7×10^{-1}Pa（5×10^{-3}Torr）とし、直流電力を2kWとし、基板上に形成される酸化ケイ素（SiOx）の屈折率が1.46となるように酸素流量を調整した以外は前記実施例1と同様の方法でDCマグネトロンスパッタ法によりターゲットにスパッタリングを行って基板上に膜厚1000Åの酸化ケイ素（SiOx）膜を形成した。

【0031】そして異常放電回数を負電位のターゲットに印加する正電位の周波数毎に測定した。得られた測定結果を図4に示す。

【0032】図4から明らかなように負電位に印加する正電位の周波数は約5kHzで異常放電をほぼ防止し得ることが分かる。

【0033】尚、図4におけるSiNx の測定結果（黒丸印）は前記実施例1の測定結果を参考のために記載したものである。

【0034】実施例3
導電性ターゲットとしてグラファイト（C）を用い、反応ガスとしてメタン（CH_4）ガスを用い、スパッタ圧を 6.7×10^{-1}Pa（5×10^{-3}Torr）とし、直流電力を2kWとした以外は前記実施例1と同様の方法でDCマグネトロンスパッタ法によりターゲットにスパッタリングを行って基板上に膜厚 200Åのダイヤモンドライクカーボン（DLC）膜を形成した。

【0035】そして異常放電回数を負電位のターゲットに印加する正電位の周波数毎に測定した。得られた測定結果を図4に示す。

【0036】図4から明らかなように負電位に印加する正電位の周波数は約5kHzで異常放電をほぼ防止し得ることが分かる。

【0037】前記実施例1，2，3の結果から、導電性ターゲット材料、放電状態によりプラス（＋）の電荷の蓄積量が異なるため、異常放電はターゲットに印加する周波数に大きく依存する。従って、周波数5kHz以上であれば、種々のターゲット材料でもスパッタリング中の異常放電を大幅に減少することが出来ることになる。

【0038】実施例4
導電性ターゲットとしてアルミニウム（Al）、チタン（Ti）、タンタル（Ta）、またはこれらの合金例えばAl－2at％Tiを用い、反応ガスとして窒素（N_2）、酸素（O_2）、水素（H_2）、一酸化炭素（CO）、二酸化炭素（CO_2）、アンモニア（NH_3）、水（H_2O）を単独、或いは2種以上を用い、これらを種々組み合わせし、その他の条件を前記実施例1と同様にしてDCマグネトロンスパッタ法により基板上に酸化物、窒化物、炭化物のいずれかの薄膜を形成したが、負電位に印加する正電位が周波数5kHz以上ではスパッタリング中に異常放電の発生は見られなかった。

【0039】また、前記実施例1では導電性ターゲットにSiを用い、反応ガスとして窒素ガスを用いて基板上に窒化ケイ素（SiNx）膜を形成したが、導電性ターゲットとしてSiの代わりにIn_2O_3－SnO_2焼結体（ITO）、酸化亜鉛（ZnO）、酸化スズ（SnO_2）を用い、反応ガスとして窒素ガスの代わりに酸素（O_2）、一酸化炭素（CO）、二酸化炭素（CO_2）、水（H_2O）等の酸素を含むガス、またはそのガスに水素ガス（H_2）混合したガスを用い、負電位のターゲットに印加する正電位の周波数を5～400kHzとした直流スパッタ法（DCマグネトロンスパッタ法）により基板上に透明導電膜であるITO、ZnO、SnO_2の薄膜を形成することが出来る。

【0040】図1装置では負電位に一定の周波数で正電位をパルス状に印加する電源装置として直流電源とパルス電源の組み合わせた装置としたが、これに限定されるものではなく、図2に示すような負電位に正電位が周期的（パルス状）に印加される一体型の電源装置としてもよい。

【0041】
【発明の効果】本発明のスパッタ方法によるときは、反応ガス雰囲気中で、負電位の導電性ターゲットに正電位を一定の周波数でパルス状に印加しながらスパッタリングを行うようにしたので、スパッタリング中にターゲット上に堆積した絶縁物、高抵抗膜上に蓄積するプラスイオンの電荷を中和することが出来て、アーク放電による異常放電を防止しながら長時間に亘って速い成膜速度で基板上に欠陥のない均質な薄膜を形成することが出来る効果がある。

【0042】また、本発明のスパッタ装置によるときは、導電性ターゲットに負電位に正電位を一定の周波数でパルス状に印加する電源を接続するようにしたので、アーク放電による異常放電を防止しながら長時間に亘って速い成膜速度で基板上に欠陥のない均質な薄膜を形成することが出来るスパッタ装置を提供する効果がある。

【図面の簡単な説明】

【図1】 本発明のスパッタ方法を実施するためのスパッタ装置の1例の概略截断側面図。

【図2】 図1装置による導電性ターゲットに印加される電位のモデル図。

【図3】 本発明スパッタ方法の1実施例における成膜時の周波数と異常放電回数との関係、並びに周波数と成膜速度との関係を示す特性線図。

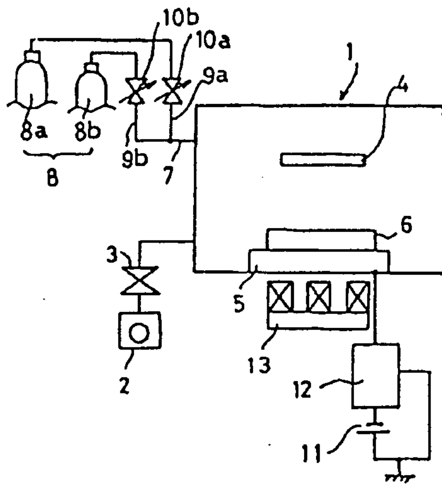
【図4】 本発明スパッタ方法の他の実施例における成膜時の周波数と異常放電回数との関係を示す特性線図。

【符号の説明】

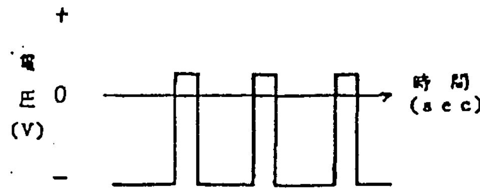
1 真空処理室、 2 真空排気系、 4 基板、 6 導電性ターゲット、 7 ガス導入管、 8 スパッタガス供給源、 11 直流電源、 12 パルスユニット。

Best Available Copy

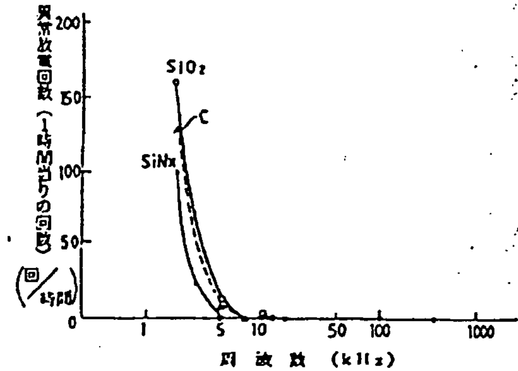
【図1】



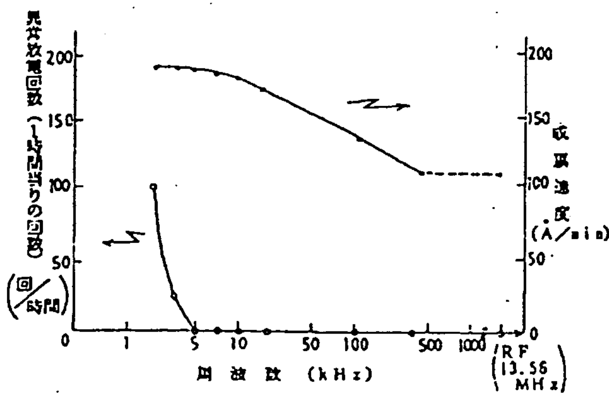
【図2】



【図4】



【図3】



フロントページの続き

(72)発明者 鄒 紅▲こう▼
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 小松 孝
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 中村 久三
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 桃野 健
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 川村 裕明
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 鈴木 郁生
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 池山 智
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 石川 道夫
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 太田 賀文
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

(72)発明者 松本 昌弘
千葉県山武郡山武町横田523 日本真空技術株式会社千葉超材料研究所内

RCE Filed 6-24-06

PTO/SB/06 (12-04)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875 Effective December 8, 2004

Application or Docket Number: 10/101,863

APPLICATION AS FILED – PART I

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	SMALL ENTITY RATE ($)	SMALL ENTITY FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY FEE ($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	150.00		N/A	300.00
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	$250		N/A	$500
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	$100		N/A	$200
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X$ 25 =		OR	X$50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X100 =			X200 =	
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))			+180=			+360=	
			TOTAL			TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

AMENDMENT A — 2-24-06

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 17	Minus	** 39	=	X$ 25 =		OR	X$50 =	
Independent (37 CFR 1.16(h))	* 2	Minus	*** 5	=	X100 =		OR	X200 =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					+180=		OR	+360=	
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B — 6-12-06

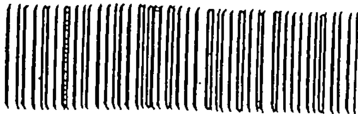
	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 27	Minus	** 39	= —	X$ 25 =	—	OR	X$50 =	
Independent (37 CFR 1.16(h))	* 3	Minus	*** 5	= —	X100 =	—	OR	X200 =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					+180=	—	OR	+360=	
					TOTAL ADD'L FEE	—	OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Index of Claims



Application No. 10/101,863

Applicant(s)

Examiner

Art Unit

√	Rejected	–	(Through numeral) Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

Claim Final	Claim Original	Date 2/5/04
	1	-
	2	-
	3	-
	4	-
	5	-
	6	-
	7	-
	8	-
	9	-
	10	-
	11	-
	12	-
	13	-
	14	-
	15	-
	16	-
	17	-
	18	-
	19	-
	20	-
	21	-
	22	-
	23	-
	24	-
	25	-
	26	-
	27	-
	28	-
	29	-
	30	-
	31	-
	32	-
	33	-
	34	-
	35	-
	36	-
	37	-
	38	-
	39	-
	40	-
	41	-
	42	-
	43	-
	44	√
	45	√
	46	√
	47	√
	48	√
	49	√
	50	

Claim Final	Claim Original	Date
	51	
	52	
	53	
	54	
	55	
	56	
	57	
	58	
	59	
	60	
	61	
	62	
	63	
	64	
	65	
	66	
	67	
	68	
	69	
	70	
	71	
	72	
	73	
	74	
	75	
	76	
	77	
	78	
	79	
	80	
	81	
	82	
	83	
	84	
	85	
	86	
	87	
	88	
	89	
	90	
	91	
	92	
	93	
	94	
	95	
	96	
	97	
	98	
	99	
	100	

Claim Final	Claim Original	Date
	101	
	102	
	103	
	104	
	105	
	106	
	107	
	108	
	109	
	110	
	111	
	112	
	113	
	114	
	115	
	116	
	117	
	118	
	119	
	120	
	121	
	122	
	123	
	124	
	125	
	126	
	127	
	128	
	129	
	130	
	131	
	132	
	133	
	134	
	135	
	136	
	137	
	138	
	139	
	140	
	141	
	142	
	143	
	144	
	145	
	146	
	147	
	148	
	149	
	150	

2823
IFW

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
	)
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
	)
Filed: March 16, 2002	)
	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938
	)

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

TENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Tenth Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

07/18/2006 RMEBRAHT 00000101 060916 10101863
01 FC:1806 180.00 DA

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

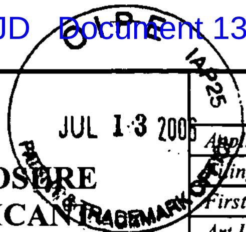
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 13, 2006

By: ____________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 860818417 US**



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	2	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 4,710,940	12-01-1987	Sipes, Jr.	
		US 4,785,459	11-15-1988	Baer	
		US 5,435,826	07-25-1995	Sakakibara et al.	
		US 5,512,147	04-30-1996	Bates et al.	
		US 5,569,520	10-29-1996	Bates	
		US 5,597,660	01-28-1997	Bates et al.	
		US 5,612,152	03-18-1997	Bates	
		US 6,168,884 B1	01-02-2001	Neudecker et al.	
		US 6,236,793 B1	05-22-2001	Lawrence et al.	
		US 6,242,132 B1	06-05-2001	Neudecker et al.	
		US 6,365,300 B1	04-02-2002	Ota et al.	
		US 6,760,520 B1	07-06-2004	Medin et al.	
		US 6,818,356 B1	11-16-2004	Bates	
		US 2001/0031122 A1	10-18-2001	Lackritz et al.	
		US 2003/0185266 A1	10-02-2003	Henrichs	
		US 2006/0134522 A1	06-22-2006	Zhang et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 860818417 US**

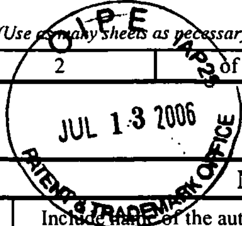
IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00



NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		COCORULLO, G. et al., "Amorphous silicon waveguides and light modulators for integrated photonics realized by low-temperature plasma-enhanced chemical-vapor deposition," *Optics Lett. 21*(24):2002-2004 (1996).	
		Notice of Allowance mailed August 6, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140.0002-01).	
		Final Office Action mailed June 9, 2006 in U.S. Appl. No. 11/100,856 (Atty. Docket No. 09140.0015-01).	
		Office Action issued on March 23, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00).	
		Specification as filed September 2, 2005, for U.S. Appl. No. 11/218,652 (Atty. Docket No. 09140.0052-00000).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 860818417 US**

IFW 2823

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

ELEVENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Eleventh Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

English translations of the non-English language documents are enclosed.

4

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

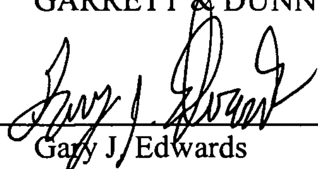
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: August 15, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 746096525 US**

O I P E, AUG 15 2006, PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	2	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 5,433,835	07/18/1995	Demaray	
		US 6,288,835 B1	09/11/2001	Nilsson et al.	
		US 6,452,717 B1	09/17/2002	Endo	
		US 2002/0014406 A1	02/07/2002	Takashima	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		DE 37 38 738 C1	01/26/1989	Degussa AG		Yes
		JP 5-230642 A	09/07/1993	Nissin High Voltage Co., Ltd.		Yes
		WO 99/61674 A1	12/02/1999	Universiteit Gent		
		WO 2006/063308 A2	06/15/2006	Symmorphix, Inc.		

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		AGRAWAL, G.P., in: Fiber-Optic Communication Systems, 2nd Edition, John Wiley & Sons, New York, pp. 361-399 and 415 (1997).	
		ASM Handbook, Formerly Ninth Edition, Metals Handbook, Volume 15, Casting, Davis et al. (Eds.), ASM International, pp. 372-373, 376-383, and 410-411 (1988).	
		MASUDA, H. & KAWAI, S., "Wide-band and gain-flattened hybrid fiber amplifier consisting of an EDFA and a multiwavelength pumped raman amplifier," *IEEE Photonics Technology Lett. 11*(6):647-649 (1999).	
		SNOEKS, E. et al., "Cooperative upconversion in erbium-implanted soda-lime silicate glass optical waveguides," *J. Opt. Soc. Am. B 12*(8):1468-1474 (1995).	
		Response to Office Action filed July 27, 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
		Notice of Allowance mailed March 25, 2004 for US Patent No. 6,827,826 (Atty. Docket No. 09140.0002-02).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746096525 US

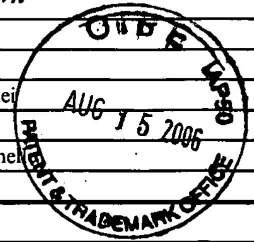
IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michel
Attorney Docket Number	9140.0016-00



NON PATENT LITERATURE DOCUMENTS			
		Notice of Allowance issued on October 8, 2002, in U.S. Patent No. 6,533,907 (Atty. Docket No. 09140-0004-00).	
		Notice of Allowance issued on October 21, 2004, in U.S. Application No. 10/101,492 (Atty. Docket No. 09140-0015-00).	
		Response to Office Action filed on August 9, 2006 in Application No. 10/954,182 (Atty. Docket No. 09140.0016-01).	
		Office Action issued on August 2, 2006, in U.S. Application No. 10/101,341 (Atty. Docket No. 09140-0017-00).	
		Response to Office Action filed on July 24, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00).	
		Response to Office Action filed July 26, 2006 in U.S. Application No. 10/851,542 (Atty. Docket No. 09140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 746096525 US**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 June 2006 (15.06.2006)

PCT

(10) International Publication Number
WO 2006/063308 A2

(51) International Patent Classification:
B05D 5/12 (2006.01) *H01M 10/38* (2006.01)
H01M 4/52 (2006.01) *C23C 14/34* (2006.01)

(21) International Application Number:
PCT/US2005/044781

(22) International Filing Date:
7 December 2005 (07.12.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/634,818 8 December 2004 (08.12.2004) US
60/651,363 8 February 2005 (08.02.2005) US

(71) Applicant *(for all designated States except US)*: SYMMORPHIX, INC. [US/US]; 1278 Reamwood Avenue, Sunnyvale, CA 94089-2233 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: ZHANG, Hongmei [US/US]; 1330 Rodney Drive, San Jose, CA 95118 (US). DEMARAY, Richard, E. [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). SHAO, May [US/US]; 5401 Nectar Circle, Elk Grove, CA 95757 (US).

(74) Agent: EDWARDS, Gary, J.; Finnegan, Henderson, Farabow, Garrett & Dunner LLP, 901 New York Avenue, Washington, D.C.., District of Columbia 20001-4413 (US).

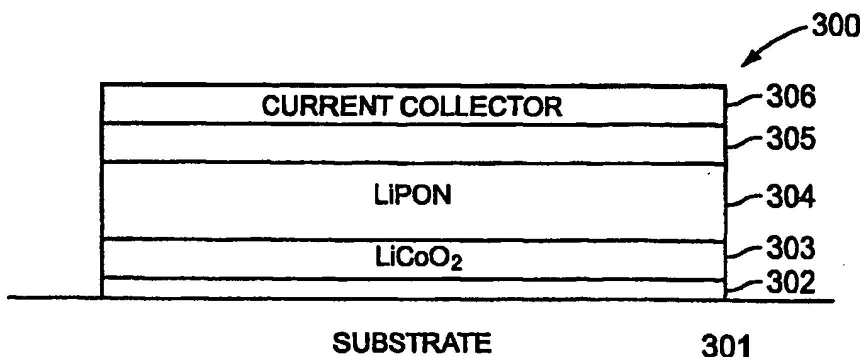
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DEPOSITION OF LICoO2



(57) Abstract: In accordance with the present invention, deposition of $LiCoO_2$ layers in a pulsed-dc physical vapor deposition process is presented. Such a deposition can provide a low-temperature, high deposition rate deposition of a crystalline layer of $LiCoO_2$ with a desired <101> or <003> orientation. Some embodiments of the deposition addresses the need for high rate deposition of $LiCoO_2$ films, which can be utilized as the cathode layer in a solid state rechargeable Li battery. Embodiments of the process according to the present invention can eliminate the high temperature (>700°C) anneal step that is conventionally needed to crystallize the $LiCoO_2$ layer. Some embodiments of the process can improve a battery utilizing the $LiCoO_2$ layer by utilizing a rapid thermal anneal process with short ramp rates.

WO 2006/063308 A2

66

DEPOSITION OF LICoO_2

RELATED APPLICATION

[001] The present application claims priority to Provisional Application No. 60/651,363, filed on February 8, 2005, by Hongmei Zhang and Richard E. Demaray, and to Provisional Application No. 60/634,818, filed on December 8, 2004, by the same inventors, each of which are herein incorporated by reference in their entirety.

BACKGROUND

1. Field of the Invention

[002] The present invention is related to thin-film solid-state batteries and, in particular, the deposition of $LiCoO_2$ films and layers for battery manufacture.

2. Discussion of Related Art

[003] Solid-state thin-film batteries are typically formed by stacking thin films on a substrate in such a way that the films cooperate to generate a voltage. The thin films typically include current collectors, a cathode, an anode, and an electrolyte. The thin films can be deposited utilizing a number of deposition processes, including sputtering and electroplating. Substrates suitable for this application have conventionally been high temperature materials capable of withstanding at least one high temperature anneal process to at least 700 °C for up to about 2 hours in air so as to crystallize the $LiCoO_2$ film. Such a substrate can be any suitable material with appropriate structural and material properties, for example a semiconductor wafer, metallic sheet (e.g., titanium or zirconium), ceramic such as alumina, or other material capable of withstanding subsequent high temperature processing in

the presence of the $LiCoO_2$, which can experience significant interfacial reactions with most materials utilized in a battery during these temperature cycles.

[004] Other lithium containing mixed metal oxides besides $LiCoO_2$, including Ni, Nb, Mn, V, and sometimes also Co, but including other transition metal oxides, have been evaluated as crystalline energy storage cathode materials. Typically, the cathode material is deposited in amorphous form and then the material is heated in an anneal process to form the crystalline material. In $LiCoO_2$, for example, an anneal at or above 700°C transforms the deposited amorphous film to a crystalline form. Such a high temperature anneal, however, severely limits the materials that can be utilized as the substrate, induces destructive reaction with the lithium containing cathode material and often requires the use of expensive noble metals such as gold. Such high thermal budget processes (i.e., high temperatures for extended periods of time) are incompatible with semiconductor or MEM device processing and limit the choice of substrate materials, increase the cost, and decrease the yield of such batteries. The inventors are unaware of a process disclosed in the art that allows production of cathodic lithium films for a battery structure where a post-deposition anneal process has a low enough thermal budget to allow production of functional structures on low temperature materials such as stainless steel, aluminum, or copper foil.

[005] It is known that crystallization of amorphous $LiCoO_2$ on precious metals can be achieved. An example of this crystallization is discussed in Kim et al., where a conventional furnace anneal at 700°C for 20 minutes of an amorphous layer of $LiCoO_2$ on a precious metal achieves crystallization of the $LiCoO_2$ material, as shown by x-ray diffraction data. Kim, Han-Ki and Yoon, Young Soo, "Characteristics of rapid-thermal-annealed $LiCoO_2$, cathode film for an all-solid-state thin film microbattery," J. Vac. Sci. Techn. A 22(4), Jul/Aug 2004. In Kim et al., the $LiCoO_2$ film was deposited on a platinum film that was deposited on a high-temperature MgO/Si substrate. In Kim et al, it was shown that such

a crystalline film is capable of constituting the Li+ ion containing cathode layer of a functional all solid-state Li+ ion battery. However, it is of continuing interest for the manufacture of solid state Li+ ion batteries to further reduce the thermal budget of the post deposition anneal, both in time and in temperature, so as to enable the manufacture of such batteries without the need for expensive precious metal nucleation, barrier layers, or expensive high-temperature substrates.

[006] There are many references that disclose an ion beam assisted process that can provide a $LiCoO_2$ film that demonstrates some observable crystalline composition by low angle x-ray diffraction (XRD). Some examples of these are found in U.S. Patent Applications 09/815,983 (Publication No. US 2002/001747), 09/815,621 (Publication No. US 2001/0032666), and 09/815,919 (Publication No. US 2002/0001746). These references disclose the use of a second front side ion beam or other ion source side-by-side with a deposition source so as to obtain a region of overlap of the flux of ions with the flux of $LiCoO_2$ vapor at the substrate surface. None of these references disclose film temperature data or other temperature data of the film during deposition to support an assertion of low temperature processing.

[007] It is very difficult to form a uniform deposition either by sputtering a material layer or by bombardment with an ion flux. Utilization of two uniform simultaneous distributions from two sources that do not occupy the same position and extent with respect to the substrate enormously increases the difficulties involved in achieving a uniform material deposition. These references do not disclose a uniform materials deposition, which is required for reliable production of thin-film batteries. A well understood specification for material uniformity for useful battery products is that a 5% one-sigma material uniformity is standard in thin film manufacturing. About 86% of the films with this uniformity will be found acceptable for battery production.

[008] It is even more difficult to scale a substrate to manufacturing scale, such as 200 mm or 300 mm. Indeed, in the references discussed above that utilize both a sputtering deposition and an ion beam deposition, only small area targets and small area substrates are disclosed. These references disclose a single feasibility result. No method for achieving a uniform distribution from two separate front side sources has been disclosed in these references.

[009] Further, conventional materials and production processes can limit the energy density capacity of the batteries produced, causing a need for more batteries occupying more volume. It is specifically desirable to produce batteries that have large amounts of stored energy per unit volume in order to provide batteries of low weight and low volume.

[010] Therefore, there is a need for a low temperature process for depositing crystalline material, for example $LiCoO_2$ material, onto a substrate.

SUMMARY

[011] In accordance with the present invention, deposition of $LiCoO_2$ layers in a pulsed-dc physical vapor deposition process is presented. Such a deposition can provide a low-temperature, high deposition rate deposition of a crystalline layer of $LiCoO_2$ with a desired <101> orientation. Some embodiments of the deposition address the need for high rate deposition of $LiCoO_2$ films, which can be utilized as the cathode layer in a solid state rechargeable Li battery. Embodiments of the process according to the present invention can eliminate the high temperature (>700 °C) anneal step that is conventionally needed to crystallize the $LiCoO_2$ layer.

[012] A method of depositing a $LiCoO_2$ layer according to some embodiments of the present invention includes placing a substrate in a reactor; flowing a gaseous mixture including argon and oxygen through the reactor; and applying pulsed-DC power to a target

formed of $LiCoO_2$ positioned opposite the substrate. In some embodiments, a $LiCoO_2$ layer is formed on the substrate. Further, in some embodiments the $LiCoO_2$ layer is a crystalline layer of orientation <101>.

[013] In some embodiments, a stacked battery structure can be formed. The stacked battery structure includes one or more battery stacks deposited on a thin substrate, wherein each battery stack includes: a conducting layer, a crystalline $LiCoO_2$ layer deposited over the conducting layer, a LiPON layer deposited over the $LiCoO_2$ layer; and an anode deposited over the LiPON layer. A top conducting layer can be deposited over the one or more battery stacks.

[014] In some embodiments, a battery structure can be formed in a cluster tool. A method of producing a battery in a cluster tool includes loading a substrate into a cluster tool; depositing a conducting layer over the substrate in a first chamber of the cluster tool; depositing a crystalline $LiCoO_2$ layer over the conducting layer in a second chamber of the cluster tool; depositing a LiPON layer over the $LiCoO_2$ layer in a third chamber of the cluster tool; depositing an anode layer over the $LiCoO_2$ layer in a fourth chamber; and depositing a second conducting layer over the LiPON layer in a fifth chamber of the cluster tool.

[015] A fixture for holding a thin substrate can include a top portion and a bottom portion, wherein the thin substrate is held when the top portion is attached to the bottom portion.

[016] These and other embodiments of the invention are further discussed below with reference to the following figures. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed. Further, specific explanations or theories regarding the deposition or performance of certain layers during deposition processes or in the performance of devices incorporating those layers are presented for explanation only and

are not to be considered limiting with respect to the scope of the present disclosure or the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[017] Figures 1A and 1B illustrate a pulsed-DC biased reactive deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[018] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B.

[019] Figure 3 illustrates a thin-film battery design according to some embodiments of the present invention.

[020] Figures 4A and 4B show an x-ray diffraction analysis of and an SEM photograph of a $LiCoO_2$ film deposited according to embodiments of the present invention.

[021] Figures 5A through 5F show SEM photographs of $LiCoO_2$ films according to some embodiments of the present invention.

[022] Figure 5G shows x-ray diffraction data corresponding to the depositions shown in Figures 5B-5F.

[023] Figure 6A illustrates a layer of $LiCoO_2$ deposited according to some embodiments of the present invention on a thin substrate.

[024] Figure 6B illustrates a layer of $LiCoO_2$ deposited according to some embodiments of the present invention over a conducting layer on a thin substrate.

[025] Figures 7A, 7B, 7C, and 7D illustrate a thin substrate mount and mask arrangement that can be utilized in the deposition of $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[026] Figure 8 illustrates a cluster tool that can be utilized to form batteries with $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[027] Figures 9A and 9B illustrate examples of stacked batter structures with $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[028] Figures 10A through 10D illustrate deposition and anneal steps for $LiCoO_2$ deposited over an iridium layer on a silicon wafer.

[029] Figures 11A through 11D illustrate a single layer battery formed over an iridium layer according to some embodiments of the present invention.

[030] Figures 12A through 12L illustrate deposition of a crystalline LiCoO2 layer on a silicon or alumina substrate.

[031] Figures 13A through 13F illustrate rapid thermal anneal processes for $LiCoO_2$ layers deposited according to the present invention.

[032] Figures 14A through 14D illustrate several anneal processes utilized with a $LiCoO_2$ film deposited according to embodiments of the present invention.

[033] Figures 15A and 15B illustrate the effects of ramp-time in a rapid thermal anneal of $LiCoO_2$ films deposited according to the present invention.

[034] Figure 16 illustrates thickness uniformity of a LiCoO2 film deposited according to some embodiments of the present invention.

[035] Figure 17 illustrates battery charge and discharge profiles of a battery formed utilizing a $LiCoO_2$ film according to some embodiments of the present invention.

[036] In the figures, elements having the same designation have the same or similar functions.

DETAILED DESCRIPTION

[037] In accordance with embodiments of the present invention, $LiCoO_2$ films are deposited on a substrate by a pulsed-dc physical vapor deposition (PVD) process. In contrast to, for example, Kim et al., $LiCoO_2$ films according to some embodiments of the present

invention provide a crystalline $LiCoO_2$ film as deposited on a substrate at a substrate temperature as low as about 220 °C during deposition, without the use of a metallic nucleation or barrier underlying film. The as-deposited crystalline $LiCoO_2$ films can be easily ripened to very high crystalline condition by anneal at about 700 °C for as little as 5 minutes without the use of an underlying precious metal film. In addition, the as deposited crystalline films, when positioned on a noble metal film can be annealed at much further reduced temperatures, for example as low as 400 to 500 °C, providing for deposition, annealing, and production of solid state batteries on lower temperature substrates.

[038] In the present application, a single, extended source is described which has been scaled to 400mm X 500mm for production achieving a $LiCoO_2$ uniformity of 3% one-sigma measured at 25 points at a deposition rate of 1.2 microns thickness an hour over an area of 2000 cm^2, without the need for secondary front side ion source or ion assistance.

[039] In one example process, a $LiCoO_2$ film was deposited utilizing a conductive ceramic $LiCoO_2$ target as described herein, with pulsed-dc power of 4 kW, no bias, with 60 sccm Ar and 20 sccm O_2 gas flows. A 3000 Angstrom layer of crystalline $LiCoO_2$ was deposited on a substrate area of 400 X 500 mm. As demonstrated in Figure 16, film thickness uniformity was located at about 25 locations spaced uniformly across the substrate using a felt marker pen to lift off a portion of the film in each location. High precision white-light interferometry was utilized to measure the film thickness in each location by measuring the step height from the substrate to film surface. All 25 thickness measurements demonstrated a 3% one-sigma uniformity in the film thickness over 400 X 500 mm substrate area. As shown in Figure 16, a film was deposited with average thickness of about 2.96 μm with a maximum of 3.09 μm and a minimum of 2.70 μm and standard deviation of 0.093. Thickness data was taken at points spaced 0.65 mm apart on the surface of the film. The film thickness therefore showed 3% one-sigma uniformity over the shown surface area.

[040] On other depositions utilizing this process, a temperature measurement of the substrate during deposition showed that the substrate remained at less than 224 °C. Temperature measurements were performed utilizing a temperature sticker purchased from Omega Engineering, Stamford, Ct (Model no. TL-F-390, active from 199-224 °C).

[041] Moreover, in some embodiments, films deposited according to the present invention can have a deposition rate of from about 10 to about 30 times higher than processes in conventional films. Deposition thicknesses and times of deposition for films deposited according to the present invention are illustrated in Table I. Furthermore, films according to the present invention can be deposited on wide area substrates having a surface area from 10 to 50 times the surface area of prior sputtering processes, resulting in much higher productivity and much lower cost of manufacture, thereby providing high-volume, low-cost batteries.

[042] Further, conventional deposition processes without ion sources are capable of depositing amorphous $LiCoO_2$ layers, but do not deposit crystalline $LiCoO_2$ layers. Surprisingly, depositions according to some embodiment of the present invention, deposit a $LiCoO_2$ layer with substantial crystallinity readily measured by x-ray diffraction techniques. In some embodiments, the crystallinity of the as-deposited $LiCoO_2$ layers is sufficient to be utilized in a battery structure with no further thermal processing. In some embodiments, crystallinity of the as-deposited $LiCoO_2$ layers are improved by thermal processes with low thermal budgets, which can be compatible with films deposited on low-temperature substrates.

[043] Further, as-deposited the stoichiometry of some $LiCoO_2$ layers deposited according to some embodiments of the present invention shows that this layer is sufficient for utilization in a battery. With the demonstrated ability to deposit a $LiCoO_2$ film with crystallinity and with sufficient stoichiometry, a battery utilizing as-deposited $LiCoO_2$ films

can be produced. Heat treating the $LiCoO_2$ layers may improve the crystallinity and lower the impedance.

[044] In some embodiments, a crystalline layer of $LiCoO_2$ with a <101> or a <003> crystalline orientation is deposited directly on the substrate. Deposition of crystalline material can eliminate or lessen the need of a subsequent high temperature anneal or precious-metal layers to crystallize and orient the film. Removing the high temperature anneal allows for formation of battery structures on light-weight and low temperature substrates such as stainless steel foil, copper foil, aluminum foil, and plastic sheet, reducing both the weight and the cost of batteries while retaining the energy density storage capabilities of Li-based batteries. In some embodiments, a crystalline $LiCoO_2$ layer can be deposited on a precious metal layer, such as platinum or iridium, resulting in a further significant lowering of the ripening thermal budget required to improve crystallinity.

[045] Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films can be deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101863.

[046] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film. Apparatus 10 can also be a Phoenix Gen III PVD cluster tool made by Symmorphix, which is specifically designed for pulsed-dc processes such as is described herein.

[047] Apparatus 10 includes target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it from the pulsed DC power supply 14 and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[048] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[049] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 kHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics, and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[050] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[051] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 14 and allow passage of the pulsed-dc power and frequency.

[052] Pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications such as barrier films and dielectric films, where high density is important, due to the boundaries between the columns. The columns act to lower the dielectric strength of the material, but may provide diffusion paths for transport or diffusion of electrical current, ionic current, gas, or other chemical agents such as water. In the case of a solid state battery, a columnar structure containing crystallinity as derived from processes according to the present invention is beneficial for battery performance because it allows better Li transport through the boundaries of the material.

[053] In the Phoenix system, for example, target 12 can have an active size of about 800.00 X 920.00 mm by 4 to 8 mm in order to deposit films on substrate 16 that have

dimension about 600 X 720 mm. The temperature of substrate 16 can be adjusted to between –50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm (in some embodiments, between 4.8 and 6 cm are used). Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 milliTorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the Phoenix reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 800 mm.

[054] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity, oxide film uniformity, or metallic film uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity, which is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity to the deposited film. In optimized processes, however, regions 52 and 24 may be coextensive.

[055] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[056] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface, and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform electrical, mechanical, or optical properties such as index of refraction, stoichiometry, density, transmission, or absorptivity.

[057] Target 12 can be formed of any materials that provide the correct stoichiometry for $LiCoO_2$ deposition. Typical ceramic target materials include oxides of Li and Co as well as metallic Li and Co additions and dopants such as Ni, Si, Nb, or other suitable metal oxide additions. In the present disclosure, target 12 can be formed from $LiCoO_2$ for deposition of $LiCoO_2$ film.

[058] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 and 60 individual tiles. Tiles can be finished to a size so as to provide a margin of edge-wise non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[059] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further herein, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[060] Figure 3 shows a battery structure with a $LiCoO_2$ layer deposited according to some embodiments of the present invention. As shown in Figure 3, a metallic current collection layer 302 is deposited on a substrate 301. In some embodiments, current collection layer 302 can be patterned in various ways before deposition of a $LiCoO_2$ layer 303. Also according to some embodiments, $LiCoO_2$ layer 303 can be a deposited crystalline layer. In some embodiments of the invention, layer 303 is crystalline without the necessity of a crystallizing heat treatment. Therefore, substrate 301 can be a silicon wafer, titanium metal, alumina, or other conventional high temperature substrate, but may also be a low temperature material such as plastic, glass, or other material which could be susceptible to damage from the high temperature crystallizing heat treatment. This feature can have the great advantage of decreasing the expense and weight of battery structures formed by the present invention. The low temperature deposition of the $LiCoO_2$ allows for successive depositions of battery layers, one upon another. Such a process would have the advantage that successive layers of battery structure would be obtained in a stacked condition without the inclusion of a substrate

layer. The stacked layered battery would provide higher specific energy density as well as low impedance operation for charging and discharging.

[061] In some embodiments, an oxide layer can be deposited on substrate 301. For example, a silicon oxide layer can be deposited on a silicon wafer. Other layers can be formed between conducting layer 302 and substrate 301.

[062] As further shown in Figure 3, a LiPON layer 304 ($Li_xPO_yN_z$) is deposited over $LiCoO_2$ layer 303. LiPON layer 304 is the electrolyte for battery 300 while $LiCoO_2$ layer 303 acts as the cathode. A metallic conducting layer 305 can be deposited over the LiPON layer 304 in order to complete the battery. Metallic conducting layer 305 can include lithium adjacent to LiPON layer 304.

[063] An anode 305 is deposited over LiPON layer 304. Anode 305 can be, for example an evaporated lithium metal. Other materials such as, for example, nickel can also be utilized. A current collector 306, which is a conducting material, is then deposited over at least a portion of anode 305.

[064] A Li based thin film battery operates by transport of Li ions in the direction from current collector 306 to current collector 302 in order to hold the voltage between current collector 306 and current collector 302 at a constant voltage. The ability for battery structure 300 to supply steady current, then, depends on the ability of Li ions to diffuse through LiPON layer 304 and $LiCoO_2$ layer 303. Li transport through bulk cathode $LiCoO_2$ layer 303 in a thin film battery occurs by the way of grains or grain boundaries. Without being restricted in this disclosure to any particular theory of transport, it is believed that the grains with their planes parallel to substrate 302 will block the flow of Li ions while grains oriented with planes perpendicular to substrate 301 (i.e., oriented parallel to the direction of Li ion flow) facilitate the Li diffusion. Therefore, in order to provide a high-current battery

structure, $LiCoO_2$ layer 303 should include crystals oriented in the <101> direction or <003> direction.

[065] In accordance with the present invention, $LiCoO_2$ films can be deposited on substrate 302 with a pulsed-DC biased PVD system as was described above. In addition, an AKT 1600 PVD system can be modified to provide an RF bias, which is available in the Phoenix system, and an Advanced Energy Pinnacle plus 10K pulsed DC power supply can be utilized to provide power to a target. The pulsing frequency of the power supply can vary from about 0 to about 350 KHz. The power output of the power supply is between 0 and about 10 kW. A target of densified $LiCoO_2$ tiles having a resistivity in the range of about 3 to about 10 kΩ can be utilized with dc-sputtering.

[066] In some embodiments, $LiCoO_2$ films are deposited on Si wafers. Gas flows containing Oxygen and Argon can be utilized. In some embodiments, the Oxygen to Argon ratio ranges from 0 to about 50% with a total gas flow of about 80 sccm. The pulsing frequency ranges from about 200 kHz to about 300 kHz during deposition. RF bias can also be applied to the substrate. In many trials, the deposition rates vary from about 2 Angstrom/(kW sec) to about 1 Angstrom/(kW sec) depending on the O_2/Ar ratio as well as substrate bias.

[067] Table I illustrates some example depositions of $LiCoO_2$ according to the present invention. XRD (x-Ray Diffraction) results taken on the resulting thin films illustrate that films deposited according to the present invention are crystalline films, often with highly textured grain sizes as large as about 150 nm. The dominant crystal orientation appears to be sensitive to the O_2/Ar ratio. For certain O_2/Ar ratios (~10%), as-deposited films exhibit a preferred orientation in the <101> direction or the <003> direction with poorly developed <003> planes.

[068] Figures 4A and 4B illustrate an XRD Analysis and SEM cross section, respectively, of the $LiCoO_2$ film deposited as Example 15 in Table I. Such a $LiCoO_2$ film was deposited on Si wafer with 2kW of target power, a frequency of 300 kHz, with 60 sccm Ar and 20 sccm of O_2 for a substrate with an initial temperature of about 30°C. As shown in the XRD analysis of Figure 4A, a strong <101> peak is indicated showing a strong orientation of $LiCoO_2$ crystals in the desired <101> crystallographic direction. The SEM cross section shown in Figure 4B further shows the columnar structure of the film having the <101> direction and the grain boundaries of the resulting $LiCoO_2$ crystals.

[069] Figures 5A through 5F show SEM cross sections of further example depositions of $LiCoO_2$ crystals according to the present invention. In each of the examples, deposition of the $LiCoO_2$ film was performed on a Si wafer with target power of about 2 kW and frequency of about 250 kHz. The $LiCoO_2$ film shown in Figure 5A corresponds to the example deposition Example 1 in Table I. In the deposition of the $LiCoO_2$ film shown in Figure 5A, no bias power was utilized with an argon flow rate of about 80 sccm and an oxygen flow rate of about 0 sccm. A deposition rate of about 1.45 μm/hr was achieved over the full substrate area of 400 X 500 mm. Further, as is indicated in the cross section shown in Figure 5A, a <101> orientation of the $LiCoO_2$ was achieved.

[070] The rate of deposition of the $LiCoO_2$ layer shown in Figure 5A is very high, likely due to the relatively high conductivity or low resistivity of the ceramic $LiCoO_2$ oxide sputter target. A target resistance of 10 kOhms was measured by means of an Ohm meter over a distance of about 4 cm on the surface of target 12. This high rate allows the manufacture of the 3 micron or thicker $LiCoO_2$ layer required for the battery at high rate over a wide area in short times, resulting in very high productivity and very low cost. Target resistance on the order of about 500 kΩ over the same distance by the same measurement technique or higher would not allow for such a high sputter efficiency or high rate of

deposition at such a low target power. The resistance of conventional target materials can be unmeasurably high. A resistance of 100 kΩ over about 4 cm of surface will result in high sputter efficiency and high rate of deposition. Further, because deposition rates typically scale nearly linearly with target power, a deposition at 6 kW will yield a deposition rate of approximately 3 μm/hr, which is a very desirable rate of deposition for manufacturability of Li-based thin-film solid-state batteries on a surface area of 400 X 500 mm^2.

[071] The $LiCoO_2$ layer shown in Figure 5B is deposited under the conditions listed as Example 7 in Table I. Again, no bias was utilized in the deposition. An argon flow rate of about 72 sccm and an oxygen flow rate of about 8 sccm was utilized. The deposition rate was significantly reduced to about 0.85 μm/hr. Further, although a <101> crystallinity can be discerned, that <101> crystallinity is not as pronounced as that exhibited in the deposition of the film shown in Figure 5A.

[072] The $LiCoO_2$ film shown in Figure 5C was deposited according to Example 3 in Table I. In this deposition, 100 W of bias power is applied to the substrate. Further, an argon flow rate of 72 sccm, and an oxygen flow rate of 8 sccm was utilized. The deposition rate was about 0.67 μm/hr. Therefore, the application of bias in comparison with the $LiCoO_2$ film shown in Figure 5B further reduced the deposition rate (from 0.85 μm/hr of the example shown in Figure 5B to 0.67 μm/hr of the example shown in Figure 5C). Further, the desired <101> directionality of formed crystals appears to be further degraded.

[073] The $LiCoO_2$ film shown in Figure 5D corresponds to Example 4 in Table I. In this deposition, the Ar/O_2 ratio was increased. As is shown in Figure 5D, increasing the Ar/O_2 ratio improves crystallinity. With respect to the example illustrated in Figure 5C, the deposition illustrated in Figure 5D was performed with an argon flow of about 76 sccm and an oxygen flow of about 4 sccm as well as retaining the 100 W bias to the substrate. The

$LiCoO_2$ deposition rate was improved to 0.79 μm/hr from a rate of 0.67 μm/hr illustrated in Figure 5C.

[074] In the example deposition illustrated in Figure 5E corresponding to Example 5 in Table I. The substrate temperature was set at about 200°C while the bias power remained at about 100 W. The argon flow rate was set at about 76 sccm and the oxygen flow rate was set at about 4 sccm. The resulting deposition rate for the $LiCoO_2$ layer was about 0.74 μm/hr.

[075] In the example deposition illustrated in Figure 5F, which corresponds with Example 6 of Table I, the argon flow rate was set at about 74 sccm and the oxygen flow rate was set at about 6 sccm, resulting in a $LiCoO_2$ deposition rate of about 0.67 μm/hr. Therefore, increasing both argon and oxygen flow rate over the deposition illustrated in Figure 5E resulted in a lower deposition rate.

[076] Figure 5G illustrates XRD data corresponding to Figures 5F, 5D, 5C, 5E, and 5B, respectively. As illustrated in Figure 5G, as-deposited crystalline $LiCoO_2$ is deposited in these processes.

[077] The data show clearly that an as-deposited crystalline film of $LiCoO_2$ can be obtained under several of the process conditions, as shown in Table II. In particular, very high rates of deposition with low power are obtained along with the oriented crystalline structure for the process conditions according to embodiments of the present invention.

[078] Figure 6A illustrates a layer of $LiCoO_2$ 602 deposited on a thin substrate 601 according to some embodiments of the present invention. Higher lithium-ion mobilities can be achieved utilizing crystalline $LiCoO_2$ cathode films 602 deposited on a thin substrate 601 that has thickness comparable to that of the battery stack itself, rather than a thickness many or tens of times that of the battery stack. Such a film can lead to faster charging and discharging rates. Substrate 601 can be formed of a thin metallic sheet (e.g., aluminum,

titanium, stainless steel, or other suitable thin metallic sheet), can be formed of a polymer or plastic material, or may be formed of a ceramic or glass material. As shown in Figure 6B, if substrate 601 is an insulating material, a conducting layer 603 can be deposited between substrate 601 and $LiCoO_2$ layer 602.

[079] Depositing materials on a thin substrate involves holding and positioning the substrate during deposition. Figures 7A, 7B, 7C, and 7D illustrate a reusable fixture 700 for holding a thin film substrate. As shown in Figure 7A, reusable fixture 700 includes a top portion 701 and a bottom portion 702 that snap together. Thin substrate 601 is positioned between top portion 701 and bottom portion 702. As shown in Figure 7B, top portion 701 and bottom portion 702 are such that substrate 601 is brought into tension and subsequently clamped as top portion 701 is closed into bottom portion 702. Substrate 601 can be easily held by fixture 700 so that substrate 601 can be handled and positioned. In some embodiments, the corners of substrate 601, areas 703, are removed so that substrate 601 is more easily stretched by avoiding "wrap-around" corner clamping effects when top portion 701 is closed into bottom portion 702.

[080] As shown in Figure 7C, a mask 712 can be attached to fixture 700. In some embodiments, fixture 700 includes guides in order to align fixture 700 with respect to mask 712. In some embodiments, mask 712 may be attached to fixture 700 and travel with fixture 700. Mask 712 can be positioned at any desired height above substrate 601 in fixture 700. Therefore, mask 712 can function as either a contact or proximity mask. In some embodiments, mask 712 is formed of another thin substrate mounted in a fixture similar to fixture 700.

[081] As shown in Figure 7C and 7D, fixture 700 and mask 712 can be positioned relative to mount 710. Mount 710, for example, can be a susceptor, mount, or an electrostatic chuck of a processing chamber such as that shown in Figures 1A and 1B. Fixture 700 and

mask 712 can have features that allow for ready alignment with respect to each other and with respect to mount 710. In some embodiments, mask 712 is resident in the processing chamber and aligned with fixture 700 during positioning of fixture 700 on mount 710, as shown in Figure 7D.

[082] Utilizing fixture 700 as shown in Figures 7A, 7B, 7C, and 7D allows processing of a thin film substrate in a processing chamber. In some embodiments, thin film substrates can be about 10 μm or more. Further, thin film substrate 601, once mounted within fixture 700, can be handled and moved from process chamber to process chamber. Therefore, a multiprocessor chamber system can be utilized to form stacks of layers, including one or more layers of $LiCoO_2$ deposited according to embodiments of the present invention.

[083] Figure 8 illustrates a cluster tool 800 for processing thin film substrates. Cluster tool 800 can, for example, include load lock 802 and load lock 803, through which mounted thin film substrate 601 is loaded and a resultant device is removed from cluster tool 800. Chambers 804, 805, 806, 807, and 808 are processing chambers for depositions of materials, heat treatments, etching, or other processes. One or more of chambers 804, 805, 806, 807, and 808 can be a pulsed-DC PVD chamber such as that discussed above with respect to Figures 1A and 1B and within which a $LiCoO_2$ film deposited according to embodiments of the present invention may be deposited.

[084] Processing chambers 804, 805, 806, 807, and 808 as well as load locks 802 and 803 are coupled by transfer chamber 801. Transfer chamber 801 includes substrate transfer robotics to shuttle individual wafers between processing chambers 804, 805, 806, 807, and 808 and load locks 802 and 803.

[085] In production of a conventional thin-film battery, ceramic substrates are loaded into load lock 803. A thin metallic layer can be deposited in chamber 804, followed

by a $LiCoO_2$ deposition performed in chamber 805. The substrate is then removed through load lock 803 for an in-air heat treatment external to cluster tool 800. The treated wafer is then reloaded into cluster tool 800 through load lock 802. A LiPON layer can be deposited in chamber 806. The wafer is then again removed from cluster tool 800 for deposition of the lithium anode layer, or sometimes chamber 807 can be adapted to deposition of the lithium anode layer. A second metallic layer is deposited in chamber 808 to form a charge collector and anode collector. The finished battery structure is then off-loaded from cluster tool 800 in load lock 802. Wafers are shuttled from chamber to chamber by robotics in transfer chamber 801.

[086] A battery structure produced according to the present invention could utilize thin film substrates loaded in a fixture such as fixture 700. Fixture 700 is then loaded into load lock 803. Chamber 804 may still include deposition of a conducting layer. Chamber 805 then includes deposition of a $LiCoO_2$ layer according to embodiments of the present invention. A LiPON layer can then be deposited in chamber 806. Chamber 807 may still be adapted to deposition of a lithium rich material such as lithium metal and chamber 808 can be utilized for deposition of the conducting layer of the current collector. In this process, no heat treatment is utilized to crystallize the $LiCoO_2$ layer.

[087] Another advantage of a thin film battery process is the ability to stack battery structures. In other words, substrates loaded into cluster tool 800 may traverse process chambers 804, 805, 806, 807, and 808 multiple times in order to produce multiply stacked battery structures. Figures 9A and 9B illustrate such battery structures.

[088] Figure 9A illustrates a parallel coupled stacking. As shown in Figure 9A, a substrate 601, which for example can be a plastic substrate, is loaded into load lock 803. A conducting layer 603, for example about 2 μm of aluminum, copper, iridium or other material, acts as a bottom current collector. Conducting layer 603, for example, can be

deposited in chamber 804. A $LiCoO_2$ layer 602 is then deposited on conducting layer 603. $LiCoO_2$ layer 602 can be about 3-10 μm and can be deposited in chamber 805 according to embodiments of the present invention. The wafer can then be moved to chamber 806 where a LiPON layer 901 of thickness of about .5 to about 2 μm can be deposited. In chamber 807, an anode layer 902, for example a lithium metal layer of up to about 10 μm, can then be deposited in chamber 807. A second conducting layer 903 can then be deposited over anode layer 902. A second battery stack can then be deposited over the first battery stack formed by metal layer 603, LiCoO2 layer 602, LiPON layer 901, lithium layer 902, and current collection conduction layer 903. Over current collection conducting layer 903, another lithium layer 902 is formed. Another LiPON layer 901 is formed over lithium layer 902. Another LiCoO2 layer 602 is formed over LiPON layer 901 and finally another metal layer 603 is formed over LiCoO2 layer 602. In some embodiments, further stackings can be formed. In some embodiments, metal layers 603 and 903 differ in the mask utilized in deposition so that tabs are formed for electrical coupling of layers.

[089] As discussed above, any number of individual battery stacks can be formed such that parallel battery formations are formed. Such a parallel arrangment of battery stacking structure can be indicated as Current collector/LiCoO2/LiPON/Anode/current collector/Anode/LiPON/LiCoO2/current collector/LiCoO2 . . . /current collector. Figure 9B illustrates an alternative stacking corresponding to the battery structure current collector/LiCoO2/LiPON/anode/current collector/LiCoO2/LiPON/anode/current collector . . . /current collector. In this case, a series arrangement battery stacking structure is formed because the individual battery stacks share anodes.

[090] To form the structures shown in Figures 9A and 9B, substrates are rotated again through the chambers of cluster tool 800 in order to deposit the multiple sets of batteries. In general, a stack of any number of batteries can be deposited in this fashion.

[091] In some embodiments, stoichiometric $LiCoO_2$ can be deposited on iridium. Figures 10A through 10D illustrate an anneal procedure for Li-Co deposition over an iridium layer that has been deposited on a Si wafer. The $LiCoO_2$ deposition was accomplished as discussed above with a target power of 2 kW, no bias power, reverse time of 1.6 μs, a pulsing frequency of 300 kHz, with 60 sccm Ar flow and 20 sccm of O_2 flow, with no pre-heat for 7200 sec. As a result, a layer of $LiCoO_2$ of about 1.51 μm was deposited.

[092] Figures 10A through 10D show XRD analysis of both as-deposited and annealed layers of $LiCoO_2$ deposited as discussed above. The XRD analysis of the as-deposited layer demonstrates a shallow peak at $2\theta = 18.85°$ denoting a <003> orientation of crystalline $LiCoO_2$, a sharper peak at about $2\theta = 38.07°$ corresponding with the desired <101> crystallographic direction, and a peak at $2\theta = 40.57°$ corresponding to the <111> direction of iridium. However, the position of the <101> $LiCoO_2$ peak indicates that the <101> $LiCoO_2$ peak is nonstoichiometric $LiCoO_2$. In order to be useful as a battery layer, stoichiometric $LiCoO_2$ provides for the best Li transport. One of ordinary skill in the art will notice that careful adjustment of deposition parameters can provide stoichiometric $LiCoO_2$ of desired orientation.

[093] Figure 10B shows an XRD analysis of the sample shown in figure 10A after a 300°C anneal in air for 2 hours. As shown in Figure 10B, the XRD peak corresponding to <003> $LiCoO_2$ grows, indicating crystallization of $LiCoO_2$ into the <003> direction. Further, the <101> peak of $LiCoO_2$ shifts slightly to $2\theta = 38.53°$, indicating a more stoichiometric crystallization of the <101> $LiCoO_2$. However, the crystalline $LiCoO_2$ is still not stoichiometric after this anneal. One of ordinary skill in the art will notice that longer anneals and/or further adjustment of the deposited stoichiometry may result in usefully oriented stoichiometric $LiCoO_2$ layers with anneal temperatures at 300 °C or less. Consequently, low temperature materials such as polymers, glass, or metal may be utilized as the substrate.

[094] Figure 10C illustrates an XRD analysis from the sample after a subsequent 500°C anneal in air for 2 hours. As shown in Figure 10C, more of the $LiCoO_2$ crystalizes into the <003> layer. Further, the <101> $LiCoO_2$ peak shifts again to $2\theta = 39.08°$, indicating crystallization of a <012> layer of $LiCoO_2$. In this case, the <012> $LiCoO_2$ cyrstal is stoichiometric and therefore allows for efficient Li transport. One of ordinary skill in the art will notice that longer anneals and/or further adjustment of the deposited stoichiometry may result in usefully oriented stoichiometric $LiCoO_2$ layers with anneal temperatures at 500°C or less. Consequently, low temperature materials such as polymers, glass, or metal may be utilized as the substrate.

[095] Figure 10D illustrates an XRD analsysis of the sample after a subsequent anneal of 700°C in air for 2 hours. As shown in Figure 10D, the <003> $LiCoO_2$ peak disappears, but the <012> $LiCoO_2$ peak remains relatively the same as that shown in the 500° anneal illustrated in Figure 10C.

[096] Figures 10A through 10D demonstrate deposition of <101> $LiCoO_2$ at low temperature over an iridium layer. Subsequent anneals to 500°C may be desired to change the stoichiometry of the <101> $LiCoO_2$ layer, but anneals to 700 °C do not appear to be necessary. With anneal temperatures less than 500°C, depositions of a $LiCoO_2$ layer over a conducting iridium layer can be accomplished on glass, aluminum foil, plastic, or other low temperature substrate material. Anneal temperatures of less than 500°C but greater than 300°C or lengthening the time of lower temperature anneals may also result in desired orientations of stoichiometric crystalline $LiCoO_2$.

[097] Figures 11A through 11D illustrate formation of a single-layer battery according to some embodiments of the present invention. As shown in Figure 11A, a lift-off layer 1102 can be deposited on a substrate 1101. Further, an iridium layer 1103 can be

deposited over lift-off layer 1102. In some embodiments, substrate 1101 can be plastic, glass, Al foil, Si wafer, or any other material. Lift-off layer 1102 can be any lift off layer and can be a polymer layer such as polyimide, an inorganic layer such as CaF_2 or carbon, or an adhesive layer that loses its adhesion as a result of, for example, oxidation, heat, or light. Lift-off layers are well known. Iridium layer 1103 can be from about 500 Å or more.

[098] As shown in Figure 11B, a $LiCoO_2$ layer is deposited over iridium layer 1103 as was discussed above. In some embodiments, an anneal can be performed at this step. In some embodiments, further layers of the battery may be deposited before an anneal step is performed. In some embodiments, a stoichiometric $LiCoO_2$ layer of a useful crystalline orientation may result in the as-deposited $LiCoO_2$ with no further anneals necessary.

[099] Figure 11C illustrates deposition of a LiPON layer 1105 over the $LiCoO_2$ layer, deposition of a Li layer 1106 over LiPON layer 1105, and deposition of an electrode layer 1107 over Li layer 1106. In some embodiments, an anneal step of up to 500°C as discussed above may be performed here.

[0100] As shown in Figure 11D, the resulting single-layer battery formed from iridium layer 1103, $LiCoO_2$ layer 1104, LiPON layer 1105, Li layer 1106, and electrode layer 1107 can be "lifted off" from substrate 1101. Such a single-layer battery can be a free-standing battery of thickness about 5 μm or greater. Such a battery, without the requirement of a substrate 1101, is well known to have the potential of energy storage of greater than about 1 kW-hr/liter.

[0101] As an alternative to a lift-off process as described in Figures 11A through 11D, a substrate may be removed during anneal leaving a single-layer battery. Further, in some embodiments, substrate 1101 can be removed by a solvent, etching, or a photo process. Further, single-layer batteries may be combined or stacked in any fashion to provide a device of greater energy storage at a particular voltage.

[0102] Figures 12A through 12L illustrate the crystallinity of as-grown and post anneal $LiCoO_2$ layers according to samples 31 and 32 illustrated in Table I. Samples 31 and 32 were formed in the same deposition, utilizing a silicon substrate and an alumina substrate, respectively.

[0103] Figure 12A illustrates an XRD analysis of the as-deposited $LiCoO_2$ film on Al_2O_3 substrate (Example 32 in Table I). A broad <003> crystalline $LiCoO_2$ peak is observed. The remaining peaks in the analysis, which are not labeled in Figure 12A, result from the Al_2O_3 substrate. The <003> peak is characteristic of the layered structure in the as-deposited crystalline $LiCoO_2$ film according to embodiments of the present invention.

[0104] Figure 12B illustrates the crystallinity of the LiCoO2 film shown in Figure 12A after a 2 hr 700 °C anneal. As shown in Figure 12B, the <003> peak becomes sharper and higher, indicating better crystallinity. As shown in Figures 12G through 12J, in comparison with figures 12C through 12F, the columnar structure ripens with the anneal and the grain size becomes larger with anneal. Figure 12B also shows <012> and <006> crystallinity peaks.

[0105] Figure 12C through 12F show SEM photos of the granularity of the as-deposited film corresponding to Example 32 in Figure I. Figures 12G through 12J show SEM photos of the granularity of the annealed film, as illustrated in Figure 12B. A comparison of Figures 12C through 12F with 12G through 12J illustrate the increased granularity resulting from the anneal process.

[0106] Figure 12K illustrates a fracture cross-section SEM that illustrates the morphology of the as-deposited crystalline film corresponding to Example 31 in Table I. Figure 12L illustrate a similar cross-section SEM corresponding to the film grown according to Example 32 in Table I.

[0107] Figures 13A through 13J illustrate rapid thermal anneal processes applied to a $LiCoO_2$ layer as in Example 49 of Table I. In that example, $LiCoO_2$ is deposited on alumina with a 2 kW pulsed DC power with no bias. Argon flow as set to 60 sccm and oxygen flow was set to 20 sccm. The deposition parameters are nearly identical with those of Example 32 in Table I, therefore XRD data for the as-deposited films are shown in Figure 12A. Figure 13A shows XRD data after a 15 minute 700 °C anneal in an argon atmosphere. Ramp-up time (room temperature to 700 °C) is 45 sec and ramp-down time (700 °C to about 300 °C) occurred over 10 min. At 300 °C, the sample is removed from the rapid-thermal-anneal (RTA) oven and cooled in air to room temperature. As shown in Figure 13A, substantial crystallinity is obtained. Figure 13B shows XRD data after a RTA as described with Figure 13A in an argon/oxygen atmosphere. The argon/oxygen ratio was 3:1.

[0108] As shown in a comparison of Figures 13A and 13B, more crystallinity is observed in an argon only RTA than with a RTA performed in the presence of oxygen. This is further illustrated in a comparison of Figures 13C and 13D with Figures 13E and 13F. Figures 13C and 13D show the granularity of the $LiCoO_2$ film after the RTA illustrated in Figure 13A. Figures 13E and 13F show the granularity of the $LiCoO_2$ film after the RTA illustrated in Figure 13B. As is observed, the granularity shown in Figures 13C and 13D (which differ in magnification) is better than that shown in Figures 13E and 13F (which also differ in magnification).

[0109] Figures 14A through 14D illustrate several anneal processes with the Example 37 of Table I. In that example, LiCoO2 was deposited on alumina utilizing a pulsed-dc process with 2kW of power and 100 W of bias with an argon flow of 60 sccm and an oxygen flow of 20 sccm.

[0110] Figure 14A shows an SEM photo of an as-deposited $LiCoO_2$ film according to the process illustrated in Example 37 of Table I. Figure 14B shows an SEM photo of

$LiCoO_2$ film according to the process illustrated in Example 37 of Table I, annealed conventionally with a two-hour 700 °C anneal. Figures 14C and 14D show SEM photos of a $LiCoO_2$ film according to the process illustrated in Example 37 of Table I, annealed in an RTA process at 700 °C. The ramp-up and ramp-down times in the RTA process is illustrated above. Figure 14C shows an SEM photo of a $LiCoO_2$ film after an RTA process at 700 °C for five minutes whereas Figure 14D shows an SEM photo of a $LiCoO_2$ film after an RTA process at 700 °C for fifteen minutes. It is clear from a comparison of Figures 14C and 14D with Figure 14B, that much better granularity is achieved with the low thermal-budget RTA process rather than the conventional furnace anneal. A low thermal-budget RTA process allows for deposition of such films on low temperature substrates.

[0111] Figures 15A and 15B show SEM photos of a $LiCoO_2$ film that was annealed in an RTA process utilizing two different ramp-up times, illustrating the effects of the ramp time in the RTA process. A $LiCoO_2$ film was deposited on an alumina substrate according to the process described as Example 51 in Table I. The film shown in Figure 15A was annealed with a 45 sec ramp-up time (i.e., room temperature to 700 °C in 45 sec). The film shown in Figure 15B was annealed with a 240 sec ramp-up time. Both films were held at 700 °C for five minutes. As shown in a comparison between Figures 15A and 15B, it is clear that a short anneal ramp-up times yield better granularity than longer ramp-up times.

[0112] Figure 17 illustrates battery charge and discharge profiles of a battery structure formed utilizing $LiCoO_2$ films according to embodiments of the present invention. The $LiCoO_2$ film in the battery profiled in Figure 17 was deposited according to Example 54 in Table I. The $LiCoO_2$ film was deposited on an alumina substrate with a gold current collector. The $LiCoO_2$ film was annealed utilizing a fast-ramp (45 sec) RTA process as was described above. A 1.5 μm LiPON layer was then deposited with a standard RF deposition process without bias in a modified AKT reactor. A lithium anode and a nickel current

collector were then deposited. Data was taken at 0.33 mA, 1.65 mA, 3.3 mA, 16.5 mA, 33 mA, and 66 mA. As observed, the battery was capable of storing an exceptional 25 mA/cm^2 at voltages greater than 2.0 V.

[0113] One skilled in the art will recognize variations and modifications of the examples specifically discussed in this disclosure. These variations and modifications are intended to be within the scope and spirit of this disclosure. As such, the scope is limited only by the following claims.

TABLE I

Example #	Target Power (kW)	Bias Power (W)	Reverse Time (µs)	Frequency (kHz)	Ar (sccm)	O_2 (sccm)	Initial Substrate Temperature (temperature during deposit) (°C)	Deposition Time (sec)	Film Thickness (µm)
1	2	0	1,6	250	80	0	30	10000	3.9
2	2	0		250	72	8	30	7200	1.7
3	2	100		250	72	8	30	7200	1.34
4	2	100		250	76	4	30	7200	1.57
5	2	100		250	76	4	200	7200	1.3
6	2	100		250	74	6	200	7200	1.3
7	2	0		300	72	8	30	7200	1.58
8	2	0		300	74	6	30	7200	
9	2	100		300	74	6	30	7200	
10	2	100		300	72	8	30	7200	
11	2	100		300	70	10	30	7200	
12	2	0		300	70	10	30	7200	
13	2	0		300	72	8	30	7200	1.58
14	2	0		300	74	6	30	7200	
15	2	0		300	60	20	30	7200	
16	2	0		300	50	30	30	7200	
17	2	200		300	60	20	30	7200	
18	2	50		300	60	20	30	7200	
19	2	0		300	70	10	30	7200	
20	2	0		300	65	15	30	7200	
21	3	0		300	65	15	30	7200	
22	2	0	1.6	250	60	20	30	7200	
23	3	0	1.6	250	60	20	30	7200	
24	2	0	1.6	250	60	20	30 (NPH)	7200	

25	2	0	1.6	250	60	20	10min heat 30min coc	7200	
26	2	0	1.6	250	60	20	no preheat	9000	
27	2	0		300	60	20	no preheat	7200	
28	2	0		300	60	20	15min heat, 10min	7200	
29	2	0		250	60	20	no preheat		
30	2	0		250	60	20	10min, 10min		
31	2	0	1.3	300	60	20	30 (220)	7200	4.81
32	2	0	1.3	300	60	20	30 (220)	7200	4.74
33	2	0	1.3	300	22.5	7.5	30 (220)	7200	3.99
34	2	0	1.3	300	22.5	7.5	30 (220)	7200	3.93
35	2	0	1.3	300	37.5	12.5	30 (220)	7200	3.64
36	2	0	1.3	300	37.5	12.5	30 (220)	7200	3.54
37	2	100	1.3	300	60	20	30 (220)	7200	4.54
38	2	200	1.3	300	60	20	30 (220)	7200	4.84
39	2	100	1.3	300	37.5	12.5	30 (220)	7200	4.30
40	2	100	1.3	300	22.5	7.5	30 (220)	7200	3.77
41	2	200	1.3	300	37.5	12.5	30 (220)	7200	3.92
42	2	200	1.3	300	60	20	400	7200	3.77
43	2	0	1.3	300	22.5	7.5	30(220)	7200	3.24
44	2	0	1.3	300	60	20	30(220)	7200	3.88
45	2	0	1.3	300	60	20	30(220)	3600	1.78
46	2	200	1.3	300	60	20	30(220)	3600	1.87
47	2	200	1.3	300	22.5	7.5	30(220)	3600	1.52
48	2	0	1.3	300	60	20	30(220)	6000	1.12
49	2	0	1.3	300	60	20	30(220)	10800	1.89
50	2	0	1.3	300	60	20	30(220)	14400	2.52
51	2	100	1.3	300	60	20	30(220)	10000	1.57
52	2	100	1.3	300	60	20	30(220)	10000	2.11
53	2	100	1.3	300	60	20	30(220)	6000	2.70

54	2	100	1.3	300	60	20	30(220)	6000	2.70

TABLE II

Example #	Phase	Lattice	Texture	d_{101} [Å]	2θ [°]	crystallite size [Å]
15	$LiCoO_2$	rhombohedral	strong [101]	2.376(1)	37.83	~1300
16	$LiCoO_2$	Rhombohedral	strong [101]	2.375(1)	37.85	~750
17	Co	cubic	random	--	--	<50
18	Co	cubic	random	--	--	<50
19	$LiCoO_2$	rhombohedral	strong [101]	2.370(1)	37.93	~1400
20	$LiCoO_2$	rhombohedral	strong [101]	2.372(1)	37.90	~1500
21	$LiCoO_2$	rhombohedral	strong [101]	2.370(1)	37.92	~1700
PDF	$LiCoO_2$	Rhombohedral	random	2.408(1)	37.31	--

WHAT IS CLAIMED IS:

1. A method of depositing a $LiCoO_2$ layer, comprising:

placing a substrate in a reactor;

flowing a gaseous mixture including argon and oxygen through the reactor; and

applying pulsed DC power to a target formed of $LiCoO_2$ positioned opposite the substrate,

wherein a crystalline layer of $LiCoO_2$ is deposited over the substrate.

