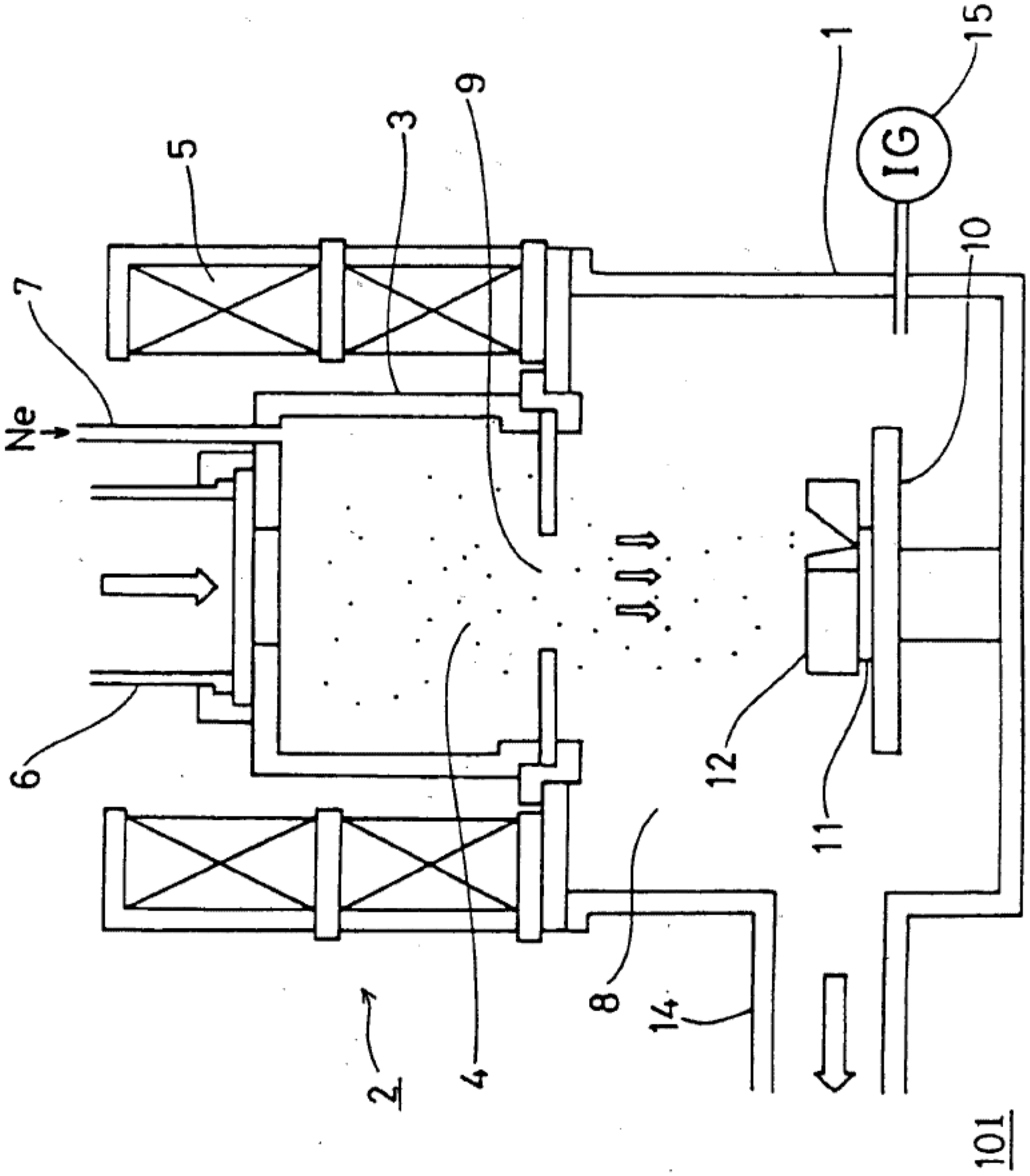


FIG. 4

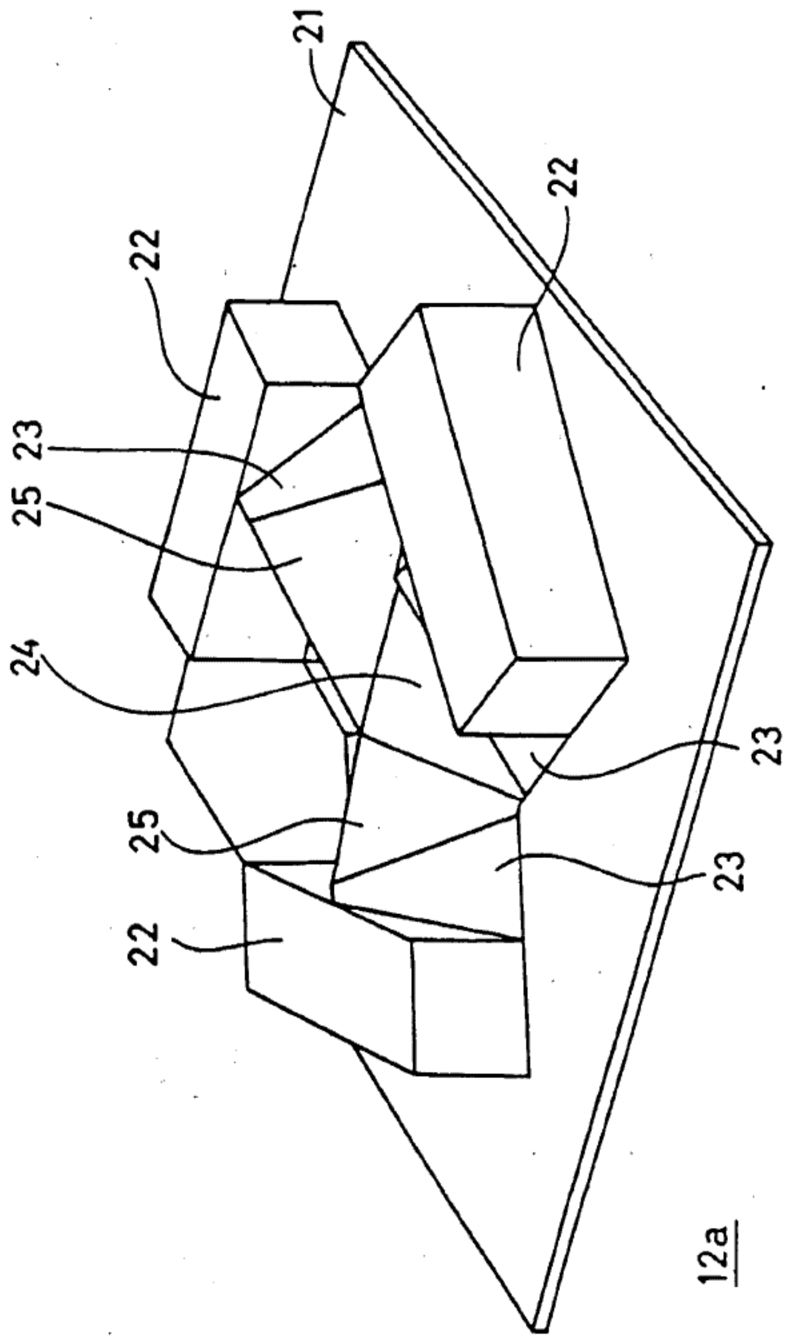


FIG. 5

FIG.6A

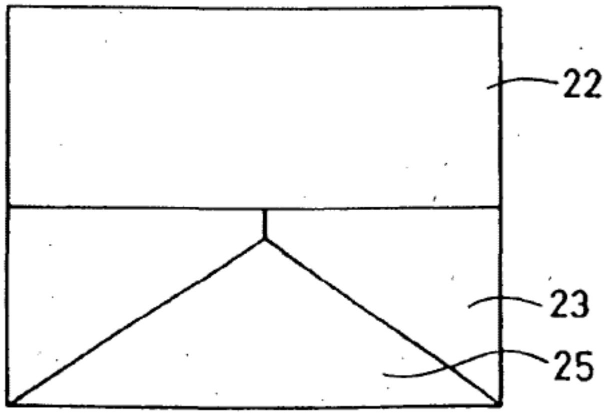


FIG.6B

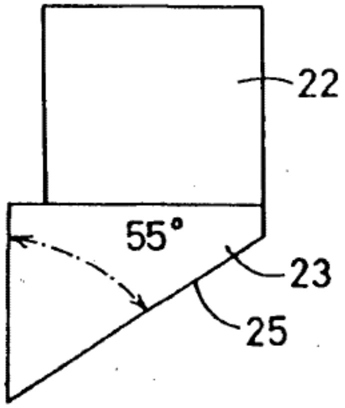
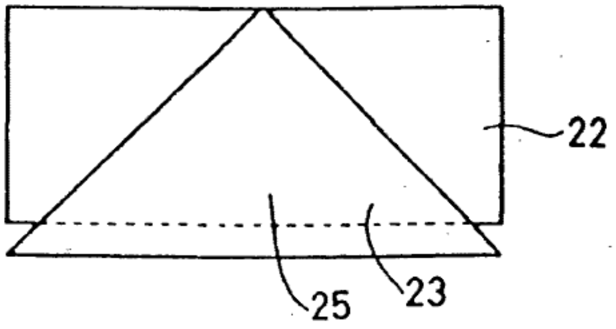