2. The method of claim 1, further including applying an RF bias to the substrate.

3. The method of claim 1, wherein the crystalline layer is <101> oriented.

4. The method of claim 1, wherein the crystalline layer is <003> oriented.

5. The method of claim 1, wherein a grain size of the crystalline layer is between about 750 Å and about 1700 Å.

6. The method of claim 1 wherein the substrate is a material chosen from a set comprised of silicon, polymers, glasses, ceramics, and metals.

7. The method of claim 1, further including preheating the substrate to a temperature of about 200 °C.

8. The method of claim 1, wherein the substrate is a low temperature substrate.

9. The method of claim 8, wherein the low temperature substrate is one of a set of substrates including glass, plastic, and metal foil.

10. The method of claim 1, further including depositing an oxide layer on the substrate.

11. The method of claim 10, wherein the oxide layer is a silicon dioxide layer.

12. The method of claim 3, wherein the crystalline layer is deposited at a rate of greater than 1 μm per hour.

13. The method of claim 1 wherein the target is a ceramic $LiCoO_2$ sputter target with a resistance measured across about 4 cm of surface of less than about 500 kΩ.

14. The method of claim 1, further including depositing a metal layer on the substrate.

15. The method of claim 14, wherein the metal layer is iridium.

16. The method of claim 14, wherein the metal layer is platinum.

17. The method of claim 1, further including annealing the crystalline layer with a low thermal budget.

18. The method of claim 17, wherein annealing the crystalline layer includes annealing to 700°C in a rapid thermal anneal process for a period of time less than about 10 minutes.

19. The method of claim 14, further including annealing the $LiCoO_2$ layer at a temperature of less than or equal to about 500°C.

20. The method of claim 14, further including annealing the $LiCoO_2$ layer at a temperature of less than or equal to about 400°C.

21. A battery structure, comprising:

a crystalline $LiCoO_2$ layer deposited over a low-temperature substrate.

22. The structure of claim 21, further including a conducting layer deposited between the crystalline $LiCoO_2$ layer and the low-temperature substrate.

23. The structure of claim 22, wherein the conducting layer is an iridium layer.

24. The structure of claim 22, wherein the conducting layer is a platinum layer.

25. The structure of claim 21, further including a LiPON layer deposited over the $LiCoO_2$ layer.

26. The structure of claim 21, further including a second conducting layer deposited over the $LiCoO_2$ layer.

27. A stacked battery structure, comprising:

one or more battery stacks deposited on a thin substrate, wherein each battery stack comprises:

a conducting layer,

a $LiCoO_2$ layer deposited as a crystalline layer over the conducting layer,

a LiPON layer deposited over the crystalline $LiCoO_2$ layer,

an anode layer deposited over the LiPON layer; and

a top conducting layer deposited over the one or more battery stacks.

28. The stacked battery structure of claim 27, wherein the battery stacks form a parallel stacked battery structure.

29. The stacked battery structure of claim 27, wherein the battery stacks form a series stacked battery structure.

30. The stacked battery structure of claim 27, wherein the conducting layer is a metal layer deposited on a substrate.

31. The stacked battery structure of claim 30, wherein the metal layer is an iridium layer.

32. The stacked battery structure of claim 30, wherein the metal layer is a platinum layer.

33. The stacked battery structure of claim 30, wherein the substrate is a low temperature substrate.

34. The stacked battery structure of claim 27, wherein the conducting layer is a metallic foil.

35. The stacked battery structure of claim 34, wherein the metallic foil is formed of a metal from a group consisting of copper, gold, platinum, aluminum, stainless steel and other nickel or cobalt based super alloy.

36. A method of producing a battery, comprising:

loading a substrate into a cluster tool;

depositing a crystalline $LiCoO_2$ layer over a conducting layer in a chamber of the cluster tool with a pulsed-dc PVD process.

37. The method of claim 36, wherein depositing a crystalline $LiCoO_2$ layer includes depositing crystalline $LiCoO_2$ through a mask.

38. The method of claim 36, further including

depositing a conducting layer on the substrate.

39. The method of claim 36, further including depositing a LiPON layer over the $LiCoO_2$ layer.

40. The method of claim 39, further including deposition an anode over the LiPON layer.

41. The method of claim 40, further including depositing a conducting layer over the anode.

42. The method of claim 36, wherein the conducting layer is an iridium layer.

43. A fixture for holding a thin substrate, comprising:

a top portion; and

a bottom portion, wherein

the thin substrate is held when the top portion is attached to the bottom portion.

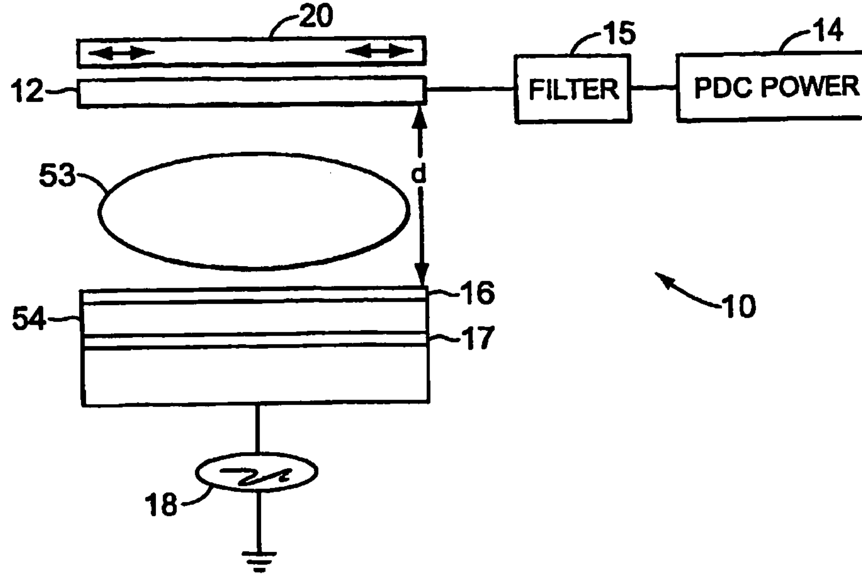


FIG. 1A

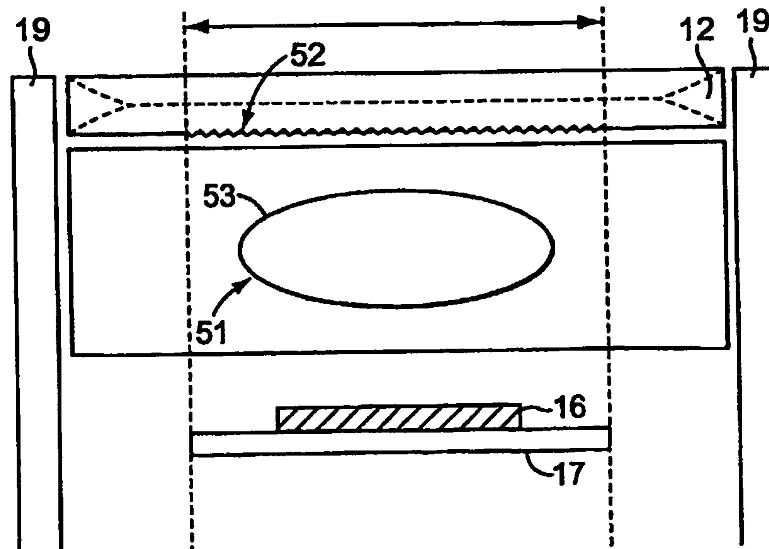


FIG. 1B

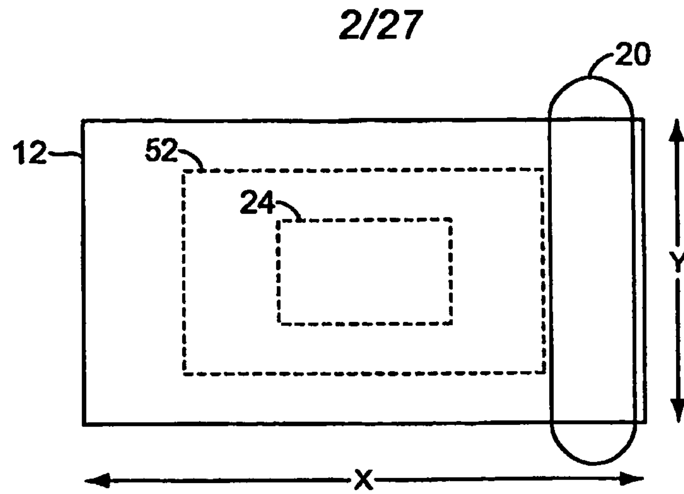


FIG. 2

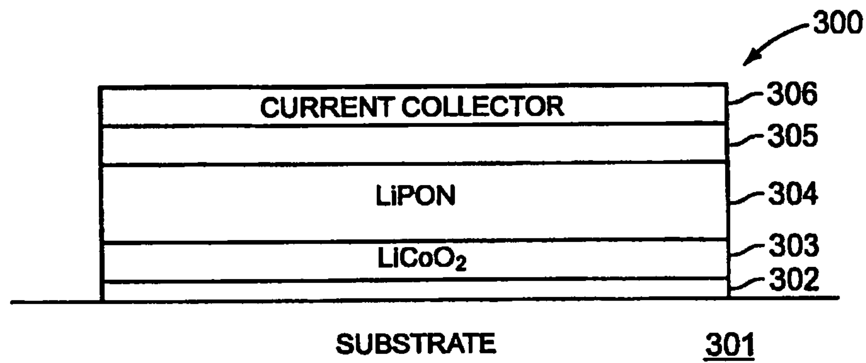


FIG. 3

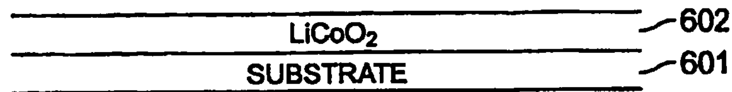


FIG. 6A

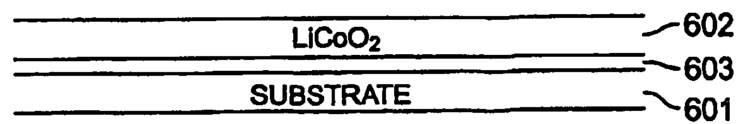


FIG. 6B

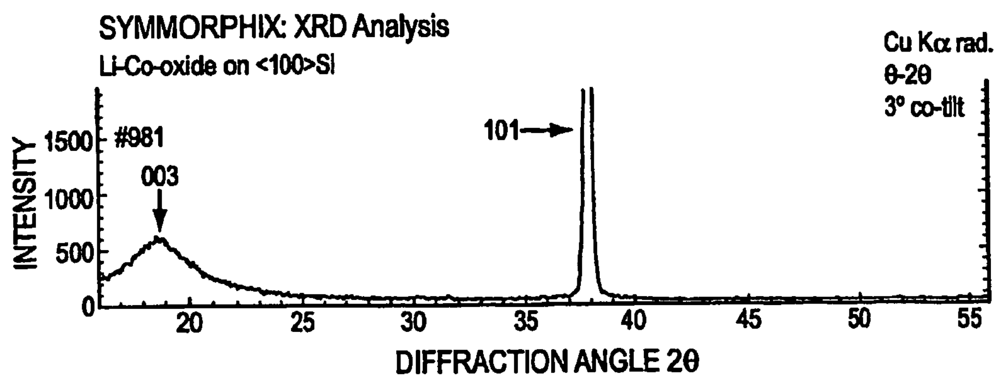


FIG. 4A

FIG. 4B

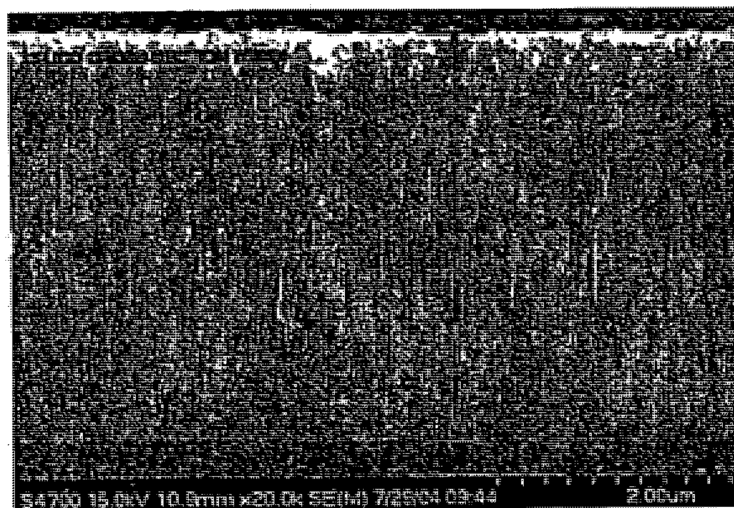


FIG. 5A

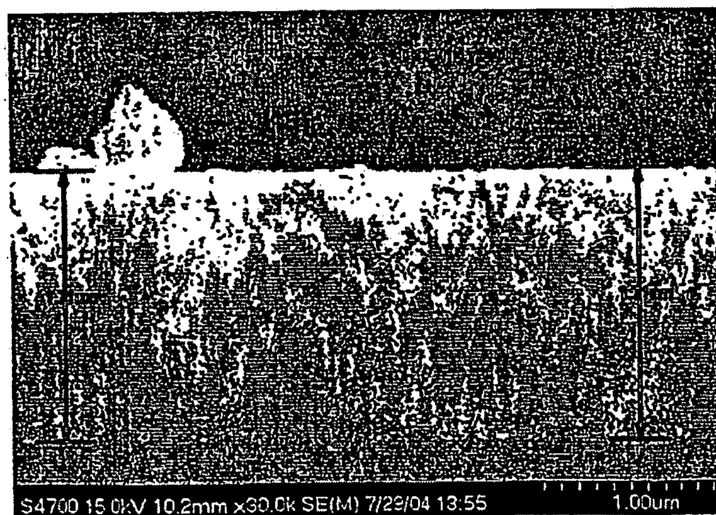


FIG. 5B

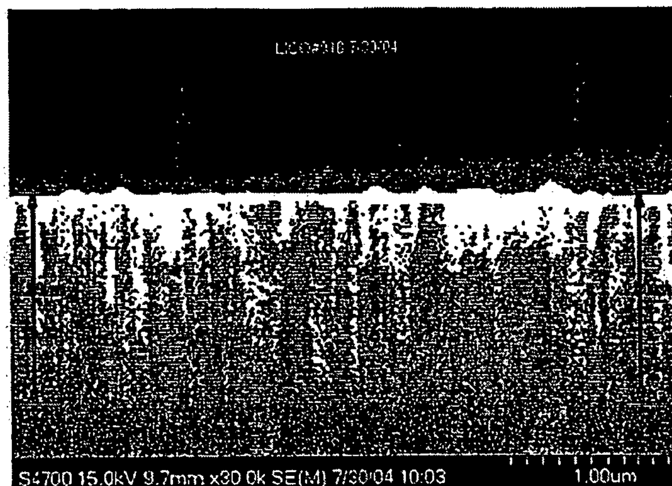


FIG. 5C

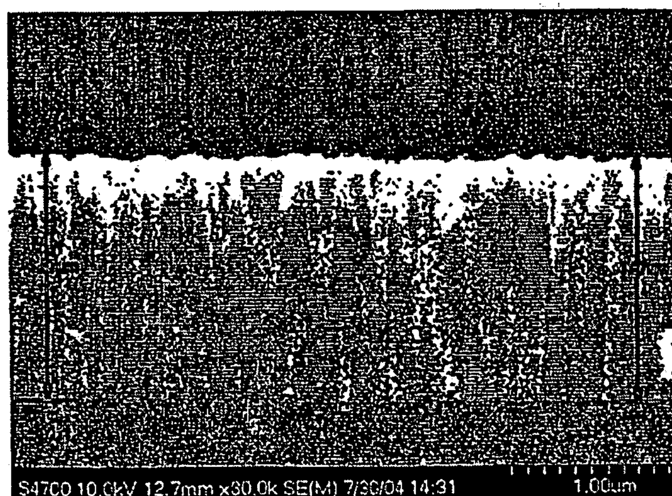


FIG. 5D

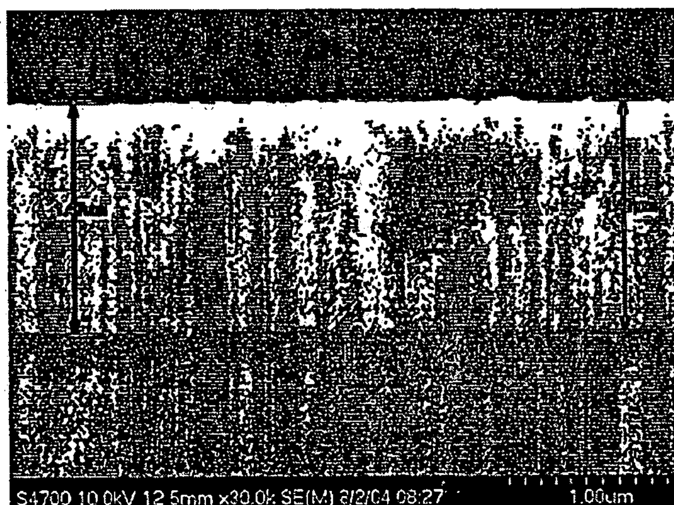


FIG. 5E

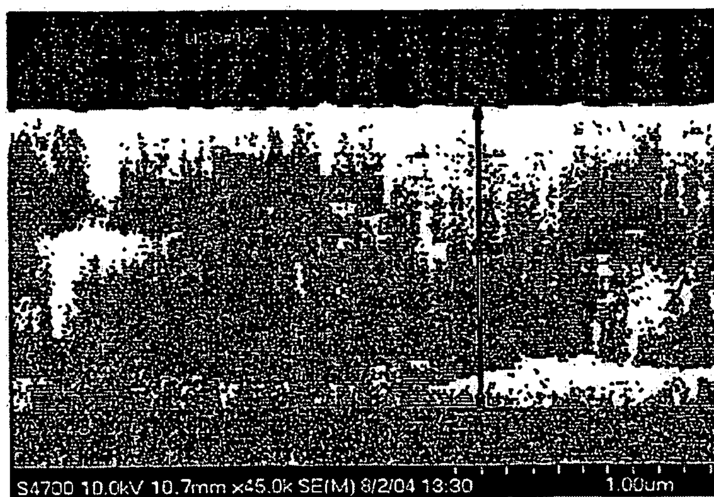


FIG. 5F

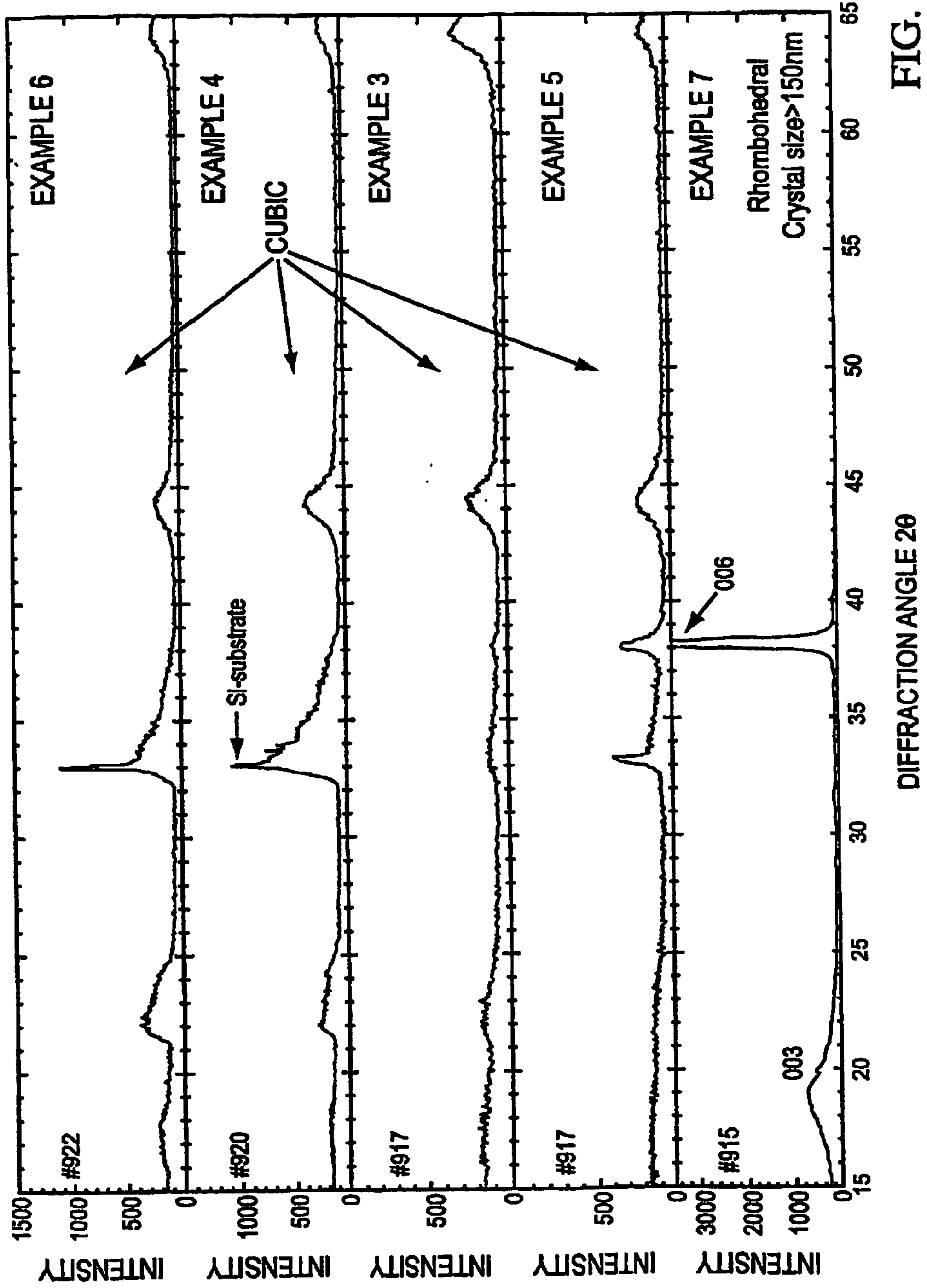


FIG. 5G

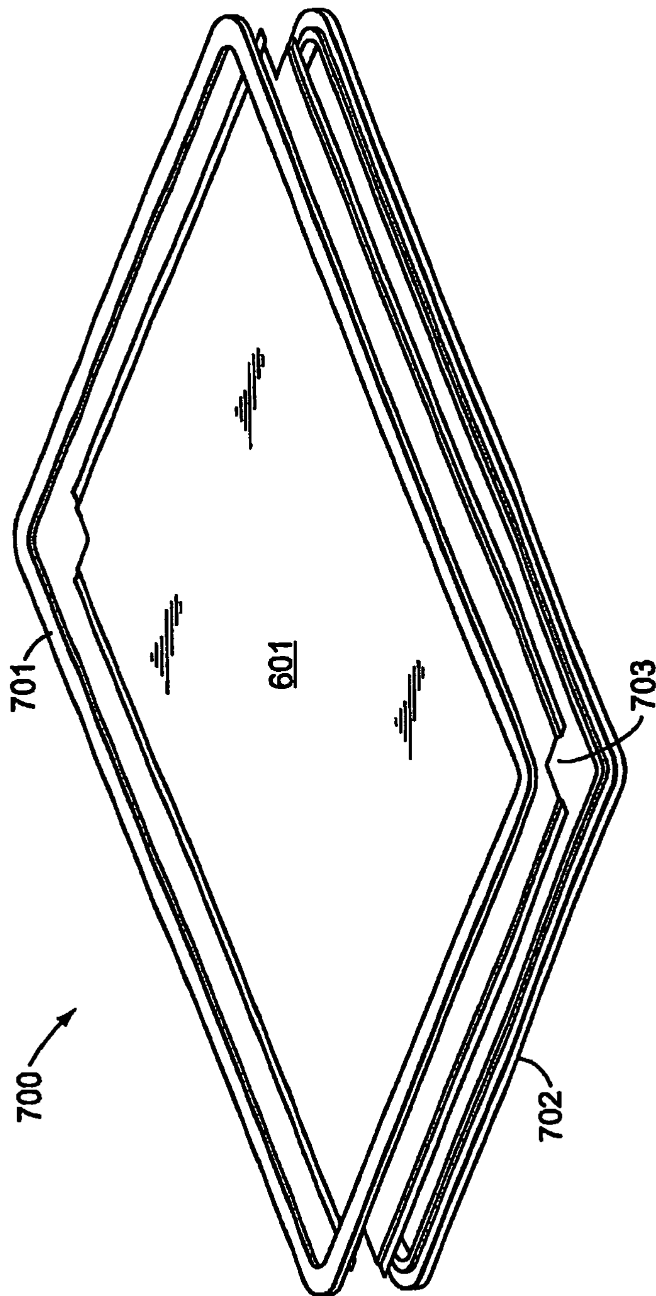


FIG. 7A

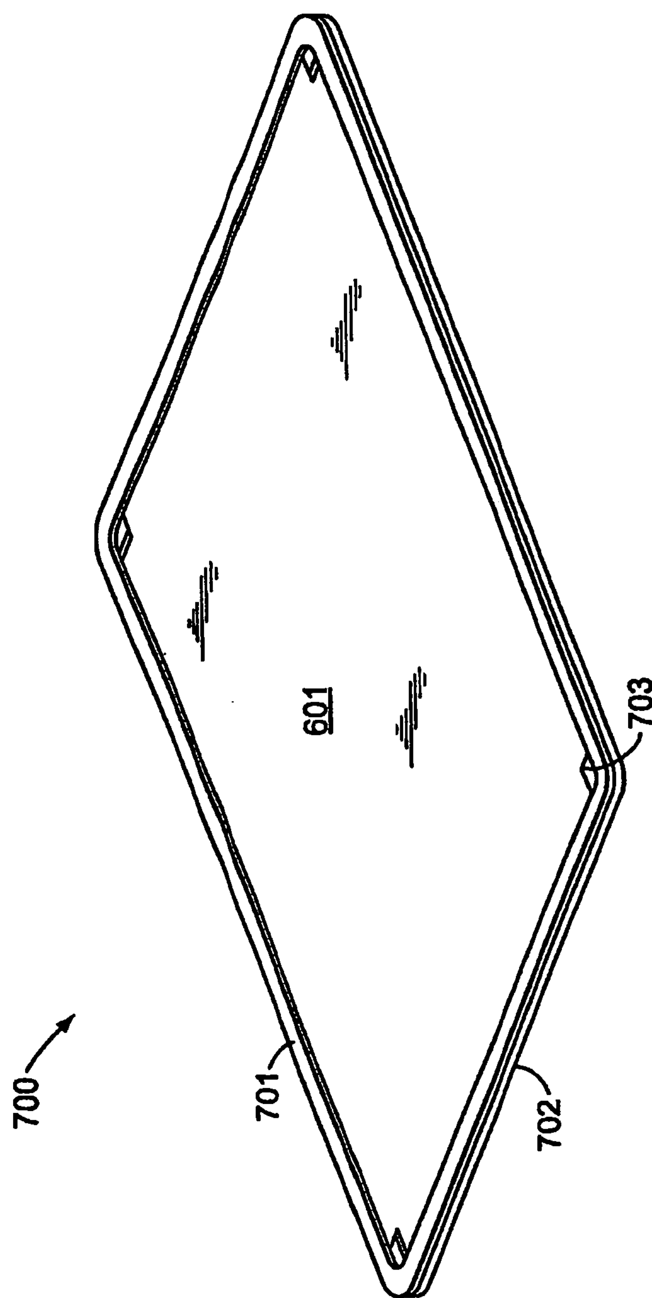


FIG. 7B

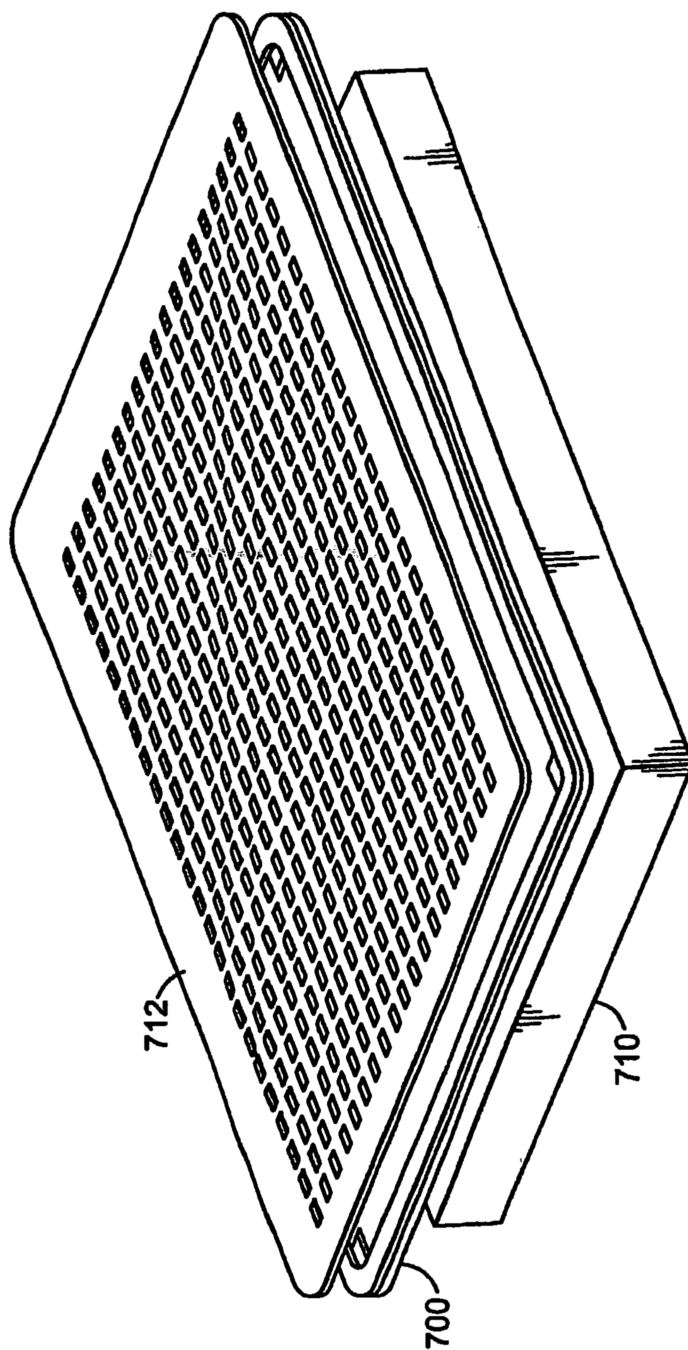


FIG. 7C

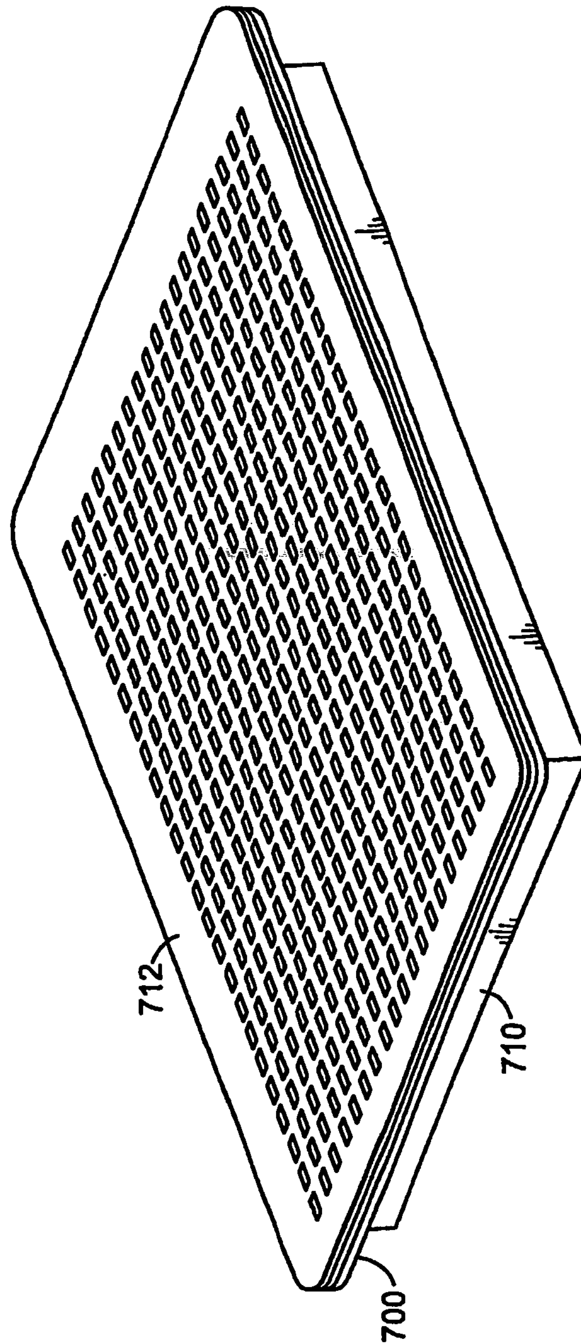


FIG. 7D

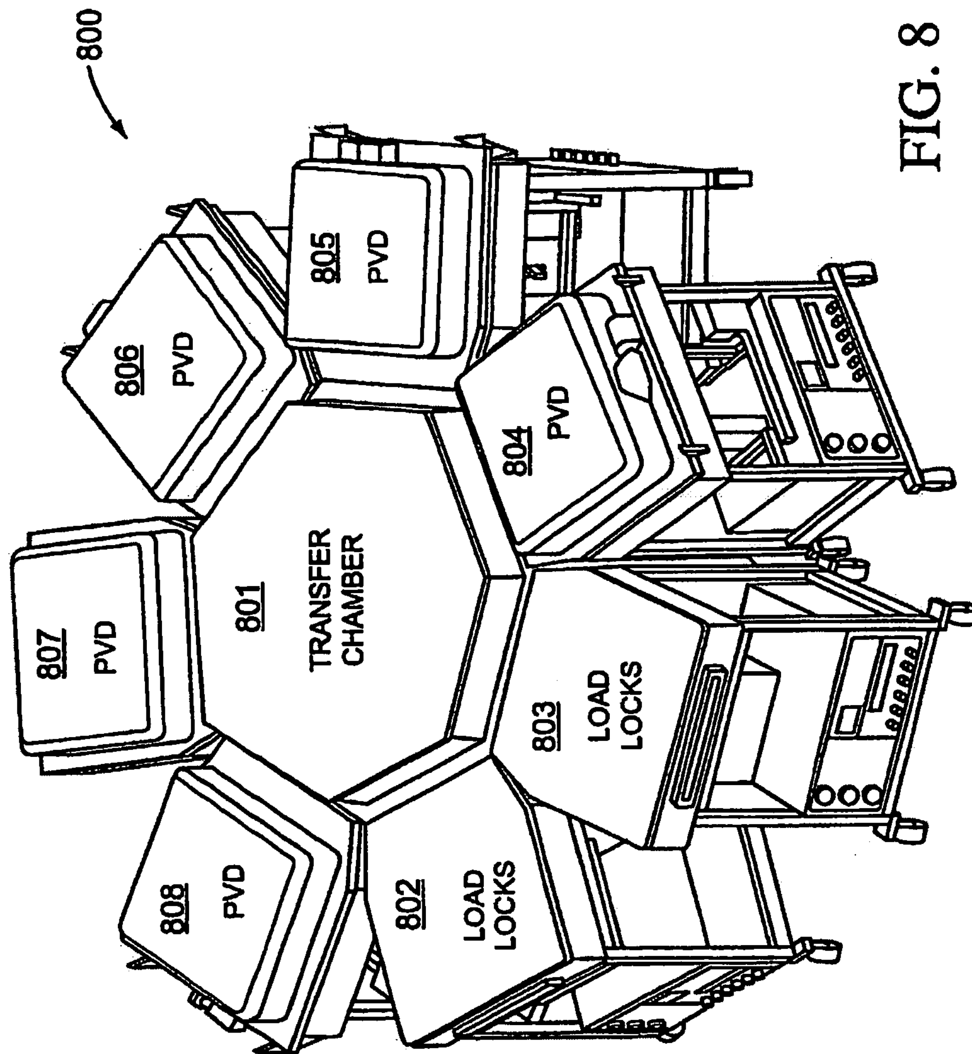


FIG. 8

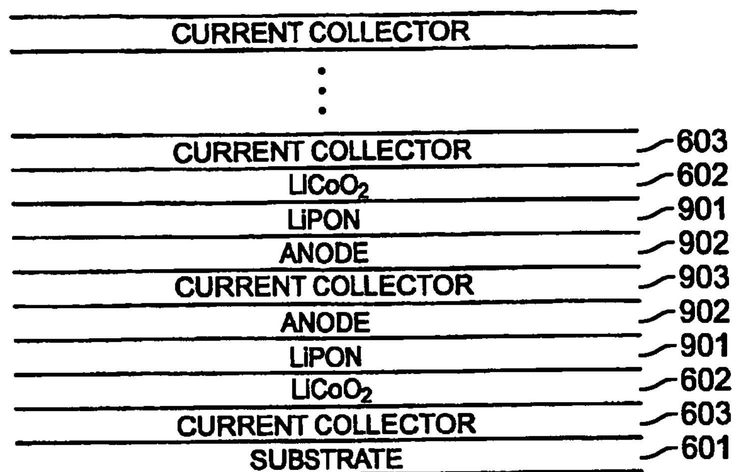


FIG. 9A

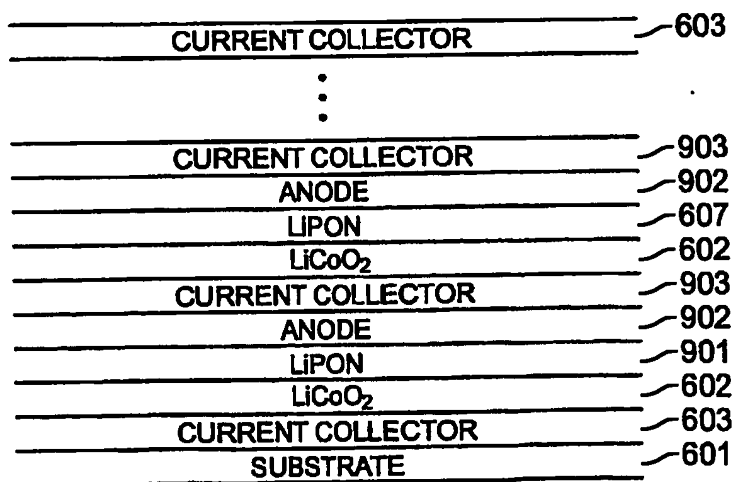
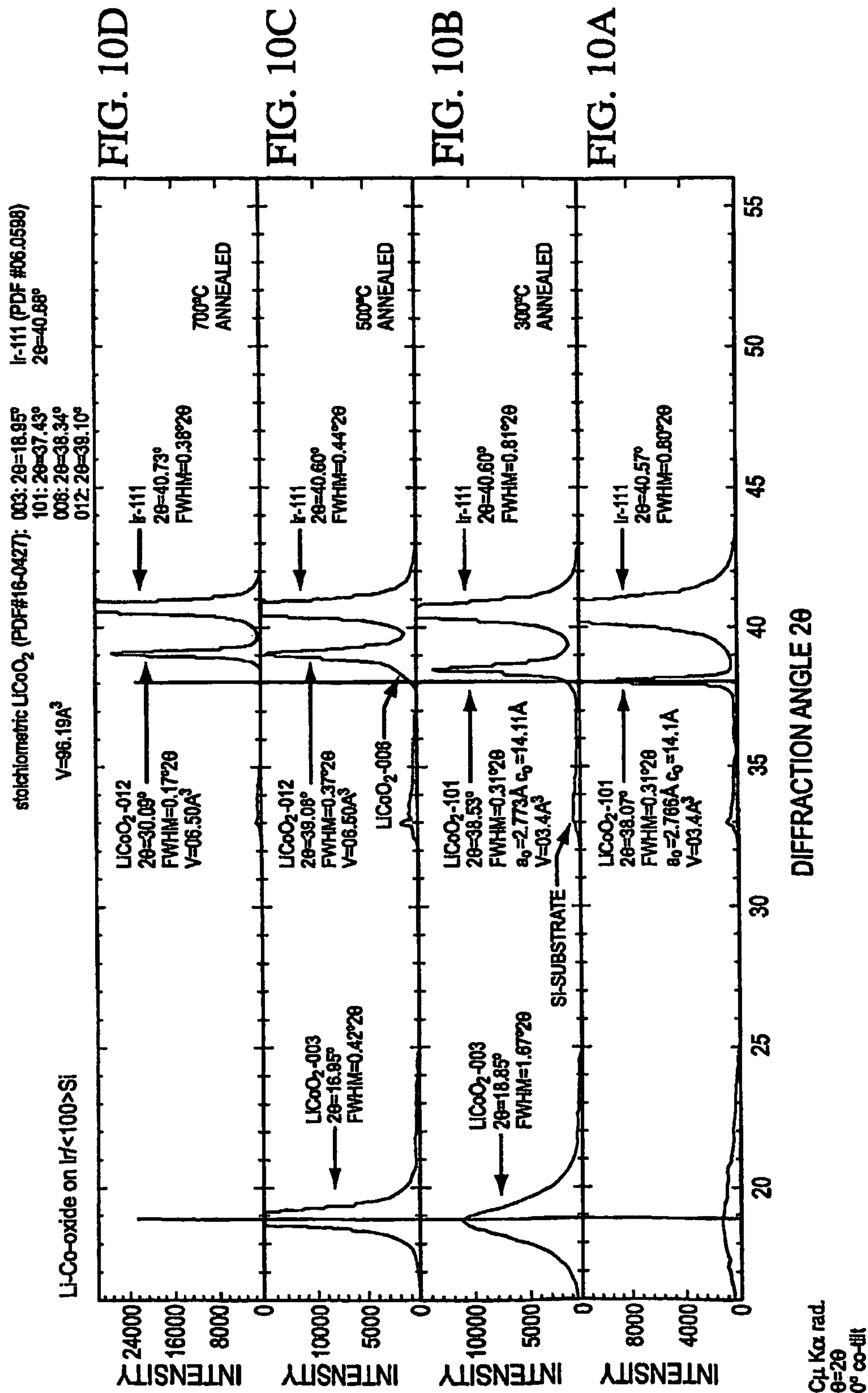


FIG. 9B



Li-Co-oxide on Ir/<100>Si
stoichiometric LiCoO2 (PDF#16-0427): 003: 2θ=18.95° 101: 2θ=37.43° 006: 2θ=38.34° 012: 2θ=39.10°
V=96.19A3
Ir-111 (PDF #06.0598) 2θ=40.68°
LiCoO2-012 2θ=30.09° FWHM=0.17°2θ V=06.50A3
Ir-111 2θ=40.73° FWHM=0.38°2θ
700°C ANNEALED
LiCoO2-003 2θ=16.95° FWHM=0.42°2θ
LiCoO2-012 2θ=39.08° FWHM=0.37°2θ V=06.50A3
LiCoO2-006
Ir-111 2θ=40.60° FWHM=0.44°2θ
500°C ANNEALED
LiCoO2-003 2θ=18.85° FWHM=1.67°2θ
LiCoO2-101 2θ=38.53° FWHM=0.31°2θ a0=2.773Å c0=14.11Å V=03.4A3
Si-SUBSTRATE
Ir-111 2θ=40.60° FWHM=0.81°2θ
300°C ANNEALED
LiCoO2-101 2θ=38.07° FWHM=0.31°2θ a0=2.766Å c0=14.1A V=03.4A3
Ir-111 2θ=40.57° FWHM=0.80°2θ
INTENSITY
24000 16000 8000 0
10000 5000 0
10000 5000 0
8000 4000 0
20 25 30 35 40 45 50 55
DIFFRACTION ANGLE 2θ
Cμ Kα rad. θ=2θ 0° co-tilt
FIG. 10D
FIG. 10C
FIG. 10B
FIG. 10A

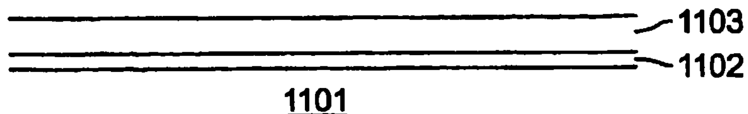


FIG. 11A

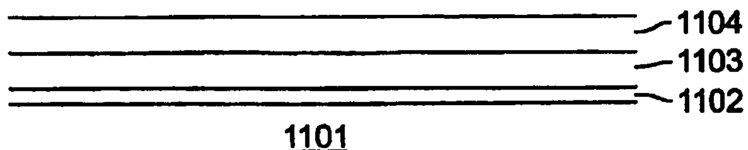


FIG. 11B

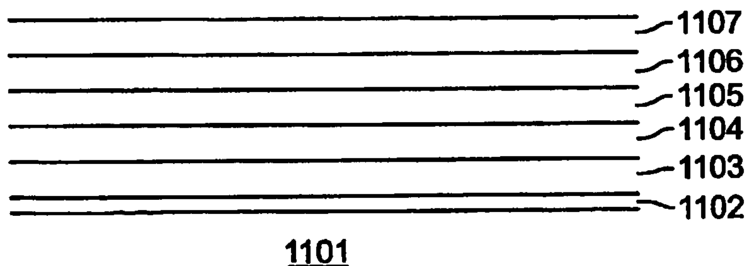


FIG. 11C

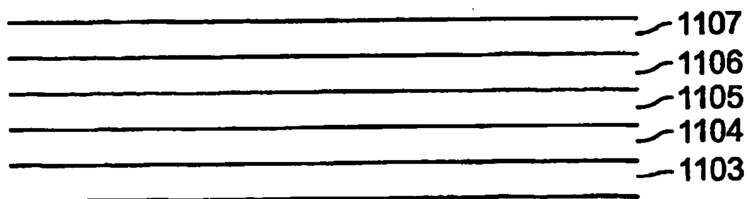


FIG. 11D

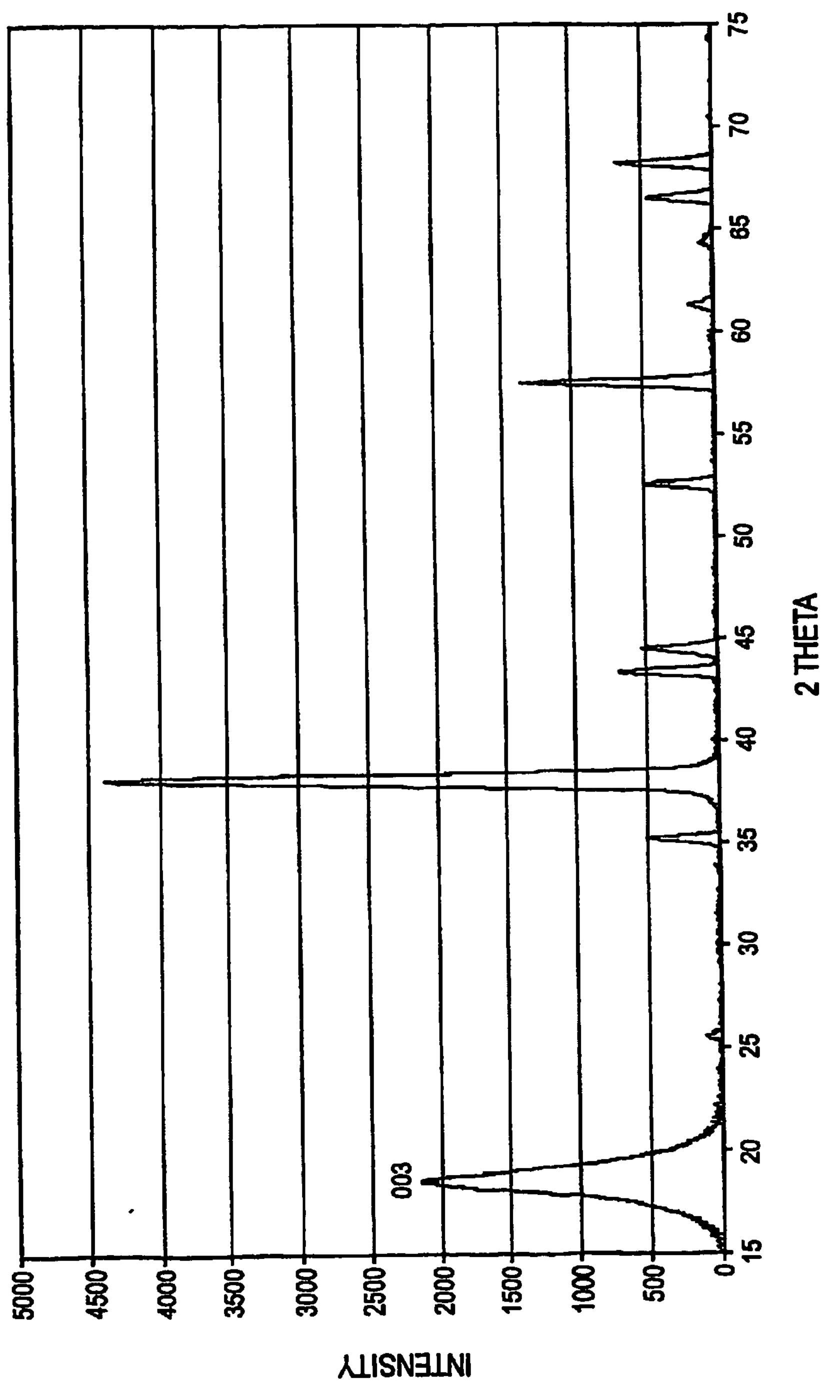


FIG. 12A

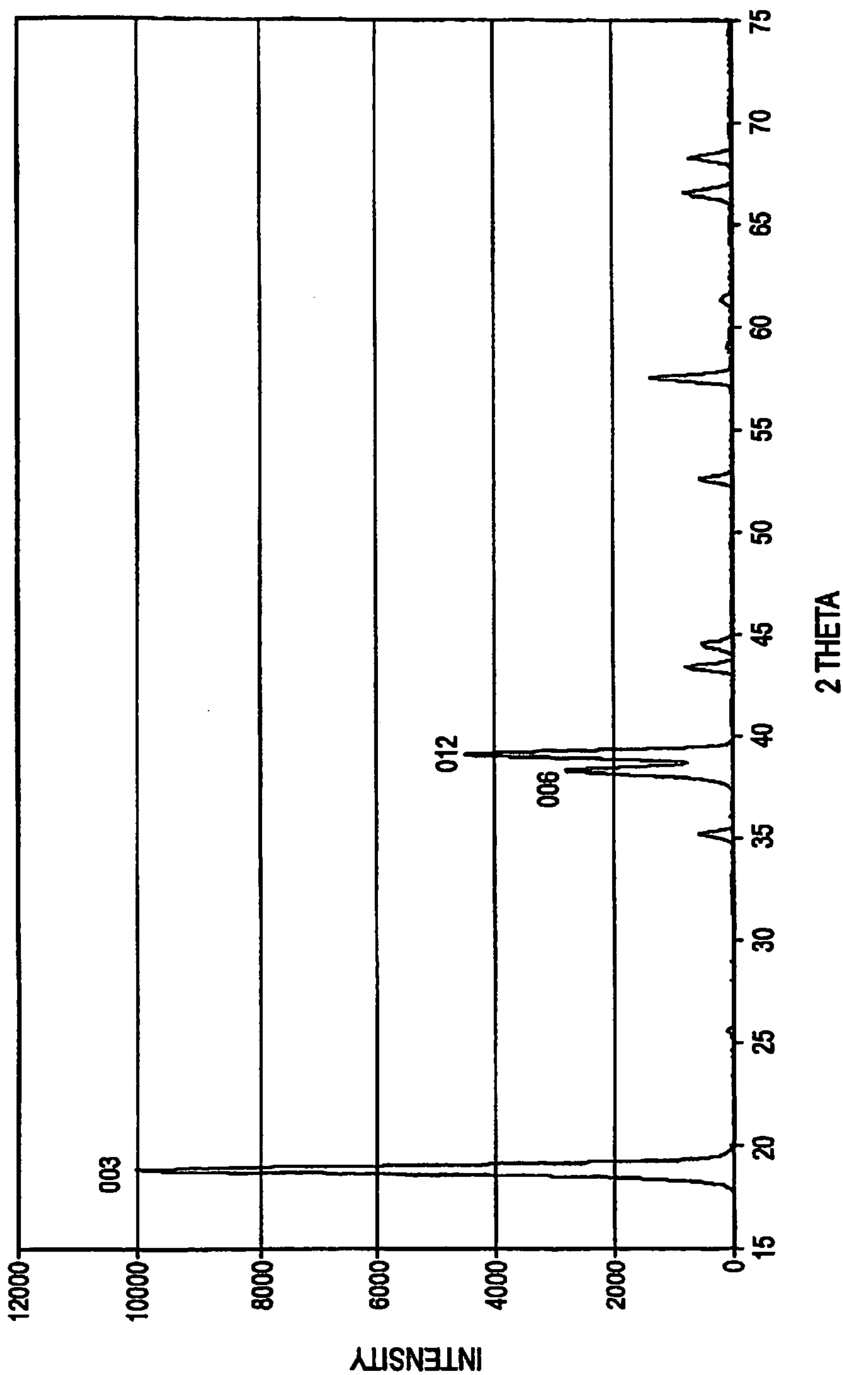


FIG. 12B

FIG. 12C

FIG. 12D

FIG. 12E

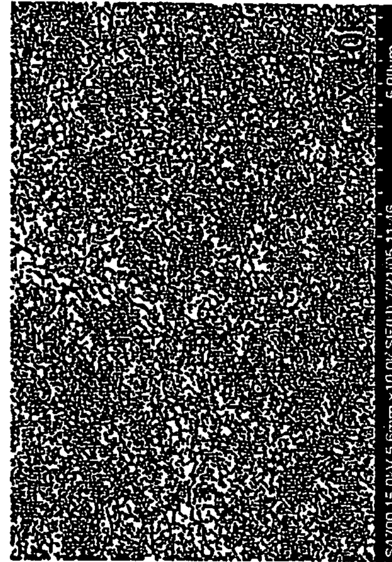


FIG. 12F

BEST AVAILABLE COPY

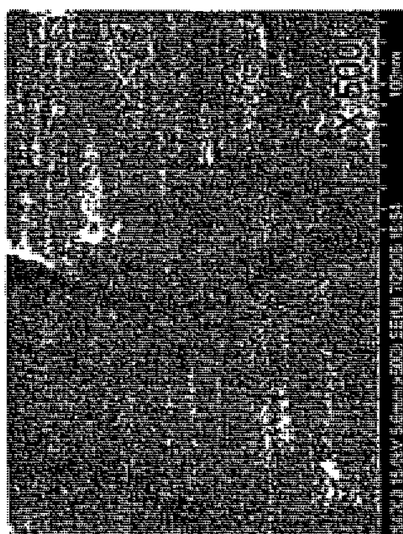


FIG. 12G

FIG. 12H

FIG. 12I

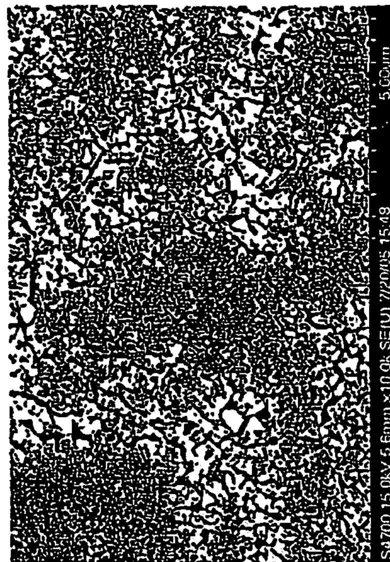
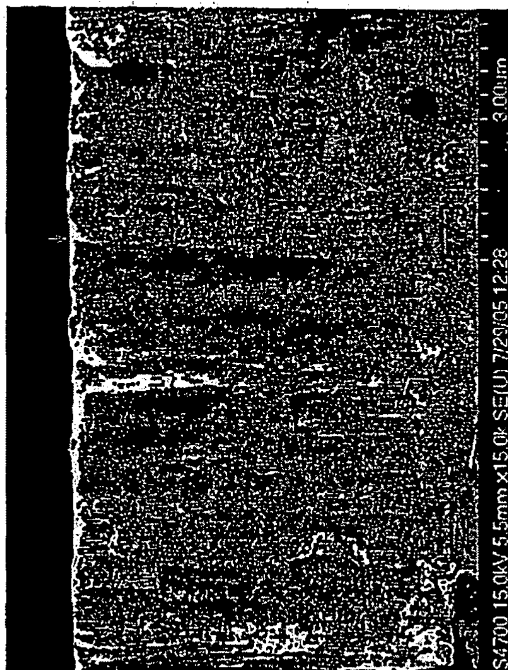


FIG. 12J

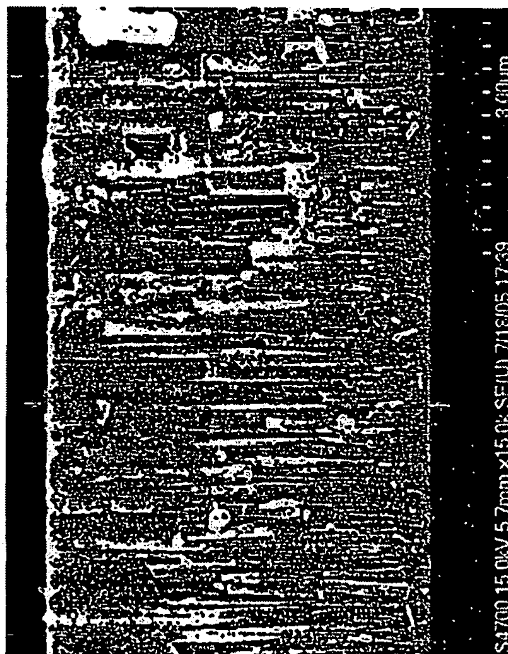
BEST AVAILABLE COPY

FIG. 12L



On alumina

FIG. 12K



On Si

BEST AVAILABLE COPY

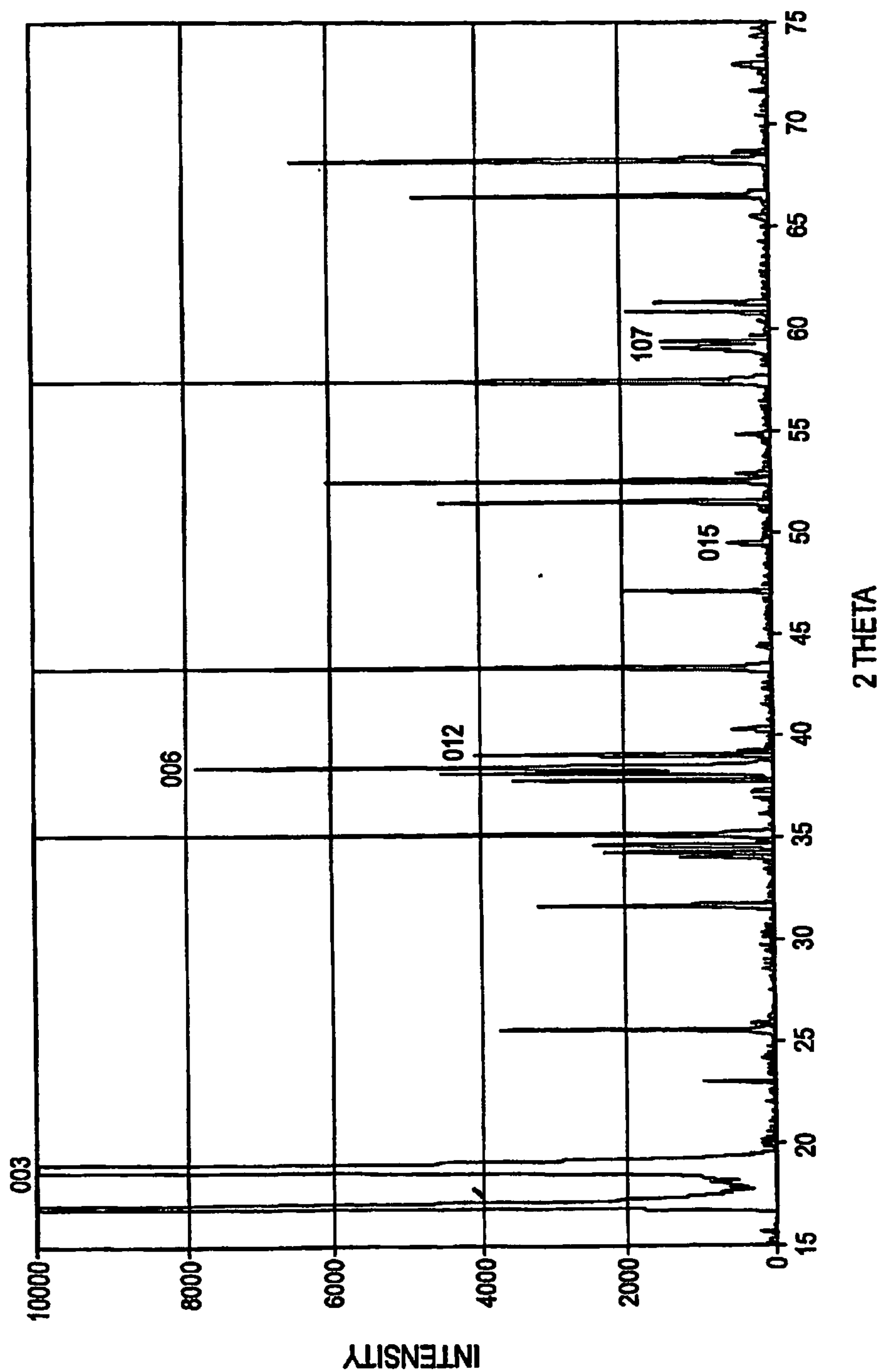


FIG. 13A

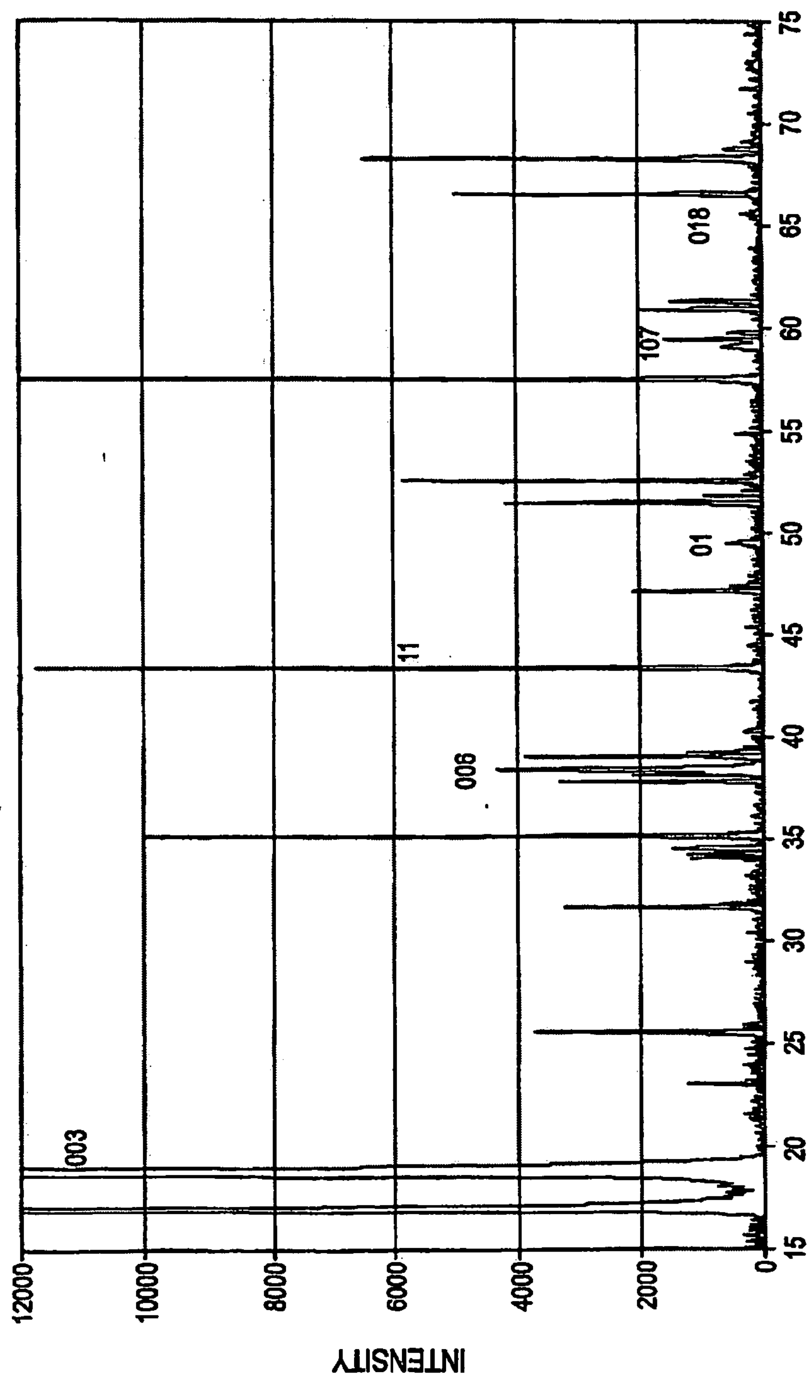


FIG. 13B

FIG. 13C

FIG. 13D

In Ar

FIG. 13E

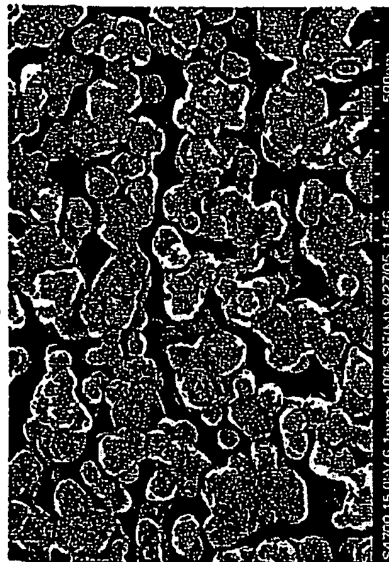


FIG. 13F

In Ar/O_2 (3/1)

BEST AVAILABLE COPY

FIG. 14A

As deposited

FIG. 14B

700CX2h

FIG. 14C

RTA-5m

FIG. 14D

RTA-700C15m

BEST AVAILABLE COPY

FIG. 15A

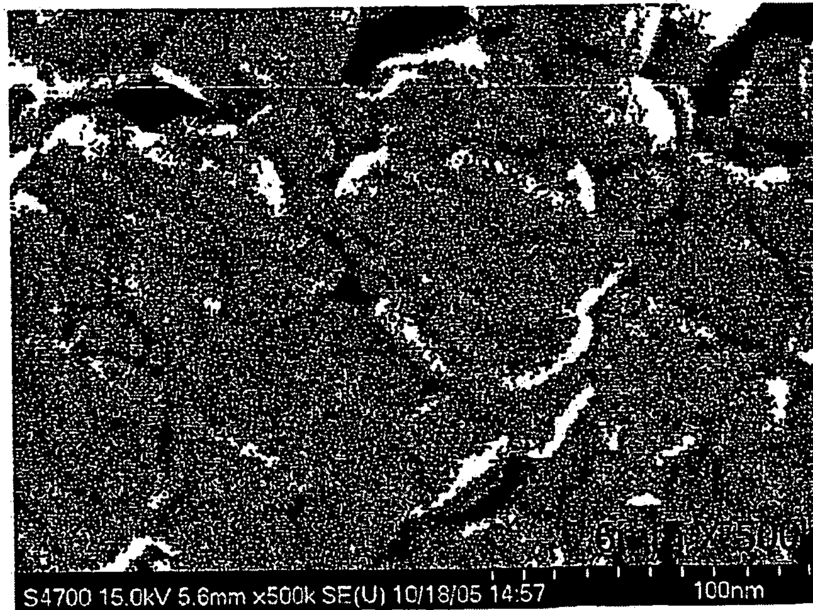


FIG. 15B

BEST AVAILABLE COPY

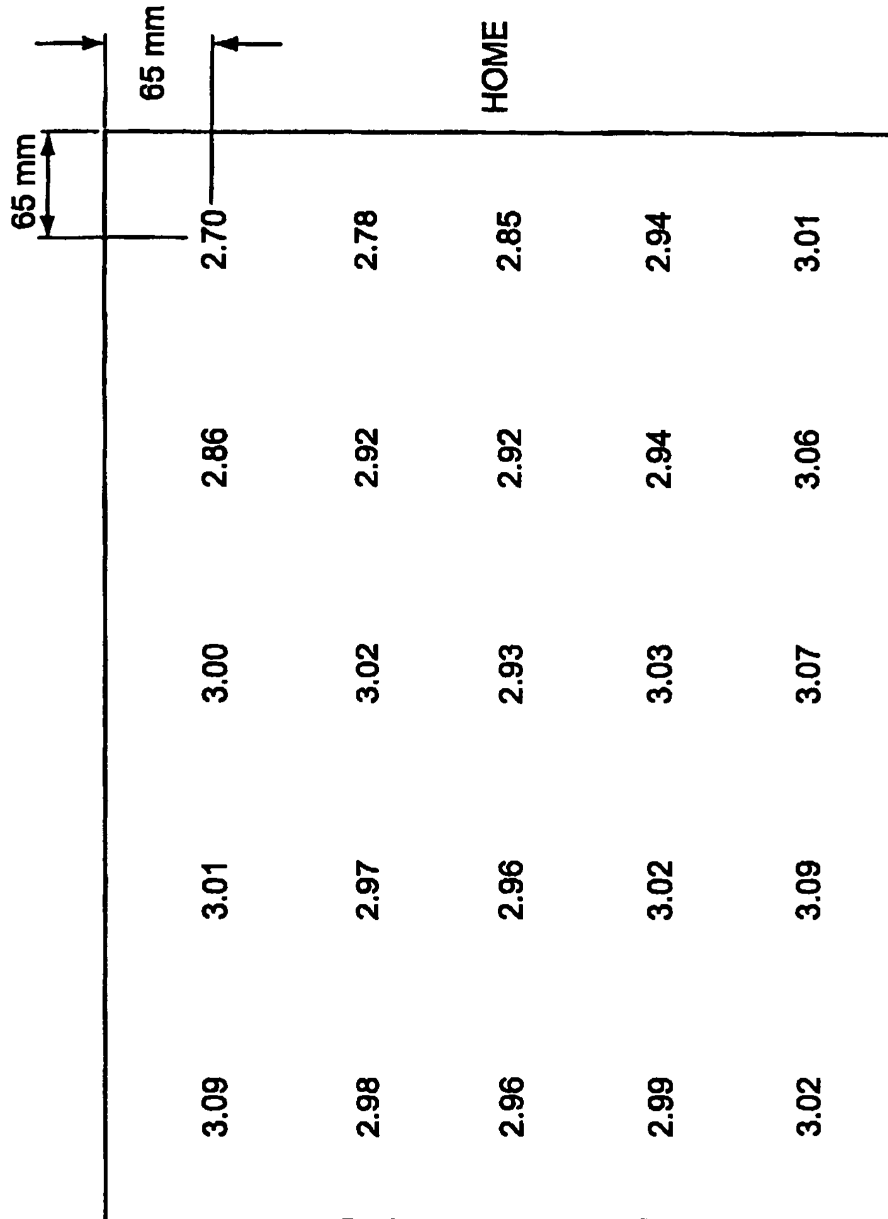


FIG. 16

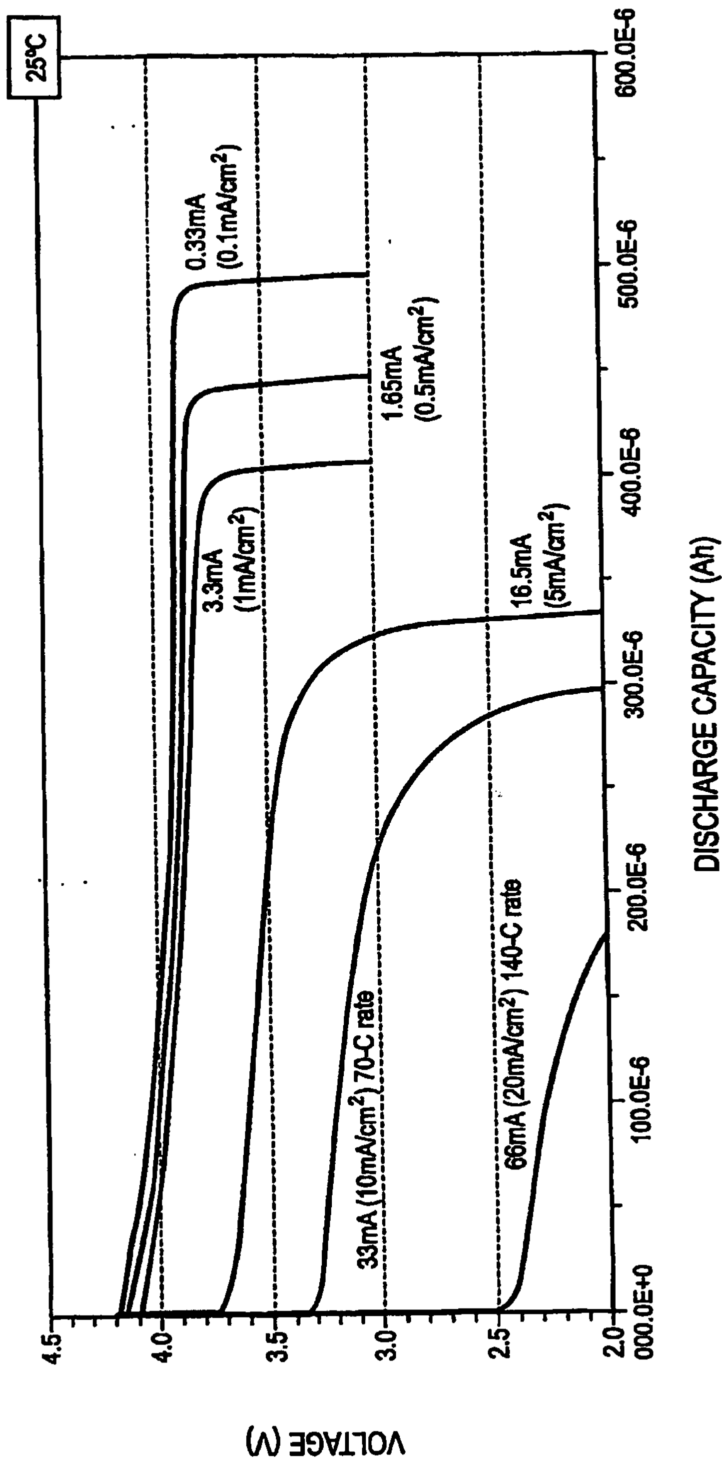


FIG. 17

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C23C 4/10, 4/12, 14/34

A1

(11) International Publication Number: WO 99/61674

(43) International Publication Date: 2 December 1999 (02.12.99)

(21) International Application Number: PCT/EP99/03599

(22) International Filing Date: 26 May 1999 (26.05.99)

(30) Priority Data:
98870120.7 26 May 1998 (26.05.98) EP

(71) Applicant *(for all designated States except US)*: UNIVERSITEIT GENT [BE/BE]; St. Pietersnieuwstraat 25, B–9000 Gent (BE).

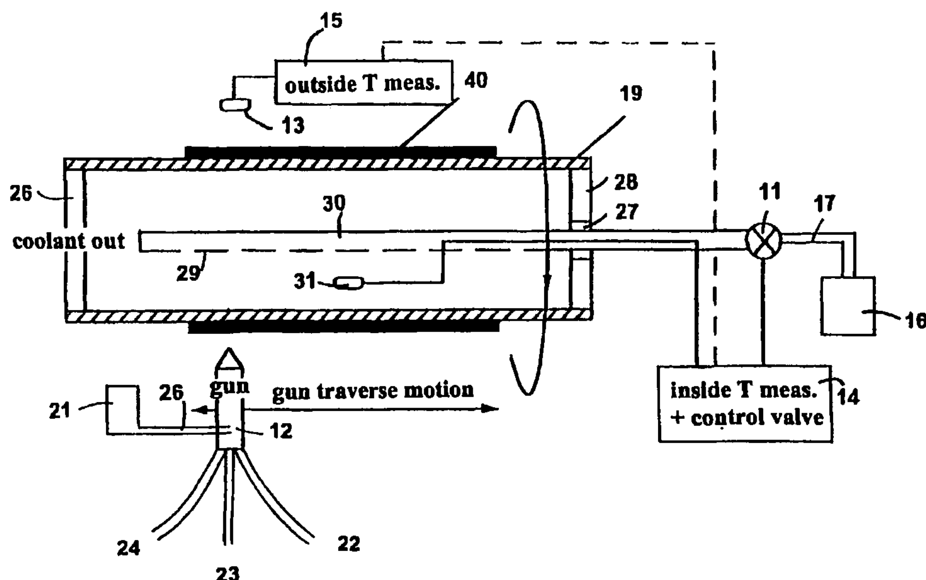
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: HOSTE, Serge [BE/BE]; Gaverse steenweg 579, B–9280 Merelbeke (BE). PERSYN, Frans [BE/BE]; Oude boomgaardlaan 23, B–9080 Lochrist (BE). VAN DRIESSCHE, Isabel [BE/BE]; Wareslagstraat 94, B–9250 Waasmunster (BE).

(74) Agents: BIRD, William et al.; Bird Goën & Co., Termerestraat 1, B–3020 Winksele (BE).

(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: SPRAYING METHOD TO FORM A THICK COATING AND PRODUCTS OBTAINED



(57) Abstract

A method and an apparatus for spraying materials onto a substrate to produce a coating thereon is described which allows very thick layers of complex metal oxides to be produced. The apparatus and method are particularly suitable for producing superconducting coatings.

32

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	Country	Code	Country	Code	Country	Code	Country
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

SPRAYING METHOD TO FORM A THICK COATING AND PRODUCTS OBTAINED

The present invention relates an apparatus and a method of spraying to form a coating on flat or curved substrates, for example, either as part of the direct
5 formation of metallic or ceramic coatings such as superconductive or piezo-electric layers or for the production of targets for sputtering magnetrons having coatings which are precursors of such layers.

TECHNICAL BACKGROUND

10 From EP-A-286 135 it is known to flame spray complex ceramic materials onto a substrate such as a tape to form a superconducting layer. It is suggested to pre-heat the substrate to temperatures above 540°C and to cool the coating slowly. It is further recommended to treat the coating in an atmosphere containing one of the components of the superconducting ceramic. An oxy-acetylene flame is
15 used for the flame spraying. Thickness of up to 3 mm are described.

It is also known from US 5,196,400 to plasma spray a coating onto a target for use in a sputtering magnetron to sputter a Y-Ba-CuO superconductor coating. Deposition of only a thin target coating of 0.5 mm is reported.

The production of superconducting powders using flame spraying is
20 reported in US 5,140,005. An oxy-acetylene flame is used. It is tacitly accepted that the high temperature of the flame changes the stoichiometric ratios of the components and that this has to be compensated by increasing the more volatile components in the original mixtures. US 5,045,365 describes a method of cooling a oxy-acetylene flame-sprayed substrate with water. Without special precautions,
25 water cooling is unsuitable for superconductors due to the water vapour produced.

EP-A-355 736 describes production of flat targets with metal oxides up to a layer thickness of 3 mm. WO 98/0833 describes the production of < 20 micron thick layers of superconducting metal oxide mixtures.

The article by Murakami et. al. "Rapidly Solidified Thick Deposit Layers
30 of Fe-C-Mo Alloys by Flame Spraying" describes up to 1.5 mm thick rapidly

cooled thick layers of Fe-C-Mo alloys by flame spraying. Special precautions were taken to produce dense layers, e.g. direct application of cryogenic gas on the coating during application.

EP-A-586 809 describes the metal spraying application of a layer of
5 relatively homogeneous material (nickel coated silicon) which is much easier to handle than the heterogeneous oxide mixtures contemplated by the present invention. Layer thicknesses of up to 8 mm are described but 3 to 5 mm is preferred. Various layers are proposed including a Ni-Al layer for improving adhesion between the deposited layer and the substrate. A Ni-Al adhesion
10 promoter is known from DE-A-33 18 828.

Plasma spraying of superconducting materials is described in EP-A-288711 up to a thickness of 250 micron.

It is an object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a ceramic coating on flat
15 or curved substrates.

It is a further object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a thick walled ceramic coating on flat or curved substrates which is structurally sound.

It is a further object of the present invention to provide an apparatus and a
20 method of spraying to form a thick walled coating of a superconducting ceramic material.

It is still a further object of the present invention to provide an apparatus and a method of spraying suitable for forming a thick walled ceramic coating on flat or curved targets to be used in a sputtering magnetron.

25 It is still another object of the present invention to provide a method of producing a (magnetron) vacuum sputtering target as well as the target itself with improved thermal and electrical conductivity and high mechanical strength using a spraying process employing dedicated powder formulations.

30 SUMMARY OF THE INVENTION

One aspect of the present invention is to provide a substrate with a coating of a combination of metal oxides having a thickness greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. Preferably, the coating is deposited by spraying, e.g. flame or plasma spraying. Preferably, 5 the substrate is cylindrical and is more preferably is suitable as a cylindrical target substrate for a sputtering magnetron. The combination of oxides preferably comprises at least a superconductive precursor or a superconductor. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity of the composite 10 preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. 15 withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical 20 resistivity of the deposited layer is lower than 15×10^{-6} Ohm.m, more preferably lower than 10×10^{-6} and most preferably less than 5×10^{-6} Ohm.m. Values below 1×10^{-6} Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

25 The electrical , thermal and mechanical properties of the coating deposited in accordance with the present invention should be sufficient that the deposited layer can be applied to a suitable substrate by means of a sputtering magnetron preferably at a static sputtering deposition speed of at least 5 nm/minute, more preferably, at 20 nm/minute and most preferably at at least 40 nm/minute.

30 When a superconductor precursor or a superconductive material is

deposited, at least 10% of the coating is in the superconducting phase, more preferably 15%. This may be assisted by a subsequent limited thermal treatment, e.g. 3 hours and 940°C, after deposition.

The present invention also includes a method of depositing by spraying a superconductor precursor layer onto a cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase. The present invention also includes a method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

In accordance with one aspect of the present invention a flame spraying apparatus is provided for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a burner for producing a flame; an inlet for feeding material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm.

Another aspect of the present invention is to provide a flame spraying apparatus for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a flame spraying gun; and a cooling system for the substrate, the cooling system including a device for bringing a cryogenic fluid into contact with the substrate. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. The input material for the sprayer may be a liquid solution of soluble compounds (e.g. nitrates) which decompose thermally into ceramic component oxides, liquid slurries of the ceramic components or metal powders, or dry metal or ceramic powders or precursors of the ceramic components, e.g. nitrates, of such powders.

The present invention may provide a method of flame spraying a

combination of metal oxide materials onto a substrate to produce a coating thereon, comprising: generating a flame; feeding the material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted
5 may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides.

The present invention may also provide a method of flame spraying metal oxide combinations onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the materials; and cooling the substrate by
10 bringing a cryogenic fluid into contact with the substrate.

The present invention may also provide a method of flame spraying a superconducting ceramic material or a precursor thereof onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the ceramic material; depositing the coating on the substrate; and during deposition of
15 the coating, cooling the substrate so that the solidified coating thereon has a temperature between room temperature (~25°C) and 150°C, preferably room temperature (~25°C) and 100°C. Water or cryogenic fluid cooling are particularly preferred.

One linking concept between the above methods and apparatus is control
20 of the total heat energy into the spraying/coating system. This can be achieved by careful control of parameters which influence the energy input such as spraying distance, spray head traverse speed, rotation speed of a cylindrical substrate, powder dwell time in the hot exit plume from the spray head, particle velocity exiting the spray head, cooling method and rate of cooling the substrate during
25 coating deposition.

The present invention also includes a method of reconditioning a target for a sputtering magnetron by flame spraying or atmospheric plasma spraying as well as a reconditioned target as made in accordance with the method. The target material or coating is preferably a ceramic coating, in particular a
30 superconducting or superconductor precursor coating.

The final coating is preferably a metallic or ceramic layer, in particular a superconducting or piezo-electric layer or a precursor thereof. The present invention includes a method of spray drying a liquid to form a powder suitable for flame spraying. The spray dried powder may be sintered. The present invention
5 also includes a manufacturing method for depositing a coating on a substrate comprising the steps of: spray drying a precursor liquid to form a powder and flame spraying the powder to form a coating on a substrate. The substrate may be a target for a sputtering magnetron and the final coating may sputtered onto a final substrate in the sputtering magnetron. The ceramic powder may be sintered after
10 the spray drying step. The flame of the flame spray gun preferably imparts a temperature to the powder to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. During flame spraying the target is preferably cooled by bringing a cryogenic
15 fluid into contact with the target. In particular the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The present invention includes an apparatus for spray drying a liquid to form a powder suitable for flame spraying. The present invention may also
20 include an apparatus for depositing a coating on a substrate comprising: a spray drier for drying a precursor liquid to a powder, and a flame sprayer for flame spraying the powder to form a coating on a substrate. The substrate may be a target for a magnetron. Additionally, a sputtering magnetron for sputtering the final coating onto the final substrate using the target may be provided. The flame
25 of the flame spray gun preferably imparts a temperature to the powder to be sprayed of slightly above the melting point of the sprayed material. Preferably the temperature imparted is 1500°C or less, preferably 1200°C or less. Temperatures of 600 to 850 °C may be suitable for some metal oxides. In the flame sprayer a cooling system for the target is preferably provided, the cooling system including
30 a device for bringing a cryogenic fluid into contact with the target. In particular

the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The above methods may be used, for example, either as part of the direct
5 formation of superconductive or piezo-electric layers on the substrate, e.g. a tape, or for the production of coatings on targets for use in a sputtering magnetron to sputter a superconducting layer onto a final substrate. The present invention may provide oxide sputtering targets supporting very high power dissipation thus enabling high sputter deposition rates of at least 50 nm/min.

10 The dependent claims describe additional individual embodiments of the present invention. The present invention will now be described with reference to the following drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a schematic representation of a flame spraying apparatus in accordance with one embodiment of the present invention.

Fig. 2 is a schematic representation of a flame spraying apparatus in accordance with another embodiment of the present invention.

Fig. 3 is a schematic representation of a spray drying apparatus in
20 accordance with another embodiment of the present invention.

DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

The present invention will be described with reference to certain specific embodiments and with reference to certain specific drawings but the invention is
25 not limited thereto but only by the claims. In particular, the present invention will mainly be described with reference to the deposition of a superconductor precursor or superconductive coatings but the invention is not limited thereto but may be used advantageously with other heterogeneous coatings such as ceramic coatings, particularly those having special properties such as piezo-electric
30 coatings and in particular coatings which contain components which can be

degraded by high temperatures or which are more volatile than other components. More particularly the present invention will be described with reference to the manufacture of $YBa_2Cu_3O_7$ superconducting powders and coatings but the invention is not limited thereto but only by the claims. Further one way of
5 carrying out the present invention will be described with reference to low temperature flame spraying but the present invention is not limited thereto. By carrying out the invention in accordance with the processing details and principles described below thick layer (greater than 3 mm, more preferably greater than 5 mm and most preferably greater than 8 mm) metal oxide combination coatings
10 suitable for use as a sputtering magnetron target have been applied by oxy-acetylene flame spraying with water cooling or by atmospheric pressure or low-pressure plasma spraying to substrates including cylindrical substrates used in rotating cathode magnetrons. During plasma spraying gasses may be used such as argon or mixtures of argon and other gasses to shield the plasma spray. Also the
15 present invention will mainly be described with reference to an input to the flame spraying head of spray dried powder. The present invention is not limited thereto but includes other forms of input materials such as a mixture of the metal oxides, including slurries thereof or mixtures of precursors of metal oxides such as metal nitrates as well as slurries and solutions thereof.

20 Fig. 1 is a schematic diagram of the flame spraying apparatus 10 in accordance with a first embodiment of the present invention. A flame spraying gun is represented schematically at 12. The gun 12 may be a commercially available flame spraying gun as for instance available from Sulzer Metco, Westbury, NY, USA or a high velocity oxy-fuel spraying gun available from the
25 same company. The gun 12 may be provided with an air pincher. The gun 12 may be fed with fuel gas in pipe 22, oxygen in pipe 23 and gun cooling air in pipe 24. Additional gases may be supplied to the gun 12 as described for instance in US 5,273,957 or EP-A-413 296. Material to be coated is fed in powder or liquid form, e.g. a dry powder, a slurry of the powder and a liquid or in solution, to the
30 gun via conduit 26 from hopper 21. Gun 12 is mounted on a drive (not shown)

which provides the necessary movements of the gun 12 to coat the substrate 19. When substrate 19 is a cylindrical target, for instance, for a rotating cathode magnetron, this may be rotated and the movements of the gun 12 may be simple reciprocating movements parallel to the axis of the target 19. If the substrate 19 is
5 a flat rectangular or circular plate, the movements may be provided by a suitable robot and may be complex, e.g. including rotational cycloidal motions. For rapid deposition several guns 12 may spray the same substrate 19 at the same time.

The fuel gas for the gun 12 may be selected from one of acetylene, propylene, hydrogen or similar fuels but the present invention is not necessarily
10 limited thereto. Particularly preferred in one embodiment of the present invention is a fuel with a lower calorific value such as one of ethylene, natural or town gas, butane or propane as these provide a lower temperature flame than acetylene and butane is particularly preferred as it gives a stable easily controllable flame and is considered safer than acetylene if powders containing copper compounds are
15 used. It is generally accepted that oxy-acetylene flames have temperatures of 2000 °C and more. It is preferred in accordance with an embodiment of the present invention if the flame of the flame spraying gun 12 imparts a temperature only sufficient to just melt the powder to be sprayed. Temperatures of 1500 °C or less and preferably 1200 °C or less are preferred and temperatures between 600 and
20 1000 °C may be more preferable. These low flame temperatures minimise decomposition of the ceramic powder components during flame spraying. Moreover, they limit the impact of evaporation of the materials to be flame sprayed and allow a deposition efficiency of more than 80%, i.e. more than 80% of the solid mass originally introduced into the gun 12, becomes attached to the
25 substrate 19. Mechanically stable, scratch resistant flame sprayed coatings are produced with these low temperatures.

The gun 12 is preferably held at 7 to 15 cm from the substrate 19 to be coated but this depends upon the size of the flame. Similar coatings have been obtained using both oxy-acetylene flame spraying and plasma spraying. Attention
30 must be paid to the energy taken up by the sprayed particles during the spraying

and the transfer of this energy to the substrate. Intensive cooling of the substrate is preferred which may be on the side of the substrate remote from the deposited layer and/or on the same side. By altering the velocity of the particles in the flame or plasma the dwell time therein may be altered, thus limiting the energy uptake 5 by the particles.

The material of substrate 19 preferably has a high melt temperature and a high thermal conductivity and when the substrate 19 is to be used as a target for a sputtering magnetron a good electrical conductivity is preferable. It is also preferred if the thermal expansion of the substrate material is similar to that of the 10 ceramic coating to be applied. In accordance with embodiments of the present invention low temperature flame spraying and/or intense cooling of the substrate 19 allows the use of substrates 19 with a thermal expansion coefficient up to at least twice or down to at least a half of the thermal expansion coefficient of the ceramic coating. A non-limiting list of suitable materials may be steel, iron, 15 stainless steel, copper or copper alloys, however the low temperature flame spraying process in accordance with the present invention, either independently or in combination with intense cryogenic cooling of the substrate 19, allows other materials to be used such as paper, cardboard or polymeric materials. Preferably, the substrate 19 should be free of grease and dry before deposition. Preferably, 20 the outer surface of metals is sand blasted and then lapped with abrasive materials. Buffer layers between the substrate and the sprayed coating may be used such as Ni-Al or an In-alloy. These may be applied by flame or plasma spraying before application of the metal oxide coating. .

Where the substrate 19 is rigid it may be mounted in a suitable jig. For 25 example, a cylindrical substrate 19 is preferably mounted in a rotating device such as a lathe. The substrate 19 may be held by rotatable chucks at each end thereof. The temperature of the solidified flame sprayed coating 40 on the surface of the substrate 19 is preferably measured by a temperature sensor 13, 15. The sensor head 13 is preferably a remote sensing optical head which is not in contact with 30 the surface 40 of the flame sprayed coating. The temperature to be measured is of

the solidified coating 40 and not that of the coating immediately on impacting the substrate 19 which may have a higher temperature. Hence, the temperature sensor 13 is preferably mounted so that it lags behind the impact position of the flame sprayed materials a little. In addition a temperature sensor 31 may be provided
5 inside the substrate 19 for further control of the deposition process. Control of deposition temperature is an important aspect of the present invention. Control of temperature affects the amount of thermal stress in the coating, a low stress reducing the possibility of cracks forming in the coating.

In accordance with one embodiment of the present invention a means for
10 intense cooling of the substrate 19 is provided. This is preferably a cryogenic cooler comprising a supply 16 of cryogenic fluid and a delivery system 11, 14, 17, 29, 30. The delivery system may be adapted to the form of the substrate 19. For example, for a cylindrical substrate 19 the cooling device may be a conduit 17 for supplying the cryogenic fluid to a control valve 11, a conduit 30 with regularly
15 spaced holes 29 for distribution of the cryogenic fluid inside the substrate 19 and a control device 14 for receiving the output of the temperature sensor 13, 15 and for controlling the operation of the control valve 11 so as to maintain the surface temperature of the solidified coating 40 to within a certain range. Particularly preferred is a temperature range from room temperature (25 to 30°C) to 150 °C
20 and more preferably room temperature to 100 °C. These low temperatures avoid thermal stresses between the coating 40 and the substrate 19 providing a good bond and good coating density, hardness and scratch resistance thus helping to ensure the long term stability of such a coating. Using a cryogenic fluid such as liquid nitrogen (77 °K) is quite advantageous and economical as it does not
25 require the complication of perfectly sealed rotating inlets and outlets to the substrate 19 when water or other liquid coolants are used. Additionally, cryogenic fluids such as liquid nitrogen produce large temperature gradients, thus increasing the thermal sink-effect. Other liquid coolants such as water are not excluded from the present invention.

30 The cylindrical substrate 19 may be sealed by a seal 26 at one end and with

a rotating seal 28 at the other. The seal 28 may be provided with a sealed feedthrough 27 for the supply of cryogenic fluid. If water cooling is used, rotating seals at both ends of the cylindrical substrate are considered very important to prevent escape of water vapour into the deposition environment. In accordance
5 with an embodiment of the present invention it is preferred if the ends 26, 27 allow escape of a cryogenic fluid which then forms a shield gas around substrate 19 during the spraying process. Particularly preferred cryogenic fluids are liquid nitrogen, liquid oxygen and liquid air. With some complex ceramic materials, one or more components may be reduced in the spraying process. For such materials it
10 may be advantageous to use a shield gas including oxygen, e.g. liquid air or liquid oxygen, which may help to reoxidise the reduced component. On the other hand with other complex ceramics it may be advantageous to reduce the contact time with oxygen at high temperatures, under which conditions liquid nitrogen would be preferred, or a reducing gas may be included such as hydrogen. It is preferable
15 to control the atmosphere in the vicinity of the substrate 19 during coating deposition to prevent the presence of excessive water vapour and in particular to prevent condensation of water on the substrate 19. This may be achieved by generally air conditioning the air around the substrate 19 to reduce its dew point.

It is preferred if the deposition rate is selected in order to maintain the
20 substrate surface temperatures mentioned above. Assuming the cylindrical substrate as shown in Fig. 1, the rotation speed of the substrate 19, the linear speed of the gun 12 and the rate of material exiting the gun 12 may be controlled to achieve the temperatures specified above. For instance, it has been found that when using cylindrical substrates made of stainless steel of 15 cm diameter and
25 up to 40 cm long, a powder delivery of 5-10 g/min was suitable to produce 3 -10 mm coatings when depositing a $YBa_2Cu_3O_7$ layer. The rotational speed of the substrate 19 may be in the range 10 to 100 RPM with a surface speed in the range 1 to 40 m/min and the longitudinal feed of the gun 12 in the range 1-3 m/min, typically 2 m/min. The deposition rate per reciprocating pass of the gun 12 may
30 be 10 to 50 micron thickness of the coating. About 10% to 15% of the deposited

coating had maintained the lattice structure of the powder and exhibited superconducting properties. It will be appreciated by the skilled person that increasing the deposition speed, deposition thickness per pass or the flame temperature or reducing the thermal conductivity of the substrate material will increase the thermal load on the cooling system and adjustments of one or more of these parameters may be necessary to obtain satisfactory coatings. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical resistivity of the deposited layer is lower than 15 x 10^{-6} Ohm.m, more preferably lower than 10 x 10^{-6} and most preferably less than 5 x 10^{-6} Ohm.m. Values below 1 x 10^{-6} Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

Fig. 2 is a schematic representation of a further embodiment of the flame spraying process and apparatus in accordance with the present invention. Components in Fig. 2 with the same reference numbers as in Fig. 1 refer to equivalent items. The substrate 19 in accordance with this embodiment is a foil or sheet of metal, plastic or other flexible material which is wound from a pay-off spool 32 to a take-up spool 36. Where the final coating 40 cannot be spooled, the foil with coating 14 may be drawn linearly from the pay-off spool 32 and cut into lengths. The coating 40, which may be a superconducting layer, is flame sprayed

with a flame spray gun 12 similar to the one described with respect to Fig. 1. In particular it is preferable to use a fuel with a lower calorific value than acetylene such as natural or town gas, butane or propane. Preferably, the temperature of the flame of the gun 12 imparts a temperature of 1500 °C or less, more preferably 1200 °C or less to the material being sprayed through the flame. This material may be in the form of powder either of finished components of the coating 40, e.g. oxides, or precursors thereof, e.g. nitrates, or may be in the form of a slurry of powders, e.g. oxides, or a solution, e.g. of nitrates. Gun 12 may be controlled by hand or more preferably by a robot to provide zigzag motions across the width of foil 19 thus applying an even coating 40. Preferably a layer of 10 to 50 micron thickness is applied in each pass.

The temperature of the coating 40 may be monitored by one or more optical sensors 13, 15. The temperature of the foil 19 is regulated by means of a cryogenic fluid supplied from a container 16 to a series of holes or jets 29 via conduit 17, a controllable valve 11 and a conduit 30. The valve 11 is controlled by a controller 14 to maintain the temperature of the foil as determined by the sensor 13, 15 to less than 400 °C, preferably less than 150 °C and most preferably between 50 and 100 °C. Such low temperatures allow a wide range of materials for substrate 19 including polymeric materials, cellulosic materials as well as metals. Although only one controller 14 is shown the present invention includes several controllers each with its own controllable cryogenic cooling device 11, 29, 30 for individually controlling the temperature of different parts of the foil 19 or coating 40. Optionally, an optical encoder 34 may be attached to a roller 35. The optical encoder may be read with an optical sensor 37, 38, the pulse frequency generated in the sensor 37, 38 being proportional to the linear speed of the foil 19. This value may also be used by the controller 14 to control the complete process to maintain the temperatures and coating thicknesses mentioned above.

When producing superconducting coatings 40, it is preferred if there is no condensation of water onto the coating 40 nor onto the foil 19 so it is preferred if the atmosphere around the deposition equipment is air conditioned to reduce the

dew point to below ambient temperature. Preferably the coated substrates in accordance with this invention are preferably stored for long periods in a plastic bag filled with a dry inert gas such as dry nitrogen. One aspect of the present invention is the flame spraying of powders which already have superconducting
5 properties in the powder form. Using the methods in accordance with the present invention it is possible to flame spray such coatings and retain 10% to 15% of superconducting property of the coating 40 produced without extensive post-heat treatments.

The superconducting and/or ceramic powder and/or metallic powder to be
10 used for flame spraying is preferably homogeneous, exhibits the appropriate rheological properties and correct stoichiometry to generate the required properties in the final coating. Typical preferred densities for superconducting powders may lie in the range 4 to 5 g/cm^3. A non-limiting list of suitable materials which may be flame sprayed as powders, slurries or liquid solutions in
15 accordance with the present invention are: superconducting materials such as $R_1Ba_2Cu_3O_y$ where R is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu; or $Bi_{2-x}Pb_xSr_2Ca_{n-1}Cu_nO_y$, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$; or $Ba_2Ca_{n-1}O_{2n+2}$, or $CaBa_2Ca_{n-1}Cu_nO_{2n+\delta}$; or cuprate high temperature superconductors of the general formula $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ where A, E, R are selected from various
20 cations such as A= Bi, Tl, Hg, Pb, Cu or a lanthanide element, E = Ba or Sr and R = Ca or rare earth element; or piezo-electric ceramics, for example, with the general formula $M(Zr_xTi_{1-x})O_3$ where M = Pb, Ba or Sr; or refractory ceramic oxides, nitrides, carbides or phosphates, e.g. Al_2O_3, MgO, Zr_xO_y; or metals and their alloys.

25 In accordance with a further embodiment of the present invention a method is provided for production of suitable ceramic powders. By starting from aqueous solutions containing the salts of the metals in the correct proportions a reactive precursor powder can be obtained using commercially available spray drying equipment in batches of kilograms. The type of salt (mostly nitrates) should
30 preferably be compatible with thermal decomposition to oxides in further

processes such as sintering or flame spraying. In accordance with the present invention spray dried nitrate powders may be flame sprayed directly or the powders may first be sintered and then flame sprayed.

A spray drying system 50 in accordance with an embodiment of the present
5 invention for the delivery of powder suitable for subsequent flame spraying is shown schematically in Fig. 3. The input liquid is drawn from a suitable source 53 via a peristaltic pump 54 to a spray head 71. Pressurised air 51 is drawn in through an air dryer and optional pre-heater 52 to the spray head 71 by a suction device such as a fan 63 at the end of the generally closed system. The liquid from
10 source 53 enters the spray head 71 which is cooled by any suitable means 55 to prevent clogging due to early evaporation of the liquid. The liquid is atomised in a co-current two fluid nozzle 71 by the dry pressurised air 51 and discharged it into a chamber 56 where it dries to a powder. The liquid from source 53 may be a solution of suitable nitrates or a slurry of the relevant oxides with the addition of
15 other agents such as binders.

Air 65 is drawn in by fan 63 over a heater 64 and introduced into chamber 56 via a ring orifice 72 which surrounds the outlet of the spray head 71. The air 65 also heats the spray head 71. The circumferential air flow 65 guides the evaporating liquid in chamber 56 and helps to prevent the powder sticking to the
20 walls of the chamber 56. The air throughput of fan 63 is chosen so that powder of the correct grain size is swept from chamber 36 through an optional heater section 58 into a powder collector 59. Heavier particles settle out in trap 57 and are removed from the bottom of chamber 56.

The powder collector 59 may be any suitable device such as a cyclone, a
25 bag filter or an electrostatic filter although a cyclone is preferred. The cyclone discharges the powder into a removable container 60 sealed to the bottom of the cyclone 59. Spent air is removed via the trap 61 and scrubbed in scrubber 12 to remove impurities. The final clean air is exhausted to atmosphere by the fan 63 which controls air flow through the system.

30 The control system 66 - 70 for the process functions as follows. The

rotational speed of the centrifugal air pump 53, the temperature of the heating element 64 and the flow of the atomised air are set with controller 67, 70. Air flow is measured by gauge 68. The temperature of the hot air 65 and the air in the tube leading from the chamber 56 to the optional heater 58 is monitored using
5 thermocouples 66, whereas final powder temperature is monitored by temperature sensor 69.

After spray drying, the powder may be sintered in a single step. For example, to produce a superconducting powder of the general formula $YBa_2Cu_3O_7$ with optional Ag, the required nitrates are dissolved in water in the
10 correct stoichiometric proportions and spray dried as indicated above. The nitrates are then reduced to oxides by sintering at 920 - 960 °C for 40 to 60 hours. Optionally the nitrates may first be reduced by heating in air at 780 °C for 10 hours before sintering at the above temperatures and times. The $YBa_2Cu_3O_7$ powder produced by this procedure is superconducting. On aspect of the present
15 invention is to produce powders with superconducting properties by spray drying and optional sintering and then to flame spray these superconductive powders at the lowest flame temperatures necessary to obtain melting of the powder and coating formation on the substrate while cooling the coating in the fastest possible way. By this procedure the crystal structure present in the superconducting
20 powder is disturbed as little as possible by the flame spraying process. Of course, melting the powder during flame spraying causes complete loss of crystal organisation if the time in the melt is long. By lowering the flame temperature and shortening the time in the melt phase by cooling the coating very rapidly in accordance with the present invention, some local crystal organisation is kept in
25 the final flame sprayed coating, e.g. about 10% of the final coating is in the superconducting phase, thus providing a coating on the substrate with an optimum starting condition for further heat processing to develop full superconducting properties. The addition of the metallic silver enhances the thermal and mechanical properties in later flame spraying and magnetron sputtering.

30 Alternatively, the powder for flame spraying may be spray dried from

slurries of the relevant oxides in the correct stoichiometric proportions with the optional addition of silver in the above apparatus in accordance with the present invention. For instance, in the manufacture of a ceramic material the mixture of oxides may be produced by individually sieving them to 40 micron and then
5 mixing in the correct proportions to obtain the stoichiometric proportions in the final coating. A quantity of deionised water is added of about 60% by weight of the powder as well as a quantity of an organic binder such as PVA (polyvinyl acetate) equal to about 2% by weight of the powder and then mixed into a slurry. The slurry is then spray dried as described above resulting in powder with a grain
10 size from 30 to 50 micron. Generally, spray dried oxide slurries do not require sintering before flame spraying. The organic binder may be burnt out during flame spraying or in a special sintering step.

Spray drying of 10% by weight nitrate solutions generally produce grain sizes of 3 micron on average with at least 90% of the grains between 0.5 and 5
15 microns. In order to obtain the required grain size it is preferable to sinter as mentioned above. Light grinding and sieving of this sintered powder may produce a mass fraction of more than 80% with grain sizes between 40 and 80 micron. By the variation of appropriate concentrations of the solution of the aqueous media 53, and/or the addition of binders and/or the spray drying of slurries rather than
20 solutions, allows control of the grain size in the final powder to between 2 and 100 microns. For example, the present invention includes the addition of organic binders such as polyvinyl acetate (PVA) to the liquid to be spray dried to control grain size in the final powder. Such binders may be burnt out in a later high temperature process such as sintering. An average grain size of 40 to 80 microns
25 is preferred for good flame spray deposition. The final powder may be lightly milled and sieved to be improve the homogeneity of grain sizes.

One aspect of the present invention is the inclusion of silver metal in the final superconducting ceramic coating. This is achieved as mentioned above by inclusion of about 20% to 30% by weight of the ceramic materials of silver nitrate
30 when nitrate solutions are spray dried and the flame sprayed or by addition of

Ag_2O powder in an oxide slurry which is then spray dried and flame sprayed. The addition of silver in the flame sprayed material is beneficial for the inter-grain adhesion and heat dispersal during flame spraying thus yielding a strong and dense coating. The silver improves the thermal and electrical conductivity of the flame sprayed coating which is beneficial to the sputtering process when the substrate is used as a sputtering target. The improved conductivities allow higher power throughput for the magnetron than targets not containing silver.

The flame spraying process in accordance with the present invention allows the reconditioning of targets for sputtering magnetrons. It is well known that the presence of a static race-track plasma on a magnetron target during sputtering results in an erosion groove and poor target utilisation. Using the flame spraying process of the present invention such a worn target may be reconditioned by spraying the appropriate target material into the erosion groove and building up the target to its former thickness in these regions. By providing the intensive cryogenic cooling described above, the general target temperature may be kept below 400 °C, preferably below 150°C and most preferably between room temperature (~25°C) and 100°C. These low temperatures result in little damage to the existing target material while still providing a mechanically strong coating in the old erosion grooves. Such as process is particularly economic when the target material is expensive such as superconducting materials. The flame spraying gun 12 described above may be hand held and the contour of the erosion groove in the used target followed building up the lost material slowly, preferably 10 to 50 micron per pass. Preferably the gun 12 is controlled by a robot which is programmed to execute the correct motions with the gun 12 to fill up the erosion groove in the target.

While the invention has been shown and described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention as defined in the attached claims.

CLAIMS

1. A composite comprising: a substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 5 mm, more preferably greater than 8mm, the coating comprising metal oxides.

5

2. The composite according to claim 1, wherein the coating comprises a superconductor precursor and at least 10% of the coating is in a superconductive phase

10 3. The composite according to claim 1 or 2, wherein the composite is a target for a sputtering magnetron.

4. The composite according to claim 3, wherein the target is cylindrical.

15 5. The target for a sputtering magnetron comprising: a cylindrical substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 3mm, more preferably at least 5 mm, most preferably greater than 8mm, the coating comprising a superconductor precursor and at least 10% of the coating is in a superconductive phase.

20

6. The target or a composite in accordance with any previous claim, wherein the coating has a thermal conductivity of between 1 and 5 $Wm^{-1}K^{-1}$.

7. The target or a composite in accordance with any previous claim, wherein the

25 thermal conductivity of the composite or the target through the substrate and the coating is in the range 25 to 125 $Wm^{-1}K^{-1}$.

8. The target or a composite in accordance with any previous claim, wherein the coating has an electrical resistivity of lower than 15×10^{-6} Ohm.m, more preferably

30 lower than 10×10^{-6} and most preferably less than 5×10^{-6} Ohm.m.

9. The target or a composite in accordance with any previous claim, wherein the coating can withstand impact of a 0.036 kg steel ball from a height of 1 metre, preferably from 1.5 metre.

5

10. The target or a composite in accordance with any previous claim, wherein the spraying is one of plasma spraying and flame spraying.

11. A method of depositing by spraying a superconductor precursor layer onto a
10 cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase.

12. A method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

15

13. The method according to claim 11 or 12, wherein the spraying step is one of flame spraying and low-pressure or atmospheric pressure plasma spraying.

14. The method according to claim 13, wherein the spraying step includes spraying
20 a material through a spraying head, the material being in the form of a powder, a slurry or a solution.

15. A method of reconditioning a used target for a sputtering magnetron having an erosion groove in the target material, comprising the step of: flame or atmospheric
25 pressure plasma spraying target material into the erosion groove.

16. A reconditioned target for a sputtering magnetron, comprising:
an erosion groove in the target material; and target material flame sprayed or atmospheric plasma sprayed into said groove to restore the thickness of the target
30 material to that of the unused material.

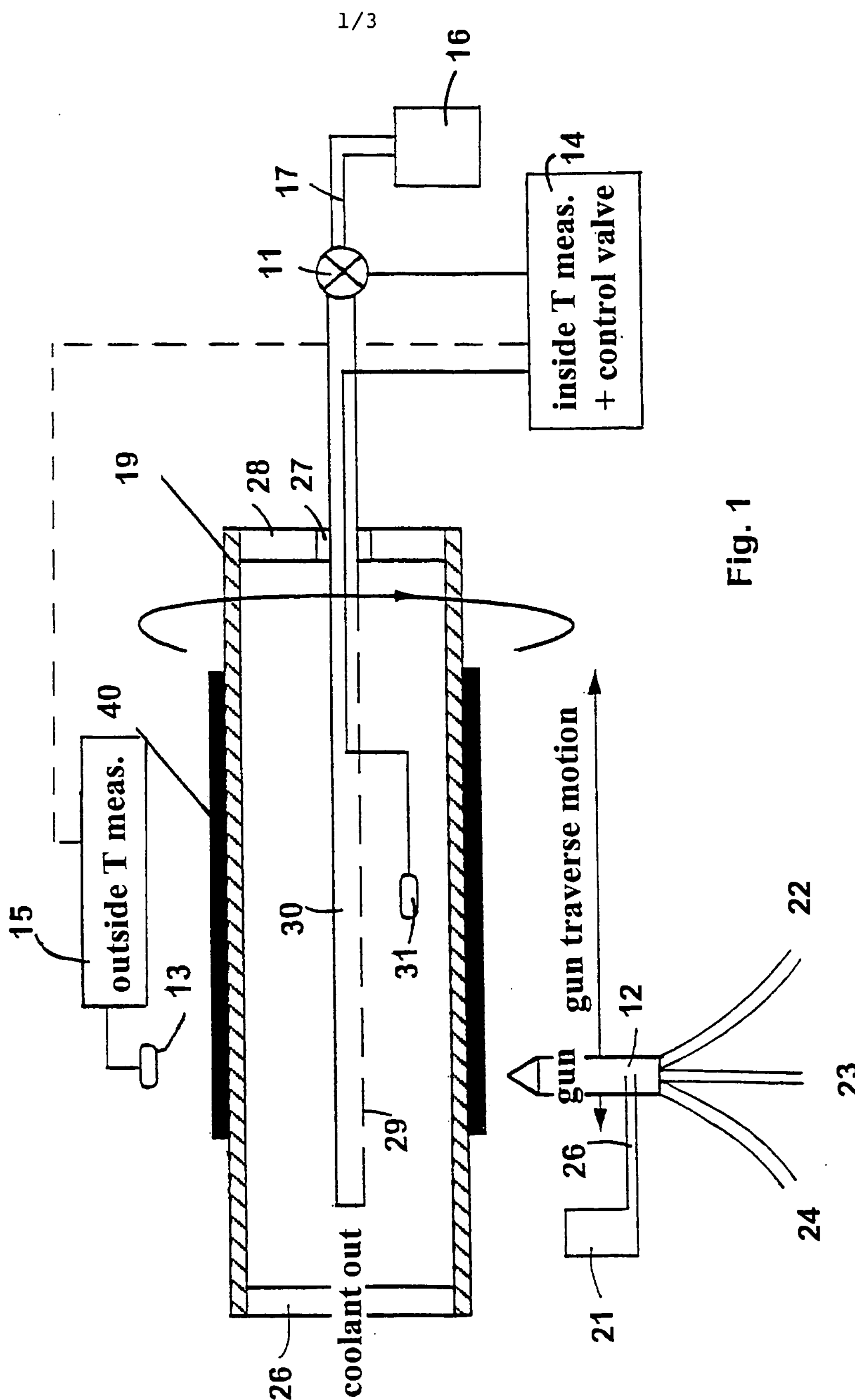


Fig. 1

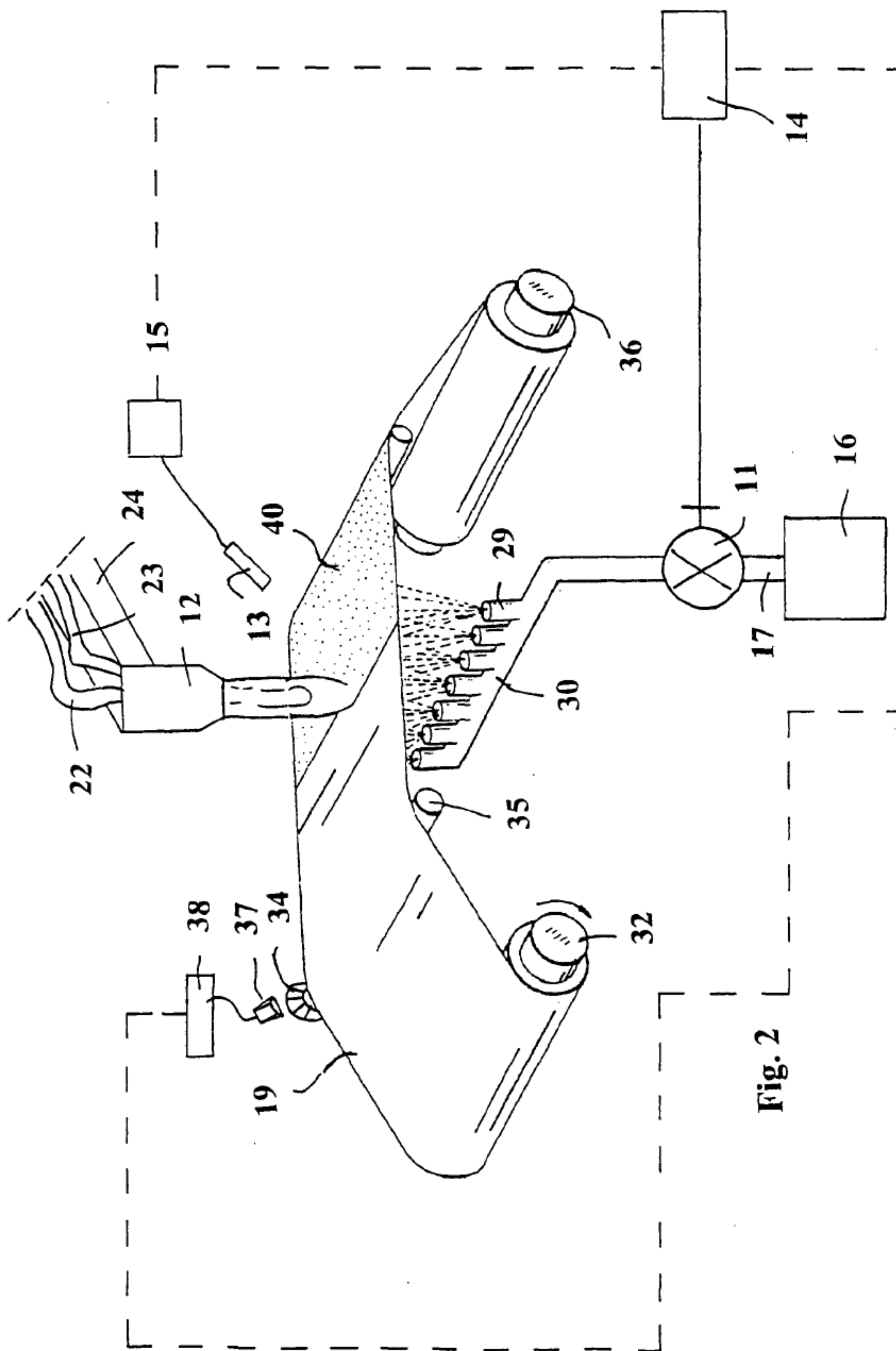


Fig. 2

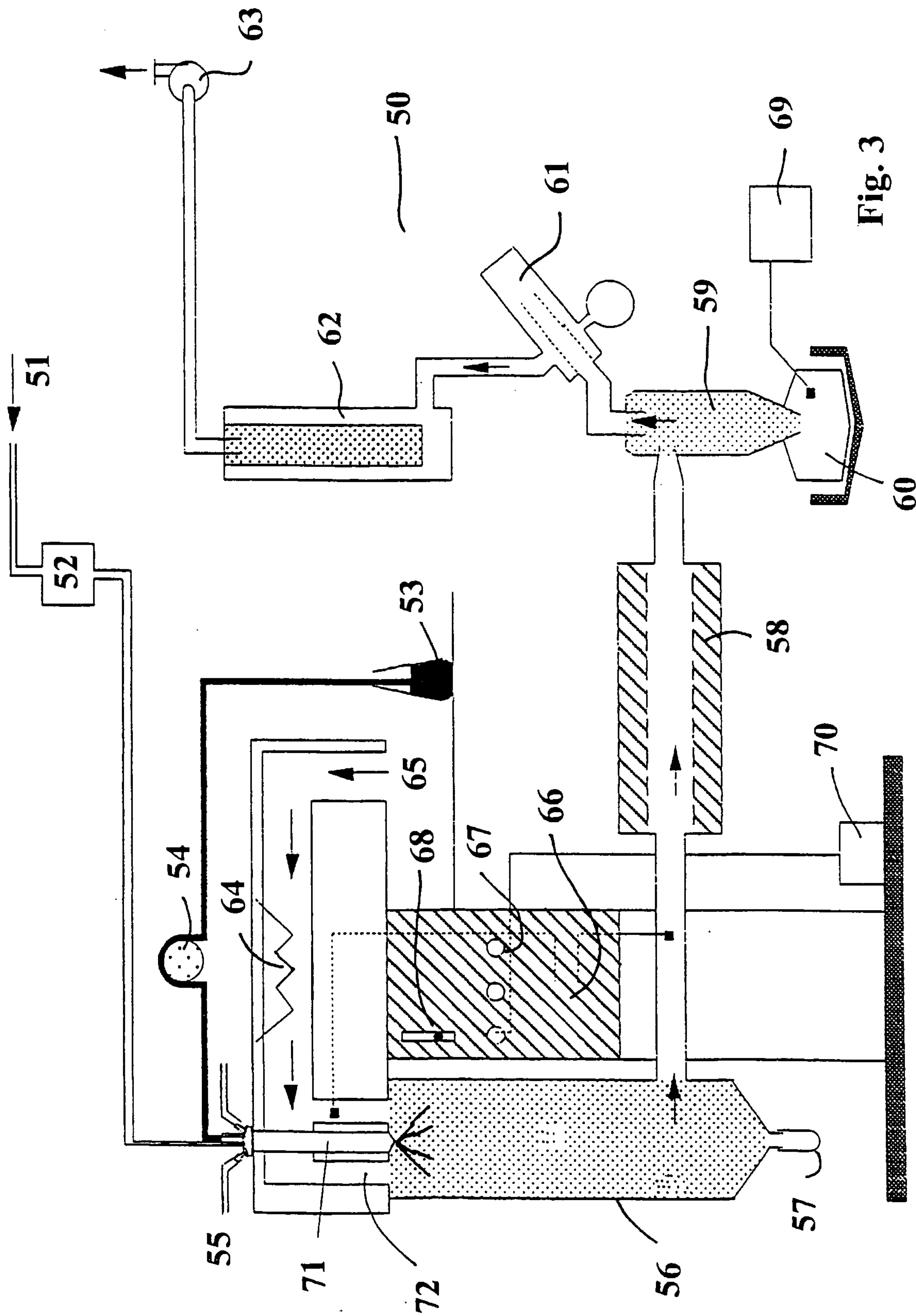


Fig. 3

INTERNATIONAL SEARCH REPORT

Int· ·ational Application No
PC·/EP 99/03599

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C4/10 C23C4/12 C23C14/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 196 400 A (CHEN CHIOU T ET AL) 23 March 1993 (1993-03-23) cited in the application column 3, line 52 - column 4, line 16	1-5, 10-14
X	EP 0 330 196 A (PERKIN ELMER CORP) 30 August 1989 (1989-08-30) page 5, line 20 - line 25; claims 1,8	1,2,10, 12-14
X	CH 648 358 A (CASTOLIN SA) 15 March 1985 (1985-03-15) claim 1	1,10, 12-14
X	DD 277 471 A (MANSFELD KOMBINAT W PIECK VEB) 4 April 1990 (1990-04-04) page 2, line 21 - line 23	15,16

-/--

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 September 1999	16/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Patterson, A

2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03599

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DE 40 15 387 A (LEYBOLD AG) 21 November 1991 (1991-11-21) the whole document ---	15,16
A	EP 0 377 073 A (MITSUBISHI METAL CORP) 11 July 1990 (1990-07-11) page 3, line 41 - line 57; table 2 page 7, line 7 - line 23; table 4 -----	5-8

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 99/03599

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: 9
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
SEE FURTHER INFORMATION SHEET

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

SEE FURTHER INFORMATION SHEET

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [X] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99 /03599

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8,10-14

   Claims for a composite comprising an oxide-containing coating deposited by spraying and having a certain minimum thickness, a sputter target having a layer of a superconductor precursor, also deposited by spraying and having a minimum thickness, and methods for producing each of these products, respectively.

2. Claims: 15,16

   Reconditioned sputter target and method for its manufacture by flame or plasma spraying material into the sputtered erosion groove.

The only common concept linking subjects 1 and 2 is the application of spraying for depositing layers of material. Since this feature is known from many prior art documents (see for example search report) there is effectively no common concept to connect the two groups of claims. Furthermore, while subject 1 addresses the problem of producing relatively thick deposits of oxides by means of spraying, subject 2 solves the unrelated problem of spraying an unspecified material to repair local damage on a target.

Therefore there is a lack of unity between the two subjects.

Nevertheless, since the EPO has already searched the subject-matter of claims 15 and 16 in connection with the priority application EP98870120, an International search report is issued for both subjects.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99/03599

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 9

Claim 9 relates to a product defined (inter alia) by reference to the following parameter:
the result of a test involving impact of a ball consisting of an unspecified steel, wherein both the weight of the ball and the height from which it is dropped are arbitrarily chosen.
The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the remaining claims

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03599

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5196400 A	23-03-1993	NONE	
EP 0330196 A	30-08-1989	CN 1036286 A	11-10-1989
		JP 1309952 A	14-12-1989
CH 648358 A	15-03-1985	NONE	
DD 277471 A	04-04-1990	NONE	
DE 4015387 A	21-11-1991	NONE	
EP 0377073 A	11-07-1990	JP 2156079 A	15-06-1990
		JP 2157150 A	15-06-1990
		KR 9507087 B	30-06-1995
		US 5077269 A	31-12-1991
		KR 9507088 B	30-06-1995

TO:Mr. Gary Edwards COMPANY:

PTO 06-6046 German Patent No. DE 37 38 738 C1

POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

Dr. Stephan Schittny et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. AUGUST 2006
TRANSLATED BY THE MCELROY TRANSLATION COMPANY

FEDERAL REPUBLIC OF GERMANY
GERMAN PATENT OFFICE
PATENT NO. DE 37 38 738 C1
(Patentschrift)

Int. Cl.[4]:	B 22 F 7/00 H 01 L 21/203
Filing No.:	P 37 38 738.3-24
Filing Date:	November 14, 1987
Publication Date of Patent Grant:	January 26, 1989

POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

[Pulvermetallurgisches Verfahren zur Herstellung von Targets]

Inventors:	Dr. Stephan Schittny et al.
Patent Holder:	Degussa AG

Publications Taken in Consideration For Judging Patentability:	DE 35 37 191 A1

Claims

1. Process for the preparation of highly pure mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum, characterized in that the rare earths are inserted with the corresponding transition metals in the form of master alloys.

2. The process of Claim 1, characterized in that master alloys having a eutectic composition are inserted.

Description

The invention pertains to a process for the preparation of highly pure, mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode

evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum

Targets are required in installations for cathode evaporation and for the vaporization of objects. With the aid of cathode evaporation (sputtering) and vaporization, a thin layer can be produced on a substrate, the applications for which span from functional layers in electronics and data systems engineering through corrosion-protective layers and anti-abrasion layers to optical layers for decorative and thermic purposes.

In cathode evaporation, an electrical gas discharge occurs between cathode (target) and counter electrode, during which impacting ions eject particles of atomic size from the target, which condense on substrates arranged in the area of the counter electrode.

Either inert gases such as argon or helium, or reactive gases, such as oxygen, nitrogen or acetylene are put in at low pressure as a gas discharge atmosphere.

In inert gas sputtering, the target commonly is composed of the material of which the layer to be formed shall be composed, while in reactive sputtering, ejected target particles react with the reaction gas and are condensed as a layer in the form of a reaction product.

In the vaporization process, the target material is thermally vaporized in a vacuum by means of electron beam heating or resistance heating and deposited as a thin layer on the substrate.

Targets commonly can be prepared using melting technology with corresponding secondary processing by means of non-cutting and tensioning processes or with powder metallurgy, by means of compressing and sintering corresponding powders or powder mixtures.

For target materials, which owing to their composition contain higher portions of brittle phases, preparation processes using melting technology prove to be problematic, since such targets when cooling after casting exhibit fissures owing to thermal stress and can crumble into pieces. In addition, such materials cannot for the most part be mechanically machined, such that certain desirable target geometries cannot be prepared.

Powder-metallurgical processes exhibit problems with those target materials containing higher portions of reaction-sensitive components and that react, e.g., with atmospheric oxygen. Due to the large specific surface area of the powder and the resulting reactivity, high-value target qualities having low oxygen content cannot be produced using powder metallurgy.

In addition, products prepared using powder metallurgy for the most part exhibit a partially open residual porosity, which is intolerable for oxygen sensitive target materials due to the potential oxidation of the entire target.

These preparation difficulties appear particularly for targets containing a predominance of rare earths and transition metals.

A powder-metallurgical process for the preparation of targets of rare earths and the transition metals iron, cobalt and nickel is known from DE-OS 35 37 191, for which a powder mixture of rare earths and the aforementioned transition metals is subjected to hot forming under decreased pressure and under inert gas at temperatures below the eutectic point, with a brittle intermetallic compound developing at the boundary between the rare earth metal and the transition metal. This process has the disadvantage that hot forming must be carried out expensively for a minimum of at least two hours, by means of which noticeable quantities of brittle intermetallic phases are formed, that powder preparation for rare earths is associated with difficulties and that the oxygen content in the powder of rare earths is still relatively high.

It was thus the problem of the present invention to develop a process for the preparation of highly pure, mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum that without great technical expense supplies a product containing limited portions of and a fine distribution of brittle phases and as little oxygen as possible.

This problem is solved in accordance with the invention by means of the fact that the rare earths are inserted with the corresponding transition metals in the form of master alloys.

Preferably, master alloys having a eutectic composition are inserted.

Reaction sensitive rare earths are processed into powders and/or shavings not as such, but as master alloys of rare earths and the corresponding transition metals, which in comparison to pure components feature lower melting points, are well intermixed with powders and/or shavings of the transition metals and are compacted into targets. The compacting of said mixture can be carried out by means of sintering, hot-rolling, hot-pressing, hot-forging, high-temperature isostatic pressing or combinations thereof in a vacuum or under inert gas.

The conditions for compacting (temperature, pressure, time, degree of defurmation) are selected such that a mechanically stable compound material emerges, the grain structure of which, as a non-equilibrium state, features only limited portions of brittle equilibrium phases formed by means of diffusion at the boundaries of the rare earth phases and the transition metal phases. Through the use of master alloys between rare earths and transition metals, relatively low compacting temperatures and brief compacting times can be selected. This leads to a decreased technical expense and to a limited formation of diffusion zones of brittle non-equilibrium phases at the contact locations of the powder grains and in the grains.

Surprisingly, it has been shown that fundamentally simpler, highly pure and low-oxygen powders or shavings can be prepared out of master alloys of rare earths with corresponding transition metals rather than out of pure rare earths. These master alloys may be used to produce shavings and powders, e.g., by means of machining, such as milling or filing under protective

gas, which is not possible without difficulty with pure rare earth metals, owing to their ductility, even with subsequent grinding. During the comminution process, the brittle phase portions of the most extremely fine grain structure of master alloys causes the formation of particles having a suitable grain shape and grain size distribution, enabling a powder preparation having a good yield and very low oxygen content (< 500 ppm).

Likewise in powder preparation by means of inert gas atomization, lower values of impurities and more limited oxygen content in the powder are achieved from lower melting master alloys owing to lower reaction rates with the crucible material and with the atmosphere at lower process temperatures and owing to the briefer residence time in the installation. Moreover, the atomization parameters (superheating, cooling rates, process gas pressure, etc.) can be optimized to a wide degree, such that the powder yield and the grain fraction can be adjusted more favorably in comparison to atomization of pure rare earths.

Surprisingly, the use of master alloys of rare earths and transition metals leads to compacting times considerably briefer in comparison to those with the use of pure rare earths, signifying a significant economic advantage of this process.

As a rule, compacting times are less than one hour and, more often than not, less than 30 minutes. Apart from this, targets prepared in accordance with the invention exhibit more favorable mechanical and magnetic properties in comparison to targets produced with powder metallurgy from pure metals. As has been shown, this is based on an advantageous distribution of portions present in the grain structure of free iron, cobalt and/or nickel, on the limited quantities of intermetallic phases and on the residual eutectic originating from the master alloys.

The following examples shall explain the process in accordance with the invention in greater detail:

1) In order to prepare highly pure, compact, mechanically stable sputter targets, first a master alloy of 80 atom% terbium and 20 atom% iron is prepared in a vacuum induction oven (10^{-5} Pa). Subsequent pulverization and further processing is carried out exclusively under argon protective gas. With the aid of a wave-milling cutter, the ingot is machined to a coarse powder. A terbium-iron powder having an average grain size ≤ 105 µm and having a yield of 70-80% is obtained by means of subsequent grinding in a ball mill. The desired target composition of, e.g., 67 atom% iron, 25 atom% terbium and 8 atom% cobalt is regulated by means of a 20 minute mixing of the corresponding iron, cobalt and master alloy powder quantities in an asymmetric moved mixer.

The processes of high-temperature isostatic pressing (HIP), hot-rolling and hot-forging in a capsule were employed in order to compact the powder mixture into targets.

For high-temperature isostatic pressing, process parameters of 820°C final temperature, 200 Mpa pressure and 20 minute residence time at the final temperature were selected. Sheet

steel cans were used as containers, which prior to being brought into the installation were evacuated at 300°C for over 3 hours. This produces mechanically stable, machinable molding bodies featuring a non-equilibrium grain structure of iron grains, zones of intermetallic phases and residual eutectic. The density is > 99% of the theoretical density, the oxygen content less than 1200 ppm. Longer residence times of, e. g., 1-2 hours at 820°C result in a wide reaching formation of large-surface zones of the intermetallic equilibrium phases, which causes an undesirable brittleness of the grain structure. It is for this reason that residence times as brief as possible are to be observed.

For compacting by means of hot-rolling, the powder mixture is filled in a sheet iron capsule, which is evacuated and welded shut. Conversion occurs at 650°C up to a degree of conversion of approximately 60% in several passes in a period of few minutes. After removal of the capsule material, a stable, highly pure target is yielded having a density of ≈ 99% of the theoretical density and an oxygen content of 1200 ppm The grain structure is of a form similar to that for compacting by means of high-temperature isostatic pressing.

For hot-forging, the powder mixture likewise is filled in a sheet steel can and evacuated. The forging process can be carried out at 800°C in a 200 ton forge. The achievable density is, at 60% conversion ≈ 99% of the theoretical density.

2. A different type of powder preparation is atomization of a melt in an inert-gas flow. For the use of low-melting point master alloys of the composition 66 atom% gadolinium, 18 atom% iron and 16 atom% cobalt having a melting temperature of approximately 620°C, an atomizing temperature of 700-800°C can be selected. This comparatively very low atomizing temperature enables, for extremely reactive rare earth materials, the preparation of low-oxygen, very pure master alloy powders, since the reaction of the melt with the crucible material and with the atmosphere is comparatively limited. Moreover, the master alloy melt exhibits a favorable viscosity and surface tension at these temperatures, such that the atomized powder features good yields of e.g., 80-90% at a grain size ≤ 88 μm. With the aid of the mixing and compacting processes described in Example 1, highly pure, compact, stable molding bodies having oxygen contents < 1000 ppm likewise are obtained. The non-equilibrium grain structures in turn are composed of iron grains, zones of intermetallic phases and residual eutectic.

Since the intermetallic phases are present in a fine distribution in the master alloys, and the grain structure is not very brittle, the blend portion of free iron can be reduced in comparison with the intermetallic phases by varying the composition of the master alloys, The magnetic properties of the targets, which are important for magnetron sputtering, can be improved by said means.

(19) BUNDESREPUBLIK DEUTSCHLAND

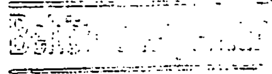
DEUTSCHES PATENTAMT

(12) **Patentschrift**

(11) **DE 37 38 738 C1**

(51) Int. Cl. 4:
B 22 F 7/00
H 01 L 21/203

(21) Aktenzeichen: P 37 38 738.3-24
(22) Anmeldetag: 14. 11. 87
(43) Offenlegungstag: –
(45) Veröffentlichungstag der Patenterteilung: 26. 1. 89



DE 37 38 738 C1

Innerhalb von 3 Monaten nach Veröffentlichung der Erteilung kann Einspruch erhoben werden

(73) Patentinhaber:

Degussa AG, 6000 Frankfurt, DE

(72) Erfinder:

Schittny, Stephan, Dr.-Ing., 8755 Alzenau, DE; Berchtold, Lorenz, Dr.-Ing., 6450 Hanau, DE; Haußelt, Jürgen, Dr.-Ing., 8755 Alzenau, DE; Kaster, Wolfgang, Dipl.-Ing., 5449 Mörsdorf, DE; Englisch, Udo, 6458 Rodenbach, DE

(56) Für die Beurteilung der Patentfähigkeit in Betracht gezogene Druckschriften:

DE 35 37 191 A1

(54) Pulvermetallurgisches Verfahren zur Herstellung von Targets

Zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets aus seltenen Erden und den Übergangsmetallen Eisen, Kobalt und Nickel auf pulvermetallurgischem Weg vermeidet man hohe Gehalte und ungünstige Verteilungen an spröden Phasen und größere Sauerstoffgehalte im Werkstoff durch Verwendung von Vorlegierungen aus seltenen Erden und den Übergangsmetallen anstelle reinen seltenen Erden.