FIG.6C



12a

FIG. 7

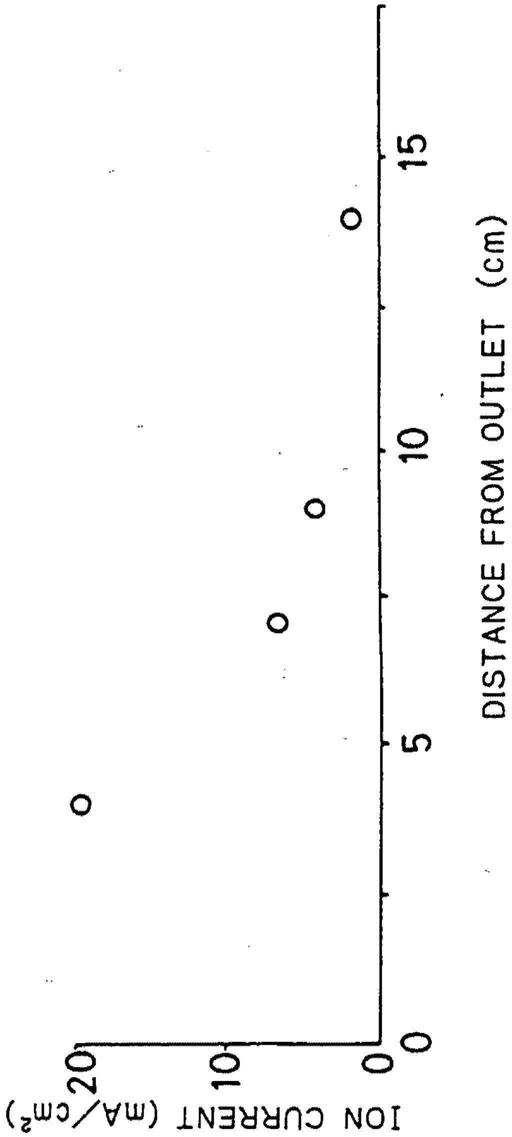


FIG. 8

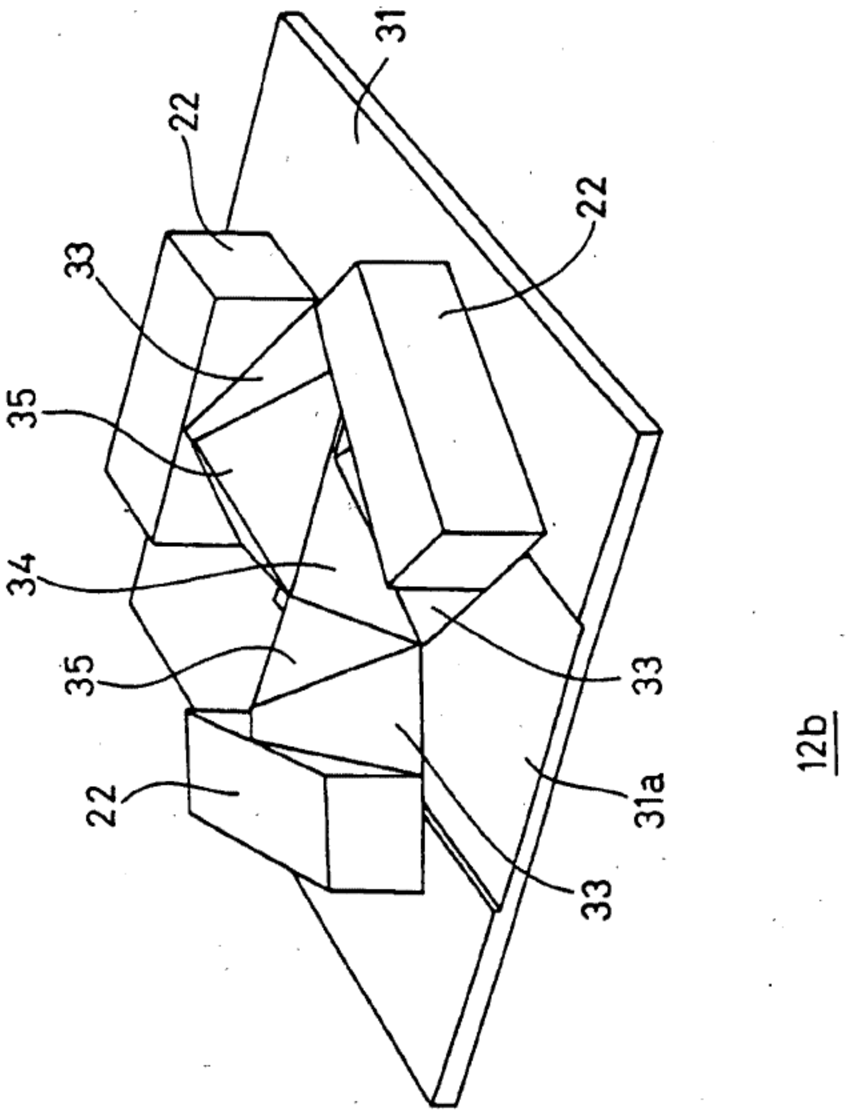


FIG. 9

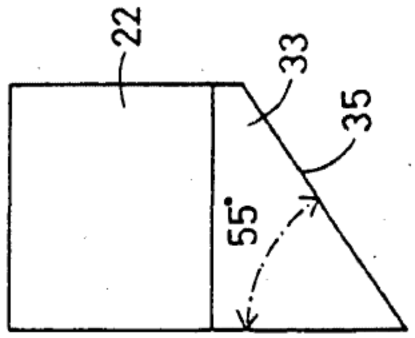


FIG. 10B

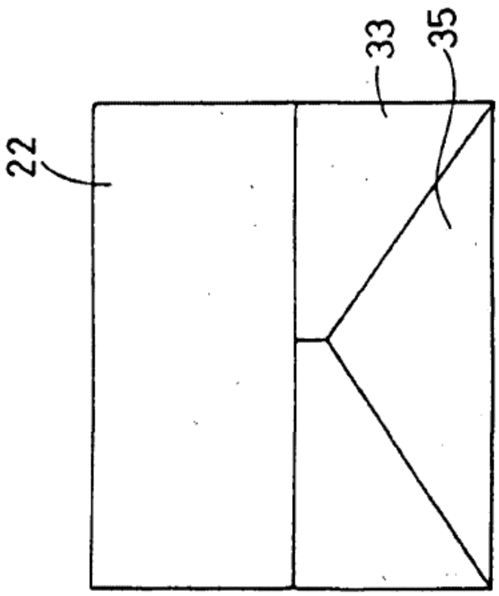


FIG. 10A

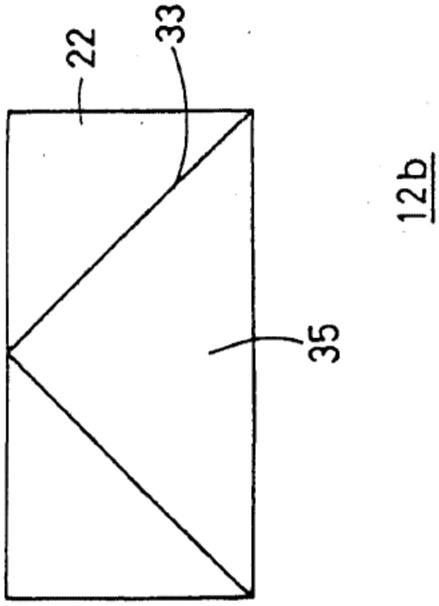


FIG. 10C

FIG. 11A

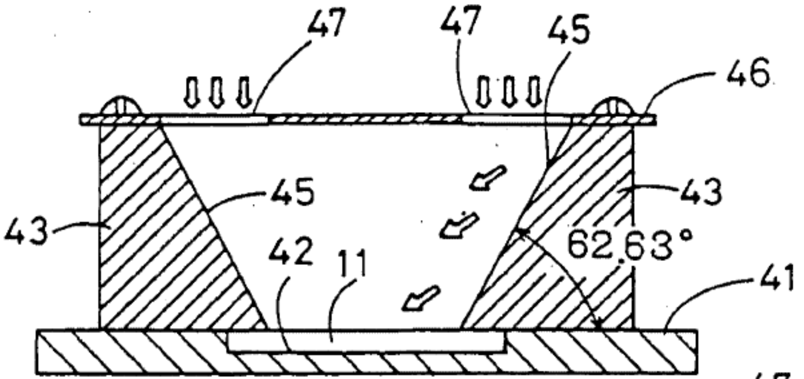
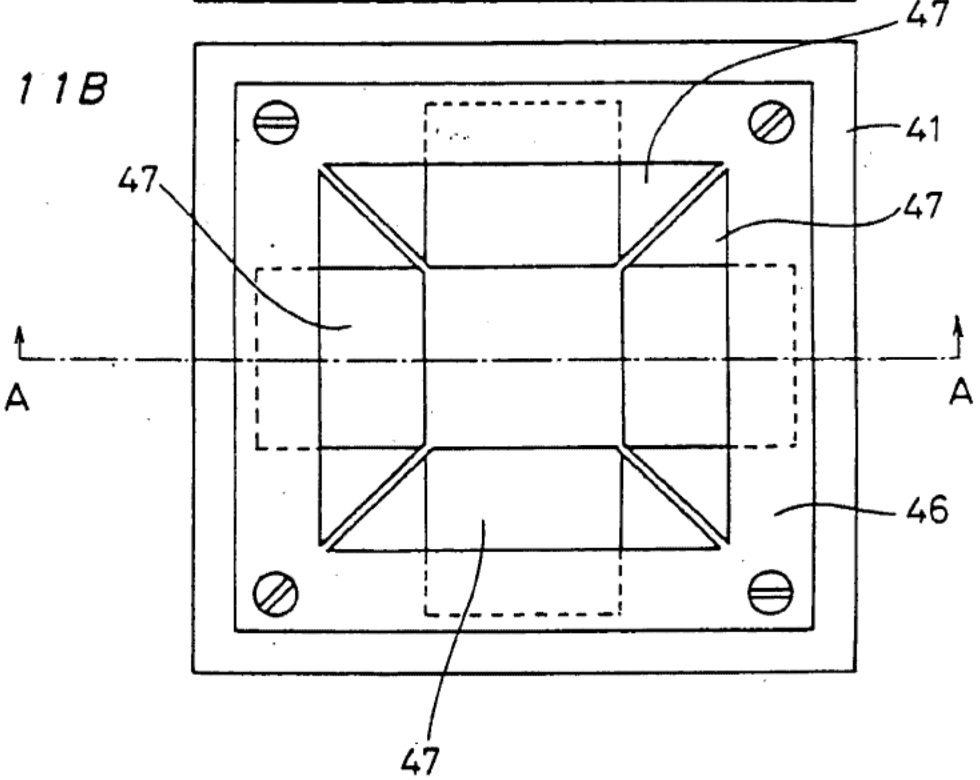