DE 37 38 738 C1

Patentansprüche

1. Verfahren zur Herstellung von hochreinen mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum, **dadurch gekennzeichnet**, daß die Seltenen Erden in Form von Vorlegierungen mit den entsprechenden Übergangsmetallen eingesetzt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Vorlegierungen mit eutektischer Zusammensetzung eingesetzt werden.

Beschreibung

Die Erfindung betrifft ein Verfahren zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum.

Targets werden in Anlagen zur Kathodenzerstäubung und zur Bedampfung von Gegenständen benötigt. Mit Hilfe der Kathodenzerstäubung (Sputtern) und des Bedampfens können dünne Schichten auf Substraten erzeugt werden, deren Anwendung von funktionalen Schichten in der Elektronik und Datentechnik über Korrosions- und Verschleißschutzschichten bis zu optischen Schichten für dekorative und wärmetechnische Zwecke reicht.

Beim Kathodenzerstäuben findet zwischen Kathode (Target) und Gegenelektrode eine elektrische Gasentladung statt, bei der von den aufprallenden Ionen aus dem Target Teilchen von atomarer Größe herausgeschlagen und auf Substraten, die im Bereich der Gegenelektrode angeordnet sind, niedergeschlagen werden.

Als Gasentladungsatmosphäre werden entweder inerte Gase, wie beispielsweise Argon oder Helium, oder reaktive Gase, wie z. B. Sauerstoff, Stickstoff oder Acetylen, bei geringem Druck eingesetzt.

Beim Inertgassputtern besteht das Target üblicherweise aus dem Material, aus dem die zu bildende Schicht bestehen soll, während beim Reaktivsputtern die herausgeschlagenen Targetteilchen mit dem Reaktionsgas reagieren und in Form eines Reaktionsproduktes als Schicht niedergeschlagen werden.

Bei den Bedampfungsverfahren wird das Targetmaterial im Vakuum durch Elektronenstrahl- oder Widerstandsbeheizung thermisch verdampft und als dünne Schicht auf dem Substrat abgeschieden.

Die Targets können üblicherweise schmelztechnisch hergestellt werden mit entsprechender Nachbearbeitung durch umformende und spannende Verfahren, oder pulvermetallurgisch durch Pressen und Sintern entsprechender Pulver bzw. Pulvergemische.

Bei Targetmaterialien, die aufgrund ihrer Zusammensetzung höhere Anteile an spröden Phasen enthalten, erweisen sich schmelztechnische Herstellverfahren als problematisch, da solche Targets beim Abkühlen nach dem Gießen aufgrund von thermischen Spannungen Risse aufweisen und in Stücke zerfallen können. Darüber hinaus sind solche Materialien meist nicht mechanisch bearbeitbar, so daß bestimmte wünschenswerte Targetgeometrien nicht herstellbar sind.

Pulvermetallurgische Verfahren zeigen bei denjenigen Targetmaterialien Probleme, die höhere Anteile an reaktionsempfindlichen Komponenten enthalten, und z. B. mit dem Luftsauerstoff reagieren. Wegen der großen spezifischen Oberfläche der Pulver und der daraus resultierenden Reaktionsfreudigkeit lassen sich keine hochwertigen Targetqualitäten mit niedrigem Sauerstoffgehalt pulvermetallurgisch herstellen.

Außerdem weisen pulvermetallurgisch hergestellte Produkte meist eine zum Teil offene Restporosität auf, die bei sauerstoffempfindlichen Targetmaterialien wegen der möglichen Oxidation des gesamten Targets nicht tolerierbar ist.

Diese Herstellungsschwierigkeiten treten insbesondere bei Targets auf, die überwiegend Seltene Erden und Übergangsmetalle enthalten.

Aus der DE-OS 35 37 191 ist ein pulvermetallurgisches Verfahren zur Herstellung von Targets aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und Nickel bekannt, bei dem ein Pulvergemisch aus Seltenen Erden und den genannten Übergangsmetallen unter vermindertem Druck und unter Inertgas bei Temperaturen unterhalb des eutektischen Punktes einer Warmverformung unterzogen wird, wobei sich eine spröde intermetallische Verbindung an der Grenzfläche zwischen dem Seltenen Erdmetall und dem Übergangsmetall ausbildet. Dieses Verfahren hat den Nachteil, daß die Warmverformung aufwendig mindestens zwei Stunden lang erfolgen muß, wodurch sich bemerkbare Mengen an spröden intermetallischen Phasen bilden, daß die Pulverherstellung bei den Seltenen Erden mit Schwierigkeiten verbunden ist und der Sauerstoffgehalt im Pulver der Seltenen Erden noch relativ hoch ist.

Es war daher Aufgabe der vorliegenden Erfindung, ein Verfahren zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum zu entwickeln, das ohne großen technischen Aufwand ein Produkt liefert, das geringe Anteile und eine feine Verteilung an spröden Phasen und möglichst wenig Sauerstoff enthält.

Diese Aufgabe wird erfindungsgemäß dadurch gelöst, daß die Seltenen Erden in Form von Vorlegierungen mit den entsprechenden Übergangsmetallen eingesetzt werden.

Vorzugsweise werden Vorlegierungen mit eutektischer Zusammensetzung eingesetzt.

Die reaktionsempfindlichen Seltenen Erden werden nicht als solche, sondern als Vorlegierungen aus Seltenen Erden und den entsprechenden Übergangsmetallen, die im Vergleich zu den reinen Komponenten niedrigere Schmelzpunkte aufweisen, zu Pulvern und/oder Spänen verarbeitet, mit Pulvern und/oder Spänen der Übergangsmetalle gut durchmischt und zu Targets kompaktiert. Die Kompaktierung dieser Mischung kann durch Sintern, Warmwalzen, Heißpressen, Warmschmieden, Heißisostatische Preßverfahren oder Kombinationen daraus im Vakuum oder unter Inertgas erfolgen.

Die Kompaktierungsbedingungen (Temperatur, Druck, Zeit, Umformungsgrad) werden so gewählt, daß ein mechanisch stabiles Verbundmaterial entsteht, dessen Gefüge als Ungleichgewichtszustand nur geringe Anteile an spröden Gleichgewichtsphasen aufweist, die durch Diffusion an den Grenzflächen der Seltenen Erd-Phasen und der Übergangsmetallphasen gebildet wer-

den. Durch die Verwendung von Vorlegierungen zwischen Seltenen Erden und Übergangsmetallen können relativ niedrige Kompaktierungstemperaturen und kurze Kompaktierungszeiten ausgewählt werden. Das führt zu einem verminderten technischen Aufwand und zu einer geringen Ausbildung von Diffusionszonen aus spröden Ungleichgewichtsphasen an den Berührungsstellen der Pulverkörner und in den Körnern.

Es hat sich überraschenderweise gezeigt, daß aus Vorlegierungen der Seltenen Erden mit den entsprechenden Übergangsmetallen wesentlich einfacher, hochreine und sauerstoffarme Pulver oder Späne herstellbar sind als aus den reinen Seltenen Erden. Aus diesen Vorlegierungen lassen sich z. B. durch spanende Bearbeitung, wie Fräsen oder Feilen, unter Schutzgas Späne und Pulver erzeugen, was bei den reinen Seltenen Erd-Metallen auf Grund ihrer Duktilität auch mit nachfolgendem Mahlen nicht ohne Schwierigkeiten möglich ist. Die spröden Phasenanteile des äußerst feinen Gefüges der Vorlegierungen bewirken beim Zerkleinerungsvorgang die Bildung von Partikeln mit geeigneter Kornform und Korngrößenverteilung, so daß eine Pulverherstellung mit guter Ausbeute und sehr niedrigem Sauerstoffgehalt (< 500 ppm) möglich ist.

Ebenso werden bei der Pulverherstellung durch Inertgasverdüsen aus den niedriger schmelzenden Vorlegierungen aufgrund der bei den tieferen Prozeßtemperaturen geringeren Reaktionsgeschwindigkeiten mit dem Tiegelmaterial und mit der Atmosphäre und aufgrund der kürzeren Verweilzeit in der Anlage, niedrigere Werte an Verunreinigungen und geringere Sauerstoffgehalte im Pulver erzielt. Desweiteren lassen sich hier die Verdüsungsparameter (Überhitzung, Abkühlrate, Prozeßgasdruck usw.) in weiten Maßen optimieren, so daß die Pulverausbeute und die Kornfraktion im Vergleich zur Verdüsung der reinen Seltenen Erden günstiger eingestellt werden können.

Die Verwendung von Vorlegierungen aus Seltenen Erden und Übergangsmetallen führt im Vergleich zur Verwendung der reinen Seltenen Erden überraschenderweise zu wesentlich kürzeren Kompaktierungszeiten, was einen bedeutenden wirtschaftlichen Vorteil dieses Verfahrens bedeutet.

Die Kompaktierungszeiten liegen in der Regel unterhalb einer Stunde, meist unterhalb von 30 Minuten. Darüber hinaus zeigen die erfindungsgemäß hergestellten Targets im Vergleich zu Targets, die pulvermetallurgisch aus den reinen Metallen hergestellt wurden, günstigere mechanische und magnetische Eigenschaften. Dies beruht, wie sich gezeigt hat, auf einer vorteilhaften Verteilung der im Gefüge vorhandenen Anteile an freiem Eisen, Kobalt und/oder Nickel, an den geringen Mengen intermetallischer Phasen und an dem aus den Vorlegierungen stammenden Resteutektikum.

Die folgenden Beispiele sollen das erfindungsgemäße Verfahren näher erläutern:

1) Zur Herstellung von hochreinen, kompakten, mechanisch stabilen Sputtertargets wird zuerst eine Vorlegierung aus 80 Atom% Terbium und 20 Atom% Eisen in einem Vakuuminduktionsofen (10^{-5} Pa) hergestellt. Die anschließende Pulverisierung und Weiterverarbeitung erfolgt ausschließlich unter Argon-Schutzgas. Mit Hilfe eines Wellenfräsers wird der Gußblock zu grobem Pulver zerspant. Durch anschließendes Mahlen in einer Kugelmühle erhält man ein Terbium-Eisenpulver mit einer mittleren Korngröße ≤ 105 µm und mit einer Ausbeute von 70—80%. Die gewünschte Targetzusammensetzung von z. B. 67 Atom% Eisen, 25 Atom% Terbium und 8 Atom% Kobalt wird durch 20 minütiges Mischen der entsprechenden Eisen-, Kobalt- und Vorlegierungspulvermengen in einem Taumelmischer eingestellt.

Zum Kompaktieren der Pulvermischung zu Targets wurden die Verfahren des Heißisostatischen Pressens (HIP) des Warmwalzens und des Heißschmiedens in einer Kapsel angewendet.

Beim Heißisostatischen Pressen werden als Prozeßparameter 820°C Endtemperatur, 200 MPa Druck und 20 min Haltezeit bei Endtemperatur gewählt. Als Behälter wurden Stahlblechkannen verwendet, die vor Einbringen in die Anlage bei 300°C über 3 Stunden evakuiert wurden. Man erhält auf diese Weise mechanisch stabile, bearbeitbare Formkörper, die ein Ungleichgewichtsgefüge aus Eisenkörnern, Zonen von intermetallischen Phasen und Resteutektikum aufweisen. Die Dichte ist >99% der theoretischen Dichte, der Sauerstoffgehalt liegt unterhalb 1200 ppm. Längere Haltezeiten von z. B. 1—2 Stunden bei 820°C haben eine weitgehende Ausbildung von großflächigen Zonen der intermetallischen Gleichgewichtsphasen zur Folge, was eine unerwünschte Versprödung des Gefüges bedingt. Es sind daher möglichst kurze Haltezeiten einzuhalten.

Für das Kompaktieren durch Warmwalzen wird das Pulvergemisch in eine Eisenblechkapsel eingefüllt, die evakuiert und zugeschweißt wird. Die Umformung erfolgt bei 650°C bis zu einem Umformgrad von ca. 60% in mehreren Stichen in einem Zeitraum von wenigen Minuten. Nach Entfernen des Kapselmaterials ergibt sich ein stabiles, hochreines Target mit einer Dichte von ≈99% der theoretischen Dichte und einem Sauerstoffgehalt von 1200 ppm. Das Gefüge ist ähnlich ausgebildet wie bei der Kompaktierung durch Heißisostatisches Pressen.

Beim Heißschmieden wird die Pulvermischung ebenfalls in eine Blechkanne gefüllt und evakuiert. Der Schmiedevorgang kann bei 800°C in einer 200 to Schmiede durchgeführt werden. Die erzielbare Dichte beträgt bei 60% Umformung ≈99% der theoretischen Dichte.

2. Eine andere Art der Pulverherstellung ist das Verdüsen einer Schmelze im Inertgasstrom. Bei Benutzung von niedrigschmelzenden Vorlegierungen der Zusammensetzung 66 Atom% Gadolinium, 18 Atom% Eisen und 16 Atom% Kobalt mit einer Schmelztemperatur von ca. 620°C kann eine Verdüsungstemperatur von 700—800°C gewählt werden. Diese vergleichsweise sehr niedrige Verdüsungstemperatur ermöglicht bei den extrem reaktionsfreudigen Seltenen Erd-Materialien die Herstellung von sauerstoffarmen, sehr reinen Vorlegierungspulvern, da die Reaktion der Schmelze mit dem Tiegelmaterial und der Atmosphäre vergleichsweise gering ist. Des weiteren zeigt die Vorlegierungsschmelze bei dieser Temperatur eine günstige Viskosität und Oberflächenspannung, so daß die verdüsten Pulver gute Ausbeuten von z. B. 80—90% bei einer Korngröße ≤88 µm aufweisen. Mit Hilfe der in Beispiel 1 beschriebenen Misch- und Kompaktierungsverfahren erhält man ebenfalls hochreine, kompakte, stabile Formkörper mit Sauerstoffgehalten <1000 ppm. Die Ungleichge-

wichtsgefüge bestehen wiederum aus Eisenkörnern, Zonen von intermetallischen Phasen und Resteutektikum.

Da die intermetallischen Phasen in den Vorlegierungen fein verteilt vorliegen, und das Gefüge nicht sehr verspröden, lassen sich die Mengenanteile an freiem Eisen im Vergleich zu den intermetallischen Phasen durch Variation der Zusammensetzung der Vorlegierungen reduzieren. Die magnetischen Eigenschaften der Targets, die für das Magnetronsputtern wichtig sind, lassen sich hierdurch verbessern.

5 10 15 20 25 30 35 40 45 50 55 60 65

JP5-230642-A

MACHINE-ASSISTED TRANSLATION (MAT):

(19)【発行国】 日本国特許庁（ＪＰ）	**(19)[ISSUING COUNTRY]** Japan Patent Office (JP)
(12)【公報種別】 公開特許公報（Ａ）	**(12)[GAZETTE CATEGORY]** Laid-open Kokai Patent (A)
(11)【公開番号】 特開平 5-230642	**(11)[KOKAI NUMBER]** Unexamined Japanese Patent Heisei 5-230642
(43)【公開日】 平成５年（１９９３）９月７日	**(43)[DATE OF FIRST PUBLICATION]** September 7, Heisei 5 (1993. 9.7)
(54)【発明の名称】 スパッタ・ターゲット	**(54)[TITLE OF THE INVENTION]** Sputter target
(51)【国際特許分類第５版】 C23C 14/34 8414-4K H01J 37/08 9069-5E 37/30 Z 9172-5E	**(51)[IPC 5]** C23C 14/34 8414-4K H01J 37/08 9069-5E 37/30 Z 9172-5E
【審査請求】 未請求	**[REQUEST FOR EXAMINATION]** No
【請求項の数】 2	**[NUMBER OF CLAIMS]** 2
【全頁数】 3	**[NUMBER OF PAGES]** 3
(21)【出願番号】 特願平 4-69981	**(21)[APPLICATION NUMBER]** Japanese Patent Application Heisei 4-69981

 Copyright (C) 2006 The Thomson Corporation.

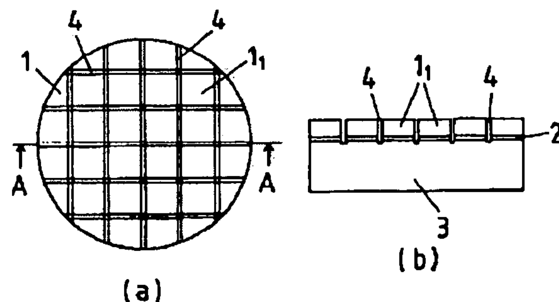
(22)【出願日】 平成４年（１９９２）２月２１日	**(22)[DATE OF FILING]** February 21, Heisei 4 (1992. 2.21)
(71)【出願人】	**(71)[PATENTEE/ASSIGNEE]**
【識別番号】 000226688	**[ID CODE]** 000226688
【氏名又は名称】 日新ハイボルテージ株式会社	**[NAME OR APPELLATION]** Nissin-High Voltage Co., Ltd.
【住所又は居所】 京都府京都市右京区梅津高畝町４７番地	**[ADDRESS OR DOMICILE]**
(72)【発明者】	**(72)[INVENTOR]**
【氏名】 馬場　隆	**[NAME OR APPELLATION]** Baba, Takashi
【住所又は居所】 京都府京都市右京区梅津高畝町４７番地　日新ハイボルテージ株式会社内	**[ADDRESS OR DOMICILE]**
(72)【発明者】	**(72)[INVENTOR]**
【氏名】 武山　邦彦	**[NAME OR APPELLATION]** Takeyama, Kunihiko
【住所又は居所】 京都府京都市右京区梅津高畝町４７番地　日新ハイボルテージ株式会社内	**[ADDRESS OR DOMICILE]**

 Copyright (C) 2006 The Thomson Corporation.

JP5-230642-A

(74)【代理人】	**(74)[AGENT]**
【弁理士】	**[PATENT ATTORNEY]**
【氏名又は名称】 成田　擴其	**[NAME OR APPELLATION]** Narita, Hiroshi

(57)【要約】	**(57)[ABSTRACT OF THE DISCLOSURE]**
【目的】 ターゲット材の加熱による割れを防止すること。	**[PURPOSE]** Prevent the crack by heat of a target material.
【構成】 所要の元素を含むターゲット材１はボンディング材２によってバッキングプレート３に固着されている。ターゲット材１にスリ割り溝（或いは切り込み、カッティングによる溝）４を設け、ターゲット材１を多数の小区画1_1に分割する。ターゲット材の厚さ方向位置での伸びの差等が小さくなり、ターゲット材の割れを防ぐことができる。予め作っておいたターゲット材の小片をバッキングプレートに貼り付けても良い。	**[CONSTITUTION]** The target material 1 containing a required element adheres to the backing plate 3 by the bonding material 2. It provides the offset rate slot (or an incision, the slot by cutting) 4 in a target material 1, and partitions a target material 1 into many subsection 1_1. The difference of the elongation in the thickness direction position of a target material etc. becomes smaller, it can prevent the crack of a target material. It is sufficient to bond on a backing plate the fragment of the target material made beforehand.



 Copyright (C) 2006 The Thomson Corporation.

【特許請求の範囲】

[CLAIMS]

【請求項１】

バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又はターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを特徴とするスパッタ・ターゲット。

[CLAIM 1]

A sputter target, in which the target material which adhered to the backing plate is partitioned into many subsections by the offset rate slot, or many fragments of a target material adhere to the backing plate in the shape of a tile sticking.

【請求項２】

請求項１のスパッタ・ターゲットを備えていることを特徴とするスパッタ型イオン源。

[CLAIM 2]

A sputter type ion source, which has the sputter target of Claim 1.

【発明の詳細な説明】

[DETAILED DESCRIPTION OF THE INVENTION]

【０００１】

[0001]

【産業上の利用分野】

本発明は、加熱によるターゲット材の割れを防いだスパッタ型イオン源等に用いるスパッタ・ターゲットに関する。

[INDUSTRIAL APPLICATION]

This invention relates to the sputter target which is used for the sputter type ion source which prevents the crack of the target material by heat.

【０００２】

[0002]

【従来の技術】

スパッタ型イオン源、イオンビームスパッタリング装置等におけるスパッタ・ターゲットは、

[PRIOR ART]

As shown in the front elevation of FIG.4(a), and sectional drawing of said (b) in the A-A, the sputter target in a sputter type ion source, an

 Copyright (C) 2006 The Thomson Corporation.

図４（ａ）の正面図、そのＡ－Ａ線での同（ｂ）の断面図に示すように、プラズマイオン、イオンビームでスパッタされる所要の元素を含む板状のターゲット材１をボンディング材２によってバッキングプレート３に固着して構成されている。ターゲット材１はスパッタ時、周囲のプラズマとプラズマイオン、或いはイオンビームの衝撃により加熱されるから、その冷却のためにバッキングプレート３は冷却ホルダーに取り付けられている。

ion-beam-sputtering apparatus, etc. adheres to a backing plate 3, and the bonding material 2 comprises the tabular target material 1 containing the required element by which a sputter is carried out from a plasma ion and an ion beam.
A target material 1 is heated by the shock of the surrounding plasma, a plasma ion, or an ion beam at the time of a sputter, therefore
The backing plate 3 is attached to the cooling holder for the cooling.

【０００３】

[0003]

【発明が解決しようとする課題】
かかるスパッタ・ターゲットのサイズが直径５０ｍｍ程度の大きさのものになると、ターゲット材１が熱伝導の悪い材質の場合には、スパッタ時、ターゲット材１の厚み方向位置での熱膨張による伸びに大きな差が生じる等の理由により、ターゲット材が割れてしまうことがある。

[PROBLEM TO BE SOLVED BY THE INVENTION]
When the size of this sputter target becomes the size which is diameter 50 mm degree and a target material 1 is the bad material of a heat conduction, a target material may break for the reasons of a big difference arising on the elongation by the thermal expansion in the thickness direction position of a target material 1 at the time of a sputter.

【０００４】
本発明は、プラズマやイオンによる加熱で、ターゲット材が割れることを防止したスパッタ・ターゲットの提供を目的とするものである。

[0004]
This invention aims to provide the sputter target which prevents the crack of a target material by heating by the plasma or an ion.

 Copyright (C) 2006 The Thomson Corporation.

【０００５】

[0005]

【課題を解決するための手段】本発明は、スパッタ・ターゲットにおいて、バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又は、ターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを主たる特徴とするものであり、そして、かかるスパッタ・ターゲットをスパッタ型イオン源に用いたことを特徴とするものでる。

[MEANS TO SOLVE THE PROBLEM]
As for this invention, in a sputter target, the target material which adhered to the backing plate is partitioned into many subsections by the offset rate slot, or many fragments of a target material adhere to a backing plate in the shape of a tile sticking.
And this sputter target is used for the sputter type ion source.
It is characterized by the above-mentioned.

【０００６】

[0006]

【作用】ターゲット材がスリ割り或いは小片のタイル貼り形式により、小さく分割されているから、各分割域における加熱による熱膨張が他の分割域に波及することがないから、ターゲット材の厚み方向位置での伸びの差等が小さく抑えられ、スパッタ・ターゲットの割れが生じない。そして、かかるターゲットをスパッタ型イオン源に用いることにより、イオンビームが安定して引出せる。

[OPERATION]
The target material is small partitioned according to an offset rate or the tile sticking form of a fragment, therefore
Since the thermal expansion by the heat in each partition region does not affect another partition region, the difference of the elongation in the thickness direction position of a target material etc. is restrained small, the crack of a sputter target does not arise.
And it can pull out an ion beam with stability by using this target for a sputter type ion source.

【０００７】

[0007]

 Copyright (C) 2006 The Thomson Corporation.

【実施例】
本考案の実施例について図面を参照して説明する。図１（ａ）、（ｂ）はスリ割り形式によるスパッタ・ターゲットの正面図及びそのＡ－Ａ線での断面図である。バッキングプレート３にボンディング材２で固着されたターゲット材１に、碁盤の目状にスリ割り溝（スリ割りないし切り込み、カッティングによる溝）４を設け、ターゲット材１を一辺が１０ｍｍ程度の多数の小区画$１_１$に小分割する。スリ割り溝４は、少なくともターゲット材部分に形成されていれば充分であるが、図１（ｂ）ではバッキングプレート３にまで達しているものを示している。

[EXAMPLES]
With reference to drawing, it demonstrates the Example of this design.
FIG. 1 (a), (b) is the front elevation of the sputter target by offset rate form, and sectional drawing in the A-A.
It provides the offset rate slot (an offset rate or an incision, slot by cutting) 4 in the target material 1 which adhered to the backing plate 3 by the bonding material 2 in a grid pattern, and one side small-partitions a target material 1 into many subsection 1_1 which are 10 mm level.
If the offset rate slot 4 is formed in the target material part at least, it is enough.
However, FIG.1(b) shows what has reached even the backing plate 3.

【０００８】
図２（ａ）、（ｂ）はタイル貼り形式のスパッタ・ターゲットの正面図とそのＡ－Ａ線での断面図であり、予めターゲット材を一辺が１０ｍｍ程度の小片$１_２$に分割しておき、かかる多数のターゲット材の小片$１_２$をボンディング材２によって、タイル貼り形式でバッキングプレート３に固着する。

[0008]
FIG. 2 (a), (b) is the front elevation and sectional drawing in an A-A of the sputter target of tile sticking form.
One side partitions the target material into fragment 1_2 which is 10 mm level beforehand, and it adheres fragment 1_2 of the target material of these many to a backing plate 3 in tile sticking form by the bonding material 2.

【０００９】
このように、ターゲット材１は、何れも一辺が１０ｍｍ程度の小区画ないしは小片$１_１$、$１_２$に分

[0009]
Thus, the target material 1 is partitioned into the subsection whose one side is all 10 mm level or fragment 1_1, and 1_2, therefore

 Copyright (C) 2006 The Thomson Corporation.

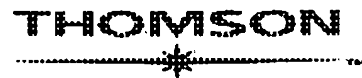
割されているから、ターゲット材１のスパッタ時に発熱、加熱が生じても、ターゲット材等の熱膨張は、各小区画、小片1_1、1_2内に限定されて、他の部分には波及せず、各小区画、小片1_1、1_2の厚み方向位置での伸びの差は小さく抑えられるから、ターゲット材に割れが発生しない。

Even if heat generation and heat arise at the time of the sputter of a target material 1, thermal expansion, such as a target material, is limited in each subsection, fragment 1_1, and 1_2, it does not affect the other part but the difference of the elongation in the thickness direction position of each subsection, fragment 1_1, and 1_2 is restrained small, therefore
A crack does not occur in a target material.

【００１０】
プラズマ・スパッタ型負イオン源では、スパッタ・ターゲット表面で発生した負イオンをイオン源の出口にビームとして集束させるために、スパッタ・ターゲットの表面を球面状にえぐった形とする場合がある。このようにすると、ターゲット材の周辺部では、その厚みは５ｍｍ程度に達し、スパッタ材が割れる可能性が高くなる。図３（ａ）及び（ｂ）は、かかる負イオン源のスパッタ・ターゲットにスリ割りを実施したものの正面図と、そのＡ－Ａ線での断面図である。図１に示したものと同様に、表面が球面状にえぐられたターゲット材１をボンディング材２によってバッキングプレート３に固着しておき、スリ割り溝４を形成することによって、ターゲット材１を多数の小区画に分割する。加熱によるスパッタ・ターゲットの割れが防止で

[0010]
In the source of a plasma sputter type negative ion, in order to converge as a beam the negative ion generated on the sputter target surface on the outlet of an ion source, it may make the surface of a sputter target into the form scooped out to the spherical shape.
If it does in this way, in the periphery part of a target material, the thickness will amount to 5 mm level, possibility that a sputter material will break becomes higher.
Although FIG.3(a) and (b) implemented the offset rate at the sputter target of this source of a negative ion, they are a front elevation and sectional drawing in the A-A.
It partitions a target material 1 into many subsections by the surface's adhering to the backing plate 3 the target material 1 scooped out by the spherical shape by the bonding material 2 like what was shown in FIG. 1, and forming the offset rate slot 4.
It can prevent the crack of the sputter target by heat, therefore
It becomes possible to pull out a beam more stably than an ion source.

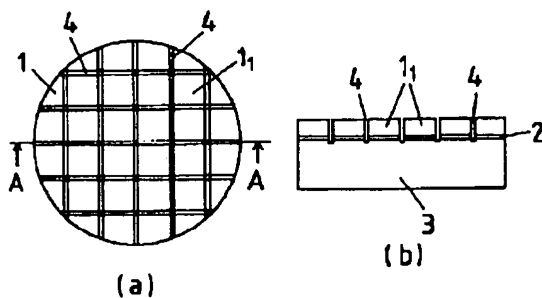
 Copyright (C) 2006 The Thomson Corporation.



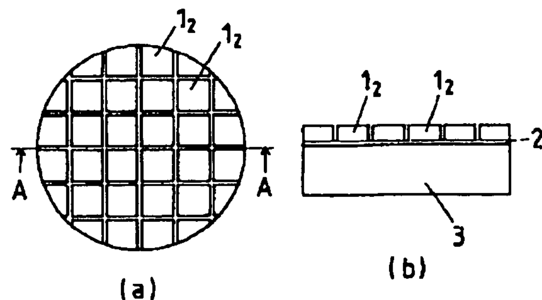
きるから、イオン源より安定にビームを引出すことが可能になる。図２と同様に、タイル貼り形式を実施してもよい。	It is sufficient to implement tile sticking form like FIG. 2.
【００１１】	**[0011]**
【発明の効果】 本発明は以上説明したように、ターゲット材が小さく分割されているから、スパッタ時に、ターゲット材における厚み方向の熱膨張による伸びの差等を小さく抑えることができ、ターゲット材の割れを防止することができる。	**[ADVANTAGE OF THE INVENTION]** As for this invention, as explained above, the target material is partitioned small, therefore At the time of a sputter, it can restrain small the difference of the elongation by the thermal expansion of the thickness direction in a target material etc., and can prevent the crack of a target material.
【００１２】 そして、本発明によるスパッタ・ターゲットをイオン源に用いることにより、イオンビームを安定に引出すことができ、特に表面が球面状にえぐられたスパッタ・ターゲットの場合に効果的である。	**[0012]** And in the case of the sputter target with which it could pull out the ion beam stably, and particularly the surface was scooped out by the spherical shape, it is effective by using the sputter target by this invention for an ion source.
【図面の簡単な説明】	**[BRIEF DESCRIPTION OF THE DRAWINGS]**
【図１】 本発明の実施例の正面図及び断面図である。	**[FIG. 1]** It is the front elevation and sectional drawing of an Example of this invention.
【図２】 他の実施例の正面図及び断面図である。	**[FIG. 2]** It is the front elevation and sectional drawing of another Example.

 Copyright (C) 2006 The Thomson Corporation.

【図３】	**[FIG. 3]**
更に他の実施例の正面図及び断面図である。	Furthermore, it is the front elevation and sectional drawing of another Example.
【図４】	**[FIG. 4]**
従来のスパッタ・ターゲットの正面図及び断面図である。	It is the front elevation and sectional drawing of a sputter target of the past.
【符号の説明】	**[DESCRIPTION OF SYMBOLS]**
$1, 1_1, 1_2$ ターゲット材	$1, 1_1, 1_2$ target material
2 ボンディング材	2 Bonding material
3 バッキングプレート	3 Backing plate
4 スリ割り溝	4 Offset rate slot
【図１】	**[FIG. 1]**

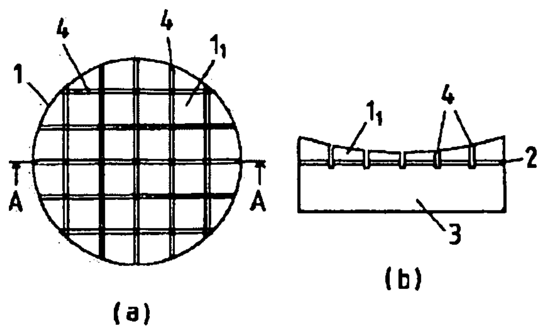


【図２】	**[FIG. 2]**

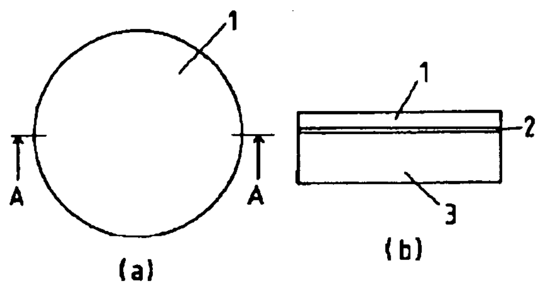


 Copyright (C) 2006 The Thomson Corporation.

【図３】 [FIG. 3]



【図４】 [FIG. 4]



 Copyright (C) 2006 The Thomson Corporation.

JP5-230642-A

THOMSON SCIENTIFIC TERMS AND CONDITIONS

Thomson Scientific Ltd shall not in any circumstances be liable or responsible for the completeness or accuracy of any Thomson Scientific translation and will not be liable for any direct, indirect, consequential or economic loss or loss of profit resulting directly or indirectly from the use of any translation by any customer.

Thomson Scientific Ltd. is part of The Thomson Corporation

Please visit our website: "www.THOMSONDERWENT.COM" (English)
"www.thomsonscientific.jp" (Japanese)

 Copyright (C) 2006 The Thomson Corporation.

(19)日本国特許庁（JP）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平5－230642

(43)公開日 平成5年(1993)9月7日

(51)Int.Cl.⁵		識別記号	庁内整理番号	FI	技術表示箇所
C23C	14/34		8414－4K		
H01J	37/08		9069－5E		
	37/30	Z	9172－5E		

審査請求 未請求 請求項の数2(全 3 頁)

(21)出願番号 特願平4－69981

(22)出願日 平成4年(1992)2月21日

(71)出願人 000226688
日新ハイボルテージ株式会社
京都府京都市右京区梅津高畝町47番地

(72)発明者 馬場 隆
京都府京都市右京区梅津高畝町47番地 日新ハイボルテージ株式会社内

(72)発明者 武山 邦彦
京都府京都市右京区梅津高畝町47番地 日新ハイボルテージ株式会社内

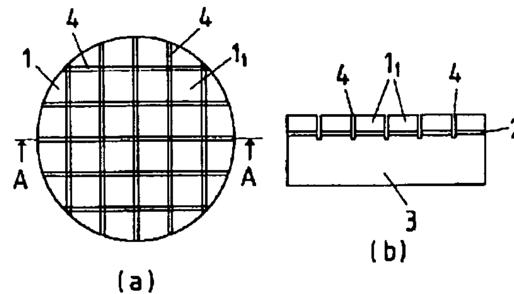
(74)代理人 弁理士 成田 據其

(54)【発明の名称】 スパッタ・ターゲット

(57)【要約】

【目的】 ターゲット材の加熱による割れを防止すること。

【構成】 所要の元素を含むターゲット材1はボンディング材2によってバッキングプレート3に固着されている。ターゲット材1にスリ割り溝（或いは切り込み、カッティングによる溝）4を設け、ターゲット材1を多数の小区画 1_1 に分割する。ターゲット材の厚さ方向位置での伸びの差等が小さくなり、ターゲット材の割れを防ぐことができる。予め作っておいたターゲット材の小片をバッキングプレートに貼り付けても良い。



(a)　(b)

【特許請求の範囲】

【請求項1】 バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又はターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを特徴とするスパッタ・ターゲット。

【請求項2】 請求項1のスパッタ・ターゲットを備えていることを特徴とするスパッタ型イオン源。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、加熱によるターゲット材の割れを防いだスパッタ型イオン源等に用いるスパッタ・ターゲットに関する。

【0002】

【従来の技術】スパッタ型イオン源、イオンビームスパッタリング装置等におけるスパッタ・ターゲットは、図4（a）の正面図、そのA－A線での同（b）の断面図に示すように、プラズマイオン、イオンビームでスパッタされる所要の元素を含む板状のターゲット材1をボンディング材2によってバッキングプレート3に固着して構成されている。ターゲット材1はスパッタ時、周囲のプラズマとプラズマイオン、或いはイオンビームの衝撃により加熱されるから、その冷却のためにバッキングプレート3は冷却ホルダーに取り付けられている。

【0003】

【発明が解決しようとする課題】かかるスパッタ・ターゲットのサイズが直径50mm程度の大きさのものになると、ターゲット材1が熱伝導の悪い材質の場合には、スパッタ時、ターゲット材1の厚み方向位置での熱膨張による伸びに大きな差が生じる等の理由により、ターゲット材が割れてしまうことがある。

【0004】本発明は、プラズマやイオンによる加熱で、ターゲット材が割れることを防止したスパッタ・ターゲットの提供を目的とするものである。

【0005】

【課題を解決するための手段】本発明は、スパッタ・ターゲットにおいて、バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又は、ターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを主たる特徴とするものであり、そして、かかるスパッタ・ターゲットをスパッタ型イオン源に用いたことを特徴とするものでる。

【0006】

【作用】ターゲット材がスリ割り或いは小片のタイル貼り形式により、小さく分割されているから、各分割域における加熱による熱膨張が他の分割域に波及することがないから、ターゲット材の厚み方向位置での伸びの差等が小さく抑えられ、スパッタ・ターゲットの割れが生じない。そして、かかるターゲットをスパッタ型イオン源に用いることにより、イオンビームが安定して引出せる。

【0007】

【実施例】本考案の実施例について図面を参照して説明する。図1（a）、（b）はスリ割り形式によるスパッタ・ターゲットの正面図及びそのA－A線での断面図である。バッキングプレート3にボンディング材2で固着されたターゲット材1に、碁盤の目状にスリ割り溝（スリ割りないし切り込み、カッティングによる溝）4を設け、ターゲット材1を一辺が10mm程度の多数の小区画1_1に小分割する。スリ割り溝4は、少なくともターゲット材部分に形成されていれば充分であるが、図1（b）ではバッキングプレート3にまで達しているものを示している。

【0008】図2（a）、（b）はタイル貼り形式のスパッタ・ターゲットの正面図とそのA－A線での断面図であり、予めターゲット材を一辺が10mm程度の小片1_2に分割しておき、かかる多数のターゲット材の小片1_2をボンディング材2によって、タイル貼り形式でバッキングプレート3に固着する。

【0009】このように、ターゲット材1は、何れも一辺が10mm程度の小区画ないしは小片1_1、1_2に分割されているから、ターゲット材1のスパッタ時に発熱、加熱が生じても、ターゲット材等の熱膨張は、各小区画、小片1_1、1_2内に限定されて、他の部分には波及せず、各小区画、小片1_1、1_2の厚み方向位置での伸びの差は小さく抑えられるから、ターゲット材に割れが発生しない。

【0010】プラズマ・スパッタ型負イオン源では、スパッタ・ターゲット表面で発生した負イオンをイオン源の出口にビームとして集束させるために、スパッタ・ターゲットの表面を球面状にえぐった形とする場合がある。このようにすると、ターゲット材の周辺部では、その厚みは5mm程度に達し、スパッタ材が割れる可能性が高くなる。図3（a）及び（b）は、かかる負イオン源のスパッタ・ターゲットにスリ割りを実施したものの正面図と、そのA－A線での断面図である。図1に示したものと同様に、表面が球面状にえぐられたターゲット材1をボンディング材2によってバッキングプレート3に固着しておき、スリ割り溝4を形成することによって、ターゲット材1を多数の小区画に分割する。加熱によるスパッタ・ターゲットの割れが防止できるから、イオン源より安定にビームを引出すことが可能になる。図2と同様に、タイル貼り形式を実施してもよい。

【0011】

【発明の効果】本発明は以上説明したように、ターゲット材が小さく分割されているから、スパッタ時に、ターゲット材における厚み方向の熱膨張による伸びの差等を小さく抑えることができ、ターゲット材の割れを防止することができる。

Case 5:20-cv-09341-EJD Document 138-6 Filed 03/18/22 Page 1279 of 1543

【0012】そして、本発明によるスパッタ・ターゲットをイオン源に用いることにより、イオンビームを安定に引出すことができ、特に表面が球面状にえぐられたスパッタ・ターゲットの場合に効果的である。

【図面の簡単な説明】

【図1】本発明の実施例の正面図及び断面図である。

【図2】他の実施例の正面図及び断面図である。

【図3】更に他の実施例の正面図及び断面図である。

【図4】従来のスパッタ・ターゲットの正面図及び断面図である。

【符号の説明】

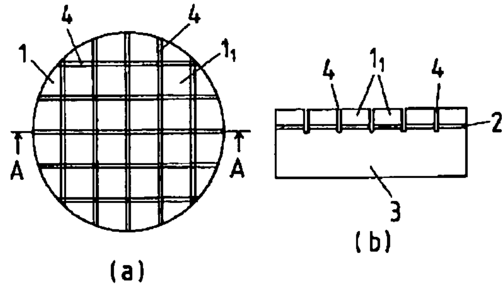
$1, 1_1, 1_2$ ターゲット材

2 ボンディング材

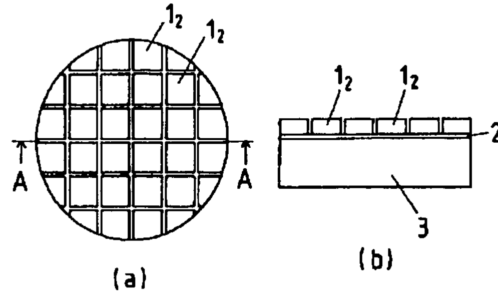
3 バッキングプレート

4 スリ割り溝

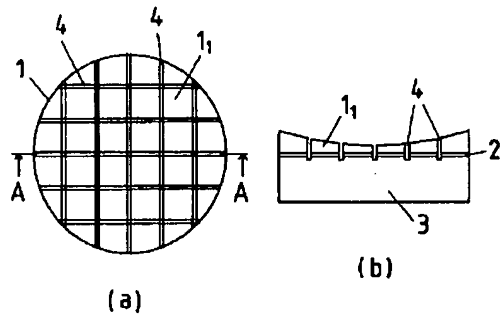
【図1】



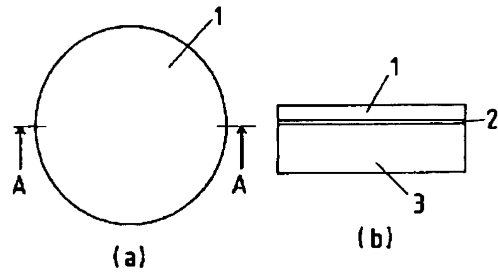
【図2】



【図3】



【図4】



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	M-12245 US	6938

22852 7590 09/06/2006

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

DATE MAILED: 09/06/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	**Application No.** 10/101,863	**Applicant(s)** ZHANG ET AL.	
	Examiner Michelle Estrada	**Art Unit** 2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *12 June 2006*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *2-4,6-14 and 21-50* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☒ Claim(s) *14* is/are allowed.

6)☒ Claim(s) *2-4,6-13 and 21-50* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1)☐ Notice of References Cited (PTO-892)

2)☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3)☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *8/15/06,6/12/06*.

4)☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5)☐ Notice of Informal Patent Application

6)☐ Other: _____.

DETAILED ACTION

The Declaration under 37 CFR 1.132 filed June 12, 2006 is insufficient to overcome the rejection of claims 21 and 43 based upon Smolanoff et al. in view of Fu et al. as set forth in the last Office action because: using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation "the filter is a band rejection filter at a frequency of the bias power" is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved.

Applicant's arguments with respect to claims 21 and 43 have been considered but are moot in view of the new ground(s) of rejection.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21 and 40-45 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claims 21, 40 and 43, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation "the filter is a band rejection filter at a frequency of the bias power" is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to

alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12 and 49, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias

power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Allowable Subject Matter

Claim 14 is allowed.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

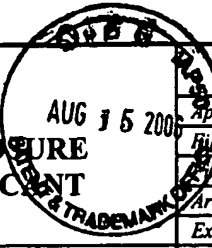
Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-

direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
September 5, 2006

IDS Form PTO/SB/08: Substitute for form 1449A/PTO



INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

Sheet 1 of 2

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
/ME/		US 5,433,835	07/18/1995	Demaray	
/ME/		US 6,288,835 B1	09/11/2001	Nilsson et al.	
/ME/		US 6,452,717 B1	09/17/2002	Endo	
/ME/		US 2002/0014406 A1	02/07/2002	Takashima	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
/ME/		DE 37 38 738 C1	01/26/1989	Degussa AG		Yes
/ME/		JP 5-230642 A	09/07/1993	Nissin High Voltage Co., Ltd.		Yes
/ME/		WO 99/61674 A1	12/02/1999	Universiteit Gent		
/ME/		WO 2006/063308 A2	06/15/2006	Symmorphix, Inc.		

NON PATENT LITERATURE DOCUMENTS

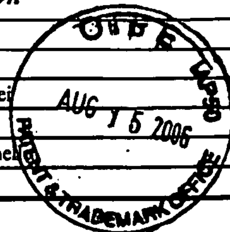
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
/ME/		AGRAWAL, G.P., in: Fiber-Optic Communication Systems, 2nd Edition, John Wiley & Sons, New York, pp. 361-399 and 415 (1997).	
/ME/		ASM Handbook, Formerly Ninth Edition, Metals Handbook, Volume 15, Casting, Davis et al. (Eds.), ASM International, pp. 372-373, 376-383, and 410-411 (1988).	
/ME/		MASUDA, H. & KAWAI, S., "Wide-band and gain-flattened hybrid fiber amplifier consisting of an EDFA and a multiwavelength pumped raman amplifier," *IEEE Photonics Technology Lett. 11*(6):647-649 (1999).	
/ME/		SNOEKS, E. et al., "Cooperative upconversion in erbium-implanted soda-lime silicate glass optical waveguides," *J. Opt. Soc. Am. B 12*(8):1468-1474 (1995).	
/ME/		Response to Office Action filed July 27, 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
/ME/		Notice of Allowance mailed March 25, 2004 for US Patent No. 6,827,826 (Atty. Docket No. 09140.0002-02).	

Examiner Signature	/Michelle Estrada/	Date Considered	8/28/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746096525 US

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	2	of	2	Attorney Docket Number	9140.0016-00

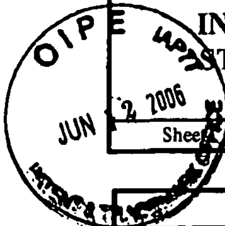


NON PATENT LITERATURE DOCUMENTS			
MME		Notice of Allowance issued on October 8, 2002, in U.S. Patent No. 6,533,907 (Atty. Docket No. 09140-0004-00).	
MME		Notice of Allowance issued on October 21, 2004, in U.S. Application No. 10/101,492 (Atty. Docket No. 09140-0015-00).	
MME		Response to Office Action filed on August 9, 2006 in Application No. 10/954,182 (Atty. Docket No. 09140.0016-01).	
MME		Office Action issued on August 2, 2006, in U.S. Application No. 10/101,341 (Atty. Docket No. 09140-0017-00).	
MME		Response to Office Action filed on July 24, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00).	
MME		Response to Office Action filed July 26, 2006 in U.S. Application No. 10/851,542 (Atty. Docket No. 09140.0033-00).	

Examiner Signature	Michelle Estrada	Date Considered	8/28/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 746096525 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
ME		US 4,082,569	04-04-1978	Evans, Jr.	
		US 5,472,795	12-05-1995	Atita	
		US 5,645,626	07-08-1997	Edlund et al.	
		US 5,702,829	12-30-1997	Paidassi et al.	
		US 6,045,626	04-04-2000	Yano et al.	
		US 6,673,716 B1	01-06-2004	D'Couto et al.	
		US 6,683,749 B2	01-27-2004	Daby et al.	
		US 6,884,327 B2	04-26-2005	Pan et al.	
		US 2002/0115252 A1	08-22-2002	Haukka et al.	
		US 2003/0035906 A1	02-20-2003	Memarian et al.	
		US 2004/0043557 A1	03-04-2004	Haukka et al.	
		US 2005/0048802 A1	03-03-2005	Zhang et al.	
		US 2005/0183946 A1	08-25-2005	Pan et al.	
		US 2006/0054496 A1	03-16-2006	Zhang et al.	
		US 2006/0057283 A1	03-16-2006	Zhang et al.	
		US 2006/0057304 A1	03-16-2006	Zhang et al.	
ME		US 2006/0071592 A1	04-06-2006	Narasimhan et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
ME		JP 7-224379 A	08-22-1995	Ulvac Japan Ltd		Abstract

Examiner Signature	*Michelle Estrada*	Date Considered	8/28/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818108 US

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
ME		BARBIER, D., "Performances and potential applications of erbium doped planar waveguide amplifiers and lasers," *Proc. OAA*, Victoria, BC, Canada, pp. 58-63 (July 21-23, 1997).	
ME		KELLY, P.J. et al., "A novel technique for the deposition of aluminum-doped zinc oxide films," *Thin Solid Films 426*(1-2):111-116 (2003).	
ME		TOMASZEWSKI, H. et al., "Yttria-stabilized zirconia thin films grown by reactive r.f. magnetron sputtering," *Thin Solid Films 287*:104-109 (1996).	
ME		Response to Final Office Action filed ~~April 14,~~ 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
ME		Office Action mailed April 27, 2006, in U.S. Appl. No. 10/291,179 (Atty. Docket No. 9140.0001-00).	
ME		Final Office Action mailed May 8, 2006 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
ME		Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01).	
ME		Office Action issued on March 9, 2006, in U.S. Appl. No. 10/954,182 (Attorney Docket No. 09140-0016-01000).	
ME		Response to Office Action filed on May 15, 2006, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
ME		Final Office Action issued on May 19, 2006 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00).	
ME		Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated March 20, 2006 (Atty. Docket No. 9140.0030-00256).	
ME		Office Action mailed April 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

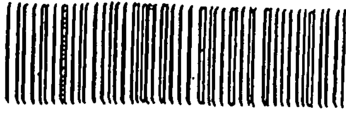
Examiner Signature	Michelle Estrada	Date Considered	8/28/06

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818108 US

BEST AVAILABLE COPY

Index of Claims



Application No.	Applicant(s)
10/101863	
Examiner	Art Unit

√	Rejected		–	(Through numeral) Cancelled		N	Non-Elected		A	Appeal
=	Allowed		÷	Restricted		I	Interference		O	Objected

Claim Final	Claim Original	2/5/04	4/5/06	Claim Final	Claim Original	Claim Final	Claim Original
	~~1~~	.			51		101
	2	.	√		52		102
	3	.	√		53		103
	4	.	√		54		104
	~~5~~	.			55		105
	6	.	√		56		106
	7	.			57		107
	8	.			58		108
	9	.			59		109
	10	-			60		110
	11	-			61		111
	12	-			62		112
	13	-	√		63		113
	(14)	-	=		64		114
	15	-			65		115
	16	-			66		116
	17	-			67		117
	18	-			68		118
	19	-			69		119
	20	-			70		120
	(21)	-	√		71		121
	22	-	√		72		122
	23	-	√		73		123
	24	-	√		74		124
	25	-			75		125
	26	-			76		126
	27	-			77		127
	28	-			78		128
	29	-			79		129
	30	-			80		130
	31	-			81		131
	32	-			82		132
	33	-			83		133
	34	-			84		134
	35	-			85		135
	36	-			86		136
	37	-			87		137
	38	-			88		138
	39	-			89		139
	40	-	√		90		140
	41	-			91		141
	42	-			92		142
	(43)	-			93		143
	44	√			94		144
	45	√			95		145
	46	√			96		146
	47	√			97		147
	48	√			98		148
	49	√	√		99		149
	50		√		100		150

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	9140.0016-00	6938

22852 7590 01/23/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER
ESTRADA, MICHELLE

ART UNIT	PAPER NUMBER
2823	

MAIL DATE	DELIVERY MODE
01/23/2007	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

Interview Summary	Application No. 10/101,863	Applicant(s) ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	

All participants (applicant, applicant's representative, PTO personnel):

(1) *Michelle Estrada*.

(2) *Gary Edwards*.

(3) *Richard Demaray*.

(4) *Hongmei Zhang*.

Date of Interview: *18 January 2007*.

Type: a)☒ Telephonic b)☐ Video Conference
c)☐ Personal [copy given to: 1)☐ applicant 2)☐ applicant's representative]

Exhibit shown or demonstration conducted: d)☐ Yes e)☒ No.
If Yes, brief description: _____.

Claim(s) discussed: *21 and 43*.

Identification of prior art discussed: *Smolanoff et al.*.

Agreement with respect to the claims f)☒ was reached. g)☐ was not reached. h)☐ N/A.

Substance of Interview including description of the general nature of what was agreed to if an agreement was reached, or any other comments: *Applicants explained the basis of the invention and the difference over Smolanoff reference with respect to the pulsed DC power. Applicants will amend claims 21 and 43 to further clarify the invention. Further consideration and search would be needed for the new limitations in the claims*.

(A fuller description, if necessary, and a copy of the amendments which the examiner agreed would render the claims allowable, if available, must be attached. Also, where no copy of the amendments that would render the claims allowable is available, a summary thereof must be attached.)

THE FORMAL WRITTEN REPLY TO THE LAST OFFICE ACTION MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a reply to the last Office action has already been filed, APPLICANT IS GIVEN A NON-EXTENDABLE PERIOD OF THE LONGER OF ONE MONTH OR THIRTY DAYS FROM THIS INTERVIEW DATE, OR THE MAILING DATE OF THIS INTERVIEW SUMMARY FORM, WHICHEVER IS LATER, TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW. See Summary of Record of Interview requirements on reverse side or on attached sheet.

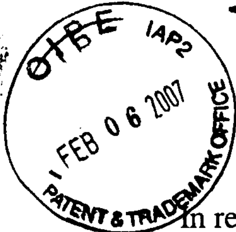
MICHELLE ESTRADA
PRIMARY EXAMINER

Examiner Note: You must sign this form unless it is an Attachment to a signed Office action.

Examiner's signature, if required

02-08-07 IFW 2823

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed September 6, 2006, and the Interview Summary, mailed January 23, 2007, the period for response having been extended to February 6, 2007, by a request for extension of one month with authorization for the Commissioner to charge the fee to Deposit Account No. 06-0916, Applicants propose that this application be amended as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 6.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 µs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Currently amended): The method of Claim 21, wherein ~~the film is an upper cladding layer of a waveguide structure and~~ the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14.-20. (Cancelled).

21. (Currently amended): A method of depositing [[a]] an oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target through a filter such that the target voltage oscillates between positive and negative voltages to create a plasma and deposit the oxide film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface, and

wherein the filter is a band rejection filter at a frequency of the bias power.

22. (Previously Presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (Previously presented): The method of claim 21, wherein the band rejection filter is a

narrow band-pass filter.

41. (Previously presented): The method of claim 21, wherein a bandwidth of the band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing [[a]] an oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power such that the target voltage oscillates between positive and negative voltages and an oxide film is deposited on the substrate.

44. (Previously presented): The method of claim 43, wherein a bandwidth of the band rejection filter is about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (Previously presented): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (New): A method of depositing an oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages; and

filtering the pulsed DC power through a narrow band rejection filter at a frequency of the bias power,

wherein the oxide film is deposited on the substrate.

52. (New): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, N_2, O_2, C_2F_6, CO_2, CO, NH_3, NO, and halide containing gasses.

53. (New): The method of claim 51, wherein the target is a metallic target.

54. (New): The method of claim 51, wherein the target is an intermetllic target.

55. (New). The method of claim 51, further including sweeping the target with a magnetic field.

56. (New): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (New): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (New) The method of claims 21, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (New) The method of claim 43, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about

350 kHz.

60. (New) The method of claim 51, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

REMARKS

Claims 2-4, 6-14, and 21-50 are pending in this application. The Examiner has allowed claim 14 and rejected claims 2-4, 6-13, and 21-50. Applicants have canceled claim 14, amended claims 21 and 43, and added new claims 51-60.

Examiner's Interview

Applicants wish to thank the Examiner for spending her time in an interview on January 18, 2007. In attendance at the Interview were Examiner Michelle Estrada, Applicant's counsel, Gary J. Edwards, and Inventors R. Ernest Demaray and Hongmei Zhang. Applicants substantially agree with the Examiner's Summary of the Interview mailed on January 23, 2007, and provide further discussion of the material discussed below.

During the interview, the inventors described to the Examiner the development of the invention, including the development of applicant's pulsed-DC processing technology, and the teachings of the cited references. In particular, the Smolanoff reference was discussed with respect to independent claims 21 and 43. Applicants discussed amending the claims to further clarify the distinctions between the claimed invention and the teachings of Smolanoff and other cited art. Those amendments are reflected in the amended claims above and in the newly added claims. The distinctions between the claimed invention and the cited prior art is further discussed below.

As pointed out to the Examiner during the interview, and as further discussed in the specification (see, e.g., Par. [0049]), the historical difficulty in deposition of insulating oxide layers is the formation of insulating layers on the target, which build up charges with the ultimate result of unwanted arcing. The arcing results in damaged power supplies and deposition of particulate matter, which degrades the properties of the resulting films deposited on the substrate.

Some embodiments of pulsed DC processing, as defined in the present application, can substantially eliminate this problem. As discussed, for example, in paragraph [0053] of Applicant's application, pulsed DC sputtering refers to a sputtering technique where the pulsed DC power supply oscillates between positive and negative potentials, driving the voltage of the target alternately to positive and negative potentials. Claims 21 and 43 of the present application have been amended to explicitly recite that "the target voltage oscillates between positive and negative voltages." New claim 51 also recites that "the target voltage oscillates between positive and negative voltages." The claims have also been amended to recite that the deposited films are oxide films. Applicants reserve the right to pursue allowable claims to the subject matter disclosed in the present application in continuation applications.

In order to further improve the quality of the deposited film, Applicant's apply a combination of pulsed DC power to the target and RF bias to the substrate. As is discussed, for example, in paragraph [0057] of the specification, application of RF bias to the substrate results in a densification of the deposited film. In order to supply both a pulsed DC power to the target and an RF bias to the substrate, a narrow band rejection filter is coupled between the pulsed DC power supply and the target. The band rejection filter is arranged to reject RF power at the frequency of the RF bias to the substrate. Applicants discovered that the use of pulsed DC power to the target and RF bias to the substrate resulted in catastrophic failure of the pulsed DC power supply due to transmission of the RF power into the pulsed DC power supply. However, a conventional high or low pass filter blocks a portion of the pulsed DC frequency to the target and therefore the benefits of using pulsed DC power are lost. Applicants discovered that a narrow band rejection filter, an embodiment of which is described in the specification at paragraph [0056], both protects the DC power supply from the RF bias power and passes the pulsed DC

frequencies which form the square pulse of the pulsed DC power to the target so that the benefits of pulsed DC deposition with RF bias can be realized. The elimination of a narrow band of frequencies about a single frequency in a narrow band rejection filter has a small effect on the square shape of the pulsed DC pulse. However, elimination of either all higher frequencies or all lower frequencies from the single frequency effectively destroys the shape of the square pulse and eliminates control of both the magnitude and duration of the positive portion of the pulse.

During prosecution of this application, several prior art publications have been raised, including Smolanoff (U.S. Patent 6,117,279) and Le (U.S. Publication No. 2003/0077914). Smolanoff was discussed during the Interview. Both publications are discussed below in particular. Neither of these references, either separately or in combination, teaches the combination of pulsed-DC deposition, where the target voltage oscillates between positive and negative voltages, and an RF bias. As a summary, Smolanoff teaches sputtering of a conducting or metallic layer and does not teach deposition of an "oxide layer," as is recited in each of claims 21, 43, and 51 above. Additionally, Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in each of claims 21, 43 and 51. Further, although Smolanoff teaches a filter between a DC power supply and the target, Smolanoff does not teach a "narrow band rejection filter" as is recited in each of claims 21, 43, and 51.

Le does not cure the defects in the teachings of Smolanoff. Le teaches "a method of depositing a titanium oxide layer on a substrate" utilizing pulsed DC voltage. (Le, Abstract) However, Le does not teach applying an RF bias to the substrate or a band rejection filter coupled between the pulsed DC power supply and the target. Further, one skilled in the art would not be motivated to combine the teachings of Smolanoff, which is directed toward

deposition of metallic layers, with the teachings of Le, which is directed toward deposition of a titanium oxide layer.

As is further discussed below, claims 2-13, 21-24, and 40-60 are allowable over the cited prior art.

Claim Rejections under 35 U.S.C. § 103[1]

The Examiner has rejected claims 2-4, 6-13, and 21-50 over combinations of Fu and Le with Smolanoff. As discussed below, claims 2-4, 6-13, and 21-50, as amended, are allowable over the cited references.

Claims 10-13, 21, and 40-45

The Examiner has rejected claims 10-13, 21, and 40-45 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,117,279 ("Smolanoff et al.") in view of U.S. Patent No. 6,306,265 ("Fu et al."). However, Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Additionally, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Further, Smolanoff does not teach deposition of "an oxide film," as is recited in claims 21 and 43.

I. Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43.

[1] The Examiner has made multiple characterizations of the claims, the cited art, and application of legal principles to those characterizations. Applicants shall not be deemed to agree with or to acquiesce in the Examiner's statements by not specifically addressing these characterizations in this response.

Smolanoff teaches that "[t]he target power supply 21 is usually a source of constant or pulsed DC power and is connected between the cathode assembly 17 and some element such as the chamber wall 13 which is at ground potential and serves as the system anode." (Smolanoff, col. 5, lines 51-54). Additionally, Smolanoff teaches that "[p]ower from the steady or pulsed DC power supply 21 and/or RF generator 24 produces a negative potential on the target 16." (Smolanoff, col. 5, line 66, through col. 6, line 1).

Applicants have explicitly defined pulsed DC power to refer to power that oscillates between positive and negative voltages. (*See*, application, par. [0053]). As described in the specification, the positive voltage period allows an insulating layer deposited on the target to discharge, resulting in an arc free deposition process. (*See,* application, par. [0053]). However, a second definition of "pulsed DC power" was also in use at the time, and the second definition is apparently the definition utilized in Smolanoff. In this second definition, which is also referred to as unipolar pulsed DC, the DC power supplied to the target is grounded on occasion, either periodically or when an impending discharge is detected. The DC power can be shunted to ground so that the voltage on the target was brought from a high negative voltage to near ground voltage until the arc condition was dissipated, while the negative voltage power supply was protected from the discharge. This process was also referred to as "pulsed DC power," but, in Smolanoff, the target remains at a negative voltage throughout the deposition.[2]

---

[2] Applicant has submitted three articles that explain various aspects of pulsed-dc technology in the Information Disclosure Statement that accompanies this amendment: *See, e.g.,* Richard A. Scholl, "Power Systems for Reactive Sputtering of Insulating Films," Advanced Energy Industries, Inc., While Paper, September, 2001, page 3, paragraph 3; *See also,* Richard A. Scholl, "Advanced Supplies for Pulsed Plasma Technologies: State-Of-The-Art and Outlook," Advanced Energy Industries, Inc., White Paper, 1999; ; and A. Belkind, et al., "Pulsed-DC Reactive
(continued...)

The process of pulsed DC power as claimed in claims 21 and 43, where "the target voltage oscillates between positive and negative voltages," then, differs from the teachings of Smolanoff at least in that Smolanoff teaches that the target remains at a negative potential. Such pulses occur only, generally, when an impending discharge from the target is sensed and may not be periodic. Therefore, Smolanoff does not teach "that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43.

II. Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43.

Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Smolanoff teaches that "[t]he power supply 21 preferably is connected to the cathode assembly 17 through an RF filter 22." (Smolanoff, col. 5, lines 56-58). However, no further description of filter 22 is provided. Therefore, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43.

The Examiner has commented that "using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies." (OA, page 2). Additionally, the Examiner commented that "the limitation 'the filter is a band rejection filter at a frequency of the bias power' is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved." (OA, page 2). Applicants disagree.

(...continued)
Sputtering of Dielectrics: Pulsing Parameter Effects," Society of Vacuum Coaters 43rd Annual Technical Conference Proceedings, Denver, CO, April 15-20, 2000.

Although it is true that "the filter is going to work at certain frequencies," as suggested by the Examiner, the recited "band rejection filter" works at the frequency of the RF bias supply and blocks only a narrow band of frequencies around the frequency of the RF bias supply. This allows the square wave pulse of the DC power, which is formed of all frequencies both higher and lower than the biased frequency, to be transmitted through the filter to the target. Otherwise, the pulse that would reach the target is distorted so that the benefits of the pulsed DC power are not realized. Therefore, utilization of a band rejection filter at the frequency of the bias power is neither taught nor obvious from the teachings of Smolanoff. Furthermore, use of a band rejection filter at the frequency of the bias power places a distinct limitation on the claim.

Therefore, Smolanoff does not teach "applying pulsed DC power to the target through a filter . . . wherein the filter is a band rejection filter at a frequency of the bias power," as is recited in claims 21, or "applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power," as is recited in claim 43.

III. Smolanoff teaches deposition of metallic films and does not teach "an oxide film," as is recited in claims 21 and 43.

Smolanoff teaches "a sputter coating apparatus" that is generally directed to deposition of conducting films. In particular, Smolanoff "relates to sputter coating, and more particularly, to the Ionized Physical Vapor Deposition (IPVD) of coating material onto substrates." (Smolanoff, col. 1, lines 6-8). Smolanoff teaches that

> For some sputtering processes, such as those used for coating contacts at the bottoms of high aspect ratio holes and other features on the substrate 15 and for metallizing such holes by filling them with sputtered conductive material, it is highly preferred in VLSI semiconductor device manufacturing that the particles impinge onto the substrate 15 in a narrow angular distribution around the

> normal to the substrate so that they can proceed directly into the features and onto the feature bottoms without striking or being shadowed by the feature sides.

(Smolanoff, col. 6, lines 34-43).

As stated in Smolanoff,

> The present invention is further predicated in part upon a principle that a substantial loss of positive ions from a secondary plasma and a resulting reduction in the ionization fraction of sputtered ions by the secondary plasma, are prevented when electrically conductive shields employed in ionized physical deposition processes on the periphery of the secondary plasma used for the ionization of the puttered material are prevented from developing a substantial negative DC potential. The invention is further predicated in part upon the concept that the existence of conductive shields or chamber walls bounding the secondary plasma, if prevented from developing a strongly negative DC potential or if kept far from the center of the chamber, will reduce the steering of positive ions from the secondary plasma into the walls or shields, and decrease the width of the plasma sheath. The invention is particularly predicated on the concept of providing these effects while maintaining an RF shield that will allow effective and efficient coupling of energy into the secondary plasma.

Further, Smolanoff teaches that

> For sputter processing, the gas from the supply 40 is typically an inert gas such as argon. For reactive processes, additional gases, such as nitrogen, hydrogen, ammonia, oxygen or other gas, can be introduced through auxiliary flow controllers.

(Smolanoff, col. 7, lines 23-26). Further, Smolanoff teaches that "[a] metal shield positioned inside of the window shields the window from the deposition of conductive sputtered material thereon which, if permitted to accumulate on the window, would isolate the chamber from the coil." (Smolanoff, col. 4, lines 19-22). Additionally, Smolanoff teaches that

> While the window 60 itself is not electrically conductive, it is susceptible to the accumulation of a coating of conductive material sputtered from the target 16. . . .
>
> To prevent such buildup of conductive sputtered material on the window 60, a shield 70 is provided in the vacuum of the

> chamber 12 between the space 11 and the window 60, in close proximity to the inside surface of the window 60.

(Smolanoff, col. 7, line 61, -col. 8, line 9).

As indicated in Smolanoff, and discussed above, the shield taught in Smolanoff can not be made insulating and must remain electrically conducting in order for the Smolanoff invention to function. Any deposition of insulating material, which would occur during deposition of an oxide material, would cause the invention taught in Smalanoff to become nonfunctional. Smolanoff, therefore, teaches away from deposition of dielectric materials such as oxide materials. Therefore Smolanoff teaches sputtering of conductive materials and does not teach deposition of oxide materials.

IV. Fu does not cure the defects in the teachings of Smolanoff.

As discussed above, Smolanoff teaches deposition of conducting films and does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Additionally, Smolonoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Fu does not cure the defects in the teachings of Smolonoff.

Fu teaches "sputtering of materials." (Fu, col. 1, line 13). As shown in Figure 1, Fu teaches applying DC power to the target. (*See*, Fu, Fig. 1; col. 1, lines 30-32). However, Fu does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Therefore, Fu does not teach the combination of "applying pulsed DC power to the target through a filter . . . wherein the filter is a band rejection filter at a frequency of the bias power," as is recited in claim 21, or "applying pulsed DC power to a target through a band rejection filter at a frequency of the

bias power," as is recited in claim 43. Although Fu mentions that oxygen can be supplied to the reactor to produce oxides such as Al_2O_3 (*See*, Fu, col. 1, lines 39-40), Fu concentrates on ionized metal deposition (*See, e.g.,* Fu, title).

Therefore, claims 21 and 43 are allowable over the combination of Fu and Smolanoff. Claims 10-13 and 40-42 depend from claim 21 and are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 21. Claims 44-45 depend from claim 43 and are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 43.

Claims 2-4, 5, and 22-24

The Examiner has rejected claims 2-4, 6, and 22-24 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of the Examiner's comments.