FIG. 11B



12c

FIG. 12A

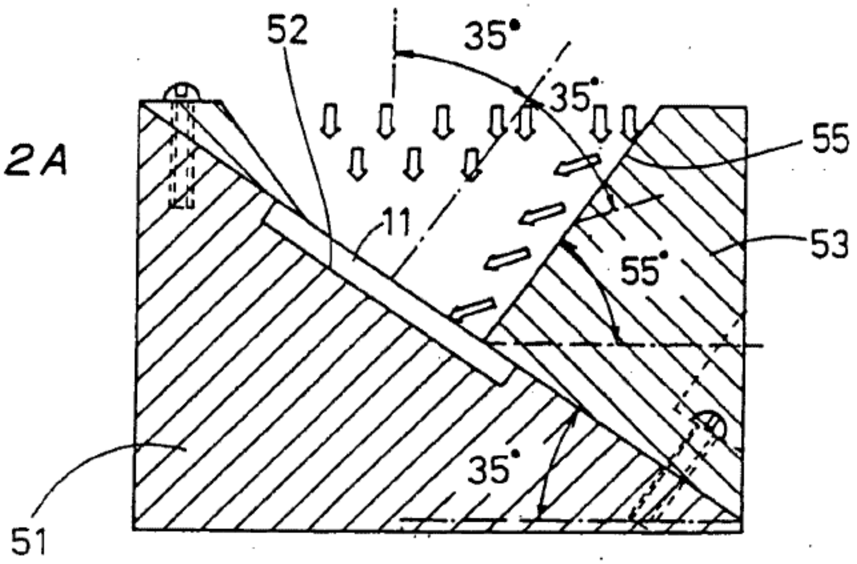
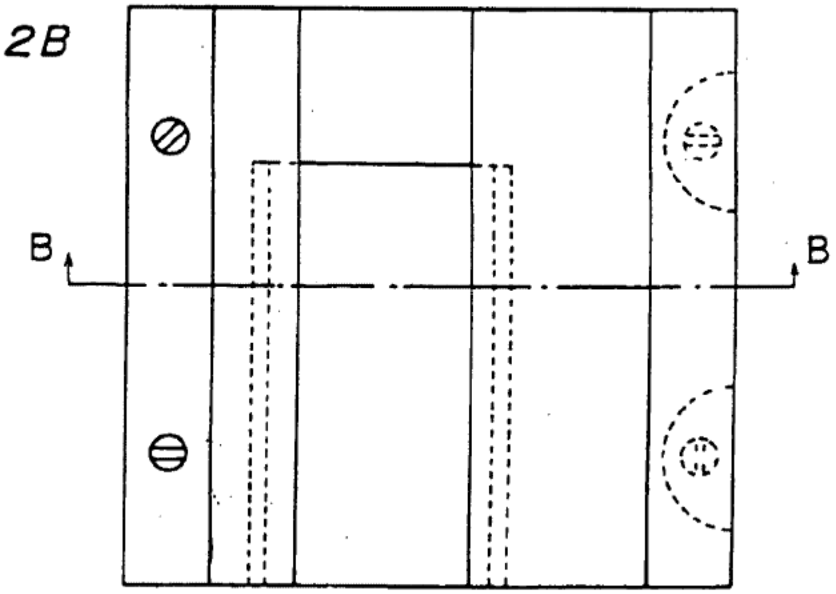


FIG. 12B



12d

FIG. 13

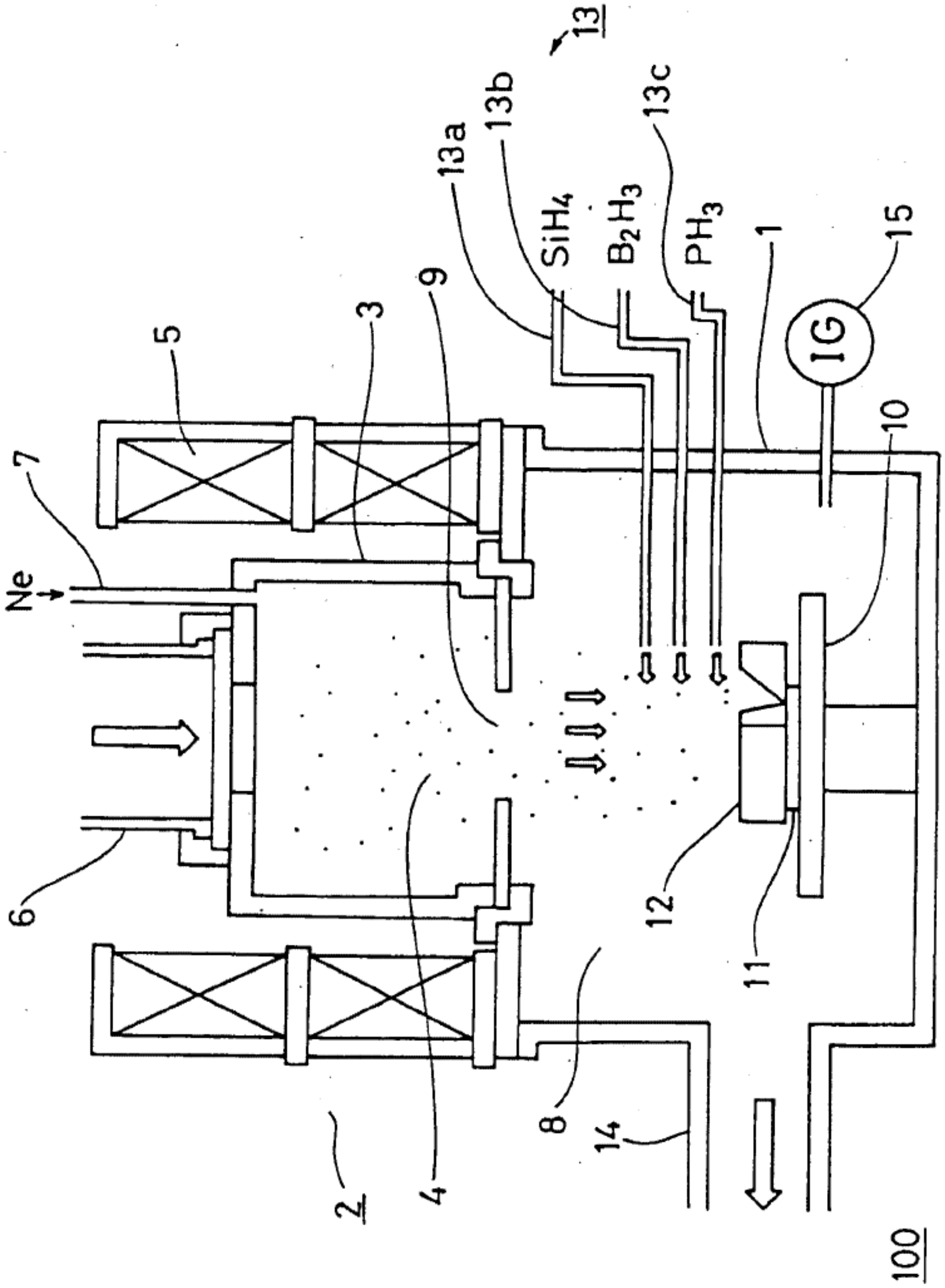


FIG. 14

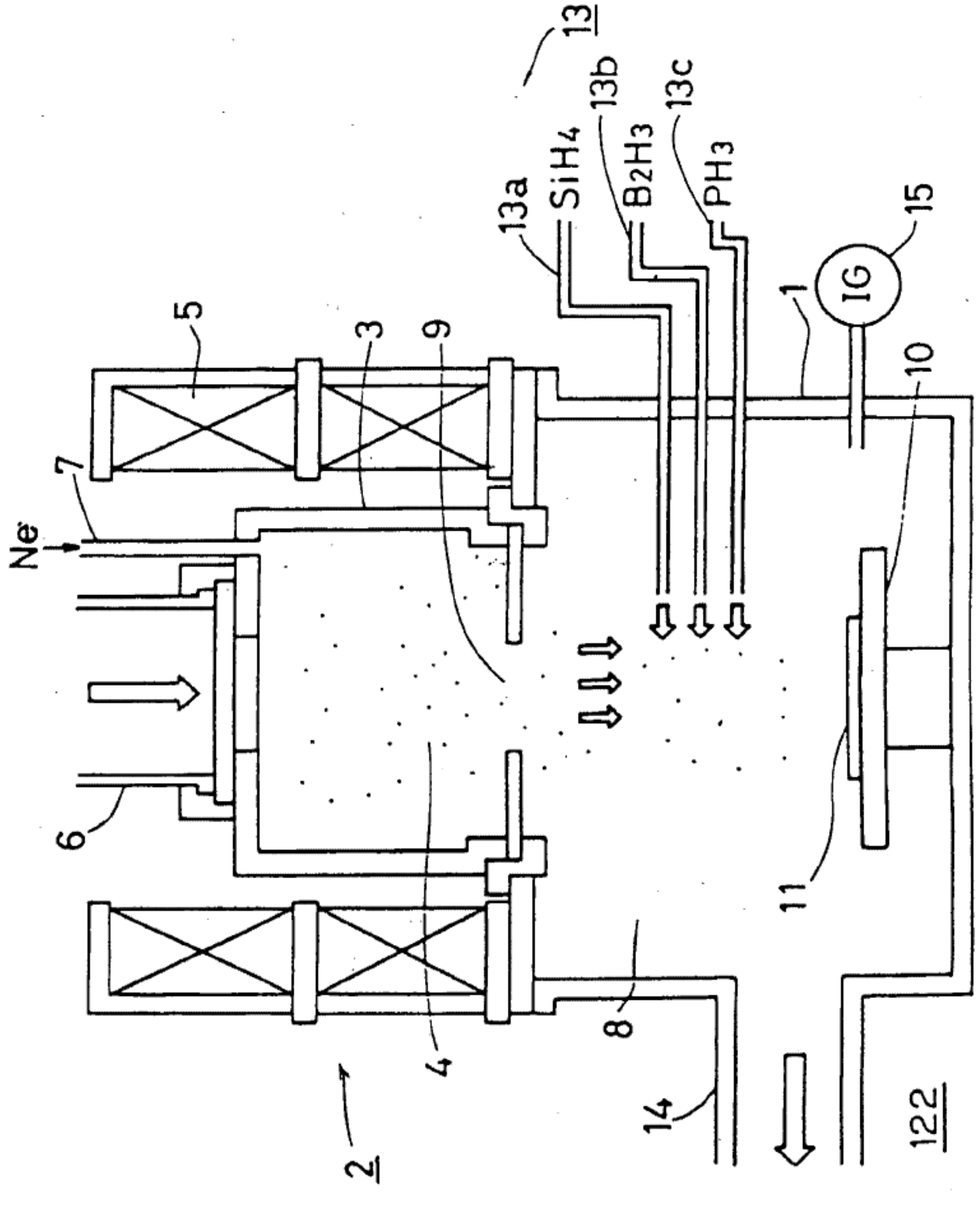


FIG. 15

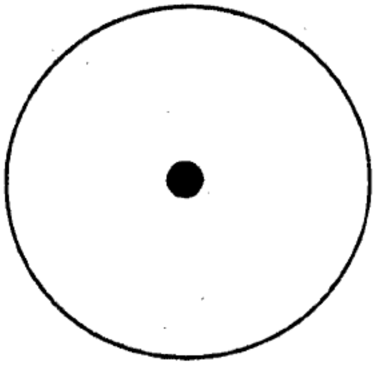