However, claims 2-4, 6, and 22-24 depend from claim 21, which is allowable over the combination of Fu and Smolanoff as discussed above. Therefore, claims 2-4, 6, and 22-24 are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 21.

The Examiner's comments regarding the prima facie obviousness of claiming different ranges are not appropriate with regard to claims 2-4, 6, and 22-24 because the recited ranges are directed to the process claimed, which as discussed above is allowable over the cited prior art. Therefore, the recited ranges in claims 2-4, 6, and 22-24 are not related to the ranges provided in the prior art, which is directed towards different processes.

Claims 7 and 9

The Examiner has rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of U.S. Application No. 2003/0077914 ("Le et al.").

As discussed above with respect to claim 21, the combination of Smolanoff and Fu does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages" and "a band rejection filter at a frequency of the bias power," as is recited in claims 21. Le does not cure the defects in the teachings of Smolanoff and Fu.

Le teaches "a method of depositing a titanium oxide layer on a substrate" utilizing pulsed DC voltage. (Le, Abstract) However, Le does not teach applying an RF bias to the substrate or a band rejection filter coupled between the pulsed DC power supply and the target. Therefore, Le does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages" and "a band rejection filter at a frequency of the bias power," as is recited in claims 21.

Further, one skilled in the art would not be motivated to combine the teachings of Smolanoff, which is directed toward deposition of metallic layers, with the teachings of Le, which is directed toward deposition of a titanium oxide layer. In fact, as discussed above, Smolanoff teaches away from the deposition of oxide layers because deposition of an oxide layer on the shield, which would occur during deposition of an oxide layer, would cause the Smolanoff invention to not function.

Therefore, claims 7 and 9, which depend from claim 21, are allowable for at least the same reason as is claim 21.

New Claims

Applicants have added new claims 51-60. Independent claim 51 includes the limitations of "an oxide film," "applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages," and "filtering the pulsed DC power through a narrow band rejection filter at a frequency of the bias power," which are the limitations that were discussed with the Examiner during the Interview of January 18, 2007. Claim 51 includes limitations similar to those recited in claims 21 and 43 and discussed above. Therefore, claim 51 is allowable over the cited prior art. Claims 52-57 and claim 60, which depend from claim 51, are therefore allowable over the cited prior art for at least the same reasons as is claim 51. Claim 58 depends from claim 21 and is therefore allowable over the prior art for at least the same reasons as is claim 21. Claim 59 depends from claim 43 and is allowable over the prior art for at least the same reasons as is claim 43.

Support for claims 51-60 can be found throughout the specification. Claim 51 includes limitations similar to claims 21 and 43. Claim 52 is disclosed, for example, in paragraph [0015] and paragraph [0073]. Claims 53 and 54 are disclosed, for example, in paragraph [0062]. Claim 55 is similar to claim 12. Claim 56 includes limitations from claim 3. Claim 57 is similar to claim 4. Claims 58-60 include limitations from claim 3.

Conclusion

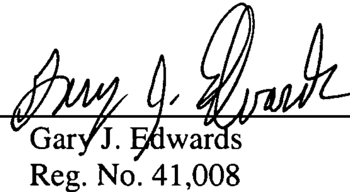
In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO. EV 955594467 US

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

TWELFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By:
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 955594467 US**

OIPE FEB 0 6 2007 PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	3	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-6,088,492	07-11-2000	Kaneko et al.	
		US-6,154,582	11-28-2000	Bazylenko et al.	
		US-2002/0191916 A1	12-19-2002	Frish et al.	
		US-2003/0044118 A1	03-06-2003	Zhou et al.	
		US 2003/0143853 A1	07-31-2003	Celii et al.	
		US 2005/0175287 A1	08-11-2005	Pan et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		KR 2003-0088236	11-19-2003	Hyundai Motor Co Ltd		Abstract
		WO 01/82297 A1	11-01-2001	Koninklijke Philips Electronics N.V.		

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		BELKIND, A. et al., "Pulsed-DC Reactive Sputtering of Dielectrics: Pulsing Parameter Effects," 43rd Annual Technical Conference Proceedings-Denver: 86-90 (April 15-20, 2000).	
		SCHOLL, R., "Power Supplies for Pulsed Plasma Technologies: State-Of-The-Art And Outlook," Advances Energy Industries, Inc., pages 1-8 (1999).	
		SCHOLLI, R., "Power Systems for Reactive Sputtering of Insulating Films," Advances Energy Industries, Inc., pages 1-8 (August 2001).	
		Final Office Action dated October 12, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Final Office Action dated November 3, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00).	
		Office Action dated December 1, 2006, in U.S. Application No. 10,291,179 (Attorney	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 955594467 US

OIPE
FEB 0 6 2007
PATENT & TRADEMARK OFFICE
IAP2

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	2	of	3	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		Docket No. 9140.0001-00).	
		Amendment dated October 19, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Office Action dated December 18, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Response to Office Action dated September 11, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Office Action dated December 1, 2006, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Office Action dated October 31, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Office Action dated December 6, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/228,834 (Attorney Docket No. 9140.0016-02).	
		Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/191,643 (Attorney Docket No. 9140.0016-04).	
		Final Office Action dated October 19, 2006, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Voluntary Amendment dated July 26, 2006 in TW Appl. No. 92123625 (Attorney Docket No. 9140.0025-00270).	
		Response to Final Office Action dated August 3, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
		Notice of Allowance dated October 23, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
		Office Action dated October 12, 2006, for U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Response to Office Action dated December 21, 2006, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Office Action dated September 22, 2006 from Korean Patent Office in Appl. No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).	
		Response to Office Action dated November 8, 2006, to the Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).	
		Response to Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated August 11, 2006 (Attorney Docket No. 9140.0030-00256).	
		Final Office Action dated October 26, 2006, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 955594467 US

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				*Complete if Known*	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	3	of	3	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		Response to Office Action dated January 26, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	
		Preliminary Amendment dated July 21, 2006, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
		Supplemental Preliminary Amendment, Substitute Specification with Markings, Substitute Specification without Markings, and Replacement Drawing Sheets dated December 6, 2006 in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
		Continuation application and Preliminary Amendment dated December 13, 2006 (Attorney Docket No. 9140.0042-01).	
		Voluntary Amendment dated August 15, 2006 in TW Appl. No. 94143175 (Attorney Docket No. 9140.0042-00270).	
		PCT International Search Report and Written Opinion for Application No. PCT/US05/44781 dated October 3, 2006 (Attorney Docket No. 9140.0042-00304).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 955594467 US

COPY

Derwent WPI
(c) 2007 The Thomson Corporation. All rights reserved. BEST AVAILABLE COPY

0014040325
WPI Acc no: 2004-222504/200421
Flywheel for radiating heat and increasing rigidity
Patent Assignee: HYUNDAI MOTOR CO LTD (HYUN-N)
Inventor: SONG J H
Patent Family: 2 patents, 1 countries

Patent Number	Kind	Date	Application Number	Kind	Date	Update	Type
KR 2003088236	**A**	**20031119**	**KR 200226187**	**A**	**20020513**	**200421**	**B**
KR 507142	B	20050809	KR 200226187	A	20020513	200662	E

Priority Applications (no., kind, date): KR 200226187 A 20020513

Patent Details

Patent Number	Kind	Lan	Pgs	Draw	Filing Notes	
KR 2003088236	A	KO	1	10		
KR 507142	B	KO			Previously issued patent	KR 2003088236

Alerting Abstract KR A
NOVELTY - A flywheel for radiating and reinforcing is provided to prevent crack by absorbing burst force with elastic force and radiating friction heat in operating the clutch because the flywheel is divided into plural portions and manufactured with different materials.
DESCRIPTION - A flywheel(10) is composed of a support plate(10a) combined with a crankshaft with pressing and fitting a ring gear(11); a cover plate(10b) fixed to the support plate and bent to form the storage space; an insert plate(10c) fastened inside the cover plate; and a friction plate(10d) contacted to the insert plate and inserted to the cover plate to receive clamping load from a clutch plate in operating the clutch. The durability is improved by preventing crack from burst force in the flywheel and radiating friction heat from clamping load.

(19)대한민국특허청(KR)
(12) 공개특허공보(A)

(51) 。Int. Cl.7
F16F 15/30

(11) 공개번호 특2003-0088236
(43) 공개일자 2003년11월19일

(21) 출원번호 10-2002-0026187
(22) 출원일자 2002년05월13일

(71) 출원인 현대자동차주식회사
서울 서초구 양재동 231

(72) 발명자 송진호
경기도안양시만안구박달2동139-101

(74) 대리인 한양특허법인

심사청구 : 있음

(54) 방열과 강성 강화용 플라이 휠

요약

본 발명은 방열과 강성 강화용 플라이 휠에 관한 것으로, 플라이휠을 서로 결합되는 여러 부분으로 분리해 제작하면서 그 재질을 달리해 버스트포스를 자체적인 탄성을 통해 흡수하면서 클러치의 조작에 의한 마찰열의 방열성도 향상시켜 균열을 방지함에 그 목적이 있다.

상기와 같은 목적을 달성하기 위한 본 발명은, 플라이휠(10)이 링기어(11)가 외주 측에 압입되면서 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 일단이 고정되면서 절곡된 내부로 수용공간을 형성하는 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 고정되는 인서트플레이트(10c) 및 이 인서트플레이트(10c)에 접촉됨과 더불어 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작에 따라 클러치플레이트(22)로부터 클램핑 로드(F')를 받는 마찰플레이트(10d)로 이루어진 것을 특징으로 한다.

대표도

도 4

명세서

도면의 간단한 설명

도 1은 일반적인 엔진의 구성도

도 2는 종래에 따른 플라이 휠부위의 구성도

도 3은 종래에 따른 플라이휠의 구성 단면도

도 4는 본 발명에 따른 플라이휠의 구성 단면도

<도면의 주요부분에 대한 부호의 설명>

1 : 실린더 2 : 피스톤

3 : 커넥팅 로드 5 : 크랭크축

6 : 워터펌프 7 : 밸브기구

8 : 크랭크풀리 9 : 타이밍 기어

10 : 플라이휠 10a : 지지플레이트

10b : 커버플레이트 10c : 인서트플레이트

10d : 마찰플레이트 10d' : 슬랏

11 : 링기어 20 : 클러치어셈블리

21 : 클러치커버 22 : 클러치플레이트

H : 휠하우징

F' : 클램핑로드 K : 갭

발명의 상세한 설명

발명의 목적

발명이 속하는 기술 및 그 분야의 종래기술

본 발명은 방열과 강성 강화용 플라이 휠에 관한 것으로, 보다 상세하게는 엔진의 회전력에 의한 균열을 방지하도록 강성을 강화함과 더불어 클러치와의 마찰에 의한 마찰열의 방열성도 향상할 수 있도록 된 방열과 강성 강화용 플라이 휠에 관한 것이다.

일반적으로 엔진은 도 1에 도시된 바와 같이 실린더(1) 내에서 혼합 가스가 폭발하여 피스톤(2)이 왕복 운동되고, 상기 피스톤(2)과 커넥팅 로드(3)로 연결된 크랭크축(5)이 회전 운동되면서 회전 동력이 발생하게 된다.

또한, 상기 크랭크축(5)에는 그 선단측에 워터펌프(6) 및 밸브기구(7)를 작동하기 위한 크랭크풀리(8) 및 타이밍기어(9)가 설치되어 있고, 반대쪽에는 하우징(H)내로 수용되어 엔진의 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)가 외주 측에 열 박음으로 압입되면서 클러치와 변속기에 회전 동력을 전달하는 플라이휠(10)이 설치되어 있다.

여기서, 상기 플라이휠(10)은 도 2에 도시된 바와 같이, 링기어(11)가 압입된 반대측으로 클러치페달에 의해 플라이휠(10)과 마찰되는 클러치플레이트(22)를 감싸는 클러치커버(21)로 이루어져 엔진과 변속기사이의 회전 전달을 분리 · 연결하는 클러치어셈블리(20)가 구비되어진다.

이러한 플라이휠(10)은 엔진의 4행정 중에서 폭발행정에서 얻어진 토크(Torque)를 흡입· 압축· 배기 행정에 고르게 분배하여 승차감 및 차량 출발성에 맞춘 형상으로 설계됨은 물론 엔진과 변속기를 연결하는 역할로 클러치의 용량에 맞게 설계됨은 물론이다.

그러나, 이와 같은 플라이휠(10)은 도 3에 도시된 바와 같이 크랭크축(5)에 보음트등을 매개로 고정된 상태에서 엔진의 회전력을 변속기로 전달하기 위해 고속으로 회전하면서, 또한 클러치의 조작에 따라 클러치플레이트(22)와 서로 강하게 마찰되면서 엔진의 회전력을 단속하는데 이에 따라, 포트(Port)형 클러치인 경우에는 클러치플레이트(22)의 취부면과 플라이휠(10)좌면 사이의 노치(C : Notch)부위가 회전에 따른 버스트 포스(Burst Force)에 의해 균열(Crack)이 발생될 소지가 있는 문제가 있게 된다.

또한, 트럭과 버스와 같이 대형 디젤엔진을 사용하는 경우에는 플라이휠(10)의 형상도 이너시아(Inertia)값이 매우 큰 형상으로 주철로 제조되는데 특히, 이와 같은 경우에는 빈번하면서 장시간동안 클러치를 조작하는 경우 클러치에서 발생되는 약 250 - 300℃ 정도의 고온에 의해 플라이휠(10)의 열변형을 가져오고 이에 따른 강도 저하는 물론 균열을 발생시킬 수 있는 문제가 있게 된다.

발명이 이루고자 하는 기술적 과제

이에 본 발명은 상기와 같은 점을 감안하여 발명된 것으로, 플라이휠을 서로 결합되는 여러 부분으로 분리해 제작하면서 그 재질을 달리해 버스트포스를 자체적인 탄성을 통해 흡수하면서 클러치의 조작에 의한 마찰열의 방열성도 향상시켜 균열을 방지함에 그 목적이 있다.

상기와 같은 목적을 달성하기 위한 본 발명은, 플라이휠이 링기어가 외주 측에 압입되면서 크랭크축에 결합되는 지지플레이트와, 이 지지플레이트에 일단이 고정되면서 절곡된 내부로 수용공간을 형성하는 커버플레이트, 이 커버플레이트의 안쪽에서 고정되는 인서트플레이트 및 이 인서트플레이트에 접촉됨과 더불어 커버플레이트내에 삽입· 고정되어 클러치 조작에 따라 클러치플레이트로부터 클램핑 로드를 받는 마찰플레이트로 이루어진 것을 특징으로 한다.

발명의 구성 및 작용

이하 본 발명의 실시예를 첨부된 예시도면을 참조로 상세히 설명한다.

도 4는 본 발명에 따른 플라리휠의 구성 단면도를 도시한 것인바, 본 발명은 피스톤(2)의 왕복 운동을 회전운동으로 변환하는 크랭크축(5)에 결합되면서 클러치어셈블리(20)가 장착되는 플라이휠(10)이 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)가 외주 측에 열 박음으로 압입됨과 더불어 보울트등의 고정부재를 통해 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 보울트등의 고정부재를 통해 고정된 일단으로부터 서로 간격을 두도록 절곡되어 그 내부로 수용공간을 형성하는 컵 형상의 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 보울트등의 고정부재를 통해 고정되는 인서트플레이트(10c) 및 이 인서트플레이트(10c)에 접촉됨과 더불어 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작 시 클러치어셈블리(20)의 클러치플레이트(22)와 접촉되어 클램핑로드(F')가 작용되는 마찰플레이트(10d)로 이루어진다.

여기서, 상기 지지플레이트(10a)와 인서트플레이트(10c)는 주철로 이루어지는 반면, 상기 커버플레이트(10b)는 강(Steel)재질로 이루어져 플라이휠(10)에 작용하는 버스트 포스(F)를 자체적인 탄성력을 통해 흡수· 완화시켜주게 된다.

또한, 상기 인서트플레이트(10c)는 클러치 조작에 따라 마찰플레이트(10d)에서 발생되는 마찰열의 전달시 열팽창에 의해 커버플레이트(10b)와의 간섭을 방지하도록 약 1.00 - 1.50mm 정도의 갭(K)을 유지하게 된다.

그리고, 상기 마찰플레이트(10d)는 클러치 조작에 따른 클러치플레이트(22)와의 마찰열을 외부로 발산하도록 그 측면 테두리를 따라 다수의 슬랏(10d')이 형성되어진다.

이하 본 발명의 작동을 첨부된 도면을 참조로 상세히 설명한다.

본 발명은 플라이휠(10)이 일체로 이루어지는 대신 여러 부품들로 이루어지는데 즉, 지지플레이트(10a)에 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)를 열 박음으로 압입시킨 상태에서 커버플레이트(10b)의 안쪽으로 보울트등의 고정부재를 이용해 인서트플레이트(10c) 와 마찰플레이트(10d) 순차적으로 고정한 후, 상기 커버플레이트(10b)와 지지플레이트(10a)를 보울트등의 고정부재를 매개로 결합시킨 상태에서 크랭크축(5)에 결합하여 플라이휠(10)을 조립하게 된다.

이때, 상기 지지플레이트(10a)와 크랭크축(5)사이에는 파이롯 베어링(Pilot Bearing)이 개재됨은 물론이다.

이어, 상기 플라이휠(10)에 클러치어셈블리(20)를 결합하여 클러치 조작시 클러치플레이트(22)에 의해 플라이휠(10)의 마찰플레이트(10d)쪽으로 강하게 작용하는 클램핑로드(F')를 통해 엔진과 변속기사이의 회전력을 단속하게 된다.

이때, 본 발명의 플라이휠(10)은 클러치의 조작에 따라 야기되는 엔진의 회전에 의해 플라이휠(10)에 발생되는 버스트 포스(F)가 강재질로 이루어진 커버플레이트(10b)의 탄성력에 의해 흡수· 완화되거나 또는 제거되고 이로 인해, 상기 커버플레이트(10b)의 모서리부위인 노치 부위로 집중되는 버스트 포스(F)에 의한 균열의 발생을 예방할 수 있게 된다.

또한, 본 발명의 플라이휠(10)은 클러치의 빈번한 조작에 의한 클램핑로드(F')에 의해 클러치플레이트(22)와 마찰플레이트(10d)사이에서 마찰열이 발생되면, 상기 마찰플레이트(10d)에 접촉된 인서트플레이트(10c)로 전달됨과 더불어 마찰플레이트(10d)의 측면 테두리를 따라 형성된 다수의 슬랏(10d')을 통해 보다 빠른 열의 방출이 이루어지게 된다.

이때, 상기 인서트플레이트(10c)로 전달된 마찰열이 방열되는 것보다 적용되는 것이 클 경우에는 인서트플레이트(10c)가 팽창하게 되지만, 이때 상기 인서트플 레이트(10c)가 이를 수용한 커버플레이트(10b)내에서 약 1.00 - 1.50mm 정도의 갭(K)을 유지하므로 열팽창에 의한 커버플레이트(10b)와의 간섭을 방지할 수 있게 됨은 물론이다.

발명의 효과

이상 설명한 바와 같이 본 발명에 의하면, 플라이휠이 링기어가 외주 측에 압입되면서 크랭크축에 결합되는 부분과 클러치 조작에 따라 클러치플레이트로부터 클램핑 로드를 받는 부분으로 분리 제작한 후 서로 조립· 결합시켜, 플라이휠이 적용되는 차종에 관계없이 플라이휠에서 발생되는 버스트포스에 의한 크랙과 클램핑로드에 따른 마찰열의 방열성을 향상시킬 수 있어 내구성을 강화할 수 있는 효과가 있게 된다.

(57) 청구의 범위

청구항 1.
링기어(11)가 압입되어 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 고정된 일단으로부터 절곡되어 그 내부로 수용공간을 형성하는 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 보고정되는 인서트플레이트(10c) 및 상기 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작 시 클러치어셈블리(20)의 클러치플레이트(22)와 접촉되어 마찰력을 발생하는 마찰플레이트(10d)로 이루어진 방열과 강성 강화용 플라이 휠.

청구항 2.
제 1항에 있어서, 상기 지지플레이트(10a)와 인서트플레이트(10c)는 주철로 이루어지는 반면, 상기 커버플레이트(10b)는 탄성을 갖는 강재질로 이루진 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

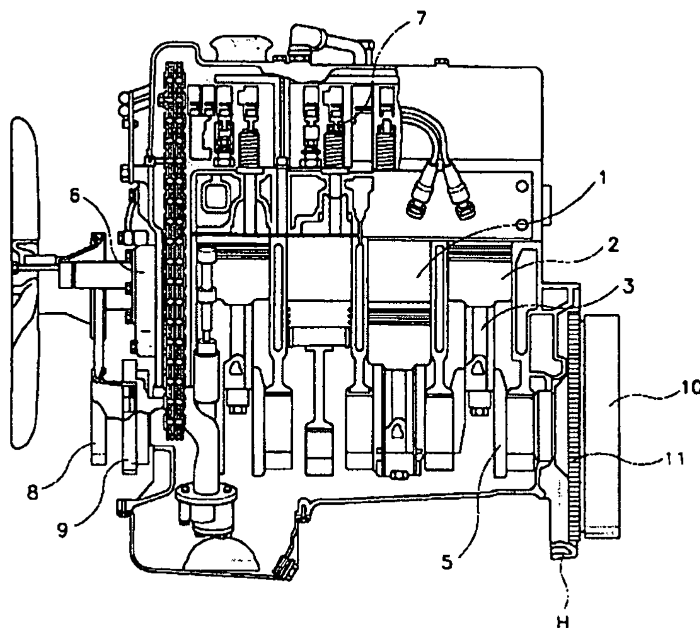
청구항 3.
제 1항에 있어서, 상기 인서트플레이트(10c)는 열팽창에 의해 커버플레이트(10b)와의 간섭을 방지하도록 갭(K)을 형성하는 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

청구항 4.
제 3항에 있어서, 상기 갭(K)은 약 1.00 - 1.50mm 정도인 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

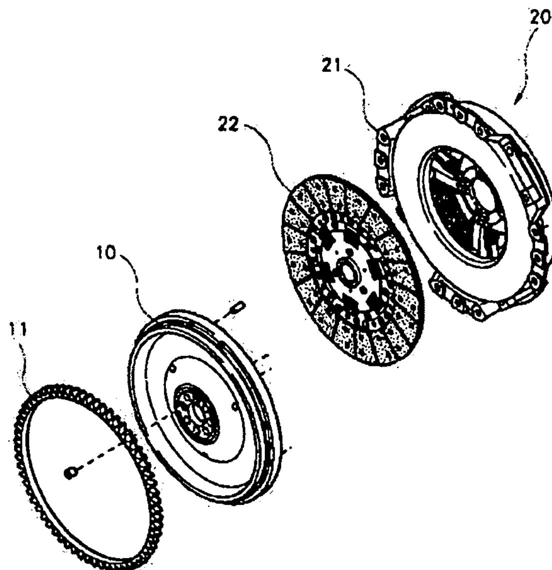
청구항 5.
제 1항에 있어서, 상기 마찰플레이트(10d)는 클러치 조작에 따른 클러치플레이트(22)와의 마찰열을 외부로 발산하도록 그 측면 테두리를 따라 다수의 슬랏(10d')이 형성되어진 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

도면

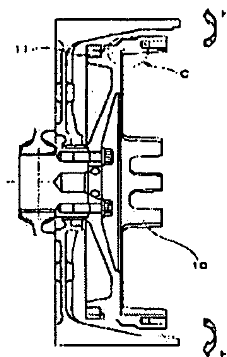
도면1



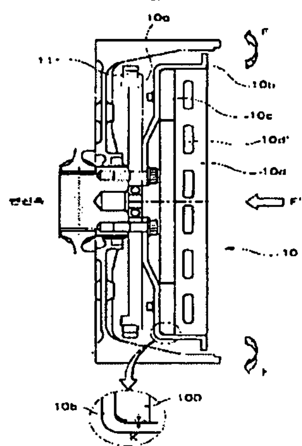
도면2



도면3



도면4



This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

COPY

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 November 2001 (01.11.2001)

PCT

(10) International Publication Number
WO 01/82297 A1

(51) International Patent Classification[7]: G11B 7/24

(21) International Application Number: PCT/EP01/04028

(22) International Filing Date: 9 April 2001 (09.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00201488.4 20 April 2000 (20.04.2000) EP

(71) Applicant: KONINKLIJKE PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).

(72) Inventor: ZHOU, Guo-Fu; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

(74) Agent: DEGUELLE, Wilhelmus, H., G.; Internationaal Octrooibureau B.V., Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

(81) Designated States *(national)*: CA, CN, JP, KR, MX, RU.

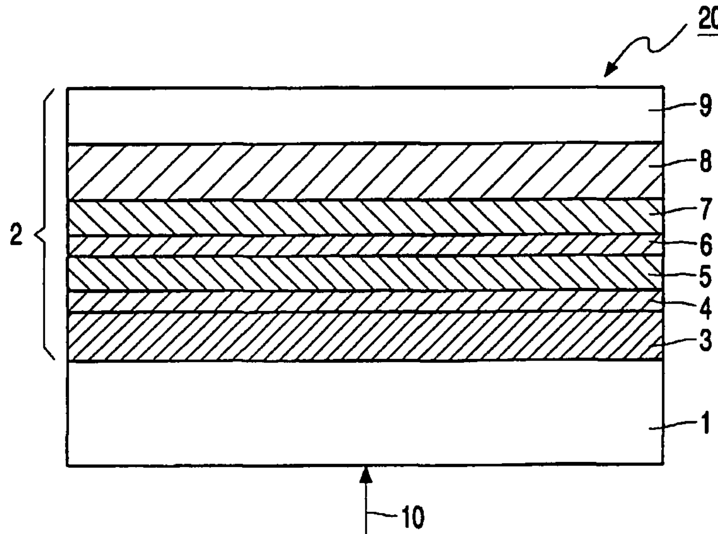
(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY

(54) Title: OPTICAL RECORDING MEDIUM AND USE OF SUCH OPTICAL RECORDING MEDIUM



(57) Abstract: The optical recording medium (20) has a substrate (1) and a stack (2) of layers provided thereon. A phase change recording layer (5), having a melting point T_{mp} is sandwiched between a first (3) and a second (7) dielectric layer. A crystallization-accelerating layer (4, 6) is being interposed in contact with the recording layer (5). Further a reflective layer (8) is present and an optional cover layer (9). The crystallization-accelerating layer (4, 6) consists of a binary metal alloy or a semiconductor and has a melting point T_{mg} at least 250 °C higher than the melting point T_{mp} of the recording layer (5) and has a crystal structure similar to the crystalline state of the recording layer (5).

WO 01/82297 A1

Optical recording medium and use of such optical recording medium

The invention relates to an optical recording medium having a substrate and a stack of layers provided thereon, the stack comprising a recording layer, having a melting point T_{mp} and being able to change between an amorphous and a crystalline state, sandwiched between a first and a second dielectric layer, the first being adjacent to the substrate, a
5 crystallization accelerating layer being interposed in contact with the recording layer, and a reflective layer.

The invention also relates to the use of such an optical recording medium.

10 An optical recording medium of the type mentioned in the opening paragraph is known from Japanese patent application JP-09161316 A. In the known medium the state of the recording layer locally changes from crystalline to amorphous when data are optically recorded.

Optical data storage based on the phase change principle is attractive, because
15 it combines the possibilities of direct overwrite (DOW) and high storage density with easy compatibility with read-only optical data storage systems. Phase-change optical recording involves the formation of submicrometer-sized amorphous recording marks in a crystalline film using a focused relatively high power laser-light beam. During recording information, the medium is moved with respect to the focused laser-light beam that is modulated in
20 accordance with the information to be recorded. Due to this, quenching takes place in the phase-change recording layer and causes the formation of amorphous information bits in the exposed areas of the recording layer that remains crystalline in the unexposed areas. Erasure of written amorphous marks is realized by recrystallizing through heating with the same laser at an intermediate power level, without melting the recording layer. The amorphous marks
25 represent the data bits, which can be read, e.g. via the substrate, by a low-power focused laser-light beam. Reflection differences of the amorphous marks with respect to the crystalline recording layer bring about a modulated laser-light beam which is subsequently converted by a detector into a modulated photocurrent in accordance with the recorded digital information.

One of the most important demands in phase-change optical recording is a high data rate, which means that data can be written in and read from the medium with a rate of at least 30Mbits/s. A high data rate requires the recording layer to have a high crystallization rate, i.e. a short crystallization time. To ensure that the previously recorded amorphous marks can be crystallized during direct overwrite, the recording layer should have a proper crystallization time to match the velocity of the medium relative to the laser-light beam. If the crystallization speed is not high enough to match the velocity of the medium relative to the laser-light beam the amorphous marks from the previous recording, representing old data, cannot be completely erased, meaning recrystallized, during DOW. This causes a high noise level. A high crystallization speed is particularly required in high-density recording and high data rate applications, such as disc-shaped DVD+RW, DVR-red and blue which are abbreviations of new generation high density Digital Versatile Disc+RW, where RW refers to the rewritability of such discs, and Digital Video Recording optical storage discs, where red and blue refer to the used laser wavelength. For these new discs the complete erasure time (CET) has to be at most 60 ns. CET is defined as the minimum duration of the erasing pulse for complete crystallization of a written amorphous mark in a crystalline environment, which is measured statically. For DVD+RW, which has a 4.7 GB recording density per 120 mm disk, a user data bit rate of 33 Mbits/s is needed, and for DVR-red said rate is 35 Mbits/s. For rewritable phase change optical recording systems such as DVR-blue, a user data rate higher than 50 Mbits/s is required.

The known medium of the phase-change type comprises a disc-shaped substrate carrying a stack of layers consisting, in succession, of a first dielectric layer, a Sb_2Te_3 layer as crystallization accelerating layer, a Sb layer as a composition correcting layer, a recording layer of a phase-change $Sb_{72}Te_{28}$ alloy, a second dielectric layer and a metal reflective layer. Such a stack of layers can be referred to as an INP'PIM structure, wherein M represents a reflective or mirror layer, I represents a dielectric layer and P represents a phase-change recording layer while P' represents a composition correction layer which mixes with the recording layer at first recording. A crystallization accelerating layer N of Sb_2Te_3, has been arranged between the first dielectric layer and the correction and the recording layer to achieve a fast crystallization of the medium during erasing information in the medium by means of a laser-light beam. In the known recording medium the N layer has a melting point of 618°C, only 68°C higher than the melting point 550°C of the P layer. The melting point of the known N layer is relatively close to the melting point of the P layer causing the N layer to dissolve in the correction and recording layer P'P after one or at best a few recording/erasure

cycles, whereafter the crystallization accelerating layer N is no longer present and its crystallization-accelerating action is lost.

For complete erasure of an amorphous mark, two processes occur, i.e. nucleation and grain (crystallite) growth. An investigation of the known recording medium
5 has revealed that the known crystallization-accelerating layer N is merely a nucleation-promoting layer.

It is a disadvantage of the known medium that its crystallization accelerating layer only functions for at most a few recording and erasing cycles. This is not sufficient for modern erasable media, which require a stable performance for at least a thousand of
10 recording and erasing cycles.

It is an object of the invention to provide an optical recording medium of the kind described in the opening paragraph, which is suitable for high speed rewritable optical
15 recording, having a CET-value of at most 60 ns.

It is another object of the invention to provide an optical recording medium of the kind described in the opening paragraph, which is suitable for rewritable optical recording, having a stable performance for at least 10^3 recording and erasing cycles.

This object is achieved in accordance with the invention by an optical
20 recording medium as described in the opening paragraph, which is characterized in that the crystallization accelerating layer

- comprises a material selected from the group consisting of binary metal alloys, semiconductors elements and semiconductor alloys and
- has a melting point T_{mg} at least 250°C higher than the melting point T_{mp} of the
25 recording layer and
- has a crystal structure similar to the crystalline state of the recording layer.

The crystallization accelerating layer according to the invention, which will also be abbreviated as G, yields a high crystallization speed of the recording layer because the amorphous marks of the recording layer are in contact with the G-layer. This accelerates the
30 crystallite growth process, leading to a higher crystallization speed. Especially because the crystal structure of the G-layer is similar to, or even the same as, the structure of the crystalline state of the recording layer the crystallization rate of amorphous marks is advantageously increased. The crystal structure of the G-layer then serves as a very good grain growth initialization or nucleation layer for crystallite growth in the recording layer.

The G-layer is always present adjacent to a thermally isolating layer, here the first or second dielectric layer, because a stack having a G-layer between the recording layer and the substrate or the reflection layer cannot realize the desired thermal properties.

An advantage of the G-layer, comprising a material selected from the group
5 consisting of binary metal alloys, semiconductors and semiconductor alloys, is that it has a high melting point. This counteracts dissolving of the G-layer in the recording layer and maintenance of the crystalline structure for a large number of recording and erasing cycles. During recording, the maximum temperature in the recording layer is about 800°C, which is about 1.4 times T_{mp} for a recording layer with a T_{mp} of 550°C. This may be deduced from a
10 temperature calculation based on the presented laser energy during recording and the physical properties of the stack. The melting temperature T_{mg} of the G-layer has to be above this maximum temperature so that the G-layer remains in crystalline state when the recording layer is melted.

Therefore, the melting temperature difference between recording layer and G-
15 layer should be 250°C or larger, but preferably 300°C or larger, taking into consideration a safety margin.

Preferred materials, which may be used as G-layer, are PbTe, Ag_2Te, CrTe, Ge and Si.

In an embodiment of the recording medium the G-layer is arranged between
20 the recording layer and the second dielectric layer. The thickness of the G-layer may be chosen between 0.1 and 10 nm. The thermal conductivity of the crystallization-accelerating layer is generally comparable to that of the recording layer, which is an alloy of metals. However this only has a small effect on the thermal behaviour of the stack because the thickness of the G-layer is generally relatively small compared to the other layers in the
25 stack. This facilitates the thermal design of the stack.

In another embodiment the crystallization time is reduced further in that a second G-layer is arranged between the recording layer and the first dielectric layer. Thus a G-layer is arranged on both sides of the recording layer. The second G-layer may be of a material similar or identical to the material of the other G-layer. The crystallization time is
30 reduced because now a crystalline layer, which accelerates the crystallite growth process, is present against the recorded amorphous mark on both sides. The thicknesses of the G-layers are between 0.1 and 10nm, preferably lower than 5 nm.

In a specific embodiment the two G-layers present on either side of the recording layer are substantially equal both in thickness and in composition. Equal in

thickness means to within 10% of each other. The equality of the thicknesses is advantageous in the manufacturing of the medium. In general the stack is deposited by evaporation or by sputtering in a vacuum chamber, where substrates move stepwise along a series of stations having targets of different compositions. The dwell time at each station is about equal, and
5 the thickness of the layer deposited at a station is determined in part by switching the deposition process on and off. Consequently, the deposition of a relatively thin layer may require less time than available at a station, whereas the deposition of a relatively thick layer may even require two adjacent stations having the same target. It is therefore advantageous to choose to replace a relatively thick layer and a relatively thin layer by two layers of about
10 equal thickness and composition, thereby reducing the number of deposition stations and the manufacturing time of a stack.

In a specific embodiment the recording layer comprises an alloy of Q, In, Sb and Te, wherein Q is selected from the group consisting of Ag and Ge.

The preferred composition comprises $Q_a\, In_b\, Sb_c\, Te_d$ (in atomic percentages),
15 wherein Q is selected from the group consisting of Ag and Ge;

$2 \leq a \leq 9$

$0 < b \leq 6$

$55 \leq c \leq 80$

$16 \leq d \leq 30$; $a + b + c + d = 100$.

20 In another specific embodiment the recording layer comprises a compound of Ge, Sb and Te. The preferred composition of this compound is defined by the formula

$Ge_{50x}Sb_{40-40x}Te_{60-10x}$ (in atomic percentages), wherein $0.166 \leq x \leq 0.444$;

the recording layer having a thickness of 5 to 35 nm;

This composition exists on a part of the line connecting the compounds GeTe
25 and Sb_2Te_3 in the triangular Ge-Sb-Te composition diagram and includes the stoichiometric compounds $Ge_2Sb_2Te_5$ (x = 4/9), $GeSb_2Te_4$ (x = 2/7) and $GeSb_4Te_7$ (x = 1/6). Especially these ternary stoichiometric compounds are preferred, because these materials crystallize rapidly since no segregation is required during crystallization.

The first and second dielectric layers are preferably made of a mixture of ZnS
30 and SiO_2, e.g. $(ZnS)_{80}(SiO_2)_{20}$. The layers may alternatively be made of SiO_2, TiO_2, Ta_2O_5, ZnS, AlN and/or Si_3N_4. The dielectric layer through which the laser light enters the stack preferably has a thickness of 70 to $(70+\lambda/2n)$ nm wherein n is the refractive index of the first dielectric layer and λ is the wavelength of the read/write laser-light beam. If the total

thickness is smaller than 70 nm, the cyclability is reduced considerably. The cyclability is measured by the relative change of the optical contrast M_0 after a large number of DOW-cycles, e.g. 10^3. The optical contrast M_0 is defined as $|R_C-R_A|/R_C$, where R_C and R_A are the reflections of the recording material in the crystalline and amorphous state respectively.
5 Another way to define cyclability is related to jitter increase of the medium. Jitter is a measure of the distortion of the shape of a recording mark, and is measured as a time shift of rising and falling edges in the information signal. The jitter of the medium should be at a low, constant level during at least 10^3 DOW-cycles.

As mentioned above the total thickness of the first dielectric layer is preferably
10 smaller than $(70+\lambda/2n)$ nm. A larger total thickness does not further increase the cyclability and is more expensive to make. If for example the wavelength is equal to 630 nm and the refractive index is 1.5, the thickness range extends from 70 nm to 280 nm.

The dielectric layer, which is closest to the reflective layer, has a thickness of 10 to 40 nm. Preferably the thickness of the dielectric layer adjacent to the reflective layer is
15 larger than or equal to 15 nm. A smaller thickness results in an increased cooling rate of the recording layer and, consequently, an undesirable increase in the write power. The thickness is preferably smaller than 40 nm. A larger thickness decreases the thermal contact between the recording layer and the reflective layer too much, resulting in too low a cooling rate of the recording layer and a worse recording performance.

20 The reflective layer may comprise metals such as Al, Ti, Au, Ni, Cu, Ag and Cr, and alloys of these metals. The reflective layer preferably has a thickness of 60 to 120 nm.

Both the reflective layers and the dielectric layers generally have been provided by vapour deposition or sputtering.

25 Optionally an outermost layer may be present on the stack as a cover layer that protects the underlying layers from the environment. The cover layer is made of, for example, an UV light-cured poly(meth)acrylate.

Another specific embodiment is characterized in that the reflective layer is present between the substrate and the first dielectric layer. Optionally a cover layer, that is
30 transparent for laser-light and has a surface which allows optical recording of information into and reading of information from the underlying recording layer with a focused laser-light beam is present on top of the stack. Thus in this embodiment the optical recording medium is written in and read out through the cover layer. This method is used in the new DVR discs that were mentioned above. The cover layer of a DVR disc has a thickness of about 100

micrometers. This cover layer allows the use, in optical disc recorders, of a read/write lens with a high numerical aperture that is necessary for high density recording and reading. Because the laser light enters the medium through the cover layer it may be necessary to adjust the thicknesses of the layers of the stack in order to optimize for optimal optical
5 contrast between recorded and unrecorded areas.

The term high-speed recording, which was mentioned above, is to be understood to mean in this context a linear velocity of the medium relative to the laser-light beam of at least 7.2 m/s, which is six times the speed according to the Compact Disc standard. The use of an optical recording medium according to the invention is therefore
10 advantageous because the crystallization rate is fast enough to permit at least this recording velocity. The important parameter is the CET (in ns), which is defined above. The CET is inversely proportional to the crystallization rate.

The substrate of the information medium generally is transparent to the laser wavelength, and is made, for example, of polycarbonate, polymethyl methacrylate (PMMA),
15 amorphous polyolefin or glass. In a typical example, the substrate is disc-shaped and has a diameter of 120 mm and a thickness of 1.2 mm, 0.6 mm or 0.1 mm for respectively low, medium and high information density applications.

Alternatively, the substrate may be in the form of a synthetic resin flexible tape, made e.g. from a polyester film. This flexible tape, with a stack of layers deposited
20 thereon, is called an optical tape and can be suited for use in an optical tape recorder, which is for example based on a fast spinning polygon. In such a device the reflected laser-light beam scans transversely across the tape surface.

The surface of the disc-shaped substrate on the side of the recording layer is, preferably, provided with a servotrack that can be scanned optically. This servotrack is often
25 constituted by a spiral-shaped groove and is formed in the substrate by means of a mould during injection moulding or pressing. This groove can be alternatively formed in a replication process in a synthetic resin layer, for example, of an UV light-cured layer of acrylate, which is separately provided on the substrate. In high-density recording such a groove has a pitch e.g. of 0.5 - 0.8 μm and a width of about half the pitch.

30 High-density recording and erasing can be achieved by using a short-wavelength laser, e.g. with a wavelength of 675 nm or shorter (red to blue).

The phase change recording layer as well as the G-layer can be applied by vapour depositing or sputtering of a suitable target. The recording layer thus deposited is amorphous and exhibits a low reflection. In order to constitute a suitable recording layer

having a high reflection, this layer must first be completely crystallized, which is commonly referred to as initialization. For this purpose, the recording layer can be heated in a furnace to a temperature just above the crystallization temperature of the e.g. Ge-In-Sb-Te or Ge-Sb-Te compound, e.g. 200°C. A synthetic resin substrate, such as polycarbonate, to which a high
5 temperature may cause damage, can alternatively be heated by a laser-light beam of sufficient power. This can be realized, e.g. in a recorder, in which case a laser beam scans the moving recording layer. The amorphous layer is then locally heated to the temperature required for crystallizing the layer, without the substrate being subjected to a disadvantageous heat load.

If desired, an additional, optically transparent, metal layer M' can be
10 interposed in the stack, thereby forming a so called MIRIM'-structure, wherein R represents a layer stack comprising a recording layer and at least one crystallization accelerating layer according to the present invention. Although the structure becomes more complicated, the additional metal layer increases the cooling rate of the recording layer as well as the optical contrast M_0.

15 Embodiments of the optical recording medium of the invention will be described with reference to the drawings.

In the drawings:

20 Fig. 1 shows a schematic cross sectional view of a first embodiment of the optical recording medium.

Fig. 2. shows a view as shown in FIG.1 of a second embodiment.

Fig. 3 shows a view as in FIG2 of a third embodiment.

25

In Fig. 1 the optical recording medium 20 has a substrate 1 and a stack 2 of layers provided thereon. The substrate 1 may be made of, for example, a sheet of plastic, e.g. polycarbonate, or glass. In Fig. 1 the stack 2 comprises a phase change recording layer 5, having a melting point T_{mp} and being able to change between an amorphous and a crystalline
30 state, that is sandwiched between a first 3 and a second 7 dielectric layer, the first 3 being adjacent to the substrate 1. In this embodiment both the first dielectric layer 3 and the second dielectric layer 7 are made of the material $(ZnS)_{80}(SiO_2)_{20}$ and have a thickness of 125 nm and 20 nm respectively. A crystallization accelerating layer 6, abbreviated as G-layer, is interposed in contact with the recording layer 5, which comprises an alloy of Q, In, Sb and

Te, wherein Q is selected from the group consisting of Ag and Ge. A reflective layer 8 is present on top of the stack 2. Reflective layer 8 is a 100 nm layer of Al or an aluminium alloy, e.g. AlCr or AlTi. The crystallization accelerating layer 6 comprises a binary metal alloy or a semiconductor element or semiconductor alloy and has a melting point T_{mg} at least
5 250°C higher than the melting point T_{mp} of the recording layer 5. The crystal structure of these materials is similar to the crystalline state of the recording layer 5. In this embodiment the recording layer 5 is made of $Ge_{6.2}In_{3.2}Sb_{71.1}Te_{19.6}$, which has a thickness of 12 nm. The embodiment shown has a cover layer 9 that may be made of an organic material, e.g. a UV-cured resin. A focused laser-light beam with a wavelength λ=405 nm enters the medium
10 through the substrate 1. This beam is diagrammatically illustrated by means of an arrow 10 in Fig. 1.

In this embodiment, when using PbTe as G-layer, which has a thickness of 3 nm, the CET has been measured to be equal to 40 ns, which is sufficiently short to allow high-speed recording. When no G-layer is present a minimal CET value of 48 ns can be
15 obtained. Other preferred materials as G-layer are Ag_2Te, CrTe, Ge or Si. The melting points T_{mg} of bulk PbTe, Ag_2Te, CrTe, Ge and Si are 914, 960, 1292, 936 and 1414°C respectively. The write power for the medium is relatively low and is 9 mW at the entrance face of the medium at a relative speed between the radiation beam and the medium of 7.2 m/s. The R_A and R_C are measured to be 4.3% and 23% respectively.
20 The cyclability is measured as the number of rewrite cycles where the jitter has increased to 12% of the clock time T_C. The jitter is the standard deviation of the difference between the rising and falling edges in the information signal and the data clock recovered from the information signal. As an example, for a standard CD format written with the so-called EFM code at the CD speed of 1.2 m/s and clock time of 230 ns, the jitter should
25 be lower than 28 ns. The number of overwrite cycles before deterioration of the medium becomes noticeable, e.g. the jitter has increased to 12% of the clock time, is larger than 10^3. The jitter of a pattern read from the medium as a function of the overwrite cycle does not show a large overshoot.

During writing, the recording layer 5 of $Ge_{6.2}In_{3.2}Sb_{71.1}Te_{19.6}$ is heated to a
30 temperature of about 750°C, well above its melting temperature, which is about 550°C. The temperature during recording is below the melting temperature of the G-layer 6 comprising PbTe. The high melting temperature of the material used for the G-layer neighbouring the recording layer 5 therefore results in an increased cyclability of the recording medium.

In application JP-09161316 A the crystallization accelerating layer N of Sb_2Te_3, which has a melting point of 618°C, is thus heated above its melting temperature, causing the atoms in the layer to become mobile. These atoms are then able to diffuse into the recording layer. The properties of the recording layer are affected by the influx of foreign
5 atoms, resulting in a deterioration of the recording process.

In Fig. 2 and Fig. 3 corresponding reference numerals denote the same layers as in Fig. 1.

In Fig. 2 a second crystallization accelerating layer 4 similar to the crystallization accelerating layer 6 is arranged between the recording layer 5 and the first
10 dielectric layer 3. Now G-layers 4, 6 are present on both sides adjacent to the recording layer 5. The G-layer 6 is made of PbTe and has a thickness of 1.5 nm. The second G-layer 4 is substantially equal both in thickness and in composition to the G-layer 6. The recording layer 5 has a thickness of 10 nm. Further the characteristics of the stack 2 are the same as in Fig. 1. The CET is measured to be 36 ns. The CET in this embodiment is smaller than in the
15 embodiment with only one G-layer. The R_A and R_C are measured to be 4.6% and 22% respectively.

In Fig. 3 the reflective layer 8 is present between the substrate 1 and the first dielectric layer 3. In this embodiment the laser light 10 is entering the stack 2 through the cover layer 9 which has a thickness of 100 μm. The cover layer 9 has a uniform thickness,
20 thereby improving the optical read and write performance in underlying recording layers when the read or write laser beam passes through said cover layer 9. For example a 100 μm cover layer 9 is used for the new 60 mm radius Digital Video Recording (DVR) disc. This disc is recorded in and read out through this cover layer 9, which therefore has to be of good optical quality. Preferably, the cover layer 9 is 100+/-3 μm thick up to radius 58.5 mm. The
25 cover layer 9 is made from a UV-cured resin. Dielectric layer 3 and 7 have a thickness of 20 nm and 125 nm respectively and are made of the same dielectric material as in Fig. 1. G-layer 4, 6 are made of the same material as in Fig. 2 and both have a thickness of 1.5 nm. Recording layer 5 has a thickness of 10 nm. For characteristics that are not specifically mentioned reference is made to the description of Fig. 1.
30 Preferably, for all embodiments, the surface of the disc-shaped substrate 1 on the side of the stack 2 is provided with a servotrack that can be scanned optically. This servotrack is often constituted by a spiral-shaped groove and is formed in the substrate by means of a mould during injection moulding or pressing. This groove can be alternatively formed in a replication process in a synthetic resin layer, for example, of an UV light-cured

layer of acrylate, which is separately provided on the substrate 1. In high-density recording such a groove has a pitch e.g. of 0.5 - 0.8 μm and a width of about half the pitch.

In a modification of the recording medium of Fig. 3, the recording layer 5 comprises an alloy of Ge, Sb and Te, e.g. $Ge_2Sb_2Te_5$.

5 It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. The word "comprising" does not exclude the presence of elements or steps other than those listed

10 in a claim. The word "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

According to the invention an optical recording medium is provided, which is

15 suitable for high speed recording, e.g. with a possible data rate higher than 50 Mbits/s, and which is suitable for direct overwrite for a least 10^3 times.

CLAIMS:

1. An optical recording medium (20) having a substrate (1) and a stack (2) of layers provided thereon, the stack comprising a recording layer (5), having a melting point T_{mp} and being able to change between an amorphous and a crystalline state, sandwiched between a first (3) and a second (7) dielectric layer, the first (1) being adjacent to the
5 substrate (1), a crystallization accelerating layer (4, 6) being interposed in contact with the recording layer (5), and a reflective layer (8), characterized in that the crystallization accelerating layer (4, 6)

- comprises a material selected from the group consisting of binary metal alloys, semiconductors elements and semiconductor alloys and
10 - has a melting point T_{mg} at least 250°C higher than the melting point T_{mp} of the recording layer (5) and
- has a crystal structure similar to the crystalline state of the recording layer (5).

2. An optical recording medium (20) as claimed in Claim 1 characterized in that
15 the crystallization accelerating layer (4, 6) comprises a material selected from the group consisting of PbTe, Ag_2Te, CrTe, Ge and Si.

3. An optical recording medium (20) as claimed in any of Claims 1 or 2, characterized in that the crystallization accelerating layer (6) is arranged between the
20 recording layer (5) and the second dielectric layer (7).

4. An optical recording medium (20) as claimed in Claim 3, characterized in that a second crystallization accelerating layer (4) similar to the crystallization accelerating layer (6) is arranged between the recording layer (5) and the first dielectric layer (3).

25

5. An optical recording medium (20) as claimed in Claim 4, characterized in that the second crystallization accelerating layer (4) is substantially equal both in thickness and in composition to the crystallization accelerating layer (6).

6. An optical recording medium (20) as claimed in Claim 1, characterized in that the recording layer (5) comprises an alloy of Q, In, Sb and Te, wherein Q is selected from the group consisting of Ag and Ge

5 7. An optical recording medium (20) as claimed in Claim 1, characterized in that the recording layer (5) comprises an alloy of Ge, Sb and Te.

8. An optical recording medium (20) as claimed in Claim 1, characterized in that the reflective layer (8) is present between the substrate (1) and the first dielectric layer (3).

10

9. The use of an optical recording medium (20), which medium is claimed in any one of the preceding claims, characterized in that the linear velocity of the medium relative to a laser-light beam (10) is at least 7.2 m/s.

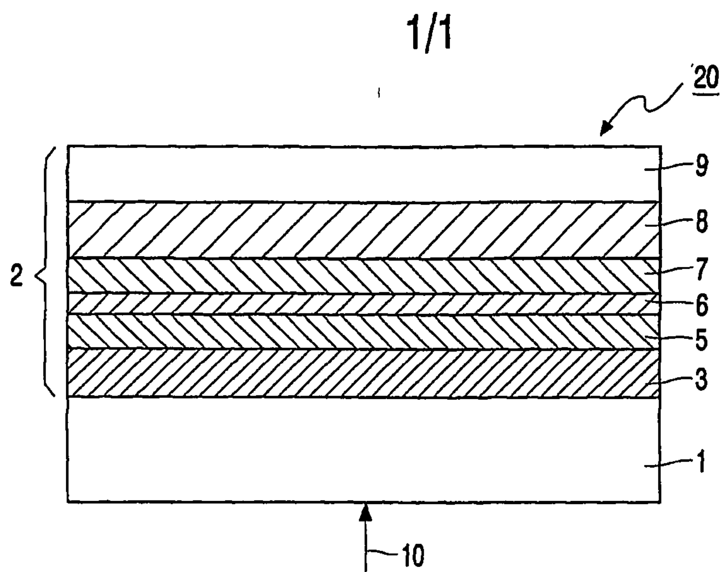


FIG. 1

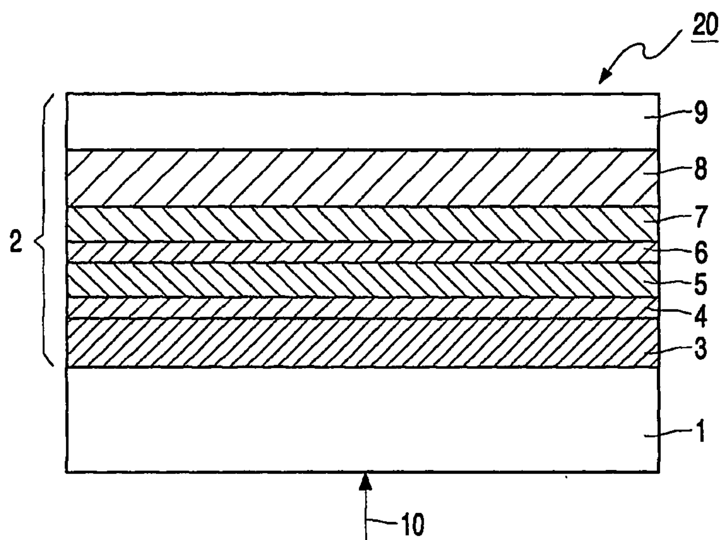


FIG. 2

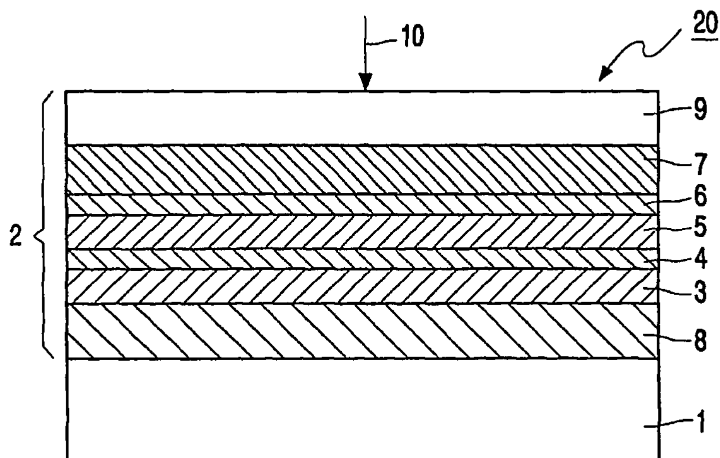


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/04028

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 980 068 A (ASAHI CHEMICAL IND) 16 February 2000 (2000-02-16) abstract paragraph '0012! - paragraph '0019! paragraph '0038!; figure 1	1,2,7
Y		8
A		3,4,9
Y	EP 0 431 489 A (HITACHI LTD) 12 June 1991 (1991-06-12) column 16, line 28 - line 56; figure 18	8

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 August 2001	16/08/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Annibal, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/04028

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 945 860 A (MATSUSHITA ELECTRIC IND CO LTD) 29 September 1999 (1999-09-29) abstract paragraph '0017! paragraph '0018! paragraph '0034! paragraph '0035! paragraph '0050! paragraph '0084!; figures 1,2	1,3-7,9
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 552 (P-1815), 20 October 1994 (1994-10-20) & JP 06 195747 A (NEC CORP), 15 July 1994 (1994-07-15) abstract	1,7,9
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 384 (P-1575), 19 July 1993 (1993-07-19) -& JP 05 062249 A (MATSUSHITA ELECTRIC IND CO LTD), 12 March 1993 (1993-03-12) abstract	1,7,9
X	EP 0 843 874 A (PHILIPS ELECTRONICS NV) 27 May 1998 (1998-05-27) column 25, line 10 -column 26, line 38; examples 10,11	1,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 01/04028

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0980068	A	16-02-2000	AU	724629 B	28-09-2000
			AU	6851698 A	11-11-1998
			CN	1252885 T	10-05-2000
			WO	9847142 A	22-10-1998
EP 0431489	A	12-06-1991	JP	2804130 B	24-09-1998
			JP	3198224 A	29-08-1991
			AU	3684393 A	17-06-1993
			AU	6770890 A	29-08-1991
			CA	2031672 A,C	07-06-1991
			DE	69032001 D	05-03-1998
			DE	69032001 T	18-06-1998
			EP	0802530 A	22-10-1997
			US	5583840 A	10-12-1996
EP 0945860	A	29-09-1999	CN	1233042 A	27-10-1999
			JP	11339311 A	10-12-1999
			TW	419654 B	21-01-2001
JP 06195747	A	15-07-1994	NONE		
JP 05062249	A	12-03-1993	JP	3049864 B	05-06-2000
EP 0843874	A	27-05-1998	WO	9745830 A	04-12-1997
			JP	11509941 T	31-08-1999
			TW	419645 B	21-01-2001
			US	6009384 A	28-12-1999

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

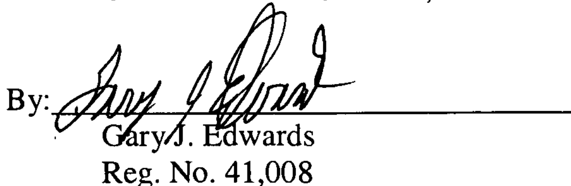
Applicant petitions for a two month extension of time to reply to the Office action of September 9, 2006. The Commissioner is hereby authorized to charge the fee of $450.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 955594467 US

02/12/2007 EFLORES 00000096 060916 10101863
01 FC:1252 450.00 DA

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 10/101,863	Filing Date 03/16/2002	☐ To be Mailed

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY ☒ RATE ($)	FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =			X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							
			TOTAL			TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

AMENDMENT	02/06/2007	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 36	Minus	** 39	= 0	X $25 =	0	OR	X $ =	
	Independent (37 CFR 1.16(h))	* 3	Minus	***5	= 0	X $100 =	0	OR	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE	**0**	OR	TOTAL ADD'L FEE	

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =		OR	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =		OR	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
Stella Little

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

TWELFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed non-patent literature documents are attached. A copy of the U.S. patent publications is not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

03/21/2007 EEKUBAY1 00000028 060916 10101863
01 FC:1806 180.00 DA

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

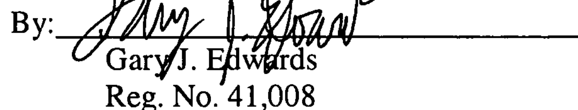
Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

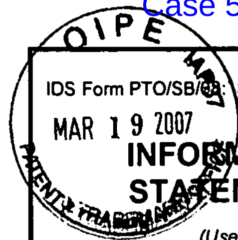
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 19, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 977728611 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	1	of	1	*Attorney Docket Number*	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-2001/0034106 A1	10-25-2001	Moise et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action and Terminal Disclaimer dated March 1, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Office Action dated March 1, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Office Action dated March 14, 2007, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Office Action dated February 20, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Office Action dated March 6, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Notice of Allowance dated February 21, 2007, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
		Notice of Allowance dated February 22, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 977728611 US**

04-03-07

2823

IFW

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

FOURTEENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed non-patent literature documents are attached. Copies of the U.S. patent and patent publication are not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

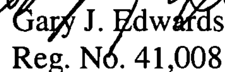
Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

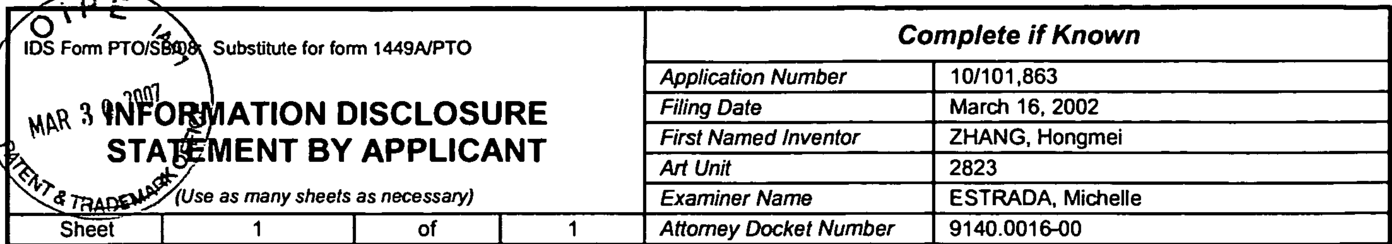
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 30, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 977728497 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

OIPE MAR 3 0 2007 PATENT & TRADEMARK OFFICE

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-6,391,166 B1	05-21-2002	Wang	
		US-20070053139 A1	03-08-2007	Zhang et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action dated March 19, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Response to Office Action dated March 30, 2007, 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Notice of Allowance dated March 26, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Supplemental Notice of Allowance dated March 15, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	
		Voluntary Amendment dated March 8, 2007, in TW Appl. No. 93114518 (Attorney Docket No. 9140.0033-00270).	
		Application filed March 22, 2007 (Attorney Docket No. 9140.0033-01).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 977728497 US

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	9140.0016-00	6938

22852 7590 05/02/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	

ART UNIT	PAPER NUMBER
2823	

MAIL DATE	DELIVERY MODE
05/02/2007	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No.	Applicant(s)	
	10/101,863	ZHANG ET AL.	
	Examiner	Art Unit	
	Michelle Estrada	2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on _06 February 2007_.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) _2-13,21-24 and 40-60_ is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) _2-13,21-24 and 40-60_ is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _2/6/07,3/30/07,3/19/07_.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

DETAILED ACTION

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21, 40-45 and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claims 21, 40, 43 and 52, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13) such that the target voltage opscillates between positive and negative voltages; and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation "the filter is a band rejection filter at a frequency of the bias power" is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claims 8 and 52, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12, 49 and 55, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claims 56-60, One of ordinary skill in the art would have been led to the recited time pulse, bias power and frequency to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of time pulse, bias power and frequency, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233

(CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed time pulse, bias power and frequency or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen time pulse, bias power and frequency or upon another variable recited in a claim, the Applicant must show that the chosen time pulse, bias power and frequency are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935,

1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Response to Arguments

Applicant's arguments filed 2/6/07 have been fully considered but they are not persuasive. Applicant argues that Smolanoff et al. do not disclose a target voltage that oscillates between positive and negative voltages. However, Smolanoff is using and RF bias power, which will make the voltage to oscillate between positive and negative voltages, it doesn't matter if they are using just the negative voltage it will oscillate.

Applicant argues that Smolanoff et al. is directed to deposit conducing layers. However, Applicant claim is directed to an oxide, it doesn't say it can't be a conducting

oxide. Therefore, the process suggested by Smolanoff et al. with the remaining references is encompassed by the instant claims.

Conclusion

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL.** See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

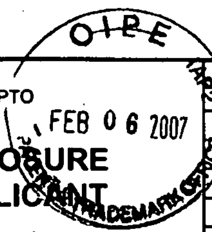
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
April 30, 2007



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	3	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
ME		US-6,088,492	07-11-2000	Kaneko et al.	
		US-6,154,582	11-28-2000	Bazylenko et al.	
		US-2002/0191916 A1	12-19-2002	Frish et al.	
		US-2003/0044118 A1	03-06-2003	Zhou et al.	
		US 2003/0143853 A1	07-31-2003	Celii et al.	
ME		US 2005/0175287 A1	08-11-2005	Pan et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
ME		KR 2003-0088236	11-19-2003	Hyundai Motor Co Ltd		Abstract
ME		WO 01/82297 A1	11-01-2001	Koninklijke Philips Electronics N.V.		

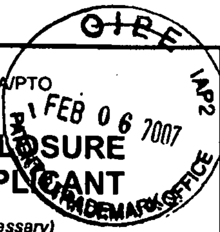
NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
ME		BELKIND, A. et al., "Pulsed-DC Reactive Sputtering of Dielectrics: Pulsing Parameter Effects," 43rd Annual Technical Conference Proceedings-Denver: 86-90 (April 15-20, 2000).	
		SCHOLL, R., "Power Supplies for Pulsed Plasma Technologies: State-Of-The-Art And Outlook," Advances Energy Industries, Inc., pages 1-8 (1999).	
		SCHOLLI, R., "Power Systems for Reactive Sputtering of Insulating Films," Advances Energy Industries, Inc., pages 1-8 (August 2001).	
		Final Office Action dated October 12, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Final Office Action dated November 3, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00).	
ME		Office Action dated December 1, 2006, in U.S. Application No. 10,291,179 (Attorney	

Examiner Signature	Michelle Estrada	Date Considered	4/26/07

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 955594467 US**



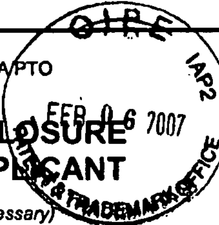
IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	2	of	3	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		Docket No. 9140.0001-00).	
ME		Amendment dated October 19, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
↓		Office Action dated December 18, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
↓		Response to Office Action dated September 11, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
↓		Office Action dated December 1, 2006, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
↓		Office Action dated October 31, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
↓		Response to Office Action dated December 6, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
↓		Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/228,834 (Attorney Docket No. 9140.0016-02).	
↓		Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/191,643 (Attorney Docket No. 9140.0016-04).	
↓		Final Office Action dated October 19, 2006, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
↓		Voluntary Amendment dated July 26, 2006 in TW Appl. No. 92123625 (Attorney Docket No. 9140.0025-00270).	
↓		Response to Final Office Action dated August 3, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
↓		Notice of Allowance dated October 23, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
↓		Office Action dated October 12, 2006, for U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
ME		Response to Office Action dated December 21, 2006, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
no translation		~~Office Action dated September 22, 2006 from Korean Patent Office in Appl. No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).~~	
ME		Response to Office Action dated November 8, 2006, to the Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).	
↓		Response to Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated August 11, 2006 (Attorney Docket No. 9140.0030-00256).	
ME		Final Office Action dated October 26, 2006, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	

Examiner Signature	Michelle Estrada	Date Considered	4/26/07

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 955594467 US



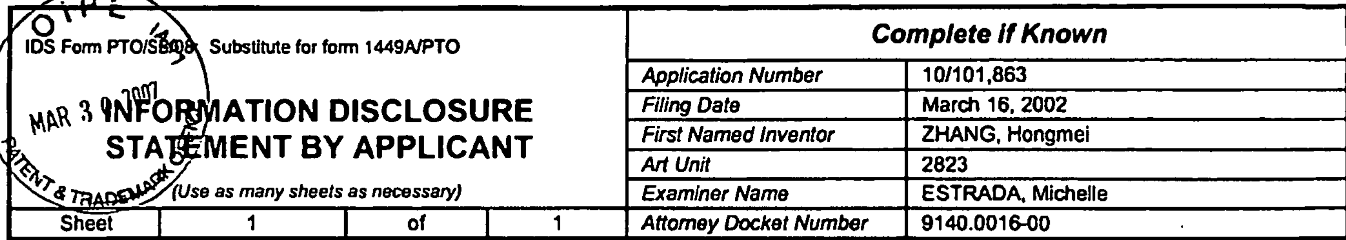
IDS Form PTO/SB/08: Substitute for form 1449A/PTO **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** *(Use as many sheets as necessary)*				***Complete if Known***	
				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
				Examiner Name	ESTRADA, Michelle
Sheet	3	of	3	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
ME		Response to Office Action dated January 26, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	
		Preliminary Amendment dated July 21, 2006, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
		Supplemental Preliminary Amendment, Substitute Specification with Markings, Substitute Specification without Markings, and Replacement Drawing Sheets dated December 6, 2006 in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
		Continuation application and Preliminary Amendment dated December 13, 2006 (Attorney Docket No. 9140.0042-01).	
		Voluntary Amendment dated August 15, 2006 in TW Appl. No. 94143175 (Attorney Docket No. 9140.0042-00270).	
ME		PCT International Search Report and Written Opinion for Application No. PCT/US05/44781 dated October 3, 2006 (Attorney Docket No. 9140.0042-00304).	

Examiner Signature	Michelle Estrada	Date Considered	4/26/07

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 955594467 US



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	1	Attorney Docket Number	9140.0016-00

OIPE MAR 3 0 2007 PATENT & TRADEMARK OFFICE

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
/ME/		US-6,391,166 B1	05-21-2002	Wang	
/ME/		US-20070053139 A1	03-08-2007	Zhang et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
/ME/		Response to Office Action dated March 19, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
/ME/		Response to Office Action dated March 30, 2007, 10/954,182 (Attorney Docket No. 9140.0016-01).	
/ME/		Notice of Allowance dated March 26, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
/ME/		Supplemental Notice of Allowance dated March 15, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	
/ME/		Voluntary Amendment dated March 8, 2007, in TW Appl. No. 93114518 (Attorney Docket No. 9140.0033-00270).	
/ME/		Application filed March 22, 2007 (Attorney Docket No. 9140.0033-01).	

Examiner Signature	/Michelle Estrada/	Date Considered	04/26/2007

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EV 977728497 US**

OIPE MAR 1 9 2007 PATENT & TRADEMARK

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
/ME/		US-2001/0034106 A1	10-25-2001	Moise et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

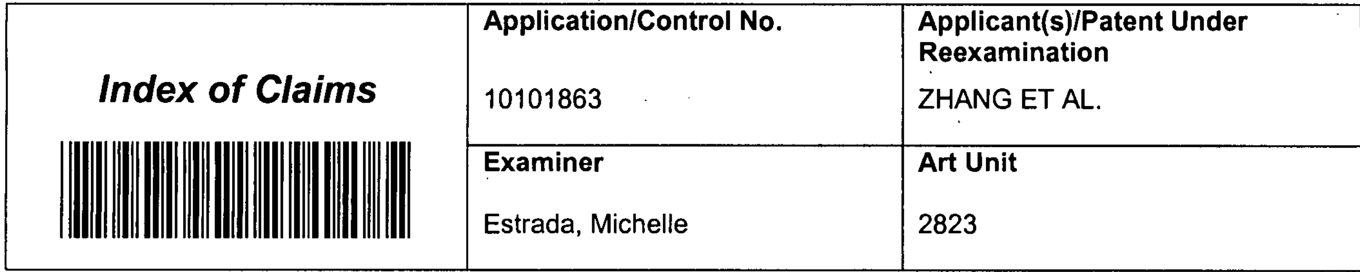
NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
/ME/		Response to Office Action and Terminal Disclaimer dated March 1, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Office Action dated March 1, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Office Action dated March 14, 2007, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Office Action dated February 20, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Office Action dated March 6, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Notice of Allowance dated February 21, 2007, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00).	
/ME/		Notice of Allowance dated February 22, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00).	

Examiner Signature	/Michelle Estrada/	Date Considered	4/26/07

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 977728611 US

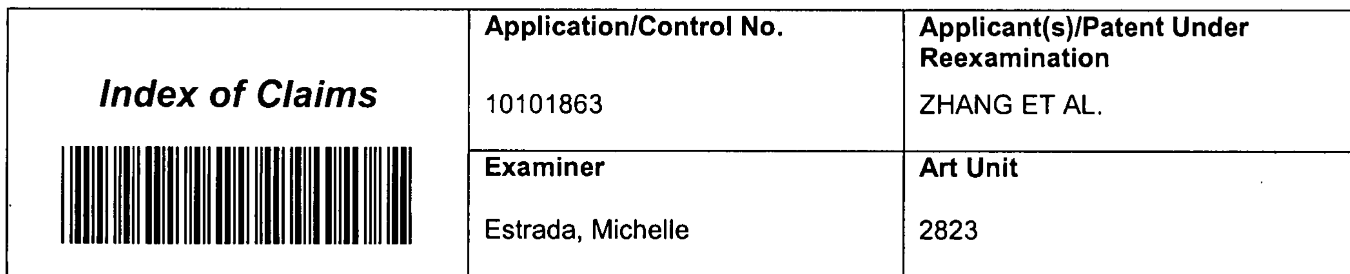


Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	Art Unit
	Estrada, Michelle	2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	04/30/2007								
	1	-								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
	12	✓								
	13	✓								
	14	-								
	15	-								
	16	-								
	17	-								
	18	-								
	19	-								
	20	-								
	21	✓								
	22	✓								
	23	✓								
	24	✓								
	25	-								
	26	-								
	27	-								
	28	-								
	29	-								
	30	-								
	31	-								
	32	-								
	33	-								
	34	-								
	35	-								
	36	-								



Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	**Art Unit**
	Estrada, Michelle	2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	04/30/2007								
	37	-								
	38	-								
	39	-								
	40	✓								
	41	✓								
	42	✓								
	43	✓								
	44	✓								
	45	✓								
	46	✓								
	47	✓								
	48	✓								
	49	✓								
	50	✓								
	51	✓								
	52	✓								
	53	✓								
	54	✓								
	55	✓								
	56	✓								
	57	✓								
	58	✓								
	59	✓								
	60	✓								

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	Confirmation No.: 6938
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	
	)	

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the document on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the listed foreign document and non-patent literature documents are attached.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicants determine that the cited documents do not constitute

"prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: ____________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EM 100825487 US**

10-04-07

REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL	Application Number: 10/101,863	Confirmation Number: 6938
	Filing Date: March 16, 2002	
	First Named Inventor: ZHANG, Hongmei	
	Group Art Unit: 2823	
	Examiner: ESTRADA, Michelle	
	Attorney Docket Number: 10655.0016-00	

Address to:
Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of the above-identified application.

Request for Continued Examination (RCE) practice under 37 C.F.R. § 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application.

1. **Submission required under 37 C.F.R. § 1.114: Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment.**
   - a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.
     - i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on ________.
     - ii. ☐ Other ________________
   - b. ☐ DO NOT ENTER the amendment(s) previously filed on ________. An alternate submission is attached.
   - c. ☒ Enclosed submission: .
     - i. ☒ Amendment/Reply
     - ii. ☐ Affidavit(s)/Declaration(s)
     - iii. ☒ Information Disclosure Statement
     - iv. ☐ Other ________

2. Miscellaneous
   - a. ☐ Suspension of action on the above-mentioned application is requested under 37 C.F.R. § 1.103(c) for a period of [number] months. (Period of suspension shall not exceed 3 months; fee under 37 C.F.R. § 1.17(i) required.)
   - b. ☐ Other ________________

3. Fees
   - a. ☒ The filing fee is calculated as follows:
     - i. ☒ $810.00 RCE fee required under 37 C.F.R. § 1.17(e)
     - ii. ☒ Petition for extension of time for (2 Months) $460.00
     - iii. ☐ Other ________________
   - b. ☒ The Commissioner is hereby authorized to charge the fee of $1,270.00 to deposit account no. 06-0916.
   - c. ☒ The Commissioner is authorized to charge any deficiencies in the filing fees, and/or credit any overpayments to Deposit Account 06-0916.

Signature of Applicant, Attorney, or Agent Required	
Name: Gary J. Edwards	Reg. No.: 41,008
Signature: Gary J. Edwards	Date: October 2, 2007

EXPRESS MAIL LABEL NO.
EM 100825487 US

10/05/2007 TNGUYEN2 00000052 060916 10101863

01 FC:1801 810.00 DA

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION FOR EXTENSION OF TIME

Applicants petition for a two-month extension of time to reply to the Final Office Action of May 2, 2007. The Commissioner is hereby authorized to charge the fee of $460.00 to Deposit Account No. 06-0916.

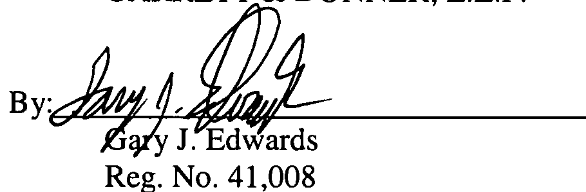
Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

10/05/2007 TNGUYEN2 00000052 060916 10101863
02 FC:1252 460.00 DA

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EM 100825487 US**

RESPONSE UNDER 37 C.F.R. § 1.116
EXPEDITED PROCEDURE REQUESTED
EXAMINING GROUP 2820
PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	Confirmation No.: 6938
	)	
For: BIASED PULSE DC REATIVE SPUTTERING OF OXIDE FILMS	)	

MAIL STOP RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT

This response is being filed with a Request for Continued Examination and is in reply to the Final Office Action mailed May 2, 2007, the period for response having been extended to October 2, 2007, by a request for extension of two months with authorization for the Commissioner to charge the fee to Deposit Account No. 06-0916. Applicant amends the application as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 7.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the

substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14.-20. (Cancelled).

21. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target ~~through a filter~~ such that ~~the~~ a target voltage oscillates between positive and negative voltages to create a plasma and deposit the oxide film; and

band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface~~, and~~

~~wherein the filter is a band rejection filter at a frequency of the bias power~~.

22. (Previously presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (Currently amended): The method of claim 21, wherein band rejection filtering utilizes the band rejection filter is a narrow band-pass filter.

41. (Currently amended): The method of claim 21, wherein a bandwidth of the narrow band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power such that the a target voltage oscillates between positive and negative voltages and an oxide film is deposited on the substrate; and

band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target.

44. (Previously presented): The method of claim 43, wherein band rejection filtering the DC power includes utilizing a band rejection filter with a bandwidth of the band rejection filter is less than about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (Previously presented): The method of Claim 43, further including holding the temperature

of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that ~~the~~ a target voltage oscillates between positive and negative voltages; and

narrow band rejection filtering the pulsed DC power ~~through a narrow band rejection filter~~ at a frequency of the bias power before applying pulsed DC power to the target,

wherein the oxide film is deposited on the substrate.

52. (Previously presented): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, N_2, O_2, C_2F_6, CO_2, CO, NH_3, NO, and halide containing gasses.

53. (Previously presented): The method of claim 51, wherein the target is a metallic target.

54. (Previously presented): The method of claim 51, wherein the target is an intermetllic target.

55. (Previously presented). The method of claim 51, further including sweeping the target with a magnetic field.

56. (Previously presented): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (Previously presented): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (Currently amended) The method of claims 21, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (Currently amended) The method of claim 43, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

60. (Currently amended) The method of claim 51, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

REMARKS

Claims 2-13, 21-24, and 40-60 are pending in this application. The Examiner has rejected claims 2-13, 21-24, and 40-60. Applicants herein have amended claims 21, 40, 43-44, 51, and 58-60 in order to further clarify the invention. No new matter has been added in this Amendment.

Claim Rejections Under 35 U.S.C § 103(a)1

To establish a *prima facie* case of obviousness the prior art reference (or references when combined) must teach or suggest all the claim limitations. *See* MPEP § 2142, 8th Ed., Rev. 5 (August 2006). Moreover, "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." USPTO Memorandum from Margaret A. Focarino, Deputy Commissioner of Patent Operations, May 3, 2007, page 2. As further discussed below, the Examiner has not established a *prima facia* case of obviousness at least because the prior art fails to teach all of the elements of each of the rejected claims.

Claims 10-13, 21, 40-45, and 51-60

Claims 10-13, 21, 40-45, and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 6,117,279 to Smolanoff et al. ("Smolanoff") in view of U.S.

1 The Examiner has made multiple characterizations of the claims, the cited art, and the application of legal principles to those characterizations. Applicants shall not be deemed to agree with or to acquiesce in the Examiner's statements by not specifically addressing these characterizations in this response.

Patent No. 6,306,265 to Fu et al. ("Fu"). Claims 21, 43, and 51 are independent claims. Applicants herein traverse these rejections.

1. Neither Smolanoff nor Fu teach applying pulsed DC power to the target so that the target voltage oscillates between positive and negative voltages.

Claims 21 and 51 each recite "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages . . ." Claim 43 recites "applying pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages . . . ." Therefore, each of the independent claims requires applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages. Neither Smolanoff nor Fu teach this limitation. In fact, both Smolanoff and Fu teach away from this feature in that both teach that the target voltage must be at a negative potential so that the target functions as a cathode.

The Examiner states that "Smolanoff et al. discloses . . . wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13) such that the target voltage opscillates [sic] between positive and negative voltages . . ." (Office Action, page 2). However, Smolanoff teaches away from the target voltage going positive. In fact, the Examiner's cited reference states exactly the opposite of the Examiner's assertion. that Smolanoff teaches that the target voltage oscillates between positive and negative voltages Smolanoff states that "[t]his main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16**, thereby ejecting particles of coating material from the target 16." (Smolanoff, col. 6, lines 8-13).

Smolanoff teaches in its background section that "[t]he plasma is typically generated by maintaining the target, either constantly or intermittently, **at a negative potential** so that the target functions as a cathode to supply electrons that excite the gas in the chamber and form a

plamsa adjacent to the target surface." (Smolanoff, col. 1, lines 33-37) (emphasis added). Further, in operation "[t]he gas ions accelerate toward the target, **which is negatively biased**, to collide with the target surface and eject from the target surface atoms and atomic clusters or particles of target material, as well as secondary electrons, which play a role in sustaining the plasma." (Smolanoff, col. 1, lines 41-46) (emphasis added).

Further, in describing Smolanoff's apparatus, as shown in Figure 1, Smolanoff teaches that "[t]he magnet structure 20 preferably includes magnets that produce a closed magnetic tunnel over the surface of the target 16 that traps electrons given off into the chamber 12 by the cathode assembly 17 **when the cathode assembly 17 is electrically energized to a negative potential as is familiar to one skilled in the art.**" (Smolanoff, col. 5, lines 39-44) (emphasis added).

In particular, Smolanoff teaches that the target is always negative:

> Power from the steady or pulsed DC power supply 21 and/or RF generator 24 **produces a negative potential on the target 16**. The negative potential accelerates ions towards the surface of the target which, upon impact, cause electrons to be emitted from the surface of the target 16. These electrons become trapped over the surface of the target 16 by the magnetic field generated by the magnet pack 20, until, eventually, the electrons strike and thereby ionize atoms of process gas in close proximity to the surface of the target 16, forming a main plasma in a region 23 of the volume 11 adjacent to the surface of the target 16. This main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16**, thereby ejecting particles of coating material from the target 16.

(Smolanoff, col. 6, line 66, through col. 6, line 12) (emphasis added).

Therefore, repeatedly Smolanoff teaches that the target must be negative in order to create the plasma. Smolanoff never teaches that the target is at a positive voltage, which according to the teachings of Smolanoff would not work because the positive ions of the plasma

would not then be attracted to the target. Smolanoff therefore teaches away from applying a positive voltage to the target. At a minimum, the Examiner can not maintain that Smolanoff teaches "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43.

Further Fu also teaches away from the target having a positive voltage. As taught in Fu, in describing a conventional PVD reactor, "[a] selectable DC power supply 22 **negatively biases the target 14 to about -600 VDC** with respect to the shield 20." (Fu, col. 1, lines 31-33) (emphasis added). Further, as was similarly taught in Smolanoff, "[w]hen the argon is admitted into the chamber, the DC voltage between the target 14 and the shield 20 ignites the argon into a plasma, and the **positively charged argon ions are attracted to the negatively charged target 14**." (Fu, col. 1, lines 51-54) (emphasis added). Therefore, Fu, like Smolanoff, teaches that the target must be negative and therefore teaches away from a positive target voltage. At a minimum, the Examiner can not maintain that Fu teaches "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43.

In responding to the remarks of Applicant's Amendment filed on February 6, 2007, the Examiner remarks that

> Applicant argues that Smolanoff et al. do not disclose a target voltage that oscillates between positive and negative voltages. However, Smolanoff is using and [sic] RF bias power, which will make the voltage to oscillate between positive and negative voltages, it doesn't matter if they are using just the negative voltage it will oscillate.

(Office Action, page 7). First, applying an RF bias to the substrate has negligible if any effect on the target voltage in a PVD deposition apparatus. Further, as seen in the discussion above, even if an RF voltage is applied to the target, the target achieves and maintains a negative voltage and never goes positive, as is well know in the art. Further, as is discussed in both Fu and Smolanoff, applying an RF bias to the substrate causes the substrate to become negative so as to attract the positive ions in the plasma. (*See* Smolanoff, col. 6, lines 51-63, "Such attraction of the positive ions of sputtered material toward the substrate 15 can be achieved, for example, **by applying a negative bias to the substrate 15 through the operation of the bias power supply 27**. Such bias attracts the positive sputtered ions . . . . For silicon semiconductor wafers, **this bias power supply 27 is preferably an RF generator** that operates in the range of from about 0.05 to 80 MHz." (emphasis added); Fu, col. 2, lines 36-45, "[t]he **pedestal 18** of FIG. 1, even if it is left electrically floating, **develops a DC self-bias**, which attracts ionized sputtered particles from the plasma across the plasma sheath adjacent to the pedestal 18 and deep into the hole 40 in the dielectral layer 42. **The effect can be accentuated with additional DC or RF biasing** of the pedestal electrode 18 to additionally accelerate the [positively] ionized particles extracted across the plasma sheath towards the wafer 16, thereby controlling the directionality of sputter deposition." (emphasis added)).

Therefore, neither Smolanoff nor Fu teach "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43. In fact, both Smolanoff and Fu teach away from a positive voltage on the target.

2. Neither Smolanoff nor Fu teach "band rejection filtering the pulsed DC power"

The Examiner identifies filter 22 shown in Figure 1 of Smolanoff as teaching the band rejection filter recited in independent claims 21, 43, and 51. Further, the Examiner comments that "using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies." (Office Action, page 2) The Examiner further comments that "the limitation 'the filter is a band rejection filter at a frequency of the bias power' is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above." (Office Action, page 2).

Claims 21, 43, and 51 have been amended such that the filtering is now a method step. Claims 21 and 43 now recite "band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target." Claim 51 now recites "narrow band rejection filtering the pulsed DC power at a frequency of the bias power before applying pulsed DC power to the target." Therefore, this limitation is now a method limitation and not a structural limitation.

Further, Smolanoff only refers to filter 22 once, and then only to identify it as "an RF filter 22." (Smolanoff, col. 5, line 58). Smolanoff does not teach that filter 22 performs the step "band rejection filtering the DC power at a frequency of the bias power" or "narrow band rejection filtering the pulsed DC power at a frequency of the bias power" as is recited in independent claims 21, 43, and 51.

Additionally, in order for the pulsed DC power applied to the target to be useful, the pulsed DC power must include substantially all of its Fourier constituents, and therefore only a band rejection filter that filters out a specific narrow band of filters can be utilized. Further, in

order that the pulsed DC power be protected from the RF bias power supply, the band rejection filter must be set to filter out the frequency of the RF bias power supply. A low pass filter, which is commonly utilized in systems such as Smolanoff, would destroy all of the low frequency components of the pulses. With a band rejection filter, all of the pulsed DC power except that within the rejected band passes to the target. Therefore, far from not mattering which filter is used, as the Examiner opines, it is extremely important that the filter be a band rejection filter that filters out the frequency of the RF bias power, as is recited in claims 21, 43, and 51. For at least this reason, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu.

3. Neither Smolanoff nor Fu teach deposition of an oxide film

Each of claims 21, 43, and 51 recite deposition of an "oxide film." Both Smolanoff and Fu are directed towards deposition of metallic films. Smolanoff teaches away from deposition of insulating materials, as deposition of insulating materials would cause Smolanoff's reactor to become non-functional for its intended purpose.

As stated in Smolanoff, "[t]hose positive ions of sputtered material that are positively charged are capable of being electrically accelerated toward the substrate, for example, by application of a negative bias to the substrate." (Smolanoff, col. 2, lines 3-6). Smolanoff also explains this feature at col. 6, lines 51-63. Similarly, Fu teaches this same operable process in col. 2, lines 37-48. As Fu states, the substrate bias "attracts ionized sputter particles from the plasma." As is well known to those skilled in the art, when oxygen is introduced to the plasma, which is necessary to forming an oxide film, the oxygen reacts with the positive ions to form neutral particles of oxide, which are not attracted to the substrate by the RF bias on the substrate.

Both Smolanoff and Fu teach processes for ionized metal deposition or ionized metal plating (*see* Fu, col. 2, lines 47-48) and do not teach formation of oxide films on the substrate. Therefore, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu for at least this reason.

4. Conclusion

For at least the reasons stated above, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu. Claims 10-13 and 40-42 depend from claim 21 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 21. Claims 44-45 depend from claim 43 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 43. Claims 52-60 depend from claim 51 and are allowable for at least the same reasons as is claim 51.

Claims 2-4, 6, and 22-24

Claims 2-4, 6, and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff in view of Fu, as applied to claims 8, 10-13, and 21. As discussed above, claim 21 is allowable over the combination of Smolanoff and Fu. Claims 2-4, 6, and 22-24 depend from claim 21 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 21.

Claims 7 and 9

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff and Fu, as applied to claims 8, 10-13, and 21, and in view of U.S. Patent Publication No.

2003/0077914 to Le et al. ("Le"). Claim 21 is allowable over the combination of Smolanoff and Fu.

Le teaches deposition of oxides using pulsed DC processes without substrate bias. Le does not teach at least "band rejection filtering the DC power at a frequency of the bias power" or "narrow band rejection filtering the pulsed DC power at a frequency of the bias power" as is recited in independent claims 21, 43, and 51. Additionally, Le does not teach the combination of pulsed DC power and a RF bias to the substrate.

Further, one skilled in the art would not find a reason to combine Le with Smolanoff or Fu. Le is directed to deposition of oxide materials. Both Smolanoff and Fu are directed to deposition of ionized metal ions. One skilled in the art would realize that the introduction of oxygen, a reactive gas, to the processes disclosed in Smolanoff and Fu would render those processes non-functional for their intended purpose.

Therefore, claims 7 and 9 are allowable over the combination of Smolanoff, Fu, and Le.

Conclusion

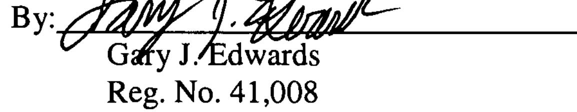
This Amendment is being filed with a Request for Continued Examination. In view of the foregoing remarks, Applicant submits that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicant therefore requests the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account 06-0916.

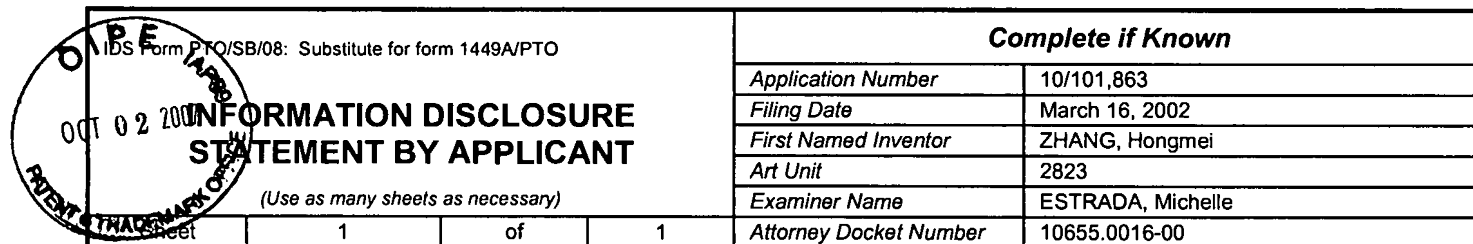
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: 
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EM 100825487 US**



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	10655.0016-00

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document — Country Code[1] Number[2] Kind Code[3] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[4]
		WO 2007/027535 A2	03-08-2007	Symmorphix, Inc.		

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Office Action dated September 22, 2006, from Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).	Yes
		Office Action mailed May 21, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Final Office Action mailed April 13, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Amendment filed August 9, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action mailed September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action mailed September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Notice of Non-Compliant Amendment mailed April 12, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Notice of Non-Compliant Amendment filed April 23, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Final Office Action mailed July 24, 2007 in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Office Action filed July 9, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Corrected Notice of Allowance mailed June 7, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Supplemental Notice of Allowance mailed July 5, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Second Supplemental Preliminary Amendment filed May 31, 2007, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
		PCT International Preliminary Report on Patentability mailed June 21, 2007, in PCT Application No. PCT/US2005/044781 (Attorney Docket No. 9140.0042-304).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 100825487 US

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 March 2007 (08.03.2007)

PCT

(10) International Publication Number
WO 2007/027535 A2

(51) International Patent Classification:
H01G 4/06 (2006.01)

(21) International Application Number:
PCT/US2006/033315

(22) International Filing Date: 24 August 2006 (24.08.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/218,652 2 September 2005 (02.09.2005) US

(71) Applicant (*for all designated States except US*): **SYMMORPHIX, INC.** [US/US]; 1278 Reamwood Avenue, Sunnyvale, California 94089-2233 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **ZHANG, Hongmei** [US/US]; 1330 Rodney Drive, San Jose, California 95118 (US). **DEMARAY, Richard, E.** [US/US]; 190 Fawn Lane, Portola Valley, California 94028 (US).

(74) Agent: **EDWARDS, Gary J.**; Finnegan, Henderson, Farabow, Garrett & Dunner LLP, 901 New York Avenue, N.W., Washington, D.C., District Of Columbia 20001-4413 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/027535 A2

(54) Title: DEPOSITION OF PEROVSKITE AND OTHER COMPOUND CERAMIC FILMS FOR DIELECTRIC APPLICATIONS

PEROVSKITE ~302
SUBSTRATE ~301

(57) Abstract: In accordance with the present invention, deposition of perovskite material, for example barium strontium titanite (BST) film, by a pulsed-dc physical vapor deposition process or by an RF sputtering process is presented. Such a deposition can provide a high deposition rate deposition of a layer of perovskite. Some embodiments of the deposition address the need for high rate deposition of perovskite films, which can be utilized as a dielectric layer in capacitors, other energy storing devices and micro-electronic applications. Embodiments of the process according to the present invention can eliminate the high temperature (>700 °C) anneal step that is conventionally needed to crystallize the BST layer.

Deposition of Perovskite and Other Compound Ceramic Films for Dielectric Applications

FIELD OF THE INVENTION

[001] The present invention is related to production and application of dielectric thin-films and, in particular, the deposition of perovskites such as Barium Strontium Titanate (BST) films and other ceramic oxides for dielectric applications.

DISCUSSION OF RELATED ART

[002] Perovskite films, for example Barium Strontium Titanate (BST) films, are one of the attractive materials to use in capacitors for high density device applications because of its relatively high dielectric constant, low leakage current density, high dielectric breakdown strength, and ferroelectric perovskite phase that does not exhibit fatigue. However, electric properties of the perovskite films are greatly dependent on the deposition process, the substrate, the post-processing, and the related film structure. For all of the potential, thin film perovskites have rarely been utilized in manufacture primarily because of difficulties in controlling physical and chemical properties of the crystalline and amorphous phases of perovskite thin-film materials and their interactions with metallic and conductive electrodes.

[003] Solid-state thin-film devices are typically formed by stacking thin films of metal and dielectric on a substrate. The thin films typically include two metallic electrodes with a dielectric layer in between. The thin films can be deposited utilizing a number of deposition processes, including sputtering, electroplating, chemical vapor deposition, sol gel, or oxidation. Substrates suitable for these applications have conventionally been high temperature materials capable of withstanding at least one high temperature anneal process to at least 650-750 °C so as to crystallize the perovskite dielectric film in order to increase its

dielectric constant. Such a substrate can be any suitable material with appropriate structural and material properties, for example a semiconductor wafer, refractory metallic sheet (e.g., titanium, zirconium, or stainless steel), ceramic such as alumina, or other material capable of withstanding subsequent high temperature processing.

[004] However, conventional materials and production processes can limit the types of materials that can be used in device manufacture. Typically, the dielectric material is deposited in amorphous form and then the material is heated in an anneal process to form the crystalline material. Conventional formation of perovskite layers, for example, require an anneal at or above 650°C to transform the deposited amorphous film to a crystalline form. Such a high temperature anneal, however, severely limits the materials that can be utilized as the substrate, and often requires the use of expensive noble metals such as platinum to protect the substrate from reaction with the electrode material. Such high heat-treat temperatures are incompatible with standard semiconductor or MEM device processing, and limit the choice of substrate materials on which the layers can be formed, increasing the cost, and decreasing the yield of such devices formed with the layers.

[005] Therefore, there is a need for a low temperature process for depositing crystalline material, for example perovskite material and other ceramic oxides, onto a substrate.

SUMMARY

[006] In accordance with the present invention, deposition of layers in a pulsed-DC physical vapor deposition process from a conductive ceramic target is presented. In some embodiments, the deposition can provide a low-temperature, high deposition-rate deposition of a dense amorphous layer of BST from a conductive BST target, which can be annealed at much lower temperature to yield crystalline BST. Some embodiments of the deposition address the need for low temperature, high rate deposition of perovskite films, for example

BST films, which can be utilized as the dielectric layer in high specific capacitance devices as, for example, de-coupling capacitors, energy storage devices, voltage tunable capacitors, or other micro-electronic devices.

[007] A method of depositing a perovskite or ceramic oxide layer according to some embodiments of the present invention includes placing a substrate in a reactor; flowing a gaseous mixture, for example argon and oxygen, through the reactor; and applying pulsed-DC power to a target formed of conductive perovskite or ceramic oxide material, such as BST, positioned opposite the substrate.

[008] In some embodiments the perovskite layer can be formed utilizing radio frequency (RF) sputtering. The perovskite is deposited by RF sputtering of a wide area target in the presence of a sputtering gas under a condition of uniform target erosion. The substrate is positioned opposite a planar target formed of perovskite, for example BST, the area of the target being larger than the area of the substrate. A central area of the target of the same size as the substrate and overlying the substrate is exposed to a uniform plasma condition, which provides a condition of uniform target erosion. A uniform plasma condition can be created without magnetic enhancement, termed diode sputtering, or by providing a time-averaged uniform magnetic field by scanning a magnet across the target in a plane parallel to the plane of the target.

[009] A film produced utilizing a pulsed dc, bias PVD process with a conductive ceramic target can be deposited at much higher rates than an insulating ceramic process, which requires an RF sputtering process. Further, deposition occurs with much less oxygen present in the gas flow to provide a fully oxidized film as opposed to a metallic target. The resulting film is much higher density than the low rate films. The films can be stoichiometric, uniform, highly dense, with low sintering temperatures and resulting high dielectric properties.

[010] In some embodiments, the substrate is preheated. The substrate can be heated to a temperature of about 400°C or below during deposition for low temperature perovskite deposition, or to higher temperatures for perovskite deposition on substrates capable of withstanding such temperature regime. Substrates suitable for low temperature perovskite deposition include glass, plastic, metal foil, stainless steel, and copper. A perovskite layer of thickness up to several microns thick can be deposited, although layers of any thickness can be formed.

[011] In some embodiments the perovskite layer formed on the substrate is later annealed. The anneal temperature can be as low as 400°C for low temperature anneal, and higher for perovskite deposition on substrates capable of withstanding such higher temperature regime. In some embodiments the perovskite target can be doped with transition metal dopants, for example manganese, transition elements, lanthanides (including the rare earth ions) and/or amphoteric elements.

[012] In some embodiments, a stacked capacitor structure can be formed. The stacked capacitor structure includes one or more capacitor stacks deposited on a thin substrate, wherein each capacitor stack includes: a bottom electrode layer, a perovskite, for example BST, dielectric layer deposited over the bottom electrode layer; and a top electrode layer deposited over the dielectric layer. A top conducting layer can be deposited over the capacitor stacks.

[013] In some embodiments, a capacitor structure can be formed in a cluster tool. An exemplary method of producing a capacitor in a cluster tool includes loading a substrate into the cluster tool; depositing an electrode layer over the substrate in a first chamber of the cluster tool; depositing a perovskite dielectric layer over the electrode layer in a second chamber of the cluster tool; depositing a second electrode layer over the dielectric layer in a

third chamber. In some embodiments the first and the second electrode layers can be deposited in the same chamber.

[014] A fixture for holding a thin substrate can include a top portion; and a bottom portion, wherein the thin substrate is held when the top portion is attached to the bottom portion.

[015] In some embodiments, the ceramic layer can be deposited on a substrate coated with iridium or other refractory conductive material to provide a low temperature anneal processed capacitive structure.

[016] These and other embodiments of the invention are further discussed below with reference to the following figures. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed. Further, specific explanations or theories regarding the deposition or performance of materials according to the present invention are presented for explanation only and are not to be considered limiting with respect to the scope of the present disclosure or the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[017] Figures 1A and 1B illustrate a pulsed-DC biased reactive deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[018] Figure 1C illustrates an RF sputtering deposition apparatus.

[019] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A, 1B, and 1C.

[020] Figures 3A and 3B illustrate a thin-film capacitor design according to some embodiments of the present invention.

[021] Figures 4A, 4B, 4C, and 4D illustrate a thin substrate mount and mask arrangement that can be utilized in the deposition of dielectric perovskite layers, for example BST films, deposited according to some embodiments of the present invention.

[022] Figure 5 illustrates a cluster tool that can be utilized to form batteries with dielectric perovskite layers deposited according to some embodiments of the present invention.

[023] Figure 6 illustrates an example of stacked capacitor structure with dielectric perovskite layers deposited according to some embodiments of the present invention.

[024] In the figures, elements having the same designation have the same or similar functions.

DETAILED DESCRIPTION

[025] In accordance with embodiments of the present invention, dielectric perovskite films or other ceramic oxide films are deposited on a substrate by a pulsed-DC physical vapor deposition (PVD) process utilizing a conductive ceramic target. In some embodiments, the film can be deposited by RF sputtering.

[026] In some embodiments, a dielectric perovskite layer, for example BST material, is deposited directly on the substrate with only low temperature anneal, eliminating the need of a subsequent high temperature anneal to crystallize the film. Removing the high temperature anneal allows for formation of capacitor structures on light-weight, low temperature, and low cost substrates such as copper foil and plastic sheet, reducing both the weight and the cost of capacitors while maintaining the high dielectric constant of the perovskite, for example BST, high-density dielectric film.

[027] Deposition of materials by pulsed-DC, RF biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101,863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002.

Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101,863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials by RF sputtering has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films can be deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101,863.

[028] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[029] Apparatus 10 includes target 12, which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it from the pulsed DC power supply 14 and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[030] For pulsed reactive DC magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[031] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 kHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[032] Filter 15 prevents the RF bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[033] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 14 while allowing the full bandwidth of the pulsed DC power supply to pass filter 15.

[034] Pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications such as barrier films and dielectric films, where high density is important, due to the boundaries between the

columns. The columns act to lower the dielectric strength of the material, but may provide diffusion paths for transport or diffusion of electrical current, ionic current, gas, or other chemical agents such as water.

[035] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be adjusted to between –50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 milliTorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 600 mm.

[036] In some embodiments of the present invention a perovskite layer is deposited by RF sputtering with a wide area target and a condition of uniform target erosion. An example apparatus 30 for RF sputtering is illustrated schematically in FIG. 1C. Apparatus 30 includes an RF power supply 60 coupled to wide area sputter source target 12 which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when RF power is applied to it and is equivalently termed the cathode. In the present disclosure, target 12 can be formed from a perovskite material, for example BST, for deposition of dielectric perovskite film. Substrate 16 is a solid, smooth surface. Substrate 16 typically is supported on a holder or carrier sheet 17 that may be larger than substrate 16.

[037] In some embodiments, a feature of the RF sputtering method is that the area of wide area target 12 is greater than the area on the carrier sheet on which physically and

chemically uniform deposition is accomplished. Secondly, a central region on target 12, overlying the substrate 16, can be provided with a very uniform condition of sputter erosion of the target material. Uniform target erosion is a consequence of a uniform plasma condition. In the following discussion, all mention of uniform condition of target erosion is taken to be equivalent to uniform plasma condition. Uniform target erosion is evidenced by the persistence of film uniformity throughout an extended target life. A uniform deposited film is defined as a film having a nonuniformity in thickness, when measured at representative points on the entire surface of a substrate wafer, of less than about 5%. Thickness nonuniformity is defined, by convention, as the difference between the minimum and maximum thickness divided by twice the average thickness. If films deposited from a target from which more than about 20% of the weight of the target has been removed under constant process conditions continue to exhibit thickness uniformity, then the sputtering process is judged to be in a condition of uniform target erosion for all films deposited during the target life.

[038] Thus, a uniform plasma condition can be created in the region between the target and the substrate overlying the substrate. The region of uniform plasma condition is indicated in the exploded view of FIG. 1B. A plasma is created in the region denoted 51, which extends under the entire target 12. The central region of the target 52 experiences the condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 will have uniform film thickness.

[039] In addition, the region in which deposition provides uniform film thickness is larger than the area in which deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In the present invention the target can be planar or approximately planar for the formation of a film on a planar substrate which is to be coated with the material of the target. In practice, planarity of the target means

that all portions of the target surface in region 52 are within a few millimeters of an ideal planar surface, typically within 0.5 mm.

[040] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity, which is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity to the deposited film. In optimized processes, however, regions 52 and 24 may be coextensive.

[041] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[042] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater

than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission, or absorption.

[043] In the present disclosure, target 12 can be formed from perovskite material, such as BST, for deposition of dielectric perovskite film. In some embodiments of the present invention the perovskite target is doped with transition metal dopants, for example Manganese, transition elements, lanthanides (including the rare earth ions) and/or amphotaric elements. In some embodiments of the present invention the percentage of the dopant in the perovskite target is from 0.1 to several percent.

[044] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 and 20 individual tiles. Tiles can be finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[045] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, in region 52 the deposition provides uniformity of deposited film that can be larger

than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[046] Reactive gases that provide a constant supply of oxygen to keep the target surface oxidized can be provided to expand the process window. Some examples of the gases that can be utilized for controlling surface oxidation are O_2, water vapor, hydrogen, N_2O, fluorine, helium, and cesium. Additionally, a feedback control system can be incorporated to control the oxygen partial pressure in the reactive chamber. Therefore, a wide range of oxygen flow rates can be controlled to keep a steady oxygen partial pressure in the resulting plasma. Other types of control systems such as target voltage control and optical plasma emission control systems can also be utilized to control the surface oxidation of the target. In some embodiments, power to target 12 can be controlled in a feedback loop at supply 14. Further, oxygen partial pressure controller 20 can control either oxygen or argon partial pressures in plasma 53. In some embodiments of the present invention, oxygen flow or partial pressure can be utilized to maintain a constant voltage of discharge from target 12.

[047] Figures 3A and 3B show a capacitor structure with a dielectric perovskite layer deposited according to some embodiments of the present invention. As shown in Figure 3A, a dielectric perovskite layer 302 is deposited on a substrate 301. In some embodiments, the dielectric layer 302 can be patterned in various ways before deposition of a substrate 301. In some embodiments, a first electrode layer 303 can be deposited on the substrate and the dielectric layer 302 is deposited over the first electrode layer. The second electrode layer 304 is then deposited over the dielectric layer 302. In some embodiments of

the invention, the dielectric perovskite layer 302 is crystalline and has sufficiently high dielectric constant without the necessity of a high temperature anneal. Therefore, substrate 301 can be a silicon wafer, titanium metal, alumina, or other conventional high temperature substrate, but may also be a low temperature material such as plastic, glass, or other material that may be susceptible to damage from the high temperature anneal. This feature can have the great advantage of decreasing the expense and weight of capacitor structures formed by the present invention. The low temperature deposition of perovskite material allows for successive depositions of perovskite and electrode layers, one upon another. Such a process would have the advantage that successive layers of capacitor structure would be obtained in a stacked condition without the inclusion of a substrate layer. The stacked layered capacitor would provide higher capacitance and higher energy storage than single layer devices with a smaller surface area. Additionally, a capacitor with a lower inductance can be obtained.

[048] In accordance with the present invention, perovskite films can be deposited on substrate 302 with a pulsed-DC biased PVD system as was described above. In particular, an AKT 1600 PVD system can be modified to provide an RF bias and an Advanced Energy Pinnacle plus 10K pulsed DC power supply can be utilized to provide power to a target. The pulsing frequency of the power supply can vary from about 0 to about 350 KHz. The power output of the power supply is between 0 and about 10 kW.

[049] A target of Barium Strontium Titanate with resistivity in the range of less than about megaohms can be utilized with high rate pulsed-dc sputtering. As discussed above, the target can be mounted on a monolithic backing plate as described in U.S. Provisional Application **{Attorney Docket No. 09140.6013}**, filed on August 26, 2005, which is also herein incorporated by reference in its entirety.

[050] In general, target 12 can be a dielectric material having a resistivity of less than about a megaohm, and therefore can be described as a conducting ceramic target. Target

12, which is formed of a dielectric perovskite material that may not be inherently conducting, is made conducting by formulation so as to contain an excess of metallic composition or by addition of a dopant that provides sufficient conductivity. Examples of suitable dopants include boron, antimony, arsenic, phosphorous, or other dopants. In the example of a BST target, the sintering process can be conducted in the presence of a reducing ambient to achieve a sufficiently conductive target material. Utilization of a conducting ceramic target material can be sputtered at high rates utilizing reactive pulsed-DC techniques so as to form dense stoichiometric dielectric films.

[051] Gas flows containing Oxygen and Argon can be utilized. In some embodiments, the Oxygen to Argon ratio ranges from 0 to about 50% with a total gas flow of between about 60 to about 80 sccm. The pulsing frequency ranges from about 200 kHz to about 350 kHz during deposition. RF bias can also be applied to the substrate. In many trials, the deposition rates varied from about 2 Angstrom/(kW sec) to about 1 Angstrom/(kW sec) depending on the O_2/Ar ratio as well as substrate bias.

[052] Figure 3A illustrates a layer of perovskite material 302 deposited on a thin substrate 301 according to some embodiments of the present invention. Substrate 301 can be formed of a thin metallic sheet (e.g., copper, titanium, stainless steel, or other suitable thin metallic sheet), can be formed of a high temperature plastic material, or may be formed of a ceramic, glass, or polymer material.

[053] Depositing materials on a thin substrate involves holding and positioning the substrate during deposition. Figures 4A, 4B, 4C, and 4D illustrate a reusable fixture 400 for holding a thin film substrate. As shown in Figure 4A, reusable fixture 400 includes a top portion 401 and a bottom portion 402 that are fastened together to secure the substrate. Thin substrate 301 is positioned between top portion 401 and bottom portion 402. As shown in Figure 7B, top portion 701 and bottom portion 702 are such that substrate 301 is brought into

a planar condition and subsequently clamped as top portion 401 is closed into bottom portion 402. Substrate 301 can be easily held by fixture 400 so that substrate 301 can be handled and positioned. In some embodiments, the corners of substrate 301, areas 403, are removed so that substrate 301 is more easily stretched by avoiding "wrap-around" corner clamping effects when top portion 401 is closed into bottom portion 402.

[054] As shown in Figure 4C, a mask 412 can be attached to fixture 400. In some embodiments, fixture 400 includes guides in order to align fixture 400 with respect to mask 412. In some embodiments, mask 412 may be attached to fixture 400 and travel with fixture 400. Mask 412 can be positioned at any desired height above substrate 301 in fixture 400. Therefore, mask 412 can function as either a contact or proximity mask. In some embodiments, mask 412 is formed of another thin substrate mounted in a fixture similar to fixture 400.

[055] As shown in Figure 4C and 4D, fixture 400 and mask 412 can be positioned relative to mount 410. Mount 410, for example, can be a susceptor, mount, or an electrostatic chuck of a processing chamber such as that shown in Figures 1A and 1B. Fixture 400 and mask 412 can have features that allow for ready alignment with respect to each other and with respect to mount 410. In some embodiments, mask 412 is resident in the processing chamber and aligned with fixture 400 during positioning of fixture 400 on mount 410, as shown in Figure 4D.

[056] Utilizing fixture 400 as shown in Figures 4A, 4B, 4C, and 4D allows processing of a thin film substrate in a processing chamber. In some embodiments, thin film substrates can be about 1 μm or more. Further, thin film substrate 301, once mounted within fixture 400, can be handled and moved from process chamber to process chamber. Therefore, a multiprocessor chamber system can be utilized to form stacks of layers,

including one or more layers of perovskite film deposited according to embodiments of the present invention.

[057] Figure 5 illustrates a cluster tool 500 for processing thin film substrates. Cluster tool 500 can, for example, include load lock 502 and load lock 503, through which mounted thin film substrate 301 is loaded and a resultant device is removed from cluster tool 500. Chambers 504, 505, 506, 507, and 508 are processing chambers for depositions of materials, heat treatments, etching, or other processes. One or more of chambers 504, 505, 506, 507, and 508 can be a pulsed-DC or RF PVD chamber such as discussed above with respect to Figures 1A, 1B, and 1C and within which a dielectric perovskite film may be deposited according to embodiments of the present invention.

[058] Processing chambers 504, 505, 506, 507, and 508 as well as load locks 502 and 503 are coupled by transfer chamber 501. Transfer chamber 501 includes substrate transfer robotics to shuttle individual wafers between processing chambers 504, 505, 506, 507, and 508 and load locks 502 and 503.

[059] In production of a thin-film capacitor, substrates are loaded into load lock 503. An electrode layer can be deposited in chamber 504, followed by a perovskite deposition performed in chamber 505. The substrate can then be removed through load lock 503 for an in-air heat treatment external to cluster tool 500. The treated wafer can then be reloaded into cluster tool 500 through load lock 502. The wafer can then again be removed from cluster tool 500 for deposition of a second electrode layer, or sometimes chamber 506 can be adapted to deposition of the second electrode layer. The process can be repeated to form a capacitor stack. The finished capacitor structure is then off-loaded from cluster tool 500 in load lock 502. Wafers are shuttled from chamber to chamber by robotics in transfer chamber 501.

[060] A capacitor structure produced according to the present invention could utilize thin film substrates loaded in a fixture such as fixture 400. Fixture 400 is then loaded into

load lock 503. Chamber 504 may still include deposition of the electrode layer. Chamber 505 then includes deposition of a perovskite layer according to embodiments of the present invention. A second electrode layer can then be deposited in chamber 506. In this process, only low temperature anneal is utilized to increase crystallinity and the dielectric constant of the perovskite layer.

[061] Another advantage of a thin film capacitor process is the ability to stack capacitor structures. In other words, substrates loaded into cluster tool 500 may traverse process chambers 504, 505, 506, 507, and 508 multiple times in order to produce multiply stacked capacitor structures. Figures 6A and 6B illustrate such structures.

[062] Figure 6A illustrates a parallel coupled stacking. As shown in Figure 6A, a substrate 301, which for example can be a high temperature plastic substrate, such as polyimide, is loaded into load lock 503. Electrode layer 303, for example, can be deposited in chamber 504. A dielectric perovskite layer 302 is then deposited on electrode layer 303. Perovskite layer 302 can be about 0.1 to 1 μm and can be deposited in chamber 505 according to embodiments of the present invention. The wafer can then be moved to chamber 506 where the next electrode layer 304 of thickness of about 0.1 μm or more is deposited. A second capacitor stack can then be deposited over the first capacitor stack formed by first electrode layer 303, perovskite layer 302, and second electrode layer 304. This capacitor stack includes second perovskite layer 305 and third electrode layer 306. In some embodiments, further stacks can be formed. In some embodiments, metal layers 303, 304, and 306 differ in the mask utilized in deposition so that tabs are formed for electrical coupling of layers.

[063] As discussed above, any number of individual capacitor stacks can be formed such that parallel capacitor formations are formed. Such a parallel arrangement of capacitor

stacking structure can be formed of alternating layers of electrode and perovskite dielectric layers and can have any number of dielectric layers.

[064] To form the structures shown in Figure 6, substrates are rotated again through the chambers of cluster tool 500 in order to deposit the multiple sets of capacitors. In general, a stack of any number of capacitors can be deposited in this fashion.

[065] Tables I and II illustrate some examples depositions of perovskite material, for example BST, according to the present invention. In these examples, the BST film is deposited using an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu. The power supply is an ENI 13.56 MHz RF power supply with a ENI matchbox. The target material is BST with resistivity in the range of kΩs or less. The target material can, for example, be sintered. Silicon wafers are used for initial experiments. 0.1-1 microns of BST films are deposited on Si wafers with various bottom electrode materials such as: n++ Si, Ir, Pt, IrO_2 and also Ti_4O_7, Ti_3O_5, Nb, Os. The Oxygen to Argon ratio ranges from 0 to 50%. Process pressure ranges from 3-10 mT. RF bias is applied to substrates for some of the examples. The dielectric constant of as deposited film range from 13 to 123 and increases after post-deposition anneal to more than 1000.

[066] One skilled in the art will recognize variations and modifications of the examples specifically discussed in this disclosure. These variations and modifications are intended to be within the scope and spirit of this disclosure. As such, the scope is limited only by the following claims.

TABLE 1

Example #	Film Thickness (nm)	Target Power (W)r	Bias Power (W)	Ar/O_2 Ratio	Vbd	Ebd	C (PF)	Dielectric Constant
BST 2	3679	1500	100	50/50	157	4.267464	167	13.35
BST 3	3736	1500	100	50/50	150	4.014989	168	13.64
BST3-N++ 550c	3736	1500	100		40	1.070664	1670	135.57
BST-Pt-1	2282	1500	100	50/25	47	2.059597	299.5	14.85
BST Pt-1 550C	2282	1500	100		16	0.701139	5722	283.74
BST-n++-4	2282	1500	100	50/25	120	5.258545	274	13.59
BST-n++550c	2282	1500	100		30	1.314636	1970	97.69
BST-IrO2-1	2310	1500	100	50/25	100	4.329004	296.2	14.87
BST-IrO2-1 750C	2310			50/25	2.4	0.103896	17700	888.46
BST-Pt-2	2310	1500	100	50/25	100	4.329004	319	16.01
BST-Pt-2 650C	2310				9.4	0.406926	9750	489.41
BST-Pt-3	2199	1500	100	75/25	7	0.318327	2580	123.28
BST-Pt-3 550	2199	1500	100	75/25	11.2	0.509322	10740	513.20
BST IrO2-2	2199	1500	100	75/25	16.7	0.759436	378	18.06
BST IrO2-2 550	2199	1500	100	75/25	1.4	0.063665	10400	496.95
BST IrO2-2 650	2199	1500	100	75/25	6.9	0.313779	11000	525.62
BST IrO2-2 750	2199			75/25	1.4	0.063665	21950	1048.85
BST Pt 1 step	2918	2000	0	50/50			1239	78.56
BST Ir 1 step	2918	2000	0	50/50			1180	74.82
BST IrO2 1 step	2918	2000	0	50/50			567	35.95
BST Pt 2 steps	1689	2000	0	100/0-50/50			1220	44.78
BST Ir 2 steps	1689	2000	0	100/0-50/50			1230	45.14
BST IrO2 2 steps	1689	2000	0	100/0-50/50			684	25.10

Table II

Sample#	thickness	target power	bias power	Ar/O2	dep time (sec)	Vbd	Ebd	C(PF)	Dielectric Constant, k	Vbd (V)		C(PF)	Dielectric Constant, k (after 500C° anneal)
ALDOEN++-1	840.4					70	8.329367	380	6.939418				
	840.4							377	6.884633				
ALDOEN++-2	5767.2							60.5	7.581825				
								1200	0				
experiment 109	1000							1200	26.07562				
	840					75	8.928571	405	7.392438				
ebonex,BST (A)	1140	900	100		3600		0		0				
Ir Coated #2	2220	900	0	50/50	5400		0	508	24.50587			16800	810.4302
												5000	
	2220											21530	1038.605
IrO2 Coated #2	2220	900	0	50/50	5400		0	365	17.60756	9	0.405	22000	1061.278
	2220						0					20000	964.7979
												19000	
												9000	
N++(1)	2220	900	0		5400	12	0.540541	290	13.98957	12		2512	121.1786
N++(2)	840	900	100	50/50	5400	10	1.190476	982	17.92438	10		2675	48.8266
N++(3)	can't meas	900	200		5400			377					
N++(4)	1490	900	100	50/25	5400		0	242	7.835289			537	17.38657
Ti4O7 (A)	910	900		50/50			0	3030	59.91525			450	8.898305
	910							2962	58.57062				
	910							2860	56.55367				
Ti4O7 (B)	1490			50/25			0	1988	64.36593			314	10.16645
	1490							2048	66.30856				
Ir # 3	650	900	1000 sec no bias/ 4400sec bias 80W	50/50	5400			very leaky					

Ir #4	870	900	500 sec no bias/ 4900 sec 50w bias	50/50	5400			very leaky					
Ir #5	2000	900	1500sec no bias/5700 sec 50W bias	50/50	7200			very leaky					
IrO2 (Tsub=450c)	2000	900	no bias	50/50	5400	10	0.5	1390	60.40852	10		5972	259.5393
	2000											6021	261.6688
n++ (6)(Tsub=450c)	934	900	75 w bias	50/50	7200	12	1.284797	870	17.65711	12		2857	57.98431
n++ (7) (room)	2541	900	no bias	50/50	5400			219		13	0.512	2210	122.0254
n++(8) (room)	2504	900	75 w bias	50/50	7200			224	12.18809	22	0.879	2218	120.6839
n++ (9) (room)	10000		75 w bias	50/50	28800			58	12.60322	55	0.55	954.7	207.4533
n++ (10) (room)	5000		75w bias	50/50	14400								

WHAT IS CLAIMED IS:

1. A method of depositing a perovskite layer on a substrate, comprising:

placing the substrate into a reactor;

flowing a gaseous mixture through the reactor; and

providing power to a target formed of a perovskite material positioned opposite the substrate.

2. The method of claim 1, wherein providing power to the conducting target includes applying pulsed-DC power to the conducting target.

3. The method of claim 2 further including filtering the pulsed-DC power to protect a pulsed DC power supply from a bias power while allowing passage of the pulsed DC power through the filter.

4. The method of claim 2, further including supplying an RF bias power to the substrate.

5. The method of claim 1, wherein providing power to the conducting target includes applying RF power to the conducting target.

6. The method of claim 1, wherein a perovskite layer is formed on the substrate.

7. The method of claim 6, wherein the perovskite layer is a barium strontium titanite (BST) layer.

8. The method of claim 6, wherein the formed perovskite layer is more than about 0.1 micron thick.

9. The method of claim 6 wherein the formed perovskite layer is less than about 1 micron thick.

10. The method of claim 6, further comprising annealing the perovskite layer formed on the substrate.

11. The method of claim 10 wherein annealing the perovskite layer includes heating the perovskite layer to an anneal temperature of between about 500°C and about 800°C.

12. The method of claim 1, further comprising preheating the substrate before applying power to the conducting target.

13. The method of claim 12, wherein preheating the substrate including heating the substrate to a temperature of about 400 °C for low temperature perovskite deposition.

14. The method of claim 1, wherein the substrate is a low temperature substrate.

15. The method of claim 14, wherein the low temperature substrate is one of a set of substrates including glass, plastic, metal foil, copper, and stainless steel.

16. The method of claim 1 wherein the conducting target is doped with a transition metal dopant, transition element, lanthanide, and/or amphotaric elements.

17. The method of claim 16 wherein the target is doped with Manganese.

18. The method of claim 17 wherein a level of Manganese in the target is at least 0.1%.

19. The method of claim 1, wherein the perovskite target is a conductive target.

20. A capacitor structure, comprising:

    a first conducting electrode layer;

    a dielectric perovskite layer deposited over the first conducting electrode layer; and

    a second conducting electrode layer deposited over the dielectric perovskite layer.

21. The capacitor of claim 20, wherein the first conducting layer is a copper sheet.

22. A stacked capacitor structure, comprising:

one or more capacitor stacks deposited on a substrate, wherein each capacitor stack comprises:

a bottom electrode layer,

a dielectric perovskite layer deposited over the electrode layer, and

a top electrode layer deposited over the one or more capacitor stacks.

23. The stacked capacitor structure of claim 22, wherein the capacitor stacks form a parallel stacked capacitor structure.

24. The stacked capacitor structure of claim 22, wherein the capacitor stacks form a series stacked capacitor structure.

25. A method of producing a capacitor, comprising:

loading a substrate into a cluster tool;

depositing a dielectric perovskite layer over a substrate in a chamber of the cluster tool.

26. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing perovskite film with a pulsed-DC PVD process.

27. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing perovskite film with an RF sputtering PVD process.

28. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing the perovskite material through a mask.

29. The method of claim 25, further including

depositing a bottom electrode layer on the substrate wherein the dielectric perovskite layer is .deposited over the bottom electrode layer.

31. The method of claim 25, further including depositing a top electrode layer over the dielectric perovskite layer.

32. A fixture for holding a thin substrate, comprising:

a top portion; and

a bottom portion, wherein

the thin substrate is held when the top portion is attached to the bottom portion.