FIG. 16

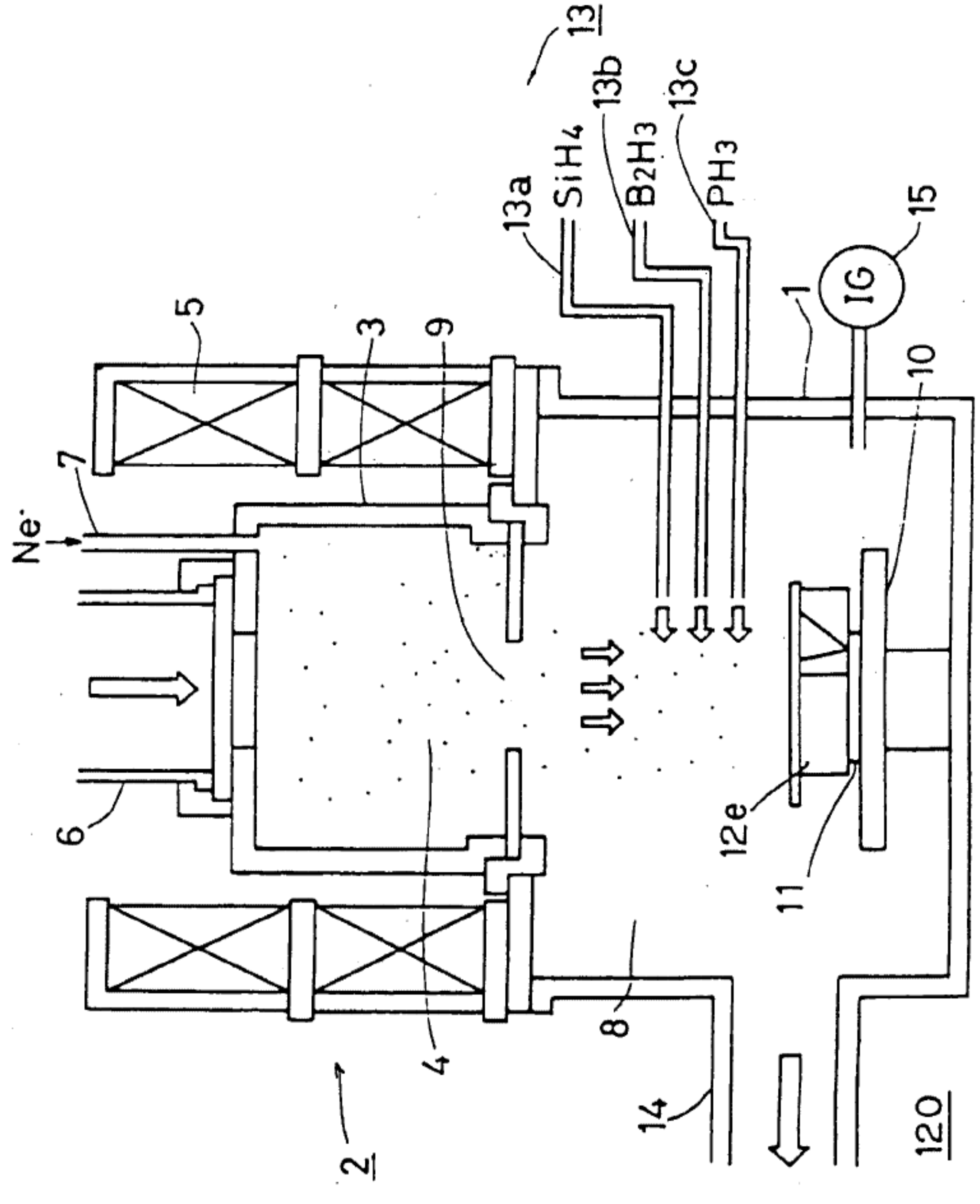


FIG. 17

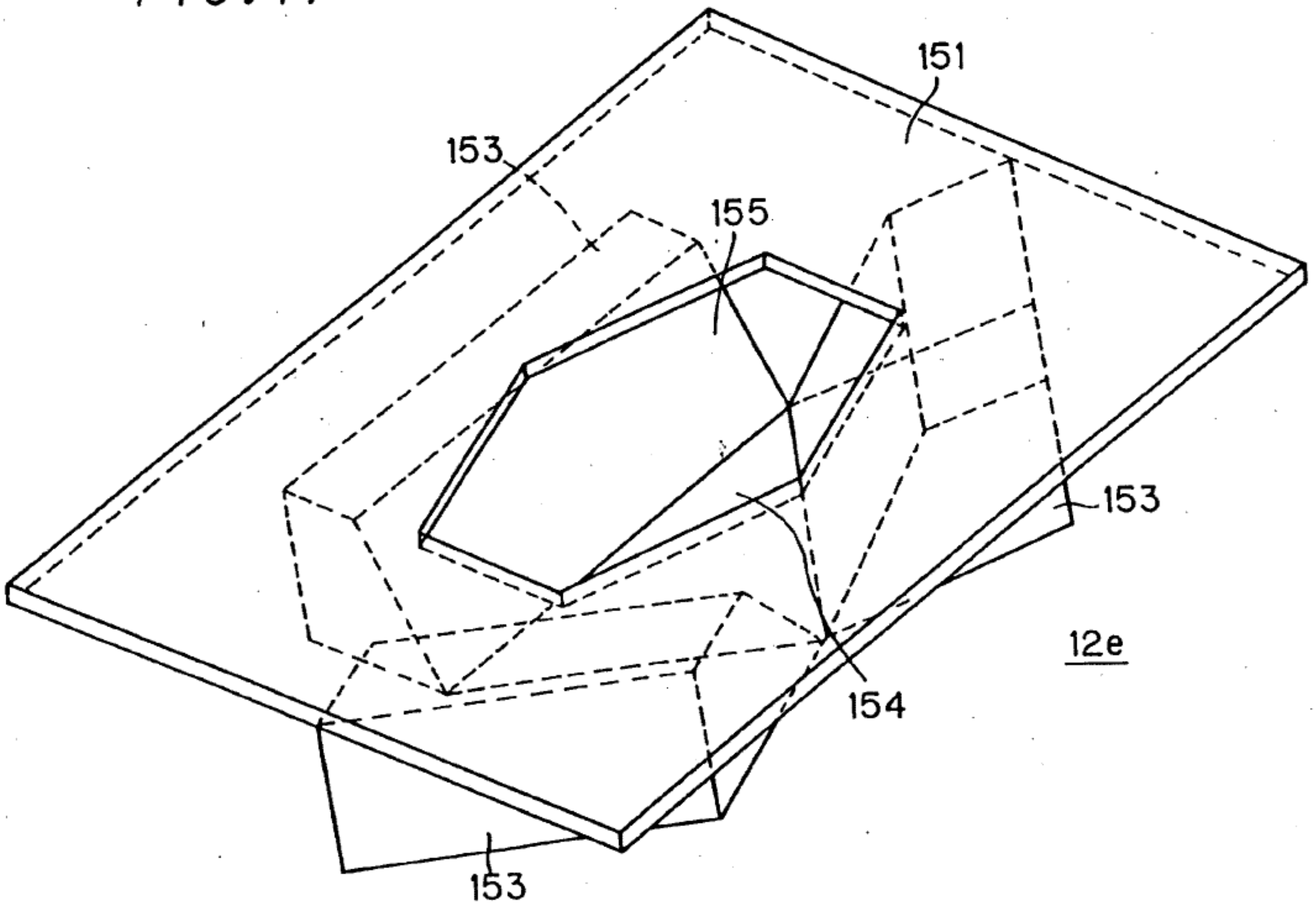


FIG. 18

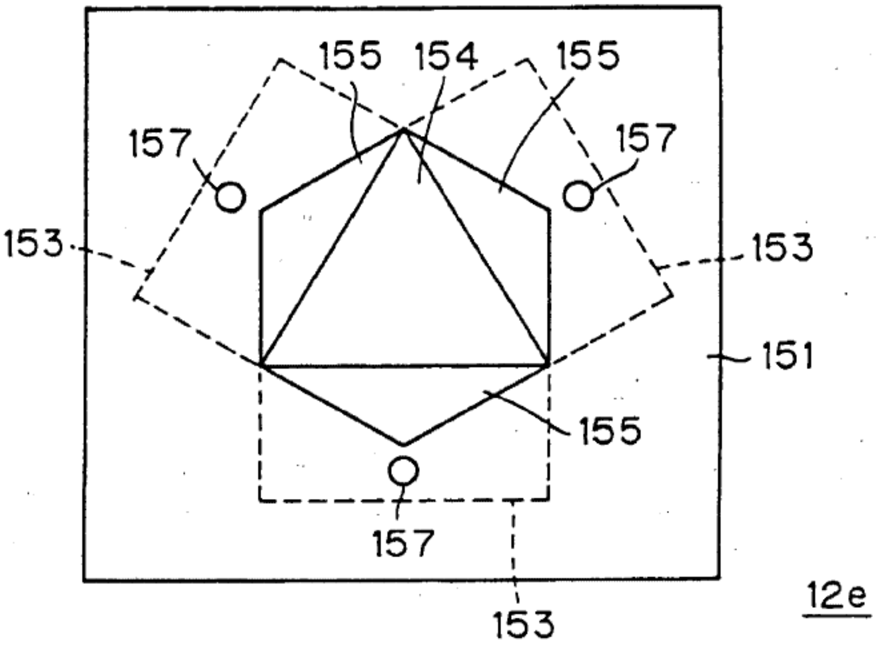


FIG. 19

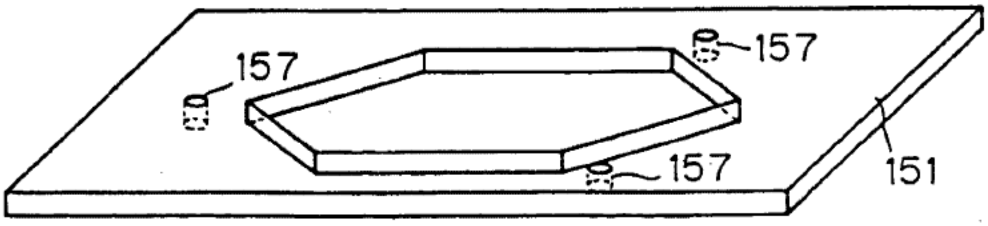


FIG.20

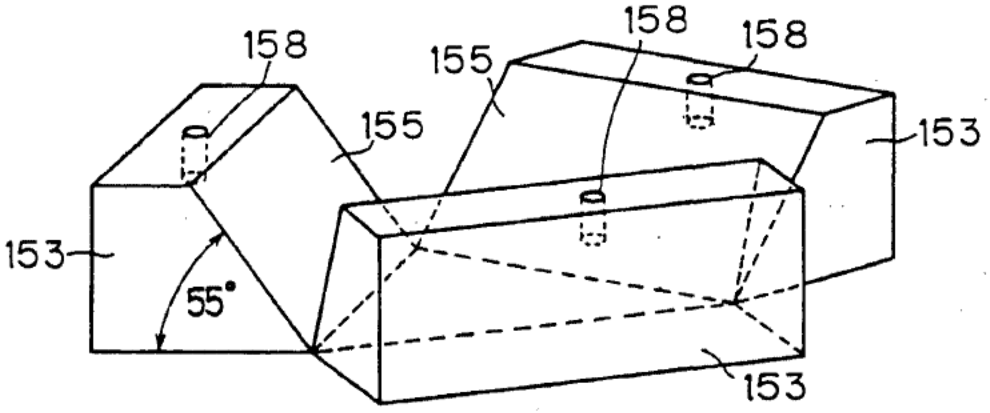

158
155
155
158
158
153
153
55°
153

FIG.21

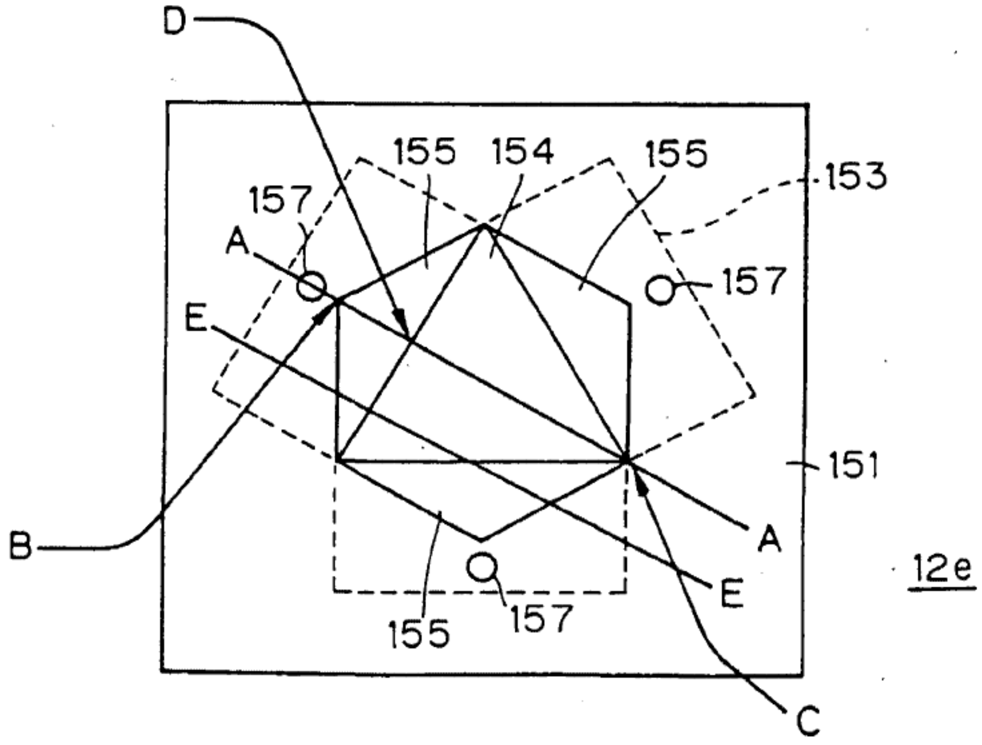