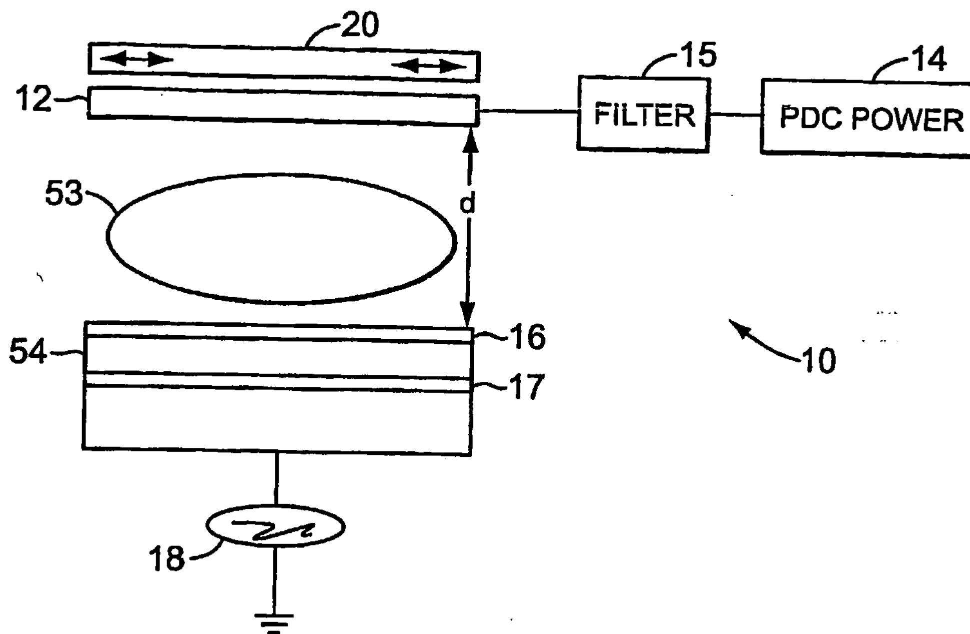


FIG. 1A

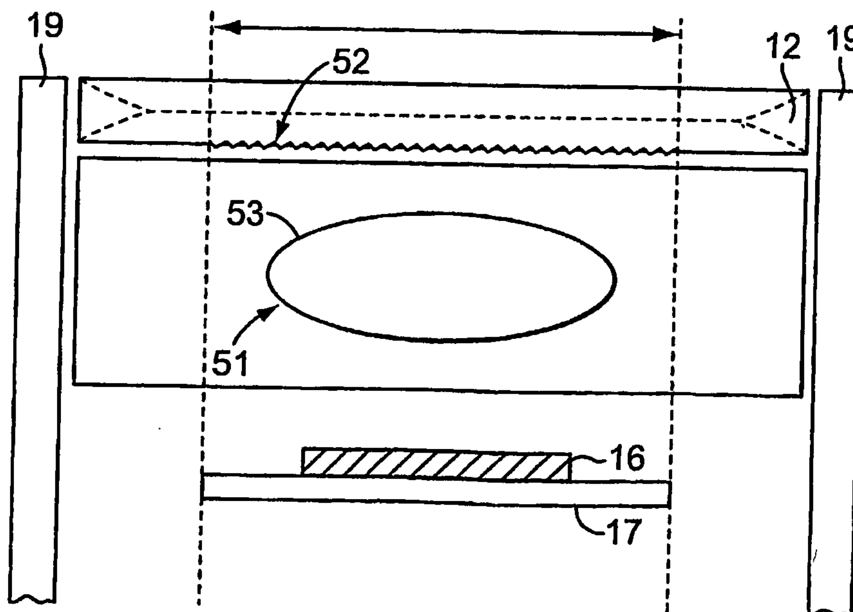


FIG. 1B

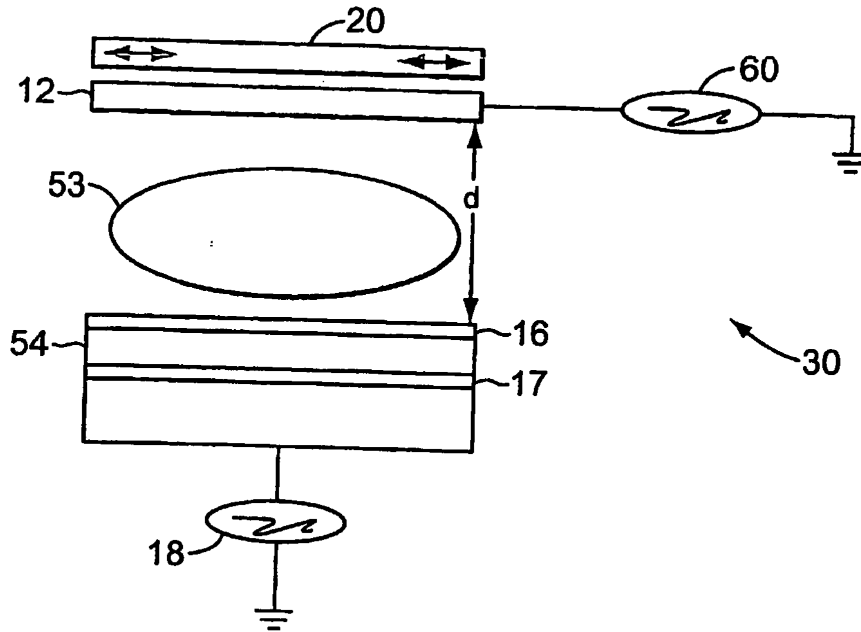


FIG. 1C

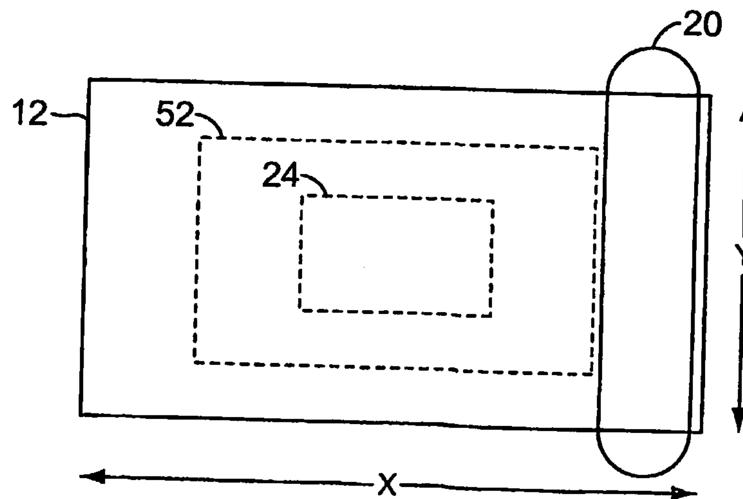


FIG. 2

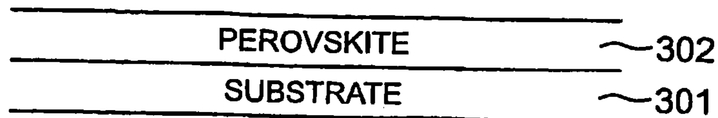


FIG. 3A

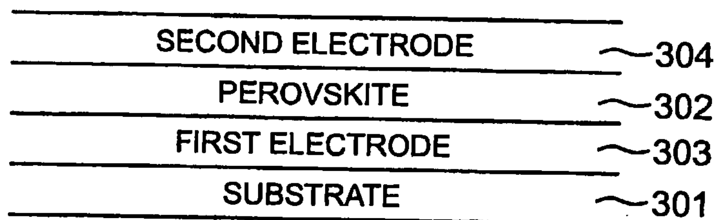


FIG. 3B

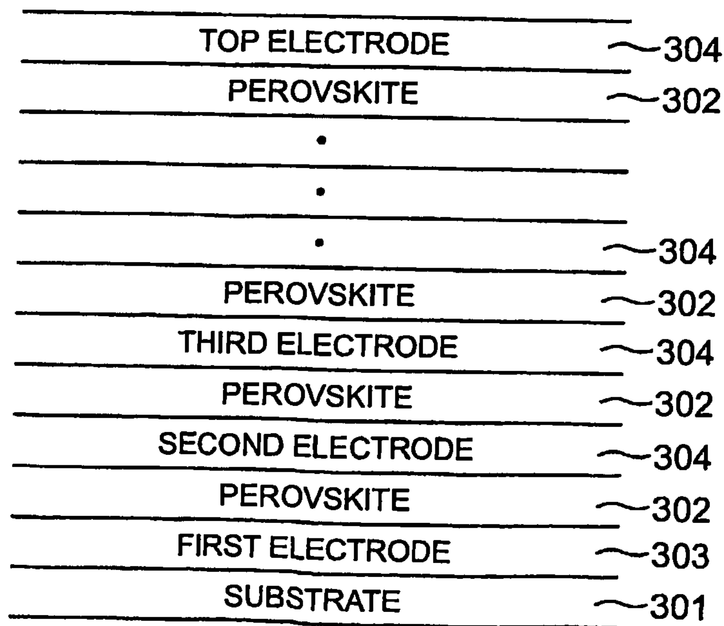


FIG. 6

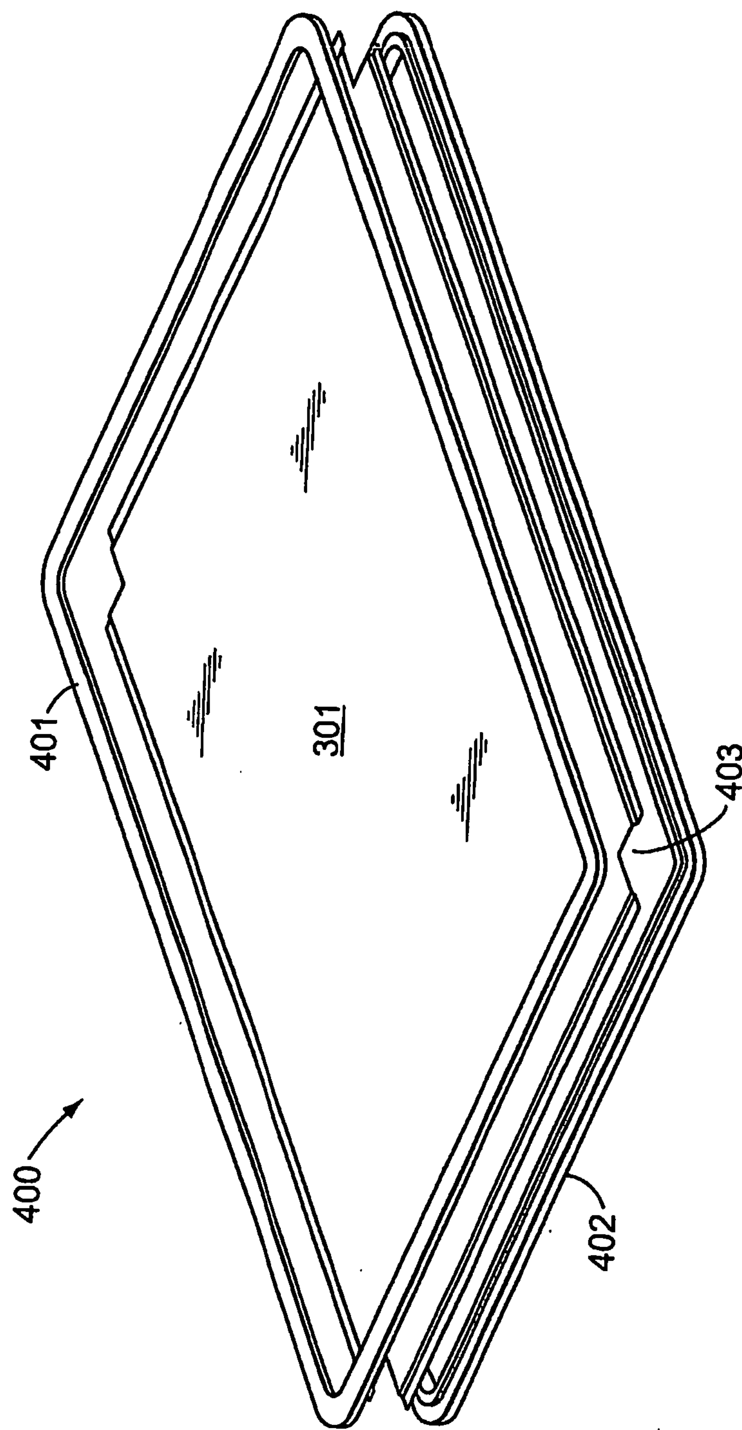


FIG. 4A

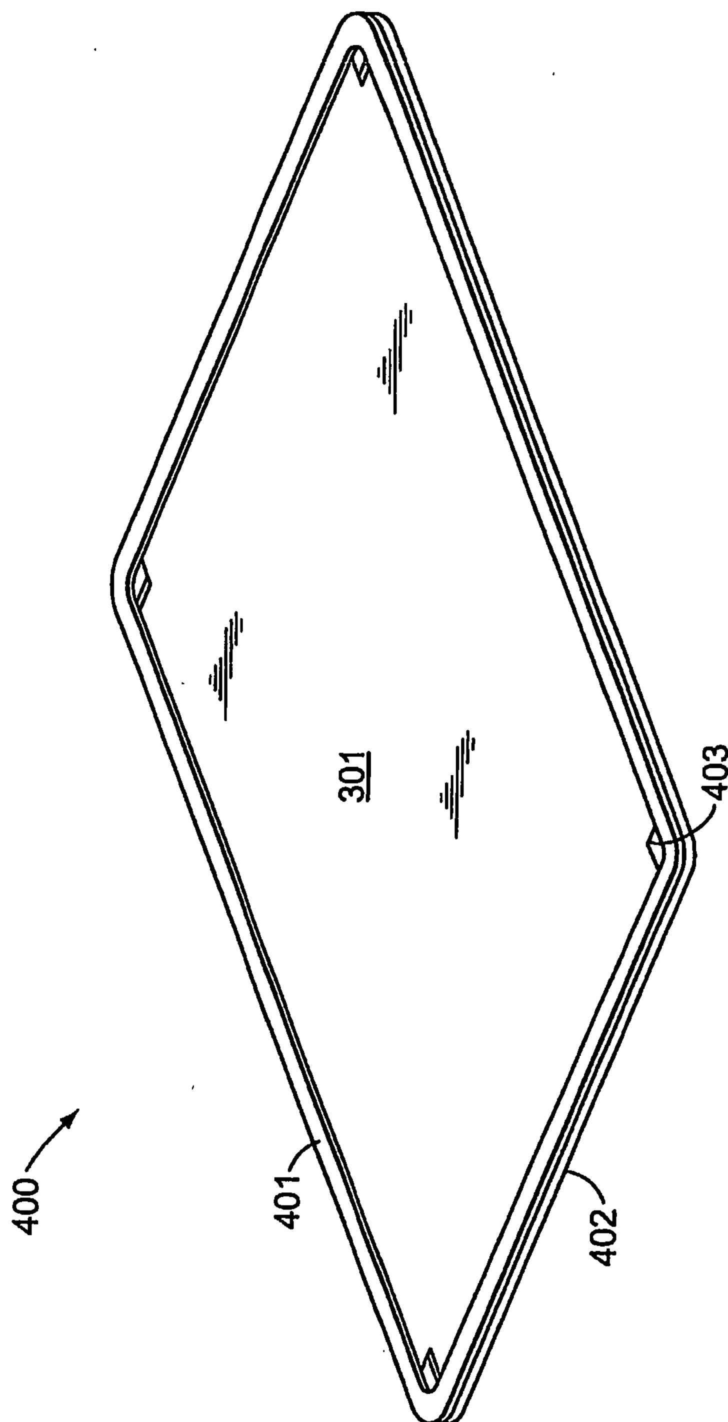


FIG. 4B

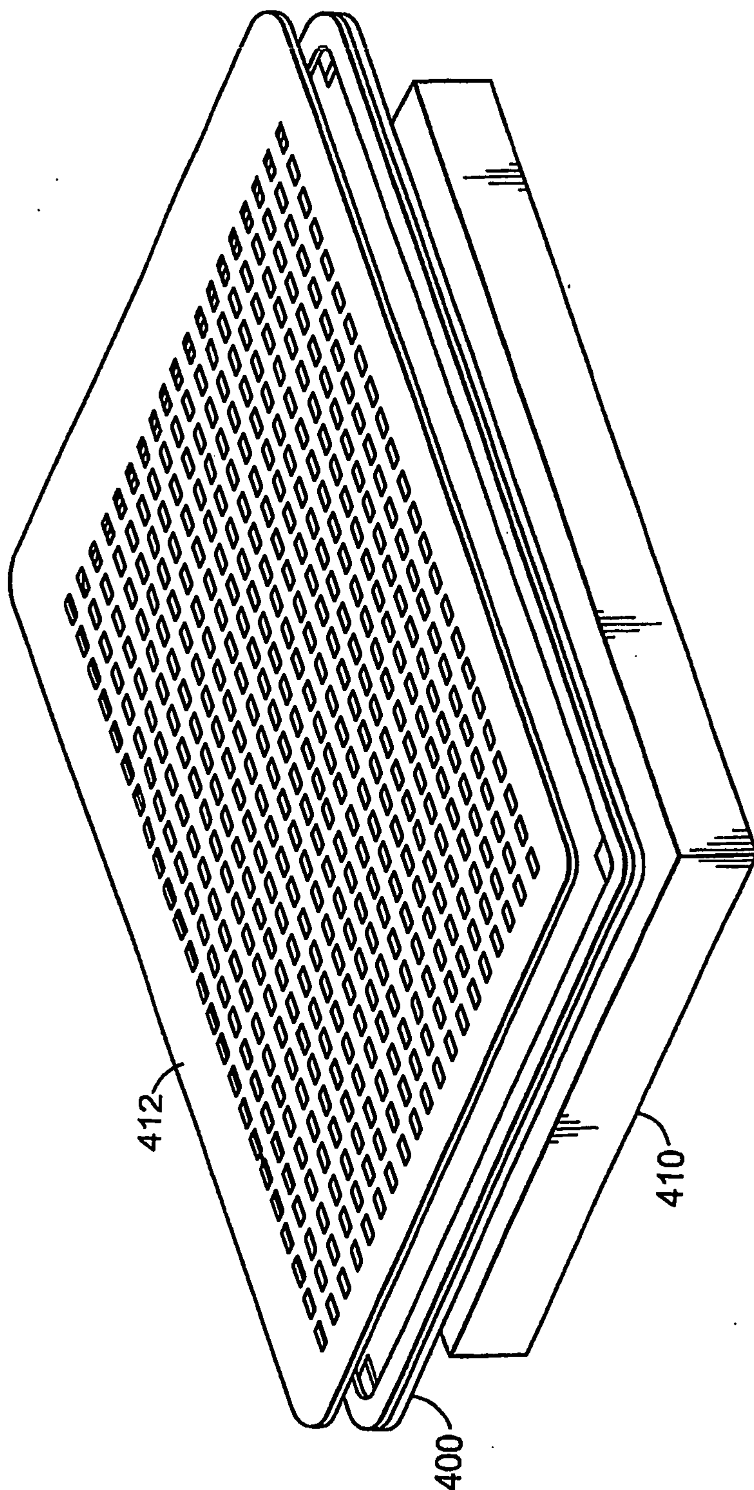


FIG. 4C

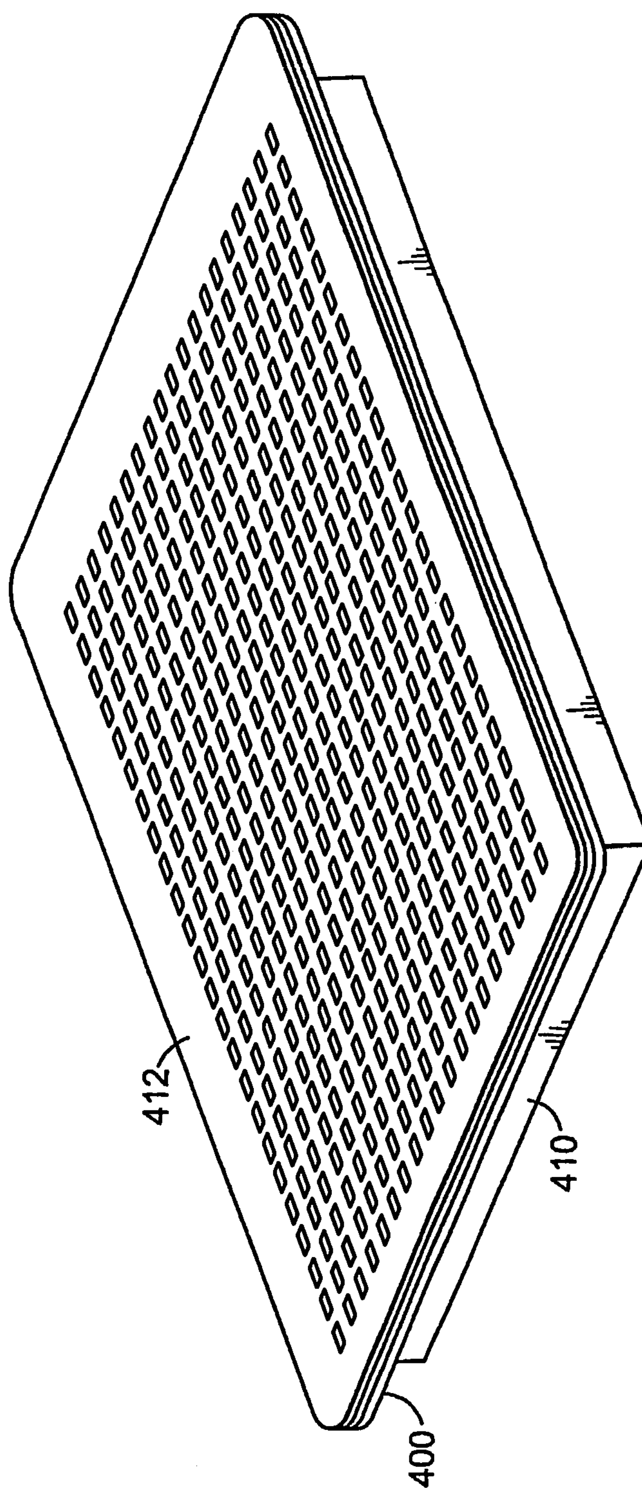


FIG. 4D

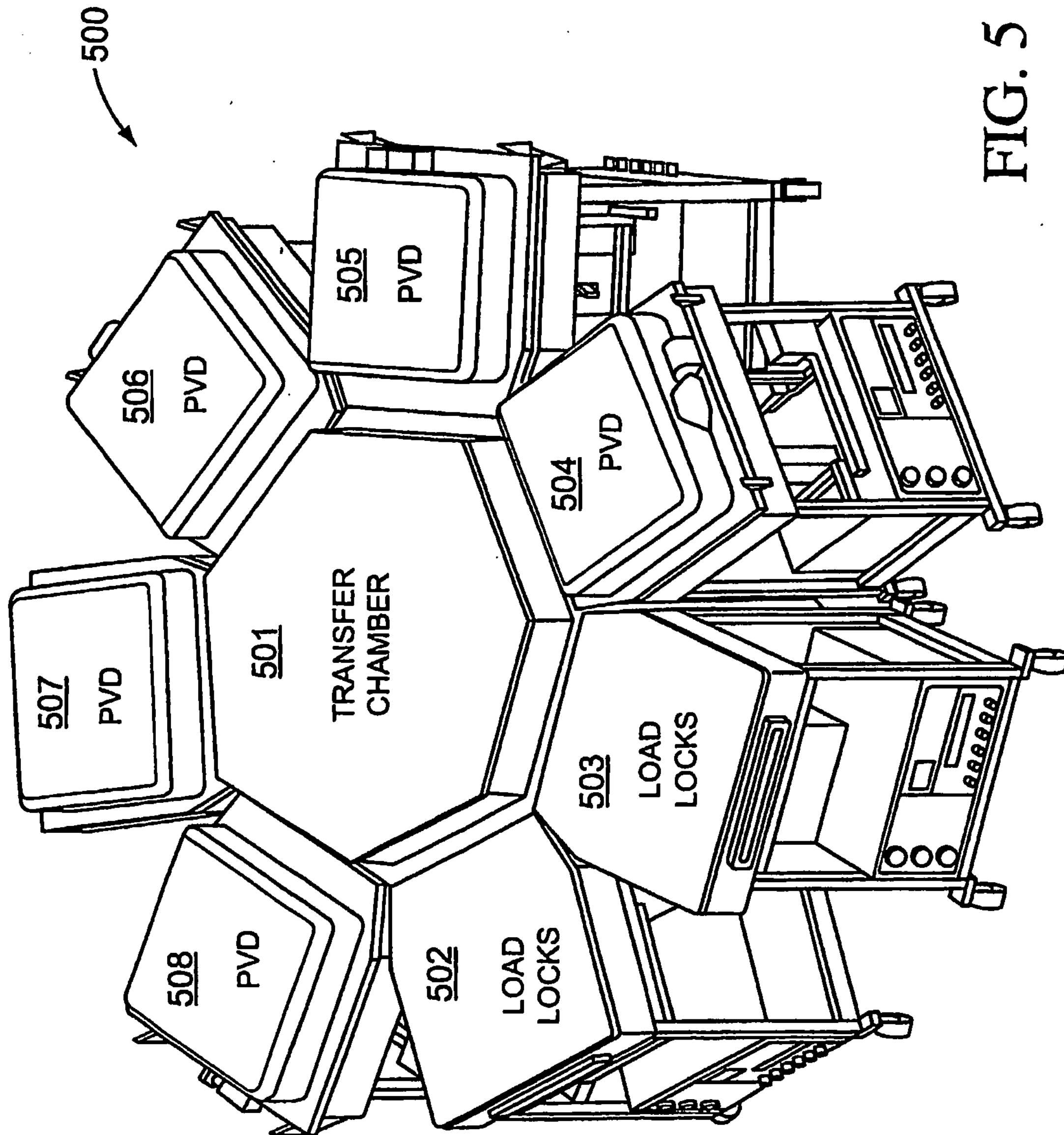


FIG. 5

PTO/SB/06 (10-07)
Approved for use through 06/30/2010. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD
Substitute for Form PTO-875

Application or Docket Number: 10/101 863

10/2/07 APPLICATION AS FILED – PART I

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	SMALL ENTITY RATE ($)	SMALL ENTITY FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY FEE ($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X =		OR	X =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X =			X =	
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $260 ($130 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))			N/A			N/A	
			TOTAL			TOTAL	810.

RCE

paid

* If the difference in column 1 is less than zero, enter "0" in column 2.

10/2/07 APPLICATION AS AMENDED – PART II

AMENDMENT A		CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE ($)	SMALL ENTITY ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 36	Minus	** 39	= —	X =		OR	X =	
	Independent (37 CFR 1.16(h))	* 3	Minus	*** 5	= —	X =		OR	X =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					N/A		OR	N/A	
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B		CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	RATE ($)	ADDITIONAL FEE ($)	OR	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X =		OR	X =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X =		OR	X =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					N/A		OR	N/A	
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	4	(pulsed with DC) with target with voltage with positive with negative	US-PGPUB; USPAT	OR	OFF	2007/11/07 11:48
L2	1848876	@ad>"20020316" or @rlad>"20020316"	US-PGPUB; USPAT	OR	OFF	2007/11/07 11:48
L3	3	1 not 2	US-PGPUB; USPAT	OR	OFF	2007/11/07 11:48

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

22852 7590 11/15/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	PAPER NUMBER
2823	
MAIL DATE	DELIVERY MODE
11/15/2007	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No.	Applicant(s)
	10/101,863	ZHANG ET AL.
	Examiner	Art Unit
	Michelle Estrada	2823

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *02 October 2007*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *2-13,21-24 and 40-60* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *2-13,21-24 and 40-60* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *10/2/07*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.

5) ☐ Notice of Informal Patent Application

6) ☐ Other: _____.

DETAILED ACTION

Continued Examination Under 37 CFR 1.114

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 10/2/07 has been entered.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21, 40-45 and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265), and further in view of Liu et al. (6,086,730) .

With respect to claims 21, 40, 43 and 51, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and

wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, if it is a band rejection, band pass, low-pass, high-pass, or stop band filter, this is a matter of design choice depending on what it is intended or needed for the desired final product or device. It is obvious that the filter is going to work at certain frequencies.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

The combination of Smolanoff et al. and Fu et al. does not clearly disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages.

Liu et al. disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages (Col. 8, lines 1-5 and Figs. 4B-4C).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Liu et al. to enable the pulsed DC power application step of the combination to be performed according to the teachings of Liu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed pulsed DC power application step of the combination and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claims 8 and 52, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12, 49 and 55, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claims 56-60, One of ordinary skill in the art would have been led to the recited time pulse, bias power and frequency to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of time pulse, bias power and frequency, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233

(CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed time pulse, bias power and frequency or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen time pulse, bias power and frequency or upon another variable recited in a claim, the Applicant must show that the chosen time pulse, bias power and frequency are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. and Liu et al. as applied to claims 10-13, 21, 40-45 and 51-60 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935,

1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. and Liu et al. as applied to claims 10-13, 21, 40-45 and 51-60 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al., Liu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

Response to Arguments

Applicant's arguments, filed 10/2/07, with respect to the rejection(s) of claim(s) 21, 43 and 51 under 35 USC 103 have been fully considered and are persuasive. Therefore, the rejection has been withdrawn. However, upon further consideration, a new ground(s) of rejection is made in view of Liu et al.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

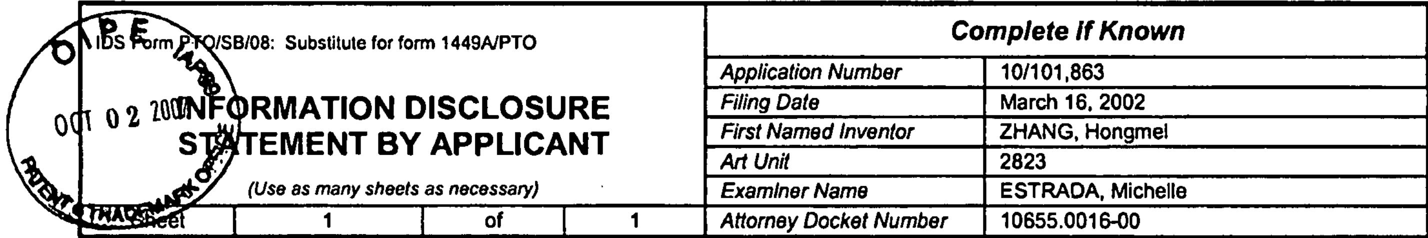
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
November 13, 2007



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete If Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	1	Attorney Docket Number	10655.0016-00

O I P E OCT 0 2 2007 PATENT & TRADEMARK OFFICE

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[1] Number[2] Kind Code[3] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[4]
ME		WO 2007/027535 A2	03-08-2007	Symmorphix, Inc.		

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
ME		Office Action dated September 22, 2006, from Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).	Yes
		Office Action mailed May 21, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Final Office Action mailed April 13, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Amendment filed August 9, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action mailed September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action mailed September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Notice of Non-Compliant Amendment mailed April 12, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Notice of Non-Compliant Amendment filed April 23, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Final Office Action mailed July 24, 2007 in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Response to Office Action filed July 9, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Corrected Notice of Allowance mailed June 7, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Supplemental Notice of Allowance mailed July 5, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01).	
		Second Supplemental Preliminary Amendment filed May 31, 2007, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00).	
ME		PCT International Preliminary Report on Patentability mailed June 21, 2007, in PCT Application No. PCT/US2005/044781 (Attorney Docket No. 9140.0042-304).	

Examiner Signature	Michelle Estrada	Date Considered	11/7/07

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EM 100825487 US**

Notice of References Cited	Application/Control No. 10/101,863	Applicant(s)/Patent Under Reexamination ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,086,730	07-2000	Liu et al.	204/192.16
*	B	US-5,584,974	12-1996	Sellers, Jeff C.	204/192.13
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

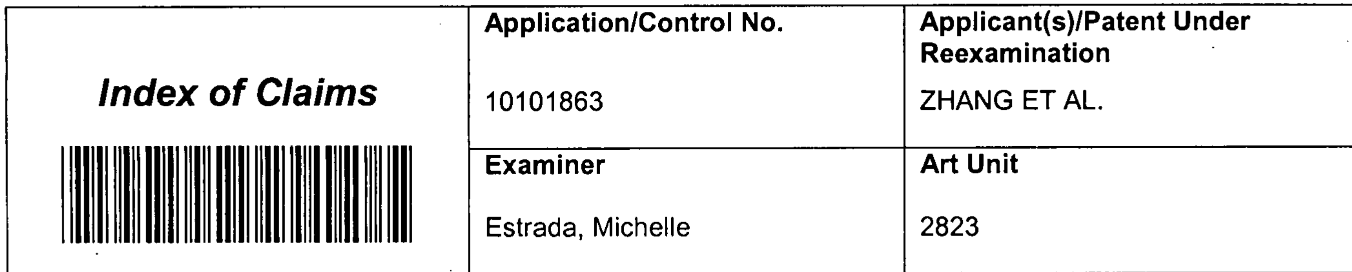
FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

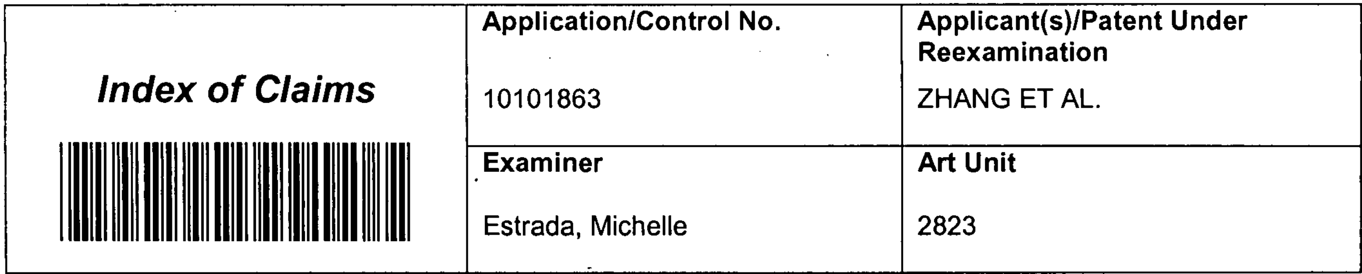


Index of Claims	Application/Control No. 10101863	Applicant(s)/Patent Under Reexamination ZHANG ET AL.
	Examiner Estrada, Michelle	Art Unit 2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	04/30/2007	11/11/2007							
	1	-	-							
	2	✓	✓							
	3	✓	✓							
	4	✓	✓							
	5	✓	✓							
	6	✓	✓							
	7	✓	✓							
	8	✓	✓							
	9	✓	✓							
	10	✓	✓							
	11	✓	✓							
	12	✓	✓							
	13	✓	✓							
	14	-	-							
	15	-	-							
	16	-	-							
	17	-	-							
	18	-	-							
	19	-	-							
	20	-	-							
	21	✓	✓							
	22	✓	✓							
	23	✓	✓							
	24	✓	✓							
	25	-	-							
	26	-	-							
	27	-	-							
	28	-	-							
	29	-	-							
	30	-	-							
	31	-	-							
	32	-	-							
	33	-	-							
	34	-	-							
	35	-	-							
	36	-	-							

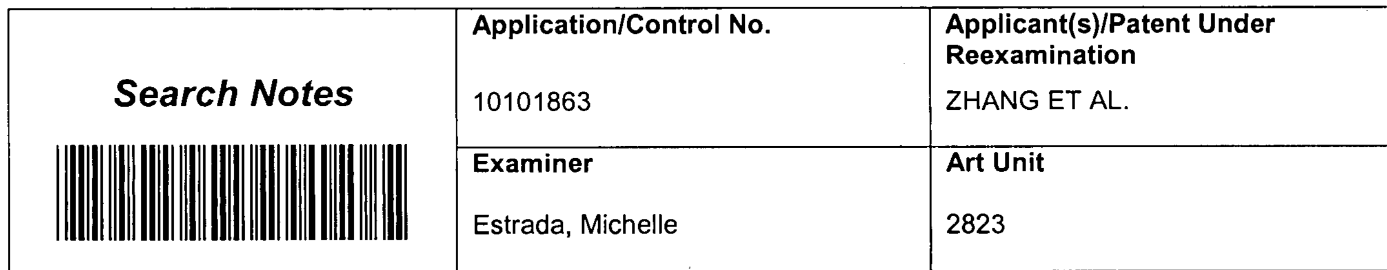


Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	**Art Unit**
	Estrada, Michelle	2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	04/30/2007	11/11/2007							
	37	-	-							
	38	-	-							
	39	-	-							
	40	✓	✓							
	41	✓	✓							
	42	✓	✓							
	43	✓	✓							
	44	✓	✓							
	45	✓	✓							
	46	✓	✓							
	47	✓	✓							
	48	✓	✓							
	49	✓	✓							
	50	✓	✓							
	51	✓	✓							
	52	✓	✓							
	53	✓	✓							
	54	✓	✓							
	55	✓	✓							
	56	✓	✓							
	57	✓	✓							
	58	✓	✓							
	59	✓	✓							
	60	✓	✓							



Search Notes	Application/Control No. 10101863	Applicant(s)/Patent Under Reexamination ZHANG ET AL.
	Examiner Estrada, Michelle	Art Unit 2823

SEARCHED

Class	Subclass	Date	Examiner

SEARCH NOTES

Search Notes	Date	Examiner
See East search attached	10/2/07	ME

INTERFERENCE SEARCH

Class	Subclass	Date	Examiner

11-29-07 1pa 2823

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
Hongmei ZHANG et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	Confirmation No.: 6938
For: BIASED PULSE DC REACTIVE	)	
SPUTTERING OF OXIDE FILMS	)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), this Supplemental Information Disclosure Statement includes a certification as specified by Section 1.97(e).

Based on reasonable inquiry, no document listed in this Supplemental Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Supplemental Information Disclosure Statement was known to any individual designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Supplemental Information Disclosure Statement.

Copies of the listed non-patent literature documents are attached. A copy of the U.S. patent is not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

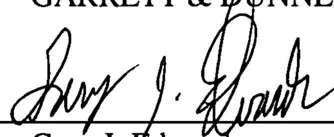
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to Deposit Account 06-0916.

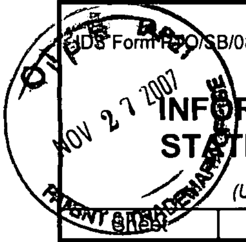
Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: November 27, 2007

By: 
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

**EXPRESS MAIL LABEL NO.
EM 074696455 US**



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	Hongmei ZHANG
Art Unit	2823
Examiner Name	Michelle ESTRADA
Attorney Docket Number	10655.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-7,262,131	08-28-2007	Narasimhan et al.	
		US-			
		US-			
		US-			
		US-			
		US-			
		US-			
		US-			

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NONPATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Amendment/RCE filed October 31, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Amendment/RCE filed October 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Office Action dated November 15, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Final Office Action dated October 10, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
		Amendment/RCE filed October 31, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 074696455 US

Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
Hongmei ZHANG et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed November 15, 2007, please amend the above-identified application as follows:

Amendments to the Claims are reflected in the listing of claims in this paper beginning on page 2.

Remarks/Arguments follow the amendment sections of this paper beginning on page 8 -

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Canceled).

¯. (Pr¯ ˙iously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14-20. (Canceled).

21. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target such that a ~~target~~ voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film; and

narrow band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poisonous mode to prepare the surface.

22. (Previously presented): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25-40. (Canceled).

41. (Previously presented): The method of claim 21, wherein a bandwidth of the narrow band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow;

applying pulsed DC power to a target such that a ~~target~~ voltage on the target oscillates

between positive and negative voltages and an oxide film is deposited on the substrate; and

narrow band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target.

44. (Previously presented): The method of claim 43, wherein band rejection filtering the DC power includes utilizing a band rejection filter with a bandwidth of less than about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed D˘ po¨er includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 µs.

˙7. (P¯¯˙iously presented): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that a ~~target~~ voltage on the target oscillates between positive and negative voltages; and

narrow band rejection filtering the pulsed DC power at a frequency of the bias power before applying pulsed DC power to the target,

wherein the oxide film is deposited on the substrate.

52. (Previously presented): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, N_2, O_2, C_2F_6, CO_2, CO, NH_3, NO, and halide containing gasses.

53. (Previously presented): The method of claim 51, wherein the target is a metallic target.

54. (Previously presented): The method of claim 51, wherein the target is an intermetllic target.

55. (Previously presented). The method of claim 51, further including sweeping the target with a magnetic field.

56. (Previously presented): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (Previously presented): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (Previously presented) The method of claims 21, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (Previously presented) The method of claim 43, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

60. (Previously presented) The method of claim 51, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

REMARKS

Claims 2-13, 21-24, and 40-60 are pending in the above-identified application. The Examiner has rejected claims 2-13, 21-24, and 40-60. In this application, claims 21, 43, and 51 are amended as discussed during an interview with the Examiner on December 11, 2007. Claim 40 is canceled.

Examiner's Interview

Applicant thanks the Examiner for meeting with us on December 11, 2007 (the "Interview"). In attendance at the Interview were Examiner Michelle Estrada, Inventor R. Ernest Demaray, and Applicant's representative Gary J. Edwards. During the interview, all of the claims were discussed as well as the art that has been cited against the claims. Agreement with respect to the claims was reached. In this Amendment, the claims have been amended as discussed during the interview. The Examiner indicated in the Interview Summary that the proposed language for the claims "would overcome the rejection on record."

The substance of the discussion with the Examiner with respect to the claims and the art is provided below.

Claim Rejections Under 35 U.S.C. § 103(a)

Claims 10-13, 21, 40-45, and 51-60

Claims 10-13, 21, 40-45, and 51-60 were rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,117,279 to Smolanoff et al. ("Smolanoff") in view of U.S. Patent No. 6,306,265 to Fu et al. ("Fu"), and in further view of U.S. Patent No. 6,086,730 to Liu et al. ("Liu"). Claims 21, 43, and 51 are independent claims. As discussed during the Interview,

Smolanoff, Fu, and Liu, either separately or in combination, do not teach or suggest "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

Further, both Smolanoff and Liu teach away from aspects of the claimed invention. As a result, there is no reason to combine Smolanoff or Liu with any other art in order to find claims 21, 43, or 51 obvious under 35 U.S.C. § 103 (a).

I. Smolanoff does not teach, and in fact teaches away from, "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages."

As discussed during the Interview, Smolanoff teaches away from a system where the target voltage becomes positive, as is recited in each of claims 21, 43, and 51. Smolanoff teaches a directed ion metal vapor source for deposition of conductive films. Although Smolanoff states that the DC source can be a pulsed DC source, Smolanoff also states that "[p]ower from the steady or **pulsed DC power supply 21** and/or RF generator 24 **produces a negative potential on the target 16.**" (Smolanoff, col. 5, line 66, -col. 6, line 1) (emphasis added). In every disclosure of target voltage, Smolanoff teaches that the target voltage must be negative. (*See, e.g.* col. 5, lines 39-44 ("[t]he magnet structure 20 preferably includes magnets that produce a closed magnetic tunnel over the surface of the target 16 that traps electrons given

off into the chamber 12 by the cathode assembly 17 when the cathode assembly 17 is **electrically energized to a negative potential** as is familiar to one skilled in the art"); col. 6, lines 9-12 ("[t]his main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16,** thereby ejecting particles of coating material from the target 16") (emphasis added)).

Smolanoff never teaches that the target can be positive and, in accordance with the teachings of Smolanoff, the target voltage must always be negative. <u>Therefore, Smolanoff teaches away from "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in each of claims 21, 43, and 51.</u> Smolanoff, then, also teaches away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

In addition, the Examiner indicated, with regard to the filter, that "if it is a band rejection, band pass, low-pass, high-pass, or stop band filter, this is a matter of design choice depending on what it is intended or needed for the desired final product or device." and then opined that "[i]t is obvious that the filter is going to work at certain frequencies." However, as explained during the Interview, that is not the case. The filter allows the combination of pulsed-DC power to the

target (where the target voltage is oscillated between positive and negative voltages) and an RF bias on the substrate. A filter that blocks too many of the constituent frequencies of the pulsed DC waveform results in the target voltage not attaining a positive voltage. A filter that does not block the RF bias voltage can result in failure of the DC power supply. Smolanoff does not teach the "narrow band rejection filtering" recited in each of claims 21, 43, and 51.

II. Liu does not teach, and in fact teaches away from, the combination of pulsed DC voltage (where a voltage on the target oscillates between positive and negative voltages) and applying RF bias to the substrate.

The Examiner stated that "[t]he combination of Smolanoff et al. and Fu et al. does not clearly disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages." (Office Action, page 4). The Examiner then relies on Liu to teach this aspect of claims 21, 43, and 51. As discussed above, Smolanoff teaches away from applying voltage to the target that causes the target voltage to become positive. Therefore, there is no reason to combine Smolanoff with Liu as suggested. Further, as discussed below, Liu also teaches away from combining a pulsed DC voltage to the target where the target voltage becomes positive and any bias voltage applied to the substrate except for a DC voltage applied to a conducting substrate.

Liu teaches deposition of conductive, diamond-like carbon thin films by sputtering with a pulsed-DC process. (*See, e.g.,* Liu, Abstract). Liu teaches that the carbon film is deposited by "a special type of pulsed DC power supply," (Liu, col. 6, lines 21-26), where the pulse characteristics provide "a positive potential to the target, by as much as, e.g. 300 volts positive," (Liu, col. 6, lines 44-45), and then "a negative potential to the target," (Liu, col. 6, line 50).

However, Liu teaches away from applying any bias to the substrate that is not a DC bias, and then only if the substrate is a conducting substrate. As taught in Liu,

> In addition to the pulsed DC sputtering with above mentioned characteristics, the substrate can also be biased in order to enhance the ta-C:H characteristics of the carbon film. **Although this can only be done with conductive substrates**, the effect is pronounced and useful. Nominally, the substrate is biased negative to the ground . . . .

(Liu, col. 6, line 66, to col. 7, line 3). Liu further teaches only DC bias voltages. (*See*, Liu, col. 7, lines 2-11).

Therefore, Liu does not teach the combination of pulsed DC where a voltage on the target oscillates between positive and negative voltages and applying an RF bias to the substrate, and in fact teaches away from such a combination especially as it applies to insulating films. As a result, Liu can not teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

There would be no reason to combine Smolanoff and Liu as suggested by the Examiner because each of these references teaches away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the

oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

III. Fu does not teach or suggest the claimed invention, and further Fu does not teach the elements for which it is being cited.

The Examiner stated that "Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface." (Office Action' page 3). Fu is relied upon to disclose "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40)." (Office Action, page 3).

As discussed above, there is no reason to combine either of Smolanoff and Liu with Fu because both Smolanoff and Liu teach away from the combination of pulsed-DC voltage to the target where the voltage on the target oscillates between positive and negative voltages and an RF bias applied to the substrate, as is recited in claims 21, 43, and 51. Additionally, Fu does not teach the elements for which it is relied or itself teach the combination of pulsed-DC power and RF bias recited in the claims.

Fu teaches high density, magnetic field enhanced ionized metal vapor deposition of conducting films. (*See* Fu, abstract). Fu, however, teaches utilization of a DC power supply (Fu, col. 1, lines 30-32) in combination with an RF bias applied to the substrate (Fu, col. 2, lines 36-

41). Therefore, Fu fails to teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

Fu does teach operation in the poison mode and operation in the metallic mode as applied to TiN deposition, but does not teach "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poison mode to prepare the surface," as is recited in claim 21. As stated by Fu,

> Reactive sputtering to produce TiN is known to operate in two modes, metallic mode and poison mode. Metallic mode produces a high-density, gold-colored film on the wafer. Poison mode, which is often associated with a high nitrogen flow, produces a purple/brown film which advantageously has low stress. However, the poison-mode film has many grain boundaries, and film defects severely reduce chip yield. Furthermore, the deposition rate in poison mode is typically only one-quarter of the rate in metallic mode. It is generally believed that in poison mode the nitrogen reacts with the target to form a TiN surface on the Ti target while in metallic mode the target surface remains clean and TiN forms only the wafer.

(Fu, col. 19, lines 28-30). Fu teaches operation in either metallic mode or poison mode, and does not teach "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poisonous mode to

prepare the surface," as is recited in claim 21. Independent claims 43 and 51 do not include this limitation.

IV. Summary

As discussed above, claims 21, 43, and 51 are allowable over the combination of Smolanoff, Fu, and Liu. Claims 10-13, 41-42, and 58 depend from claim 21 and are therefore allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 21. Claim 40 has been canceled. Claims 44-45 and 59 depend from claim 43 and are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 43. Claims 52-57 and 60 depend from claim 51 and are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 51.

Claims 2-4, 6, and 22-24

Claims 2-4, 6, and 22-24 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Fu and Liu, as applied to claims 10-13, 21, 40-45, and 51-60.

Claims 2-4, 6, and 22-24 depend from claim 21. As discussed above, claim 21 is allowable over the combination of Smolanoff, Fu, and Liu. Therefore, claims 2-4, 6, and 22-24 are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 21.

Claims 7-9

Claims 7 and 9 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Fu and Liu, as applied to claims 10-13, 21, 40-45, and 51-60, and in further view of U.S. Patent Publication No. 2003/0077914 to Le et al. ("Le").

Claims 7 and 9 depend from claim 21. As discussed above, claim 21 is allowable over the combination of Smolanoff, Fu, and Liu. Le does not cure the defects in the teachings of Smolanoff, Fu, and Liu. Further, there is no reason to combine Smolanoff and Liu with any other art in order to find claim 21 obvious because both Smolanoff and Liu teach away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21.

Le teaches deposition of an anti-reflective coating by pulsing a DC source with no bias applied to the substrate. As taught in Le,

> The pulsed DC power source 22 applies a pulsed DC (direct current) voltage to the target 14. The pulsed DC voltage may be oscillated between negative and positive states. In one version, the pulsed DC voltage is pulsed between "on" and "off" states . . . .

(Le, par. 0071). As further stated, "[t]he pulsed DC voltage alleviates this problem by maintaining "on" and "off" states during each pulse cycle." (Le, par. 0072). Therefore, Le does not teach that the target voltage goes positive, and only teaches that the DC voltage is pulsed. Further, there is no teaching of a bias applied to the substrate. Therefore, Le does not teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21.

Further, Le was apparently presented to teach "wherein the RF bias power is optimized to provide planarization," as is recited in claim 7. However, Le does not teach RF bias or planarization of a cladding layer.

Therefore, claims 7 and 9 are allowable over the cited art for at least the same reasons as is claim 21.

Conclusion

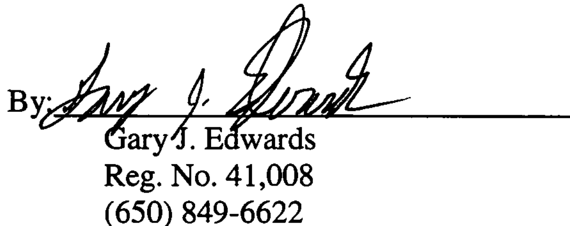
In view of the foregoing amendments, which are discussed during the Interview, and the remarks, which provides the substance of the discussion during the Interview, Applicant respectfully requests the timely allowance of the pending claims, which the Examiner indicated would be allowable after the amendments provided herein. If the Examiner has any questions or concerns regarding this Amendment or these Remarks, the Examiner is invited to call Applicant's representative.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 18, 2007

By: 
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

Electronic Acknowledgement Receipt

EFS ID:	2610189
Application Number:	10101863
International Application Number:	
Confirmation Number:	6938
Title of Invention:	Biased pulse DC reactive sputtering of oxide films
First Named Inventor/Applicant Name:	Hongmei Zhang
Customer Number:	22852
Filer:	Gary James Edwards/Annie Wong
Filer Authorized By:	Gary James Edwards
Attorney Docket Number:	10655.0016-00
Receipt Date:	18-DEC-2007
Filing Date:	16-MAR-2002
Time Stamp:	19:10:11
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes) /Message Digest	Multi Part /.zip	Pages (if appl.)
1	Amendment - After Non-Final Rejection	Amendment_Response_to_OA_10655-0016-00.pdf	237230 5b7b12a167c6082e1fe7acb03285f0060eea8dbe	no	17

Warnings:

The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing

Information:

Total Files Size (in bytes):	237230

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number	Filing Date	To be Mailed
10/101,863	03/16/2002	☐

APPLICATION AS FILED – PART I

SMALL ENTITY ☒ OR OTHER THAN SMALL ENTITY

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	RATE ($)	FEE ($)		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =			X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							
			TOTAL			TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

SMALL ENTITY OR OTHER THAN SMALL ENTITY

AMENDMENT	12/18/2007	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 35	Minus	** 39	= 0	X $25 =	0	OR	X $ =	
	Independent (37 CFR 1.16(h))	* 3	Minus	***5	= 0	X $105 =	0	OR	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE	0	OR	TOTAL ADD'L FEE	

AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =		OR	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =		OR	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
eugenia v. hardy

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

EAST Search History

S66	105	(n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench))	US-PGPUB; USPAT	OR	OFF	2004/02/17 14:39
S67	100	((n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench))) not (@ad>"20020511" or @rlad>"20020511")	US-PGPUB; USPAT	OR	OFF	2004/02/17 14:39
S68	97	(((n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench))) not (@ad>"20020511" or @rlad>"20020511")) not (438/429. ccls. not (@ad>"20020511" or @rlad>"20020511"))	US-PGPUB; USPAT	OR	OFF	2004/02/17 14:39
S69	1236723	@ad>"20020511" or @rlad>"20020511"	US-PGPUB; USPAT	OR	OFF	2006/09/05 09:32
S70	121	band with (rejection or stop or low or narrow) with filter with frequency with bias	US-PGPUB; USPAT	OR	OFF	2006/09/05 09:33
S71	93	S70 not S69	US-PGPUB; USPAT	OR	OFF	2006/09/05 09:33
S72	1	("7262131").PN.	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:13
S73	2456	(438/769,770,771,787,788).CCLS.	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:17
S74	1939945	@ad>"20020316" or @rlad>"20020316"	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:17
S75	1498	S73 not S74	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:18
S78	3342	(204/192.12,192.15).CCLS.	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:18
S79	316	(427/533).CCLS.	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:19
S80	1190	(257/E21.273,E21.278,E21.462).CCLS.	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:26
S81	550	S80 not S74	US-PGPUB; USPAT	OR	OFF	2008/01/17 12:26

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 01/25/2008

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

TITLE OF INVENTION: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

APPLN. TYPE	SMALL ENTITY	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	YES	$720	$300	$0	$1020	04/25/2008

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the SMALL ENTITY status shown above.

If the SMALL ENTITY is shown as YES, verify your current SMALL ENTITY status:

A. If the status is the same, pay the TOTAL FEE(S) DUE shown above.

B. If the status above is to be removed, check box 5b on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and twice the amount of the ISSUE FEE shown above, or

If the SMALL ENTITY is shown as NO:

A. Pay TOTAL FEE(S) DUE shown above, or

B. If applicant claimed SMALL ENTITY status before, or is now claiming SMALL ENTITY status, check box 5a on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and 1/2 the ISSUE FEE shown above.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PTOL-85 (Rev. 08/07) Approved for use through 08/31/2010.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

TITLE OF INVENTION: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

APPLN. TYPE	SMALL ENTITY	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	YES	$720	$300	$0	$1020	04/25/2008

EXAMINER	ART UNIT	CLASS-SUBCLASS
ESTRADA, MICHELLE	2823	438-788000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
   - ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
   - ☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
   (1) the names of up to 3 registered patent attorneys or agents OR, alternatively,
   (2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
   1 ____________
   2 ____________
   3 ____________

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
- ☐ Issue Fee
- ☐ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies ____________

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ☐ A check is enclosed.
- ☐ Payment by credit card. Form PTO-2038 is attached.
- ☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number ____________ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27.
- ☐ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature ____________ Date ____________

Typed or printed name ____________ Registration No. ____________

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	PAPER NUMBER
2823	

DATE MAILED: 01/25/2008

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment to date is 0 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 0 day(s).

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

PTOL-85 (Rev. 08/07) Approved for use through 08/31/2010.

Notice of Allowability	Application No. 10/101,863	Applicant(s) ZHANG ET AL.	
	Examiner Michelle Estrada	Art Unit 2823	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *12/18/07*.

2. ☒ The allowed claim(s) is/are *2-4,6-13,21-24 and 41-60*.

3. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
   a) ☐ All b) ☐ Some* c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. ______ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: ______.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

4. ☐ A SUBSTITUTE OATH OR DECLARATION must be submitted. Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL PATENT APPLICATION (PTO-152) which gives reason(s) why the oath or declaration is deficient.

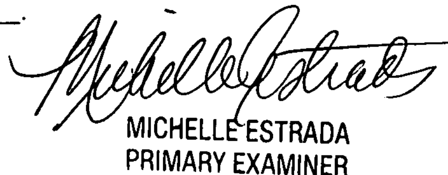
5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   (a) ☐ including changes required by the Notice of Draftsperson's Patent Drawing Review (PTO-948) attached
   1) ☐ hereto or 2) ☐ to Paper No./Mail Date ______.
   (b) ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date ______.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

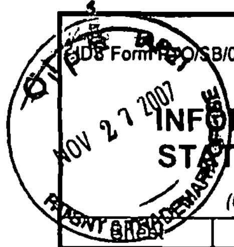
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Notice of Draftperson's Patent Drawing Review (PTO-948)
3. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 11/27/07
4. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
5. ☐ Notice of Informal Patent Application
6. ☐ Interview Summary (PTO-413), Paper No./Mail Date ______ .
7. ☐ Examiner's Amendment/Comment
8. ☐ Examiner's Statement of Reasons for Allowance
9. ☐ Other ______.



MICHELLE ESTRADA
PRIMARY EXAMINER



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	Hongmei ZHANG
Art Unit	2823
Examiner Name	Michelle ESTRADA
Attorney Docket Number	10655.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
ME		US-7,262,131	08-28-2007	Narasimhan et al.	
		US-			
		US-			
		US-			
		US-			
		US-			
		US-			
		US-			

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NONPATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
ME		Amendment/RCE filed October 31, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Amendment/RCE filed October 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Office Action dated November 15, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Final Office Action dated October 10, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	
ME		Amendment/RCE filed October 31, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00).	

Examiner Signature	Michelle Estrada	Date Considered	1/17/08

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
EM 074696455 US**

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

Bib Data Sheet

CONFIRMATION NO. 6938

SERIAL NUMBER 10/101,863	FILING DATE 03/16/2002 RULE	CLASS 438	GROUP ART UNIT 2823	ATTORNEY DOCKET NO. M-12245 US

APPLICANTS

Hongmei Zhang, San Jose, CA;

Mukundan Narasimhan, San Jose, CA;
Ravi B. Mullapudi, San Jose, CA;Richard E. Demaray, Portola Valley, CA;

** CONTINUING DATA *************************
none

** FOREIGN APPLICATIONS ********************
none

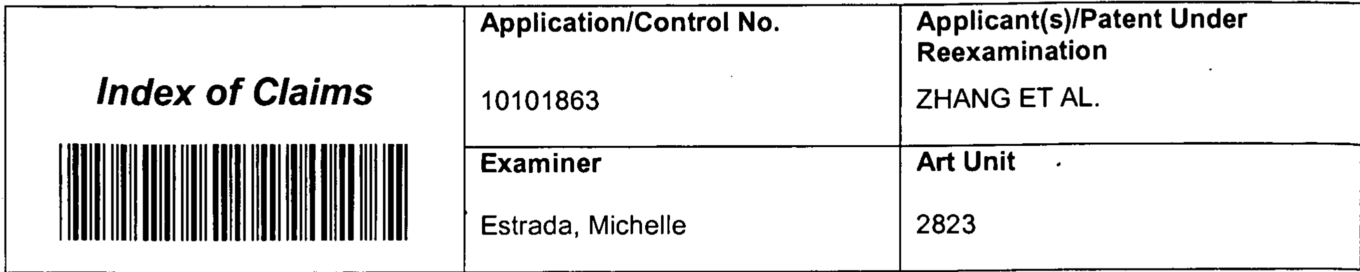
IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** SMALL ENTITY **
** 05/17/2002

Foreign Priority claimed ☐ yes ☑ no 35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance Verified and Acknowledged ______ Examiner's Signature ______ Initials	STATE OR COUNTRY CA	SHEETS DRAWING 27	TOTAL CLAIMS ~~39~~ 19	INDEPENDENT CLAIMS ~~5~~ 2

ADDRESS
22852
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON , DC
20001-4413

TITLE
Biased pulse DC reactive sputtering of oxide films

FILING FEE RECEIVED	FEES: Authority has been given in Paper No. _________ to charge/credit DEPOSIT ACCOUNT No. _________ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time)

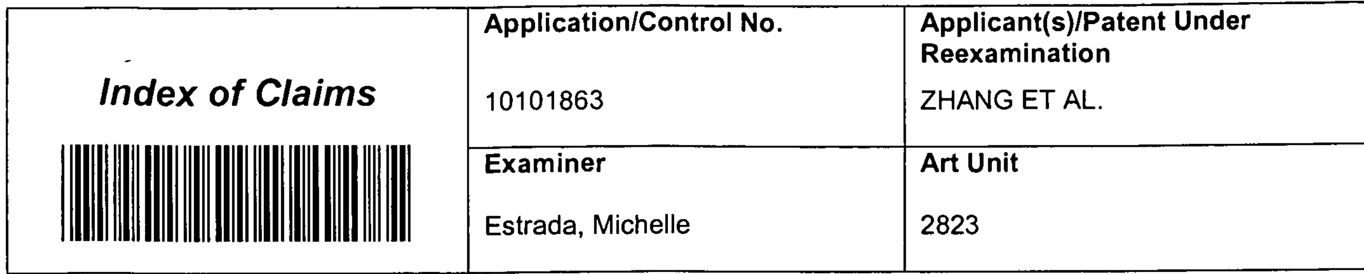


Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	Art Unit
	Estrada, Michelle	2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE									
Final	Original	04/30/2007	11/11/2007	01/17/2008							
	1	-	-								
2	2	✓	✓	=							
3	3	✓	✓	=							
4	4	✓	✓	=							
	5	✓	✓	-							
5	6	✓	✓	=							
6	7	✓	✓	=							
7	8	✓	✓	=							
8	9	✓	✓	=							
9	10	✓	✓	=							
10	11	✓	✓	=							
11	12	✓	✓	=							
12	13	✓	✓	=							
	14	-	-	-							
	15	-	-	-							
	16	-	-	-							
	17	-	-	-							
	18	-	-	-							
	19	-	-	-							
	20	-	-	-							
1	21	✓	✓	=							
13	22	✓	✓	=							
14	23	✓	✓	=							
15	24	✓	✓	=							
	25	-	-	-							
	26	-	-	-							
	27	-	-	-							
	28	-	-	-							
	29	-	-	-							
	30	-	-	-							
	31	-	-	-							
	32	-	-	-							
	33	-	-	-							
	34	-	-	-							
	35	-	-	-							
	36	-	-	-							



Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	**Art Unit**
	Estrada, Michelle	2823

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	04/30/2007	11/11/2007	01/17/2008						
	37	-	-	-						
	38	-	-	-						
	39	-	-	-						
	40	✓	✓	-						
16	41	✓	✓	=						
17	42	✓	✓	=						
18	43	✓	✓	=						
19	44	✓	✓	=						
20	45	✓	✓	=						
21	46	✓	✓	=						
22	47	✓	✓	=						
23	48	✓	✓	=						
24	49	✓	✓	=						
25	50	✓	✓	=						
26	51	✓	✓	=						
27	52	✓	✓	=						
28	53	✓	✓	=						
29	54	✓	✓	=						
30	55	✓	✓	=						
31	56	✓	✓	=						
32	57	✓	✓	=						
33	58	✓	✓	=						
34	59	✓	✓	=						
35	60	✓	✓	=						

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	Art Unit
	Estrada, Michelle	2823

ORIGINAL

CLASS	SUBCLASS
438	778

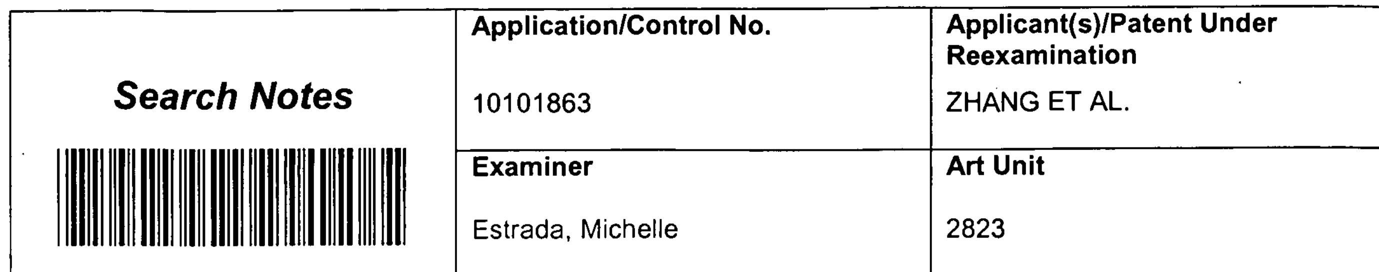
CROSS REFERENCE(S)

CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)				
438	787	788			
427	533				
204	192.12	192.15			

INTERNATIONAL CLASSIFICATION

CLAIMED					NON-CLAIMED
H	0	1	L	21 / 31 (2006.01.01)	
H	0	1	L	21 / 469 (2006.01.01)	

NONE (Assistant Examiner) (Date)	MICHELLE ESTRADA PRIMARY EXAMINER	Total Claims Allowed: 35
1-24-08 (Legal Instruments Examiner) (Date)	Estrada, Michelle 1/17/08 (Primary Examiner) (Date)	O.G. Print Claim(s): 1 O.G. Print Figure: 1A



Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	10101863	ZHANG ET AL.
	Examiner	Art Unit
	Estrada, Michelle	2823

SEARCHED

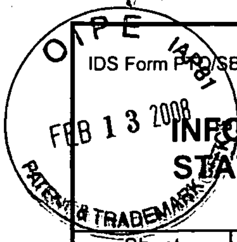
Class	Subclass	Date	Examiner
Updated as before		1/17/08	ME
257	E21.273,E21.278,E21.462	1/17/08	Me

SEARCH NOTES

Search Notes	Date	Examiner
See East search attached	10/2/07	ME
Inspected parent for pertinent prior art	1/17/08	ME

INTERFERENCE SEARCH

Class	Subclass	Date	Examiner
PG Pub text search		1/17/08	ME



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	Hongmei ZHANG
Art Unit	2823
Examiner Name	Michelle ESTRADA
Attorney Docket Number	10655.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-			

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

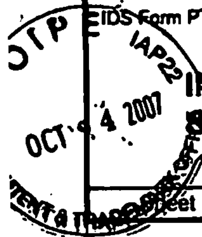
NONPATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action dated November 21, 2007, in U.S. Appl. No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Office Action dated December 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action dated January 29, 2008, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Office Action dated January 25, 2008, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Response to Office Action dated December 18, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Notice of Allowance dated February 1, 2008, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Office Action dated November 16, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 10655.0025-00).	

Examiner Signature		Date Considered	

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 074697411 US



EIDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/650,461
Filing Date	August 27, 2003
First Named Inventor	DAWES, David
Art Unit	2883
Examiner Name	DUPUIS, Derek L.
Attorney Docket Number	10655.0025-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
/DLD/		Amendment/RCE filed August 9, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
/DLD/		Office Action dated September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
/DLD/		Final Office Action dated September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
/DLD/		Response to Final Office Action filed October 2, 2007, in U.S. Application No. 10/101,863 (Attorney Docket No. 9140.0016-00).	
/DLD/		Final Office Action dated July 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	

Examiner Signature	/Derek Dupuis/	Date Considered	11/12/2007

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 100825650 US

ITW 2823

03-15-08

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	Confirmation No.: 6938
For: BIASED PULSE DC REACTIVE	)	
SPUTTERING OF OXIDE FILMS	)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(d)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(d), Applicants brings to the attention of the Examiner the documents on the attached listing. This Supplemental Information Disclosure Statement is being filed after a Notice of Allowance but before payment of the issue fee and the Commissioner is authorized to charge the fee of $180.00 to Deposit Account No. 06-0916, as specified under § 1.17(p) and a statement as specified under § 1.97(e).

Based on reasonable inquiry, no document listed in this Supplemental Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Supplemental Information Disclosure Statement was known to any individual designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Supplemental Information Disclosure Statement.

02/15/2008 EAYALEW1 00000029 060916 10101863
01 FC:1806 180.00 DA

Copies of the listed non-patent literature documents are attached. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any additional fee due in connection with the filing of this Statement, please charge the fee to Deposit Account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 13, 2008

By: Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

**EXPRESS MAIL LABEL NO.
EM 074697411 US**

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

22852 7590 03/03/2008
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	

ART UNIT	PAPER NUMBER
2823	

MAIL DATE	DELIVERY MODE
03/03/2008	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

UNITED STATES DEPARTMENT OF COMMERCE
U.S. Patent and Trademark Office
Address : COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450

APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR / PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
10101863	3/16/02	ZHANG ET AL.	10655.0016-00

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
Michelle Estrada	
ART UNIT	**PAPER**
2823	20080221

DATE MAILED:

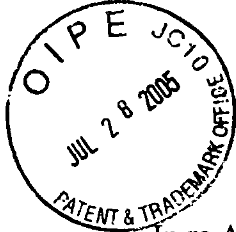
Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner for Patents

Attached are the IDS filed 7/28/05 and 7/13/06 that have been considered.

/Michelle Estrada/
Primary Examiner, Art Unit 2823

PTO-90C (Rev.04-03)



PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
ZHANG, Hongmei et al.	) Group Art Unit: 2823
Application No.: 10/101,863	) Examiner: ESTRADA, Michelle
Filed: March 16, 2002	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

Based on reasonable inquiry, no document listed in this Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Information Disclosure Statement was known to any individual

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Information Disclosure Statement.

Copies of the listed foreign patents and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and applicants determine that the cited documents do not constitute "prior art" under United States law, applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

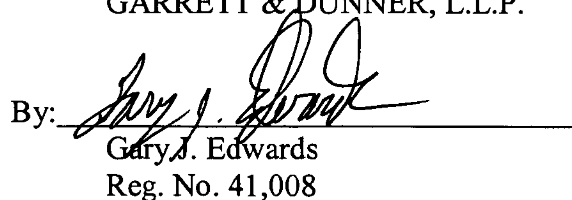
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

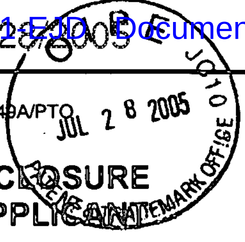
FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 28, 2005

By: 
Gary J. Edwards
Reg. No. 41,008

EXPRESS MAIL LABEL NO.
EV 727733065 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 2005/0006768 A1	01-13-2005	Narasimhan et al.	
		US 2005/0000794 A1	01-06-2005	Demaray et al.	
		US 2004/0259305 A1	12-23-2004	Demaray et al.	
		US 2004/0105644 A1	06-03-2004	Dawes	
		US 2003/0174391 A1	09-18-2003	Pan et al.	
		US 2003/0141186 A1	07-31-2003	Wang et al.	
		US 2003/0127319 A1	06-10-2003	Demaray et al.	
		US 2003/0097858 A1	05-29-2003	Strohhofer et al.	
		US 2002/0170821 A1	11-21-2002	Sandlin et al.	
		US 2001/041460 A1	11-15-2001	Wiggins	
		US 2001/0027159 A1	10-04-2001	Kaneyoshi	
		US 6,750,156 B2	06-15-2004	Le et al.	
		US 6,576,546 B2	06-10,-2003	Gilbert et al.	
		US 6,444,750 B1	09-03-2002	Touhsaent	
		US 6,433,380 B2	08-13-2002	Shin	
		US 6,423,776 B1	07-23-2002	Akkapeddi et al.	
		US 6,416,598 B1	07-09-2002	Sircar	
		US 6,413,645 B1	07-02-2002	Graff et al.	
		US 6,365,319 B1	04-02-2002	Heath et al.	
		US 6,302,939 B1	10-16-2001	Rabin et al.	
		US 6,300,215 B1	10-09-2001	Shin	
		US 6,261,917 B1	07-17-2001	Quek et al.	
		US 6,248,640 B1	06-19-2001	Nam	
		US 6,232,242	05-15-2001	Hata et al.	
		US 6,214,660 B1	04-10-2001	Uemoto et al.	
		US 6,210,544 B1	04-03-2001	Sasaki	
		US 6,204,111 B1	03-20-2001	Uemoto et al.	
		US 6,198,217 B1	03-06-2001	Suzuki et al.	
		US 6,197,167 B1	03-06-2001	Tanaka	
		US 6,165,566	12-26-2000	Tropsha	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

		US 6,157,765	12-05-2000	Bruce et al.	
		US 6,146,225	11-14-2000	Sheats et al.	
		US 6,106,933	08-22-2000	Nagai et al.	
		US 6,080,643	06-27-2000	Noguchi et al.	
		US 6,077,642	06-20-2000	Ogata et al.	
		US 6,071,323	06-06-2000	Kawaguchi	
		US 6,058,233	05-02-2000	Dragone	
		US 6,052,397	04-18-2000	Jeon et al.	
		US 6,051,296	04-18-2000	McCaulley et al.	
		US 6,046,081	04-04-2000	Kuo	
		US 6,004,660	12-21-1999	Topolski et al.	
		US 5,966,491	10-12-1999	DiGiovanni	
		US 5,952,778	09-14-1999	Haskal et al.	
		US 5,930,584	07-27-1999	Sun et al.	
		US 5,900,057	05-04-1999	Buchal et al.	
		US 5,882,946	03-16-1999	Otani	
		US 5,870,273	02-09-1999	Sogabe et al.	
		US 5,853,830	12-29-1998	McCaulley et al.	
		US 5,831,262	11-03-1998	Greywall et al.	
		US 5,811,177	09-22-1998	Shi et al.	
		US 5,771,562	06-30-1998	Harvey, III et al.	
		US 5,762,768	06-09-1998	Goy et al.	
		US 5,757,126	05-26-1998	Harvey, III et al.	
		US 5,738,731	04-14-1998	Shindo et al.	
		US 5,731,661	03-24-1998	So et al.	
		US 5,689,522	11-18-1997	Beach	
		US 5,686,360	11-11-1997	Harvey, III et al.	
		US 5,654,984	08-05-1997	Hershbarger et al.	
		US 5,607,789	03-04-1997	Treger et al.	
		US 5,591,520	01-07-1997	Migliorini et al.	
		US 5,563,979	10-08-1996	Bruce et al.	
		US 5,538,796	07-23-1996	Schaffer et al.	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	3	of	9	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS					
		US 5,499,207	03-12-1996	Miki et al.	
		US 5,457,569	10-10-1995	Liou et al.	
		US 5,355,089	10-11-1994	Treger	
		US 5,309,302	05-03-1994	Vollmann	
		US 5,306,569	04-26-1994	Hiraki	
		US 5,303,319	04-12-1994	Ford et al.	
		US 5,296,089	03-22-1994	Chen et al.	
		US 5,173,271	12-22-1992	Chen et al.	
		US 5,119,460	06-02-1992	Bruce et al.	
		US 5,107,538	04-21-1992	Benton et al.	
		US 5,085,904	02-04-1992	Deak et al.	
		US 4,587,225	05-06-1986	Tsukuma et al.	
		RE 32,449	06-30-1987	Claussen	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		EP 1 189 080 A2	03-20-2002	Agere Systems Optoelectronics Guardian Corporation		
		EP 1 092 689 A1	04-18-2001	BPS Alzenau GmbH		
		EP 1068899 A1	01-17-2001	Nippon Sheet Glass Co., Ltd.		
		EP 0 639 655 A1	02-22-1995	Asahi Glass Co, Ltd.		
		EP 0 652 308 A2	10-13-1994	Mega Chips Corp.		
		EP 0 510 883 A2	10-28-1992	AT&T		
		JP 7-233469	09-05-1995	Asahi Glass Co, Ltd.		
		JP 2-054764 A2	02-23-1990	Leybold AG		
		WO 00/21898 A1	04-20-2000	Samsung Electronics Co.		

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	4	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		AFFINITO et al., "PML/oxide/PML Barrier Layer Performance Differences Arising from Use of UV or Electron Beam Polymerization of the PML Layers," *Thin Solid Films* Vol. 308-309, pp. 19-25 (1997)	
		AFFINITO et al., "Polymer-Oxide Transparent Barrier Layers," Society of Vacuum Coaters, 39th Ann. Technical Conference Proceedings, May 5-10, 1996, Philadelphia, PA, pp. 392-397 (1996).	
		ALDER, T. et al., "High-Efficiency Fiber-to-Chip Coupling Using Low-Loss Tapered Single-Mode Fiber," IEEE Photonics Technology Letters, 12(8):1016-1018 (2000).	
		ALMEIDA, Vilson R. et al., "Nanotaper for compact mode conversion," *Optics Letters*, 28(15):1302-1304 (2003).	
		ASGHARI et al., "ASOC--A Manufacturing Integrated Optics Technology," Part of the SPIE Conference on Integrated Optics Devices III, vol. 3620, pp. 252-262 (Jan. 1999).	
		BARBIER et al, "Amplifying Four-Wavelength Combiner, Based on Erbium/Etterbium-Doped Waveguide Amplifiers and Integrated Splitters", *IEEE PHOTONICS TECHNOLOGY LETTTERS*, Vol.9, pp 315-317, 1997, 4 pages	
		BEACH R.J., "Theory and optimization of lens ducts," *Applied Optics,* 35:12:2005-15 (1996)	
		BESTWICK, T., "ASOC silicon integrated optics technology," Part of the SPIE Conferences on Photonics Packaging and Integration, SPIE vol. 3631, pp. 182-190 (Jan. 1999).	
		BORSELLA et al., "Structural incorporation of silver insoda-lime glass by the ion-exchange process: a photoluminescence spectroscopy study", *Applied Physics* A 71, pp. 125-132 (2000)	
		CAMPBELL et al., "Titanium dioxide (TiO_2)-based gate insulators," *IBM J. Res. Develop*. 43(3), 383-391, (May 1999).	
		CHANG, C.Y. (edited by), "ULSI Technology," The McGraw-Hill Companies, Inc., New York, 1996, Chapter 4, pp. 169-170, 226-231 (1996)..	
		CHEN et al. "Development of Supported Bifunctional Electrocatalysts for Unitized Regenerative Fuel Cells," *Journal of the Electrochemical Society*, 149(8), A1092-99, (2002).	
		CHOI et al., "Er-Al-codoped silicate planar light waveguide-type amplifier fabricated by radio-frequency sputtering," *Optics Letters*, vol. 25, No. 4, pp. 263-265 (Feb. 15, 2000).	
		COOKSEY et al. "Predicting Permeability & Transmission Rate for Multilayer Materials," *Foodtechnology*, Vol. 53, No. 9, pp. 60-63 (September 1999).	
		Crowder, et al., "Low-Temperature Single-Crystal Si TFT's Fabricated on Si Films Processed via Sequential Lateral Solidification," IEEE, vol. 19, no. 8 (August 1998), pages 306-308.	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO	Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	*Application Number*	10/101,863
	Filing Date	March 16, 2002
	First Named Inventor	ZHANG, Hongmei
	Art Unit	2823
(Use as many sheets as necessary)	*Examiner Name*	ESTRADA, Michelle
Sheet 5 of 9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		DELAVAUX et al., "Integrated optics erbium ytterbium amplifier system in 10 Gb/s fiber transmission experiment", 22nd European Conference on Optical Communication - ECOC' 96, Oslo, 4 pages (1996).	
		Distiributed Energy Resources: Fuel Cells, Projects, http://www.eere.energy.gov/der/fuel_cells/projects.html (2003).	
		DuPont Teijin Films, Mylar 200 SBL 300, Product Information (2000).	
		Electrometals Technologies Limited, Financial Report for the year 2002, Corporate Directory, Chairman's Review, Review of Operations (2002).	
		E-Tek website: FAQ, Inside E-Tek, E-Tek News, Products; http://www.etek-inc.com/ (2003).	
		FLYTZANIS et al, "nonlinear Optics in Composite Materials," E. Wolf, Progress in Optics XXIX (c) Elsevier Scince Publishers B.V., pp. 323-425 (1991).	
		FRAZAO et al., "EDFA Gain Flattening Using Long-Period Fibre Gratings Based on the Electric Arc Technique," (date unknown).	
		GARCIA, C. "Size Dependence of Lifetime and Absorption Cross Section of Si Nanocrystals Embedded in SiO_2," Appl. Phys. Lett., Vol. 82, No. 10, pp. 1595-7 (March 2003).	
		GOOSSENS et al., "Sensitization of TiO_2 with p-type semiconductor polymers," Delft Interfaculty Research Center, Delft University of Technology Laboratory of Inorganic Chemistry, The Netherlands (1998).	
		Greene et al., "Morphological and electrical properties of rf sputtered Y203-doped Zr02 thin films," J. Vac. Sci. Tecnol., vol. 13, no. 1 (Jan/Feb 1976), pages 72-75.	
		HAN, Hak-Seung et al. "Optical Gain at 1.54 □m in Erbium-Doped Silicon Nanocluster Sensitized Waveguide," *Appl. Phys. Lett.*, Vol. 79, No. 27, pp. 4568-70 (December 2001).	
		HAYAKAWA et al., "Enhanced fluorescence from Eu^{3+} owing to surface plasma oscillation of silver particles in glass", *Journal of Non-Crystalline Solids*, Vol. 259, pp. 16-22 (1999).	
		HAYAKAWA et al, "Field enhancement effect of small Ag particles on the fluorescence from Eu^{3+}-doped SiO_2 glass", *Appl. Phys. Lett.*, Vol. 74, No 11, pp. 1513-1515 (March 1999).	
		HAYFIELD, P.C.S., "Development of a New Material-Monolithic Ti4O7 Ebonix Ceramic," Royal Society Chemistry," (2002).	
		HEHLEN et al. "Spectroscopic Properties of Er^{3+} - and Yb^{3+}-doped Soda-Lime Silicate and Aluminosilicate Glasses," *Physical Review B*, Vol. 56, No. 15, pp. 9302-9318 (October 1997).	
		HEHLEN et al. "Uniform Upconversion in High-Concentration Er^{3+}-doped Soda Lime Silicate and Aluminosilicate Glasses," *Optics Letters*, Vol. 22, No. 11, pp. 772-774 (June 1997).	
		HORST et al., "Compact, Tunable Optical Devices in Silicon-Oxynitride Wave Guide Technology," IBM Research Division, 3 pages (1999).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	6	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		HUBNER, J. and Guldberg-Kjaer, S., "Planar Er-and Yb-Doped Amplifiers and Lasers," COM Technical University of Denmark, 10.sup.th European Conf. On Integrated Optics, Session WeB2, pp. 71-74 (2001).	
		Hwang, Man-Soo et al., "The effect of pulsed magnetron sputtering on the properties of indium tin oxide thin films," Elsevier Science B.V., P. 29-33, (2003).	
		Im, et al. "Controlled Super-lateral Growth of Si Films for Microstructural Manipulation and Optimization," Materials Science Program (1998), pages. 603-617.	
		Im, et al., "Crystalline Si Films for Integrated Active-Matrix LiquidCrystal Displays," MrS Bulletin (March 1996), pages. 39-48.	
		Im, et al., "Single-crystal Si films for thin-film transistor devices," American Institute of Physics (1997), pages. 3434-3436.	
		ITOH, M. et al., "Large reduction of singlemode-fibre coupling loss in 1.5% delta planar lightwave circuits using spot-size converters," Electronics Letters, 38(2):72-74 (2002).	
		JACKSON et al. "An Accurate Compact EDFA Model," Dept. of Electrical and Computer Engineering, University of BC (date unknown).	
		JANSSEN et al. "Photoinduced electron transfer from conjugated polymers onto nanocrystalline TiO_2," Eindhoven University of Technology, The Netherlands (date unknown).	
		JOHNSON, J.E. et al., "Monolithically Integrated Semiconductor Optical Amplifier and Electroabsorption Modulator with Dual-Waveguide Spot-Size Converter Input," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):19-25, (2000).	
		JONSSON L.B. et al. "Frequency response in pulsed DC reactive sputtering processes," *Thin Solid Films,* Vol. 365, pp. 43-48 (2000).	
		KATO et al., "Recent progress on PLC hybrid integration," Part of the SPIE Conference on Optoelectric Integrated Circuits III, SPIE. vol. 3631, pp. 28-36 (Jan. 1999).	
		KATO, Kuniharu et al., "PLC Hybrid Integration Technology and Its Application to Photonic Components," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):4-13 (2000).	
		KIK, P.G. et al. "Gain Limiting Processes in Er-doped Si Nanocrystal Waveguides in SiO_2," *J. Appl. Phys.*, Vol. 91, No. 1, pp. 534-536 (January 1, 2002).	
		KIM et al. "Frequency-dependent pulsed direct current magnetron sputtering of titanium oxide films," *J. Vac. Sci. Technol.* A 19(2); 429-434 (March 2001).	
		KIM et al. "Mixture Behaviour and Microwave Dielectric Properties in the Low-fired TiO_2-CuO System," *Jpn. J. Appl. Phys.*, 39, 2696-2700, (2000).	
		LADOUCEUR, F. et al., " 8.8 Evaluation of Results", Silica-based Buried Channel Waveguides and Devices,, Chapman & Hall, London, pp. 98-99 (1996).	
		LADOUCEUR, F. et al., "Effect of side wall roughness in buried channel waveguides," *IEEE Proc.*, vol. 141, pp. 242-248 (Aug. 1994).	
		LAMB, William B., "Designing Nonfoil Containing Skins for VIP Applications," DuPont VIA Symposium Presenation, (1999).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	7	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		LAMB, William et al. "Designing Non-Foil Containing Skins for Vacuum InsulationPanel (VIP) Applications," *Vuoto*, Vol. XXVIII, No. 1-2 - Gennaio-Giugno 1999, pp. 55-58 (1999).	
		LANGE et al, "High Gain Ultra-Short Length Phosphate glass Erbium-Doped Fiber Amplifier Material", OSA Optical Fiber Communications (OFC), 3 pages (2002).	
		LAPORTA et al, "Diode-pumped cw bulk Er: Yb: glass laser", 1952 Optics Letters/Vol. 16, No. 24/Dec. 15, 6 pages (1991).	
		LAURENT-LUND, C. et al., "PECVD Grown Multiple Core Planar Waveguides with Extremely Low Interface Reflections and Losses," *IEEE Photonics Technology Letters*, Vol. 10, No. 10, pp. 1431-1433 (Oct. 1998).	
		LEE et al., "Effect of size and roughness on light transmission in a S/SiO.sub.2 waveguide: Experiments and model," Department of Materials Science and Engineering, Massachusetts Institute of Technology, (Jul. 12, 2000).	
		LEE et al. "Effects of interfacial layer growth on the electrical characteristics of thin titanium oxide films on silicon," *Applied Physics Letters*, 74(21), 3143-3145, (May 1999).	
		LOVE, J.D. et al., "Quantifying Loss Minimisation in Single-Mode Fibre Tapers," Electronics Letters, 22(17):912-914, (1986).	
		MARDARE et al. "On the structure of Titanium Oxide Thin Films," *Analele Stiintifice Ale Universitatii AL. I. Cuza IASI*, Vol. XLV-XLVI, 201-208 (1999).	
		MARQUES, P.V.S. et al., "Planar Silica-on-Silicon Waveguide Lasers Based in Two Layer Core Devices," 10.sup.th European Conference on Integrated Optics, Session WeB2, pp. 79-82 (2001).	
		MEIJERINK et al, LUMINESCENCE OF AG^{+} IN CRYSTALLINE AND GLASSY SrB_4O_7, Journal of Physics and Chemistry of Solids, Vol. 54, No. 8, pp. 901-906, (1993).	
		MESNAOUI et al, "Spectroscopic properties of AG^{+} ions in phospage glasses of $NaPO_3$-$AgPO_3$ system", EUROPEAN JOURNAL OF SOLID STATE AND INORGANIC CHEMISTRY, Vol. 29, pages 1001-1013, 14 pages (1992).	
		MITOMI, O. et al., "Design of a Single-Mode Tapered Waveguide for Low-Loss Chip-to-Fiber Coupling,: IEEE Journal of Quantum Electronics, 30(8):1787-1793, (1994).	
		MIZUNO et al. "Temperature dependence of oxide decomposition on titanium surfaces in UHV," submitted to Journal of Vacuum Science and Technology, (October 28, 2001).	
		OHKUBO et al., "Polarization-Insensitive Arrayed-Waveguide Grating Using Pure Si)2 Cladding," Fifth Optoelectronics and Communication Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	
		OHMI et al., "Rare earth metal oxides for high-K gate insulator," Tokyo Institute of Technology,(date unknown).	
		OHTSUKI et al., "Gain Characteristics of a high concentration Er^{3+}-doped phosphate glass waveguide", *J. Appl. Phys*. 78(6), pp. 3617-3621 (1995).	
		ONO et al., "Design of a Low-loss Y-branch Optical Waveguide," Fifth Optoelectronic and Communications Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	8	of	9	*Attorney Docket Number*	9140.0016-00

		NON PATENT LITERATURE DOCUMENTS	
		PADMINI et al. "Realization of High Tunability Barium Strontium Titanate Thin Films by RF Magnetron Sputtering," College of Engineering, University of California, Santa Barbara. (date unknown).	
		PETERS et al., "Formation mechanism of silver nanocrystals made by ion irradiation of Na^{+}--Ag^{+} ion-exchanged sodalime silicate glass", Nuclear Instruments and Methods in Physics Research B 168, pp. 237-244 (2000).	
		RAJARAJAN, M. et al., "Numerical Study of Spot-Zise Expanders for an Efficient OEIC to SMF Coupling," IEEE Photonics Technology Letters, 10(8):1082-1084, (1998).	
		RAMASWAMY et al., "Ion-Exchanged Glass Waveguides: A Review", *Journal of Lightwave Technology*, Vol. 6, No. 6, pp. 984-1001 (1988)	
		Sanyo Vacuum Industries Co., Ltd. Products Info, TiO_2, (2003). http://www.sanyovac.co.jp/Englishweb/products/ETiO2.htm	
		SCHERMER, R. et al., "Investigation of Mesa Dielectric Waveguides,", Proceedings of the OSA Integrated Photonics Research Topical Meeting and Exhibit, Paper No. IWB3 (Jun 2001).	
		Second International Symposium of Polymer Surface Modification: Relevance to Adhesion, Preliminary Program (1999).	
		Seventh International Conference on TiO_2 Photocatalysis: Fundamentals & Applications, Toronto, Ontario, Canada, Final Program (November 17-21, 2002)	
		SEWELL, P. et al., "Rib Waveguide Spot-Size Transformers: Modal Properties," Journal of Lightwave Technology, 17(5):848-856, (1999).	
		SLOOFF et al, "Optical properties of Erbium-doped organic polydentate cage complexes", *J. Appl. Phys.* 83, pp. 497-503 (Jan. 1998).	
		SMITH, R.E., "Reduced Coupling Loss Using a Tapered-Rib Adiabatic-Following Fiber Coupler," *IEEE Photonics Technology Letters,* 8(8):1052-1054 (1996).	
		STROHHOFER, et al. "Energy transfer to Er^{3+}in Ag ion-exchanged glass", FOM Institute for Atomic and Molecular Physics, 10 pages (date unknown).	
		SUGIYAMA et al., "Gas Permeation Through the Pinholes of Plastic Film Laminated with Aluminium Foil," Vuoto, Vol. XXVIII, N. 1-2 - Gennaio-Guigno (1999).	
		TERVONEN, A., "Challenges and opportunities for integrated optics in optical networks," Part of the SPIE Conference in Integrated Optics Devices III, SPIE vol. 3620, pp. 2-11 (Jan. 1999).	
		TREICHEL et al., "The influence of pulsed magnetron sputtering on topography and crystallinity of TiO2 films on glass," *Space and Coatings Technology*, Vol. 123, pp. 268-272 (2000).	
		Tukamoto, H. et al., "Electronic Conductivity of $LiCoO_s$ and Its Enhancement by Magnesium Doping," J. Electrochem. Soc., vol. 44, no. 9, pages 3164-3168 (September 1997).	
		VILJANEN et al, "Planar Optical Coupling Elements for Multimode Fibers with Two-Step Ion Migration Process", Applied Physics, 24, No. 1, pp. 61-63 (January 1981).	
		VILLEGAS et al, "Optical spectroscopy ofa soda lime glass exchanged with silver", Physics and Chemistry of Glasses 37(6), pp. 248-253 (1996).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	9	of	9	*Attorney Docket Number*	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		VON ROTTKAY et al. "Influence of stoichiometry on electrochromic cerium-titanium oxide compounds," Lawrence Berkeley National Laboratory, UC Berkeley, CA, (date unknown).	
		WILKES, Kenneth T. "Gas Permeation Through Vacuum Barrier Films and its Effect on VIP Thermal Performance," Vacuum Insulation Panel Symp., Baltimore, Maryland, (May 3, 1999).	
		YANAGAWA, H. et al., "Index-and-Dimensional Taper and Its Application to Photonic Devices," Journal of Lightwave Technology, 10(5):587-591 (1992).	
		Response to Office Action filed on March 14, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Office Action issued on June 15, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Response to Office Action filed on September 3, 2002 in U.S. Patent No. 6,533,907 (Attorney Docket No. 09140-0004-00).	
		Response to Office Action filed on August 10, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on February 12, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Amendment/RCE filed on March 10, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on March 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed on June 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on July 8, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on May 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on August 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on March 3, 2004 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on February 23, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Response to Office Action filed on December 08, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on March 14, 2005 in U.S. Serial No. 10/789,953 (Attorney Docket No. 09140-0030-00).	
		Office Action issued March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

07-17-06 2823 IFW

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	)	
ZHANG, Hongmei et al.	)	Group Art Unit: 2823
	)	
Application No.: 10/101,863	)	Examiner: ESTRADA, Michelle
	)	
Filed: March 16, 2002	)	
	)	
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	)	Confirmation No.: 6938
	)	

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

TENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Tenth Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

07/18/2006 RMEBRAHT 00000101 060916 10101863
01 FC:1806 180.00 DA

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

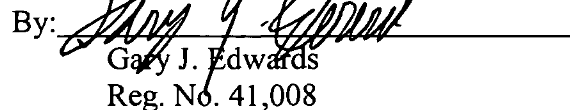
Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

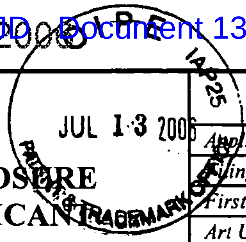
FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 13, 2006

By: 
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 860818417 US**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	2	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 4,710,940	12-01-1987	Sipes, Jr.	
		US 4,785,459	11-15-1988	Baer	
		US 5,435,826	07-25-1995	Sakakibara et al.	
		US 5,512,147	04-30-1996	Bates et al.	
		US 5,569,520	10-29-1996	Bates	
		US 5,597,660	01-28-1997	Bates et al.	
		US 5,612,152	03-18-1997	Bates	
		US 6,168,884 B1	01-02-2001	Neudecker et al.	
		US 6,236,793 B1	05-22-2001	Lawrence et al.	
		US 6,242,132 B1	06-05-2001	Neudecker et al.	
		US 6,365,300 B1	04-02-2002	Ota et al.	
		US 6,760,520 B1	07-06-2004	Medin et al.	
		US 6,818,356 B1	11-16-2004	Bates	
		US 2001/0031122 A1	10-18-2001	Lackritz et al.	
		US 2003/0185266 A1	10-02-2003	Henrichs	
		US 2006/0134522 A1	06-22-2006	Zhang et al.	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

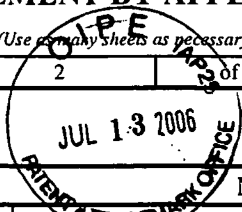
Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818417 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				*Application Number*	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				*Examiner Name*	ESTRADA, Michelle
Sheet	2	of	2	*Attorney Docket Number*	9140.0016-00



NON PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		COCORULLO, G. et al., "Amorphous silicon waveguides and light modulators for integrated photonics realized by low-temperature plasma-enhanced chemical-vapor deposition," *Optics Lett. 21*(24):2002-2004 (1996).	
		Notice of Allowance mailed August 6, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140.0002-01).	
		Final Office Action mailed June 9, 2006 in U.S. Appl. No. 11/100,856 (Atty. Docket No. 09140.0015-01).	
		Office Action issued on March 23, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00).	
		Specification as filed September 2, 2005, for U.S. Appl. No. 11/218,652 (Atty. Docket No. 09140.0052-00000).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818417 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

Bib Data Sheet

CONFIRMATION NO. 6938

SERIAL NUMBER	FILING OR 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/101,863	03/16/2002 RULE	438	2823	10655.0016-00

APPLICANTS

Hongmei Zhang, San Jose, CA;
Mukundan Narasimhan, San Jose, CA;
Ravi B. Mullapudi, San Jose, CA;
Richard E. Demaray, Portola Valley, CA;

** CONTINUING DATA *************************

** FOREIGN APPLICATIONS ********************

IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** SMALL ENTITY **
** 05/17/2002

Foreign Priority claimed ☐ yes ☐ no 35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance Verified and Acknowledged ______ Examiner's Signature Initials	STATE OR COUNTRY	SHEETS DRAWING	TOTAL CLAIMS	INDEPENDENT CLAIMS
	CA	27	39	5

ADDRESS
22852

TITLE

BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

FILING FEE RECEIVED	FEES: Authority has been given in Paper	
890	FEES: Authority has been given in Paper No. _________ to charge/credit DEPOSIT ACCOUNT No. _________ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other ____________ ☐ Credit

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

22852 7590 03/13/2008
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	
ART UNIT	**PAPER NUMBER**
2823	

MAIL DATE	DELIVERY MODE
03/13/2008	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

UNITED STATES DEPARTMENT OF COMMERCE
U.S. Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450

APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR / PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
10101863	3/16/02	ZHANG ET AL.	10655.0016-00

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
Michelle Estrada	
ART UNIT	**PAPER**
2823	20080304

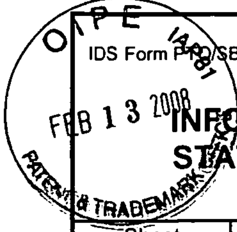
DATE MAILED:

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner for Patents

Attached is the IDS filed 2/13/08 that have been considered.

/Michelle Estrada/
Primary Examiner, Art Unit 2823



IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	1

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	Hongmei ZHANG
Art Unit	2823
Examiner Name	Michelle ESTRADA
Attorney Docket Number	10655.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-			

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NONPATENT LITERATURE DOCUMENTS

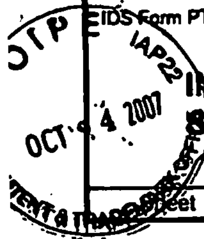
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Response to Office Action dated November 21, 2007, in U.S. Appl. No. 10/291,179 (Attorney Docket No. 9140.0001-00).	
		Response to Office Action dated December 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Final Office Action dated January 29, 2008, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
		Office Action dated January 25, 2008, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
		Response to Office Action dated December 18, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Notice of Allowance dated February 1, 2008, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	
		Office Action dated November 16, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 10655.0025-00).	

Examiner Signature	/Michelle Estrada/	Date Considered	03/04/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 074697411 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/650,461
				Filing Date	August 27, 2003
				First Named Inventor	DAWES, David
				Art Unit	2883
(Use as many sheets as necessary)				Examiner Name	DUPUIS, Derek L.
Sheet	1	of	1	Attorney Docket Number	10655.0025-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
/DLD/		Amendment/RCE filed August 9, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
/DLD/		Office Action dated September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00).	
/DLD/		Final Office Action dated September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01).	
/DLD/		Response to Final Office Action filed October 2, 2007, in U.S. Application No. 10/101,863 (Attorney Docket No. 9140.0016-00).	
/DLD/		Final Office Action dated July 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01).	

Examiner Signature	/Derek Dupuis/	Date Considered	11/12/2007

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

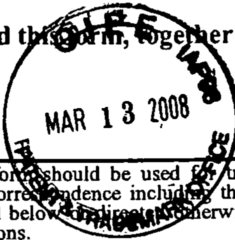
EXPRESS MAIL LABEL NO.
EM 100825650 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

PART B - FEE(S) TRANSMITTAL

03-14-08

Complete and send this form, together with applicable fee(s), to: Mail Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885



INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

03/14/2008 RMEBRAH1 00000018 060916 10101863

01 FC:2501 720.00 DA
02 FC:1504 300.00 DA

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

CERTIFICATE OF EXPRESS MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service's "Express Mail Post Office to Addressee" service under 37 CFR § 1.10, in an envelope addressed to: Mail Stop Issue Fee, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 on March 12, 2008.
Express Mail Label No.: EM 074697306 US

Signed: [signature]
Annie Wong

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

TITLE OF INVENTION: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

APPLN. TYPE	SMALL ENTITY	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	YES	$720	$300	$0	$1020	04/25/2008

EXAMINER	ART UNIT	CLASS-SUBCLASS
ESTRADA, MICHELLE	2823	438-788000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) the names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 Finnegan, Henderson,
2 Farabow, Garrett &
3 Dunner, L.L.P.

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: SpringWorks, LLC

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Minnetonka, Minnesota

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
☒ Issue Fee
☒ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies ______

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
☐ A check is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☒ The Director is hereby authorized to charge the required fee(s), any deficiency, ~~or~~ and credit any overpayment, to Deposit Account Number 06-0916 (enclose an extra copy of this form).

5. Change in Entity Status (from status indicated above)
☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27.
☒ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature [signature] Date March 12, 2008

Typed or printed name Gary J. Edwards Registration No. 41,008

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	03/16/2002	Hongmei Zhang	10655.0016-00	6938

22852 7590 03/18/2008
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
ESTRADA, MICHELLE	

ART UNIT	PAPER NUMBER
2823	

MAIL DATE	DELIVERY MODE
03/18/2008	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

UNITED STATES DEPARTMENT OF COMMERCE
U.S. Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450

APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR / PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
10101863	3/16/02	ZHANG ET AL.	10655.0016-00

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER	
Michelle Estrada	
ART UNIT	**PAPER**
2823	20080221

DATE MAILED:

Please find below and/or attached an Office communication concerning this application or proceeding.

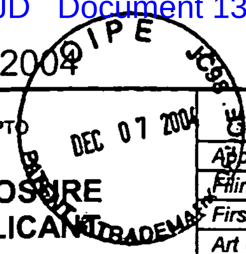
Commissioner for Patents

Attached are the IDS filed 12/7/04, 7/28/05 and 7/13/06 that have been considered.

/Michelle Estrada/
Primary Examiner, Art Unit 2823

PTO-90C (Rev.04-03)

EFS-Web Receipt date: 12/07/2004 10101863 - GAU: 2823



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG et al.
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	Michelle ESTRADA
Sheet	1	of	2	Attorney Docket Number	09140-0016-00000

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 2002/0033330 A1	Mar. 21, 2002	Demaray et al.	
		US 2002/0134671 A1	Jul. 17, 2003	Demaray et al.	
		US 2003/0063883 A1	Apr. 3, 2003	Demaray et al.	
		US 2003/0127319 A1	Jul. 10, 2003	Demaray et al.	
		US 2003/0134054 A1	Jul. 17, 2003	Demaray et al.	
		US 2003/0173207 A1	Sep. 18, 2003	Zhang et al.	
		US 2003/0173208 A1	Sep. 18, 2003	Pan et al.	
		US 2003/0174391 A1	Sep. 18, 2003	Pan et al.	
		US 2003/0175142 A1	Sep. 18, 2003	Milonopoulou et al.	
		US 2004/0105644 A1	Jun. 3, 2004	Dawes	
		US 6,506,289	Jan. 14, 2003	Demaray et al.	
		US 6,533,907	Mar. 18, 2003	Demaray et al.	
		US 6,827,826	Dec. 7, 2004	Demaray et al.	

Note: Copies of the U.S. Patent Documents are not Required in IDS filed after October 21, 2004

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		WO 2004/021532 A1	Mar. 11, 2004	Symmorphix, Inc.		
		WO 2004/077519 A2	Sep. 10, 2004	Narasimhan et al.		

Examiner Signature	/Michelle Estrada/	Date Considered	03/11/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 12/07/2004 10101863 - GAU: 2823

OIPE JC98 DEC 07 2004 PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG et al.
Art Unit	2823
Examiner Name	Michelle ESTRADA
Attorney Docket Number	09140-0016-00000

NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		Office Action issued on September 27, 2004 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Office Action issued on November 28, 2001 in U.S. Patent No. 6,506,289 (Attorney Docket No. 09140-0002-01).	
		Office Action issued on April 17,2002 in U.S. Patent No. 6,506,289 (Attorney Docket No. 09140-0002-01).	
		Quayle Action issued on November 10, 2003 in U.S. Patent No. 6,827,826 (Attorney Docket No. 09140-0002-02).	
		Office Action issued on May 2, 2002 in U.S. Patent No. 6,533,907 (Attorney Docket No. 09140-0004-00).	
		Office Action issued on February 12, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on September 10, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on September 3, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Office Action issued on October 22, 2003 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on June 10, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on May 4, 2004 in U.S. Serial No. 10/101,493 (Attorney Docket No. 09140-0021-00).	
		International Search Report issued on November 21, 2003 in PCT/US03/24809 (Attorney Docket No. 09140-0025-00).	
		International Search Report issued on October 11, 2004 in PCT/US2004/005531 (Attorney Docket No. 09140-0030-00)	
		Written Opinion issued on October 11, 2004 in PCT/US2004/005531 (Attorney Docket No. 09140-0030-00)	
		Patent Application No. 10/851,542 for ENERGY CONVERSION AND STORAGE DEVICES BY PHYSICAL VAPOR DEPOSITION OF TITANIUM AND TITANIUM OXIDES AND SUB-OXIDES filed on May 20, 2004. (Attorney Docket No. 09140-0033-00)	
		Patent Application No. 10/850,968 for TRANSPARENT CONDUCTIVE OXIDES FROM A METALLIC TARGET filed on May 20, 2004. (Attorney Docket No. 09140-0034-00)	

Examiner Signature	/Michelle Estrada/	Date Considered	03/11/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

OIPE JUL 2 8 2005 PATENT & TRADEMARK OFFICE

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	1	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS					
Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 2005/0006768 A1	01-13-2005	Narasimhan et al.	
		US 2005/0000794 A1	01-06-2005	Demaray et al.	
		US 2004/0259305 A1	12-23-2004	Demaray et al.	
		US 2004/0105644 A1	06-03-2004	Dawes	
		US 2003/0174391 A1	09-18-2003	Pan et al.	
		US 2003/0141186 A1	07-31-2003	Wang et al.	
		US 2003/0127319 A1	06-10-2003	Demaray et al.	
		US 2003/0097858 A1	05-29-2003	Strohhofer et al.	
		US 2002/0170821 A1	11-21-2002	Sandlin et al.	
		US 2001/041460 A1	11-15-2001	Wiggins	
		US 2001/0027159 A1	10-04-2001	Kaneyoshi	
		US 6,750,156 B2	06-15-2004	Le et al.	
		US 6,576,546 B2	06-10,-2003	Gilbert et al.	
		US 6,444,750 B1	09-03-2002	Touhsaent	
		US 6,433,380 B2	08-13-2002	Shin	
		US 6,423,776 B1	07-23-2002	Akkapeddi et al.	
		US 6,416,598 B1	07-09-2002	Sircar	
		US 6,413,645 B1	07-02-2002	Graff et al.	
		US 6,365,319 B1	04-02-2002	Heath et al.	
		US 6,302,939 B1	10-16-2001	Rabin et al.	
		US 6,300,215 B1	10-09-2001	Shin	
		US 6,261,917 B1	07-17-2001	Quek et al.	
		US 6,248,640 B1	06-19-2001	Nam	
		US 6,232,242	05-15-2001	Hata et al.	
		US 6,214,660 B1	04-10-2001	Uemoto et al.	
		US 6,210,544 B1	04-03-2001	Sasaki	
		US 6,204,111 B1	03-20-2001	Uemoto et al.	
		US 6,198,217 B1	03-06-2001	Suzuki et al.	
		US 6,197,167 B1	03-06-2001	Tanaka	
		US 6,165,566	12-26-2000	Tropsha	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

		US 6,157,765	12-05-2000	Bruce et al.	
		US 6,146,225	11-14-2000	Sheats et al.	
		US 6,106,933	08-22-2000	Nagai et al.	
		US 6,080,643	06-27-2000	Noguchi et al.	
		US 6,077,642	06-20-2000	Ogata et al.	
		US 6,071,323	06-06-2000	Kawaguchi	
		US 6,058,233	05-02-2000	Dragone	
		US 6,052,397	04-18-2000	Jeon et al.	
		US 6,051,296	04-18-2000	McCaulley et al.	
		US 6,046,081	04-04-2000	Kuo	
		US 6,004,660	12-21-1999	Topolski et al.	
		US 5,966,491	10-12-1999	DiGiovanni	
		US 5,952,778	09-14-1999	Haskal et al.	
		US 5,930,584	07-27-1999	Sun et al.	
		US 5,900,057	05-04-1999	Buchal et al.	
		US 5,882,946	03-16-1999	Otani	
		US 5,870,273	02-09-1999	Sogabe et al.	
		US 5,853,830	12-29-1998	McCaulley et al.	
		US 5,831,262	11-03-1998	Greywall et al.	
		US 5,811,177	09-22-1998	Shi et al.	
		US 5,771,562	06-30-1998	Harvey, III et al.	
		US 5,762,768	06-09-1998	Goy et al.	
		US 5,757,126	05-26-1998	Harvey, III et al.	
		US 5,738,731	04-14-1998	Shindo et al.	
		US 5,731,661	03-24-1998	So et al.	
		US 5,689,522	11-18-1997	Beach	
		US 5,686,360	11-11-1997	Harvey, III et al.	
		US 5,654,984	08-05-1997	Hershbarger et al.	
		US 5,607,789	03-04-1997	Treger et al.	
		US 5,591,520	01-07-1997	Migliorini et al.	
		US 5,563,979	10-08-1996	Bruce et al.	
		US 5,538,796	07-23-1996	Schaffer et al.	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	3	of	9	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

		US 5,499,207	03-12-1996	Miki et al.	
		US 5,457,569	10-10-1995	Liou et al.	
		US 5,355,089	10-11-1994	Treger	
		US 5,309,302	05-03-1994	Vollmann	
		US 5,306,569	04-26-1994	Hiraki	
		US 5,303,319	04-12-1994	Ford et al.	
		US 5,296,089	03-22-1994	Chen et al.	
		US 5,173,271	12-22-1992	Chen et al.	
		US 5,119,460	06-02-1992	Bruce et al.	
		US 5,107,538	04-21-1992	Benton et al.	
		US 5,085,904	02-04-1992	Deak et al.	
		US 4,587,225	05-06-1986	Tsukuma et al.	
		RE 32,449	06-30-1987	Claussen	

Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]
		EP 1 189 080 A2	03-20-2002	Agere Systems Optoelectronics Guardian Corporation		
		EP 1 092 689 A1	04-18-2001	BPS Alzenau GmbH		
		EP 1068899 A1	01-17-2001	Nippon Sheet Glass Co., Ltd.		
		EP 0 639 655 A1	02-22-1995	Asahi Glass Co, Ltd.		
		EP 0 652 308 A2	10-13-1994	Mega Chips Corp.		
		EP 0 510 883 A2	10-28-1992	AT&T		
		JP 7-233469	09-05-1995	Asahi Glass Co, Ltd.		
		JP 2-054764 A2	02-23-1990	Leybold AG		
		WO 00/21898 A1	04-20-2000	Samsung Electronics Co.		

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	4	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		AFFINITO et al., "PML/oxide/PML Barrier Layer Performance Differences Arising from Use of UV or Electron Beam Polymerization of the PML Layers," *Thin Solid Films* Vol. 308-309, pp. 19-25 (1997)	
		AFFINITO et al., "Polymer-Oxide Transparent Barrier Layers," Society of Vacuum Coaters, 39th Ann. Technical Conference Proceedings, May 5-10, 1996, Philadelphia, PA, pp. 392-397 (1996).	
		ALDER, T. et al., "High-Efficiency Fiber-to-Chip Coupling Using Low-Loss Tapered Single-Mode Fiber," IEEE Photonics Technology Letters, 12(8):1016-1018 (2000).	
		ALMEIDA, Vilson R. et al., "Nanotaper for compact mode conversion," *Optics Letters*, 28(15):1302-1304 (2003).	
		ASGHARI et al., "ASOC--A Manufacturing Integrated Optics Technology," Part of the SPIE Conference on Integrated Optics Devices III, vol. 3620, pp. 252-262 (Jan. 1999).	
		BARBIER et al, "Amplifying Four-Wavelength Combiner, Based on Erbium/Etterbium-Doped Waveguide Amplifiers and Integrated Splitters", *IEEE PHOTONICS TECHNOLOGY LETTTERS*, Vol.9, pp 315-317, 1997, 4 pages	
		BEACH R.J., "Theory and optimization of lens ducts," *Applied Optics*, 35:12:2005-15 (1996)	
		BESTWICK, T., "ASOC silicon integrated optics technology," Part of the SPIE Conferences on Photonics Packaging and Integration, SPIE vol. 3631, pp. 182-190 (Jan. 1999).	
		BORSELLA et al., "Structural incorporation of silver insoda-lime glass by the ion-exchange process: a photoluminescence spectroscopy study", *Applied Physics* A 71, pp. 125-132 (2000)	
		CAMPBELL et al., "Titanium dioxide (TiO_2)-based gate insulators," *IBM J. Res. Develop.* 43(3), 383-391, (May 1999).	
		CHANG, C.Y. (edited by), "ULSI Technology," The McGraw-Hill Companies, Inc., New York, 1996, Chapter 4, pp. 169-170, 226-231 (1996)..	
		CHEN et al. "Development of Supported Bifunctional Electrocatalysts for Unitized Regenerative Fuel Cells," *Journal of the Electrochemical Society*, 149(8), A1092-99, (2002).	
		CHOI et al., "Er-Al-codoped silicate planar light waveguide-type amplifier fabricated by radio-frequency sputtering," *Optics Letters*, vol. 25, No. 4, pp. 263-265 (Feb. 15, 2000).	
		COOKSEY et al. "Predicting Permeability & Transmission Rate for Multilayer Materials," *Foodtechnology*, Vol. 53, No. 9, pp. 60-63 (September 1999).	
		Crowder, et al., "Low-Temperature Single-Crystal Si TFT's Fabricated on Si Films Processed via Sequential Lateral Solidification," IEEE, vol. 19, no. 8 (August 1998), pages 306-308.	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	5	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		DELAVAUX et al., "Integrated optics erbium ytterbium amplifier system in 10 Gb/s fiber transmission experiment", 22nd European Conference on Optical Communication - ECOC' 96, Oslo, 4 pages (1996).	
		Distiributed Energy Resources: Fuel Cells, Projects, http://www.eere.energy.gov/der/fuel_cells/projects.html (2003).	
		DuPont Teijin Films, Mylar 200 SBL 300, Product Information (2000).	
		Electrometals Technologies Limited, Financial Report for the year 2002, Corporate Directory, Chairman's Review, Review of Operations (2002).	
		E-Tek website: FAQ, Inside E-Tek, E-Tek News, Products; http://www.etek-inc.com/ (2003).	
		FLYTZANIS et al, "nonlinear Optics in Composite Materials," E. Wolf, Progress in Optics XXIX (c) Elsevier Scince Publishers B.V., pp. 323-425 (1991).	
		FRAZAO et al., "EDFA Gain Flattening Using Long-Period Fibre Gratings Based on the Electric Arc Technique," (date unknown).	
		GARCIA, C. "Size Dependence of Lifetime and Absorption Cross Section of Si Nanocrystals Embedded in SiO_2," Appl. Phys. Lett., Vol. 82, No. 10, pp. 1595-7 (March 2003).	
		GOOSSENS et al., "Sensitization of TiO_2 with p-type semiconductor polymers," Delft Interfaculty Research Center, Delft University of Technology Laboratory of Inorganic Chemistry, The Netherlands (1998).	
		Greene et al., "Morphological and electrical properties of rf sputtered Y203-doped Zr02 thin films," J. Vac. Sci. Tecnol., vol. 13, no. 1 (Jan/Feb 1976), pages 72-75.	
		HAN, Hak-Seung et al. "Optical Gain at 1.54 □m in Erbium-Doped Silicon Nanocluster Sensitized Waveguide," *Appl. Phys. Lett.*, Vol. 79, No. 27, pp. 4568-70 (December 2001).	
		HAYAKAWA et al., "Enhanced fluorescence from Eu^{3+} owing to surface plasma oscillation of silver particles in glass", *Journal of Non-Crystalline Solids*, Vol. 259, pp. 16-22 (1999).	
		HAYAKAWA et al, "Field enhancement effect of small Ag particles on the fluorescence from Eu^{3+}-doped SiO_2 glass", *Appl. Phys. Lett.*, Vol. 74, No 11, pp. 1513-1515 (March 1999).	
		HAYFIELD, P.C.S., "Development of a New Material-Monolithic Ti4O7 Ebonix Ceramic," Royal Society Chemistry," (2002).	
		HEHLEN et al. "Spectroscopic Properties of Er^{3+} - and Yb^{3+}-doped Soda-Lime Silicate and Aluminosilicate Glasses," *Physical Review B*, Vol. 56, No. 15, pp. 9302-9318 (October 1997).	
		HEHLEN et al. "Uniform Upconversion in High-Concentration Er^{3+}-doped Soda Lime Silicate and Aluminosilicate Glasses," *Optics Letters*, Vol. 22, No. 11, pp. 772-774 (June 1997).	
		HORST et al., "Compact, Tunable Optical Devices in Silicon-Oxynitride Wave Guide Technology," IBM Research Division, 3 pages (1999).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	6	of	9

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS

		HUBNER, J. and Guldberg-Kjaer, S., "Planar Er-and Yb-Doped Amplifiers and Lasers," COM Technical University of Denmark, 10.sup.th European Conf. On Integrated Optics, Session WeB2, pp. 71-74 (2001).	
		Hwang, Man-Soo et al., "The effect of pulsed magnetron sputtering on the properties of indium tin oxide thin films," Elsevier Science B.V., P. 29-33, (2003).	
		Im, et al. "Controlled Super-lateral Growth of Si Films for Microstructural Manipulation and Optimization," Materials Science Program (1998), pages. 603-617.	
		Im, et al., "Crystalline Si Films for Integrated Active-Matrix LiquidCrystal Displays," MrS Bulletin (March 1996), pages. 39-48.	
		Im, et al., "Single-crystal Si films for thin-film transistor devices," American Institute of Physics (1997), pages. 3434-3436.	
		ITOH, M. et al., "Large reduction of singlemode-fibre coupling loss in 1.5% delta planar lightwave circuits using spot-size converters," Electronics Letters, 38(2):72-74 (2002).	
		JACKSON et al. "An Accurate Compact EDFA Model," Dept. of Electrical and Computer Engineering, University of BC (date unknown).	
		JANSSEN et al. "Photoinduced electron transfer from conjugated polymers onto nanocrystalline TiO_2," Eindhoven University of Technology, The Netherlands (date unknown).	
		JOHNSON, J.E. et al., "Monolithically Integrated Semiconductor Optical Amplifier and Electroabsorption Modulator with Dual-Waveguide Spot-Size Converter Input," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):19-25, (2000).	
		JONSSON L.B. et al. "Frequency response in pulsed DC reactive sputtering processes," *Thin Solid Films,* Vol. 365, pp. 43-48 (2000).	
		KATO et al., "Recent progress on PLC hybrid integration," Part of the SPIE Conference on Optoelectric Integrated Circuits III, SPIE. vol. 3631, pp. 28-36 (Jan. 1999).	
		KATO, Kuniharu et al., "PLC Hybrid Integration Technology and Its Application to Photonic Components," IEEE Journal of Selected Topics in Quantum Electronics, 6(1):4-13 (2000).	
		KIK, P.G. et al. "Gain Limiting Processes in Er-doped Si Nanocrystal Waveguides in SiO_2," *J. Appl. Phys.*, Vol. 91, No. 1, pp. 534-536 (January 1, 2002).	
		KIM et al. "Frequency-dependent pulsed direct current magnetron sputtering of titanium oxide films," *J. Vac. Sci. Technol.* A 19(2); 429-434 (March 2001).	
		KIM et al. "Mixture Behaviour and Microwave Dielectric Properties in the Low-fired TiO_2-CuO System," *Jpn. J. Appl. Phys.*, 39, 2696-2700, (2000).	
		LADOUCEUR, F. et al., " 8.8 Evaluation of Results", Silica-based Buried Channel Waveguides and Devices,, Chapman & Hall, London, pp. 98-99 (1996).	
		LADOUCEUR, F. et al., "Effect of side wall roughness in buried channel waveguides," *IEEE Proc.*, vol. 141, pp. 242-248 (Aug. 1994).	
		LAMB, William B., "Designing Nonfoil Containing Skins for VIP Applications," DuPont VIA Symposium Presenation, (1999).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	7	of	9	Attorney Docket Number	9140.0016-00

NON PATENT LITERATURE DOCUMENTS			
		LAMB, William et al. "Designing Non-Foil Containing Skins for Vacuum InsulationPanel (VIP) Applications," *Vuoto*, Vol. XXVIII, No. 1-2 - Gennaio-Giugno 1999, pp. 55-58 (1999).	
		LANGE et al, "High Gain Ultra-Short Length Phosphate glass Erbium-Doped Fiber Amplifier Material", OSA Optical Fiber Communications (OFC), 3 pages (2002).	
		LAPORTA et al, "Diode-pumped cw bulk Er: Yb: glass laser", 1952 Optics Letters/Vol. 16, No. 24/Dec. 15, 6 pages (1991).	
		LAURENT-LUND, C. et al., "PECVD Grown Multiple Core Planar Waveguides with Extremely Low Interface Reflections and Losses," *IEEE Photonics Technology Letters*, Vol. 10, No. 10, pp. 1431-1433 (Oct. 1998).	
		LEE et al., "Effect of size and roughness on light transmission in a S/SiO.sub.2 waveguide: Experiments and model," Department of Materials Science and Engineering, Massachusetts Institute of Technology, (Jul. 12, 2000).	
		LEE et al. "Effects of interfacial layer growth on the electrical characteristics of thin titanium oxide films on silicon," *Applied Physics Letters*, 74(21), 3143-3145, (May 1999).	
		LOVE, J.D. et al., "Quantifying Loss Minimisation in Single-Mode Fibre Tapers," Electronics Letters, 22(17):912-914, (1986).	
		MARDARE et al. "On the structure of Titanium Oxide Thin Films," *Analele Stiintifice Ale Universitatii AL. I. Cuza IASI*, Vol. XLV-XLVI, 201-208 (1999).	
		MARQUES, P.V.S. et al., "Planar Silica-on-Silicon Waveguide Lasers Based in Two Layer Core Devices," 10.sup.th European Conference on Integrated Optics, Session WeB2, pp. 79-82 (2001).	
		MEIJERINK et al, LUMINESCENCE OF AG^{+} IN CRYSTALLINE AND GLASSY SrB_4O_7, Journal of Physics and Chemistry of Solids, Vol. 54, No. 8, pp. 901-906, (1993).	
		MESNAOUI et al, "Spectroscopic properties of AG^{+} ions in phospage glasses of $NaPO_3$-$AgPO_3$ system", EUROPEAN JOURNAL OF SOLID STATE AND INORGANIC CHEMISTRY, Vol. 29, pages 1001-1013, 14 pages (1992).	
		MITOMI, O. et al., "Design of a Single-Mode Tapered Waveguide for Low-Loss Chip-to-Fiber Coupling,: IEEE Journal of Quantum Electronics, 30(8):1787-1793, (1994).	
		MIZUNO et al. "Temperature dependence of oxide decomposition on titanium surfaces in UHV," submitted to Journal of Vacuum Science and Technology, (October 28, 2001).	
		OHKUBO et al., "Polarization-Insensitive Arrayed-Waveguide Grating Using Pure Si)2 Cladding," Fifth Optoelectronics and Communication Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	
		OHMI et al., "Rare earth metal oxides for high-K gate insulator," Tokyo Institute of Technology,(date unknown).	
		OHTSUKI et al., "Gain Characteristics of a high concentration Er^{3+}-doped phosphate glass waveguide", *J. Appl. Phys.* 78(6), pp. 3617-3621 (1995).	
		ONO et al., "Design of a Low-loss Y-branch Optical Waveguide," Fifth Optoelectronic and Communications Conference (OECC 2000) Technical Digest, 2 pages (Jul. 2000).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/28/2005 10101863 - GAU: 2823

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	8	of	9	Attorney Docket Number	9140.0016-00

		NON PATENT LITERATURE DOCUMENTS	
		PADMINI et al. "Realization of High Tunability Barium Strontium Titanate Thin Films by RF Magnetron Sputtering," College of Engineering, University of California, Santa Barbara. (date unknown).	
		PETERS et al., "Formation mechanism of silver nanocrystals made by ion irradiation of Na^{+}--Ag^{+} ion-exchanged sodalime silicate glass", Nuclear Instruments and Methods in Physics Research B 168, pp. 237-244 (2000).	
		RAJARAJAN, M. et al., "Numerical Study of Spot-Zise Expanders for an Efficient OEIC to SMF Coupling," IEEE Photonics Technology Letters, 10(8):1082-1084, (1998).	
		RAMASWAMY et al., "Ion-Exchanged Glass Waveguides: A Review", *Journal of Lightwave Technology*, Vol. 6, No. 6, pp. 984-1001 (1988)	
		Sanyo Vacuum Industries Co., Ltd. Products Info, TiO_2. (2003). http://www.sanyovac.co.jp/Englishweb/products/ETiO2.htm	
		SCHERMER, R. et al., "Investigation of Mesa Dielectric Waveguides,", Proceedings of the OSA Integrated Photonics Research Topical Meeting and Exhibit, Paper No. IWB3 (Jun 2001).	
		Second International Symposium of Polymer Surface Modification: Relevance to Adhesion, Preliminary Program (1999).	
		Seventh International Conference on TiO_2 Photocatalysis: Fundamentals & Applications, Toronto, Ontario, Canada, Final Program (November 17-21, 2002)	
		SEWELL, P. et al., "Rib Waveguide Spot-Size Transformers: Modal Properties," Journal of Lightwave Technology, 17(5):848-856, (1999).	
		SLOOFF et al, "Optical properties of Erbium-doped organic polydentate cage complexes", *J. Appl. Phys.* 83, pp. 497-503 (Jan. 1998).	
		SMITH, R.E., "Reduced Coupling Loss Using a Tapered-Rib Adiabatic-Following Fiber Coupler," *IEEE Photonics Technology Letters*, 8(8):1052-1054 (1996).	
		STROHHOFER, et al. "Energy transfer to Er^{3+} in Ag ion-exchanged glass", FOM Institute for Atomic and Molecular Physics, 10 pages (date unknown).	
		SUGIYAMA et al., "Gas Permeation Through the Pinholes of Plastic Film Laminated with Aluminium Foil," Vuoto, Vol. XXVIII, N. 1-2 - Gennaio-Guigno (1999).	
		TERVONEN, A., "Challenges and opportunities for integrated optics in optical networks," Part of the SPIE Conference in Integrated Optics Devices III, SPIE vol. 3620, pp. 2-11 (Jan. 1999).	
		TREICHEL et al., "The influence of pulsed magnetron sputtering on topography and crystallinity of TiO2 films on glass," *Space and Coatings Technology*, Vol. 123, pp. 268-272 (2000).	
		Tukamoto, H. et al., "Electronic Conductivity of $LiCoO_s$ and Its Enhancement by Magnesium Doping," J. Electrochem. Soc., vol. 44, no. 9, pages 3164-3168 (September 1997).	
		VILJANEN et al, "Planar Optical Coupling Elements for Multimode Fibers with Two-Step Ion Migration Process", Applied Physics, 24, No. 1, pp. 61-63 (January 1981).	
		VILLEGAS et al, "Optical spectroscopy ofa soda lime glass exchanged with silver", Physics and Chemistry of Glasses 37(6), pp. 248-253 (1996).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	9	of	9	Attorney Docket Number	9140.0016-00

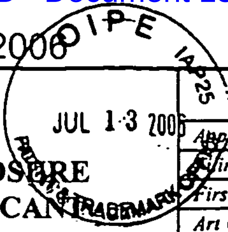
NON PATENT LITERATURE DOCUMENTS			
		VON ROTTKAY et al. "Influence of stoichiometry on electrochromic cerium-titanium oxide compounds," Lawrence Berkeley National Laboratory, UC Berkeley, CA, (date unknown).	
		WILKES, Kenneth T. "Gas Permeation Through Vacuum Barrier Films and its Effect on VIP Thermal Performance," Vacuum Insulation Panel Symp., Baltimore, Maryland, (May 3, 1999).	
		YANAGAWA, H. et al., "Index-and-Dimensional Taper and Its Application to Photonic Devices," Journal of Lightwave Technology, 10(5):587-591 (1992).	
		Response to Office Action filed on March 14, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Office Action issued on June 15, 2005 in U.S. Serial No. 10/291,179 (Attorney Docket No. 09140-0001-00).	
		Response to Office Action filed on September 3, 2002 in U.S. Patent No. 6,533,907 (Attorney Docket No. 09140-0004-00).	
		Response to Office Action filed on August 10, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on February 12, 2004 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Amendment/RCE filed on March 10, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on March 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Response to Office Action filed on June 17, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on July 8, 2005 in U.S. Serial No. 09/903,081 (Attorney Docket No. 09140-0014-00).	
		Office Action issued on May 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on August 14, 2003 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on March 3, 2004 in U.S. Serial No. 10/101,492 (Attorney Docket No. 09140-0015-00).	
		Response to Office Action filed on February 23, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Response to Office Action filed on December 08, 2004 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00).	
		Office Action issued on March 14, 2005 in U.S. Serial No. 10/789,953 (Attorney Docket No. 09140-0030-00).	
		Office Action issued March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

EFS-Web Receipt date: 07/13/2006 10101863 - GAU: 2823



IDS Form PTO/SB/08: Substitute for form 1449A/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				Application Number	10/101,863
				Filing Date	March 16, 2002
				First Named Inventor	ZHANG, Hongmei
				Art Unit	2823
(Use as many sheets as necessary)				Examiner Name	ESTRADA, Michelle
Sheet	1	of	2	Attorney Docket Number	9140.0016-00

U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] (if known)	Issue or Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US 4,710,940	12-01-1987	Sipes, Jr.	
		US 4,785,459	11-15-1988	Baer	
		US 5,435,826	07-25-1995	Sakakibara et al.	
		US 5,512,147	04-30-1996	Bates et al.	
		US 5,569,520	10-29-1996	Bates	
		US 5,597,660	01-28-1997	Bates et al.	
		US 5,612,152	03-18-1997	Bates	
		US 6,168,884 B1	01-02-2001	Neudecker et al.	
		US 6,236,793 B1	05-22-2001	Lawrence et al.	
		US 6,242,132 B1	06-05-2001	Neudecker et al.	
		US 6,365,300 B1	04-02-2002	Ota et al.	
		US 6,760,520 B1	07-06-2004	Medin et al.	
		US 6,818,356 B1	11-16-2004	Bates	
		US 2001/0031122 A1	10-18-2001	Lackritz et al.	
		US 2003/0185266 A1	10-02-2003	Henrichs	
		US 2006/0134522 A1	06-22-2006	Zhang et al.	

Note: **Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] Number[4] Kind Code[5] (if known)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	Translation[6]

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO. EV 860818417 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

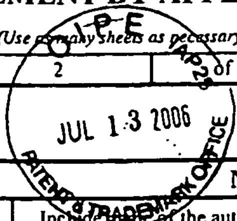
IDS Form PTO/SB/08: Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet	2	of	2

Complete if Known	
Application Number	10/101,863
Filing Date	March 16, 2002
First Named Inventor	ZHANG, Hongmei
Art Unit	2823
Examiner Name	ESTRADA, Michelle
Attorney Docket Number	9140.0016-00



NON PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	Translation[6]
		COCORULLO, G. et al., "Amorphous silicon waveguides and light modulators for integrated photonics realized by low-temperature plasma-enhanced chemical-vapor deposition," *Optics Lett. 21*(24):2002-2004 (1996).	
		Notice of Allowance mailed August 6, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140.0002-01).	
		Final Office Action mailed June 9, 2006 in U.S. Appl. No. 11/100,856 (Atty. Docket No. 09140.0015-01).	
		Office Action issued on March 23, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00).	
		Specification as filed September 2, 2005, for U.S. Appl. No. 11/218,652 (Atty. Docket No. 09140.0052-00000).	

Examiner Signature	/Michelle Estrada/	Date Considered	02/21/2008

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EV 860818417 US

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /ME/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/101,863	05/27/2008	7378356	10655.0016-00	6938

22852 7590 05/07/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Hongmei Zhang, San Jose, CA;
Mukundan Narasimhan, San Jose, CA;
Ravi B. Mullapudi, San Jose, CA;
Richard E. Demaray, Portola Valley, CA;

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. Patent No.: 7,378,356)
)
Inventors: Hongmei ZHANG et al.)
)
Issue Date.: May 27, 2008)
)
For: BIASED PULSE DC REACTIVE)
SPUTTERING OF OXIDE FILMS)

COMMISSIONER FOR PATENTS
OFFICE OF PATENT PUBLICATION
ATTN: Certificate of Correction Branch
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

REQUEST FOR CERTIFICATE OF CORRECTION

Pursuant to 35 U.S.C. § 254, and 37 C.F.R. §§ 1.322 and 1.323, this is a request for a Certificate of Correction in the above-identified patent. The mistake identified by a (*) below occurred through the fault of the U.S. Patent and Trademark Office, as clearly disclosed by the records of the application which matured into this patent. The mistakes identified by a (**) below are of a clerical or typographical nature, and resulted from errors made in good faith by the patentee. The Commissioner is hereby authorized to charge the fee of $100.00 to Deposit Account No. 06-0916 as set forth in 37 C.F.R. § 1.20(a).

(*) On the title page, item 57, Abstract, penultimate line, insert "using" before -- processes --.

(**) In claim 29, col. 24, line 43, "intermetllic" should read -- intermetallic --.

(**) In claim 33, col. 24, line 52, "claims" should read -- claim --.

The complete Certificate of Correction involves one (1) page. Issuance of a Certificate of Correction containing the correction is earnestly requested.

Please charge any required fees not included herewith to Deposit Account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 16, 2008

By:
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. 7,378,356 Page 1 of 1

APPLICATION NO.: 10/101,863

ISSUE DATE: May 27, 2008

INVENTOR(S): Hongmei ZHANG et al.

It is hereby certified that an error or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, item (57), Abstract, penultimate line, insert "using" before -- processes --.

In claim 29, col. 24, line 43, "intermetllic" should read -- intermetallic --.

In claim 33, column 24, line 52, "claims" should read -- claim --.

MAILING ADDRESS OF SENDER

Finnegan, Henderson, Farabow,
Garrett & Dunner, L.L.P.
901 New York Avenue, N.W.
Washington, D.C. 20001-4413

Electronic Patent Application Fee Transmittal

Application Number:	10101863
Filing Date:	16-Mar-2002
Title of Invention:	BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS
First Named Inventor/Applicant Name:	Hongmei Zhang
Filer:	Gary James Edwards/Annie Wong
Attorney Docket Number:	10655.0016-00

Filed as Large Entity

Utility Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Certificate of correction	1811	1	100	100
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
			Total in USD ($)	**100**

Electronic Acknowledgement Receipt

EFS ID:	3465573
Application Number:	10101863
International Application Number:	
Confirmation Number:	6938
Title of Invention:	BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS
First Named Inventor/Applicant Name:	Hongmei Zhang
Customer Number:	22852
Filer:	Gary James Edwards/Annie Wong
Filer Authorized By:	Gary James Edwards
Attorney Docket Number:	10655.0016-00
Receipt Date:	16-JUN-2008
Filing Date:	16-MAR-2002
Time Stamp:	20:19:55
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$100
RAM confirmation Number	4243
Deposit Account	060916
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes) /Message Digest	Multi Part /.zip	Pages (if appl.)
1	Request for Certificate of Correction	Request_Certificate_of_Correction_16Jun2008_7378356.pdf	37673 477a39878979d8d49754cc7405e1e016cc76b2c3	no	3
Warnings:					
Information:					
2	Fee Worksheet (PTO-06)	fee-info.pdf	8158 273e0dee7e5c5ea8dcd0679679f699d90c2c1f51	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	45831		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 7,378,356 B2
APPLICATION NO. : 10/101863
DATED : May 27, 2008
INVENTOR(S) : Hongmei Zhang et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

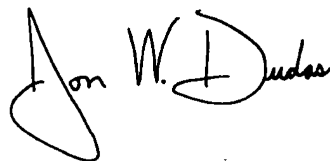
On the title page, item (57), Abstract, penultimate line or 9, insert -- using -- before "processes".

In claim 29, col. 24, line 43, "intermetllic" should read -- intermetallic --.

In claim 33, column 24, line 52, "claims" should read -- claim --.

Signed and Sealed this

Fifth Day of August, 2008



JON W. DUDAS
Director of the United States Patent and Trademark Office

PATENT
Attorney Docket No. 10655.0016-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
Hongmei ZHANG et al.	) Group Art Unit: 2823
Application No.: 10/101,863	) Examiner: Michelle ESTRADA
Filed: March 16, 2002	)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS	) Confirmation No.: 6938

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

REQUEST FOR WITHDRAWAL AS ATTORNEY OR AGENT AND CHANGE OF CORRESPONDENCE ADDRESS

I hereby apply to withdraw myself and the practitioners associated with Customer Number 22,852 as attorney or agent for the above-identified patent application.

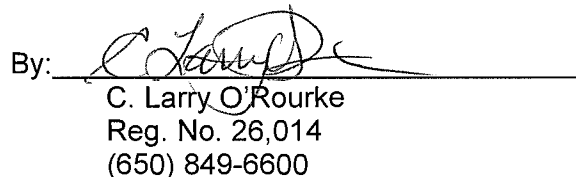
The reasons for this request are: The Assignee of Record has requested that this application be transferred to another law firm for further prosecution, therefore this request is made under the provision of 37 CFR 10.40(b)(4).

Please change the correspondence address and direct all future correspondence to: Haynes & Boone, LLP, **USPTO Customer Number 27,683**.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

Dated: July 28, 2009

By: 

C. Larry O'Rourke
Reg. No. 26,014
(650) 849-6600

Electronic Acknowledgement Receipt

EFS ID:	5782144
Application Number:	10101863
International Application Number:	
Confirmation Number:	6938
Title of Invention:	BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS
First Named Inventor/Applicant Name:	Hongmei Zhang
Customer Number:	22852
Filer:	Aaron James Capron/Drew Herndon
Filer Authorized By:	Aaron James Capron
Attorney Docket Number:	10655.0016-00
Receipt Date:	28-JUL-2009
Filing Date:	16-MAR-2002
Time Stamp:	13:44:14
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Petition to withdraw attorney or agent (SB83)	Request_for_Withdrawal_10655-0016.PDF	11918 87d0d88030358d5e5fc32a9583116dfd31f85219	no	1

Warnings:

Information:

Total Files Size (in bytes):	11918

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Via EFS-Web
COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, VA 22313-1450

POWER OF ATTORNEY TO PROSECUTE APPLIATIONS BEFORE THE USPTO

Dear Sir:

I hereby appoint practitioners associated with Haynes and Boone Customer Number **27683,** as my/our attorney(s) or agent(s) to prosecute the applications identified in Attachment A, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please recognize or change the correspondence address for the applications listed in Attachment A to Customer Number **27683**.

SpringWorks, LLC, is the Assignee of record of the entire interest in the applications identified in Attachment A by virtue of the assignment recorded in the Reel and Frame numbers listed, or for which a copy therefore is attached, in Attachment A.

SPRINGWORKS, LLC

By: ____________________

Name: Douglas A. Kelley

Title: Receiver

Attachment A
Power of Attorney to Prosecute Applications Before the USPTO

Applicant/Patent Owner: **SpringWorks LLC** hereby states that they are the assignee of the entire right, title and interest as listed below by virtue of an assignment from the inventor(s) of the patent application/patent. The assignment was recorded in the United States Patent and Trademark Office at the Reel and Frame number listed below or for which a copy therefore is attached.

Attorney Docket No.	Application Number / Patent Number	Appl. Date/ Issued Date	Inventors	Title	Current Owner	Chain of Title	Assigment Reel/Frame	Recorded Date
43668.3	11/191,643	7/27/2005	H. Zhang M. Narasimhan R. Mullapudi R. Demaray	Biased Pulse DC Reactive Sputtering Of Oxide Films	SpringWorks LLC	From Inventors to Symmorphix	014766 / 0601	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.4	11/100,856	4/6/2005	T. Pan R. Demaray Y. Chen Y. Xie R. Pethe	Mode Size Converter For A Planar Waveguide	SpringWorks LLC	From Inventors to Symmorphix	020035 / 0110	10/30/2007
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.5	10/850,968	5/20/2004	R. Demaray M. Narasimhan	Transparent Conductive Oxides	SpringWorks LLC	From Inventors to Symmorphix	014945 / 0661	8/4/2004
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.22	10/650,461	8/27/2003	D. Dawes	Optically Coupling Into Highly Uniform Waveguides	SpringWorks LLC	From Inventors to Symmorphix	014897 / 0768	1/16/2007
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.39	11/726,972	3/22/2007	R. Demaray H. Zhang M. Narasimhan V. Milonopoulou	Energy Conversion And Storage Devices By Physical Vapor Deposition Of Titanium And Titanium Oxides And Sub-Oxides	SpringWorks LLC	From Inventors to Symmorphix	014948 / 0097	8/5/2004
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.44	11/297,057	12/7/2005	H. Zhang R. Demaray M. Shao	Deposition Of LiCoO2	SpringWorks LLC	From Inventors to Symmorphix	017196 / 0699	12/21/2006
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.53	11/218,652	9/2/2005	H. Zhang R. Demaray	Deposition Of Perovskite And Other Compound Ceramic Films From Dielectric Applications	SpringWorks LLC	From Inventors to Symmorphix	016821 / 0220	11/28/2005
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.6	10/291,179 US Pat No. 7,404,877	ISSUED - 7/29/08	R. Demaray, V. Milonopoulou	Low temperature zirconia based thermal barrier layer by PVD	SpringWorks LLC	From Inventors to Symmorphix	014756 / 0416	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007

Initial: TAK

Attachment A
Power of Attorney to Prosecute Applications Before the USPTO

Applicant/Patent Owner: **SpringWorks LLC** hereby states that they are the assignee of the entire right, title and interest as listed below by virtue of an assignment from the inventor(s) of the patent application/patent. The assignment was recorded in the United States Patent and Trademark Office at the Reel and Frame number listed below or for which a copy therefore is attached.

Attorney Docket No.	Application Number / Patent Number	Appl. Date/ Issued Date	Inventors	Title	Current Owner	Chain of Title	Assigment Reel/Frame	Recorded Date
43668.8	09/903,050 US Pat No. 6,506,289	ISSUED - 1/14/03	R. Demaray, K. Wang, R. Mullapudi, D. Stadtler, H Zhang, R. Peth	Planar optical devices and methods for their manufacture	SpringWorks LLC	From Inventors to Symmorphix	012010 / 0318	07/10/2001
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.9	10/288,278 US Pat No. 6,827,826	ISSUED - 12/7/04	R. Demaray, K. Wang, R. Mullapudi, D. Stadtler, H Zhang, R. Pethe	Planar optical devices and methods for their manufacture	SpringWorks LLC	From Inventors to Symmorphix	012010 / 0318	07/10/2001
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.13	09/766,463 U.S. Pat No. 6,533,907	ISSUED - 3/18/03	R. Demaray, J. Shan, K. Wang, R. Mullapudi	Method of Producing amorphous silicon for hard mask and waveguide applications	SpringWorks LLC	From Inventors to Symmorphix	011504 / 0738	01/19/2001
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.14	09/903,081 US Pat No. 7,469,558	ISSUED - 12/30/08	R. Demaray, K. Wang, R. Mullapudi, Q. Zhu, H. Zhang, H. Ackler, J. Egermeier, R. Pethe	As-deposited planar optical waveguides with low scattering loss and methods for their manufacture	SpringWorks LLC	From Inventors to Symmorphix	012010 / 0752	07/10/2001
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.15	10/101,492 US Pat No. 6,884,327	ISSUED - 4/26/05	T. Pan, R. Demaray, Y. Chen, Y. Xie, R. Pethe	Mode size converter for a planar waveguide	SpringWorks LLC	From Inventors to Symmorphix	020035 / 0110	10/30/2007
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.17	10/101,863 US Pat No. 7,378,356	ISSUED - 5/27/08	H. Zhang, M. Narasimhan, R. Mullapudi, R. Demaray	Biased pulse DC reactive sputtering of oxide films	SpringWorks LLC	From Inventors to Symmorphix	014766 / 0601	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.21	10/954,182 US Pat No. 7,381,657	ISSUED - 6/30/08	H. Zhang, M. Narasimhan, R. Mullapudi, R. Demaray	Biased pulse DC reactive sputtering of oxide films	SpringWorks LLC	From Inventors to Symmorphix	014766 / 0601	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.19	11/228,834 US Pat No. 7,544,276	ISSUED - 6/9/09	H. Zhang, M. Narasimhan, R. Mullapudi, R. Demaray	Biased pulse DC reactive sputtering of oxide films	SpringWorks LLC	From Inventors to Symmorphix	014766 / 0601	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007

Initial:

Attachment A
Power of Attorney to Prosecute Applications Before the USPTO

Applicant/Patent Owner: **SpringWorks LLC** hereby states that they are the assignee of the entire right, title and interest as listed below by virtue of an assignment from the inventor(s) of the patent application/patent. The assignment was recorded in the United States Patent and Trademark Office at the Reel and Frame number listed below or for which a copy therefore is attached.

Attorney Docket No.	Application Number / Patent Number	Appl. Date/ Issued Date	Inventors	Title	Current Owner	Chain of Title	Assigment Reel/Frame	Recorded Date
43668.20	11/228,717 U.S. Pat No. 7,413,998	ISSUED - 8/19/08	H. Zhang, M. Narasimhan, R. Mullapudi, R. Demaray	Biased pulse DC reactive sputtering of oxide films	SpringWorks LLC	From Inventors to Symmorphix	014766 / 0601	12/2/2003
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.25	10/789,953 US Pat No. 7,205,662	ISSUED - 4/17/07	M. Narasimhan, P. Brooks, R. Demaray	Dielectric Barrier Layer Films	SpringWorks LLC	From Inventors to Symmorphix	014948 / 0111	08/05/2004
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.32	11/228,805 US Pat No. 7,262,131	ISSUED - 8/28/07	M. Narasimhan, P. Brooks, R. Demaray	Dielectric Barrier Layer Films	SpringWorks LLC	From Inventors to Symmorphix	014948 / 0111	08/05/2004
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007
43668.34	10/851,542 US Pat No. 7,238,628	ISSUED - 7/3/07	R. Demaray, H. Zhang, M. Narasimhan, V. Milonopoulou	Energy Conversion and Storage Devices by Physical Vapor Deposition of Titanium and Titanium Oxides and Sub-Oxides	SpringWorks LLC	From Inventors to Symmorphix	014948 / 0097	8/5/2004
						From Symmorphix to SpringWorks LLC	20134 / 0102	11/19/2007

SpringWorks LLC

By: Douglas A. Kelley

Name: Douglas A. Kelley

Title: Receiver

Initial: DAK

PTO/SB/122 (11-08)
Approved for use through 11/30/2011. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

CHANGE OF CORRESPONDENCE ADDRESS
Application

Address to:
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Application Number	10/101,863
Filing Date	3-16-2002
First Named Inventor	H. Zhang
Art Unit	2823
Examiner Name	Michelle Estrada
Attorney Docket Number	43668.17

Please change the Correspondence Address for the above-identified patent application to:

☑ The address associated with Customer Number: 27683

OR

☐ Firm or Individual Name

Address

City | State | Zip

Country

Telephone | Email

This form cannot be used to change the data associated with a Customer Number. To change the data associated with an existing Customer Number use "Request for Customer Number Data Change" (PTO/SB/124).

I am the:

☐ Applicant/Inventor

☐ Assignee of record of the entire interest.
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

☑ Attorney or agent of record. Registration Number 41008.

☐ Registered practitioner named in the application transmittal letter in an application without an executed oath or declaration. See 37 CFR 1.33(a)(1). Registration Number ____________.

Signature	/gary j. edwards/
Typed or Printed Name	Gary J. Edwards
Date December 2, 2009	Telephone 408-660-4120

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*.

☐ *Total of ____________ forms are submitted.

This collection of information is required by 37 CFR 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	6555033
Application Number:	10101863
International Application Number:	
Confirmation Number:	6938
Title of Invention:	BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS
First Named Inventor/Applicant Name:	Hongmei Zhang
Customer Number:	22852
Filer:	Gary James Edwards/Sheila Badon
Filer Authorized By:	Gary James Edwards
Attorney Docket Number:	43668.17
Receipt Date:	02-DEC-2009
Filing Date:	16-MAR-2002
Time Stamp:	12:26:59
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		43668_POA.pdf	482094 50be7508dee6f2cb790d6ae139f6af2655b53fda	yes	4

	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Power of Attorney		1	1	
	Assignee showing of ownership per 37 CFR 3.73(b).		2	4	
Warnings:					
Information:					
2	Change of Address	43668_17_COA.pdf	298818 93b76369c0b54a23b201bfd71810fc3dfbfbe4b5	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	780912		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	43668.17

CONFIRMATION NO. 6938

POA ACCEPTANCE LETTER

OC000000039120511

27683
HAYNES AND BOONE, LLP
IP Section
2323 Victory Avenue
Suite 700
Dallas, TX 75219

Date Mailed: 12/10/2009

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2009.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

/mnguyen/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
10/101,863	03/16/2002	Hongmei Zhang	43668.17

CONFIRMATION NO. 6938

22852
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

POWER OF ATTORNEY NOTICE

OC000000039120482

Date Mailed: 12/10/2009

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/02/2009.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

/mnguyen/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
10/101,863	03/16/2002	Hongmei Zhang	48604.18	93175

Acknowledgement of Change to Small Entity Status

The entity status change request below filed through Private PAIR on 08/06/2019 has been accepted.

CERTIFICATIONS:

Change of Entity Status:

X Applicant asserting small entity status. See 37 CFR 1.27.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

This portion must be completed by the signatory or signatories making the entity status change in accordance with 37 CFR 1.4(d)(4).

Signature:	/Gary Edwards/
Name:	Gary Edwards
Registration Number:	41008