D
155
154
155
153
157
A
157
E
151
B
A
E
12e
155
157
C

FIG.22

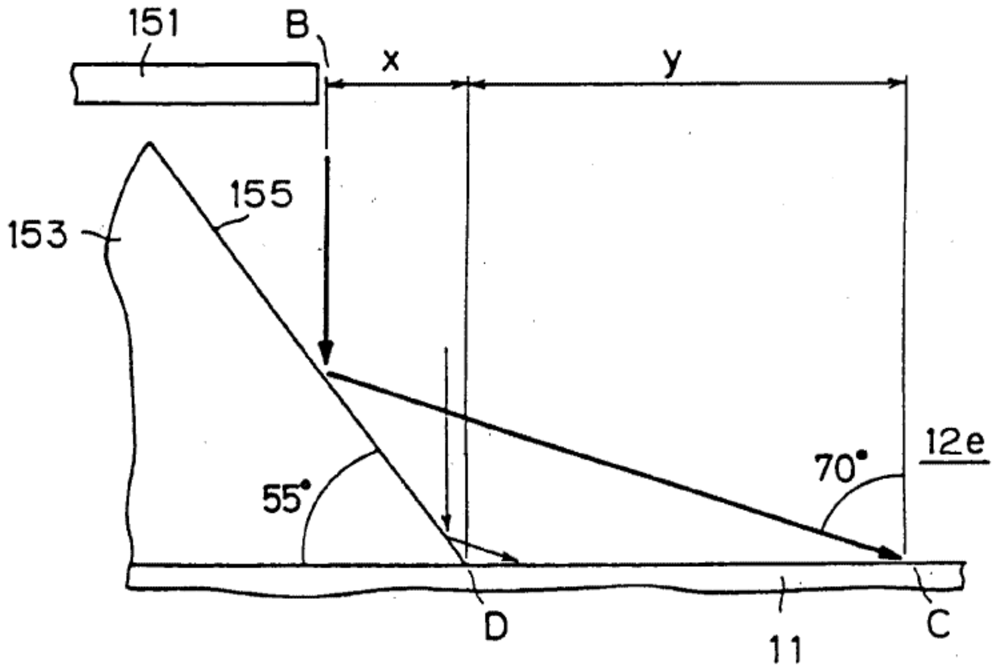


FIG.23

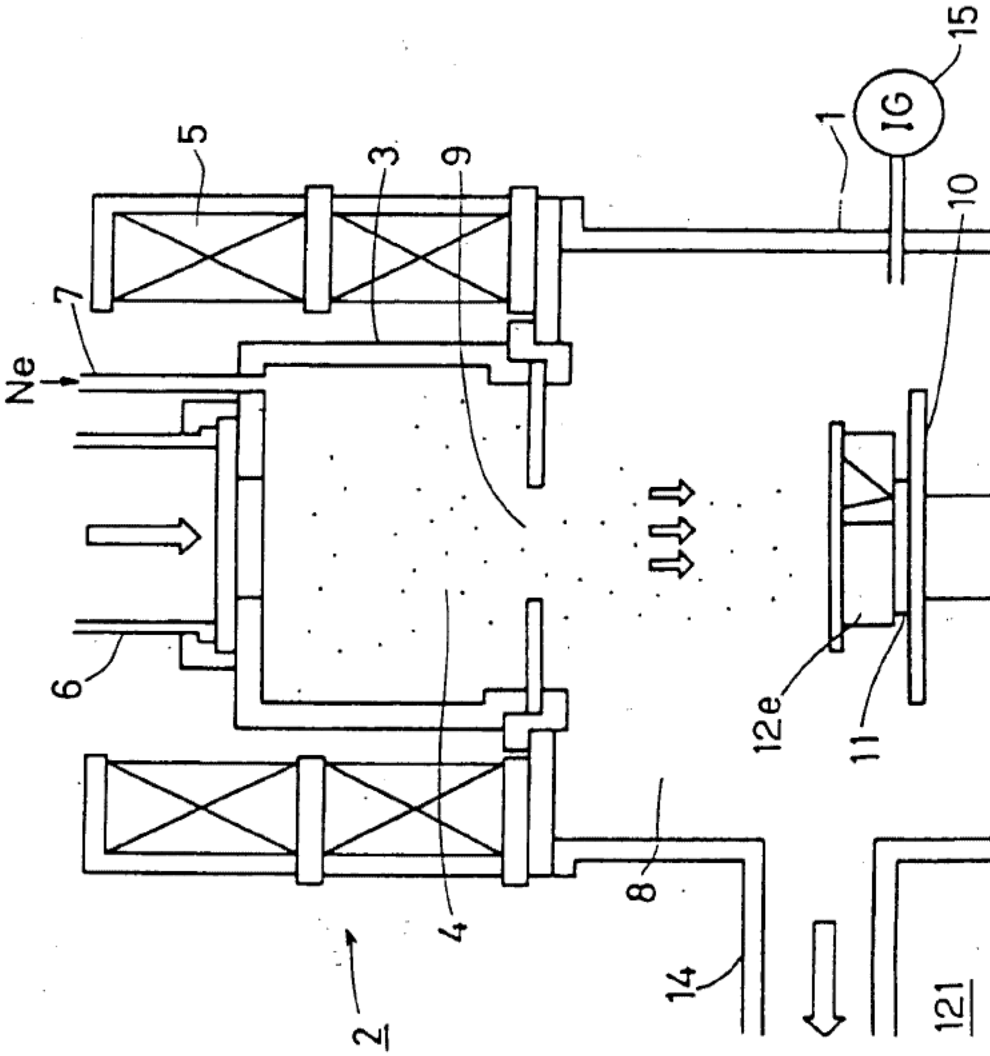


FIG. 24

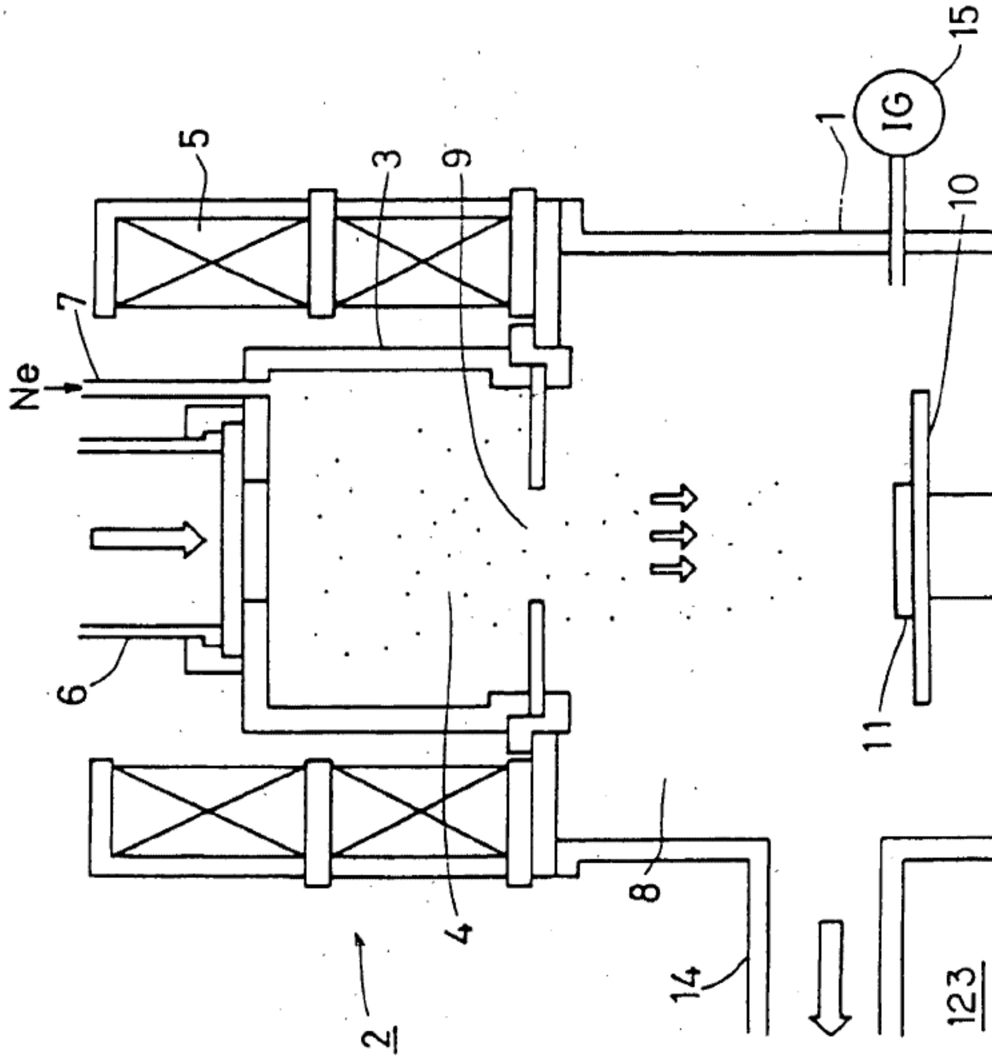


FIG. 25

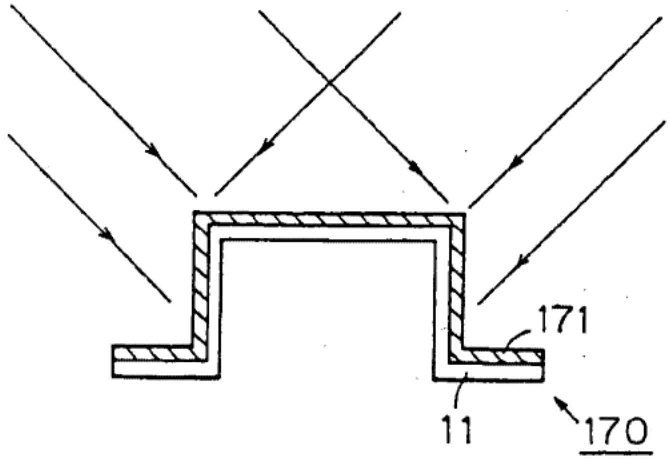


FIG. 26

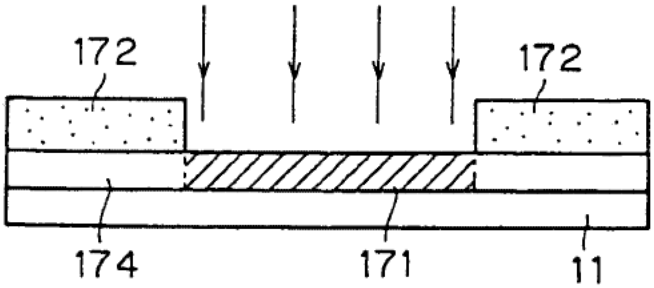


FIG. 27

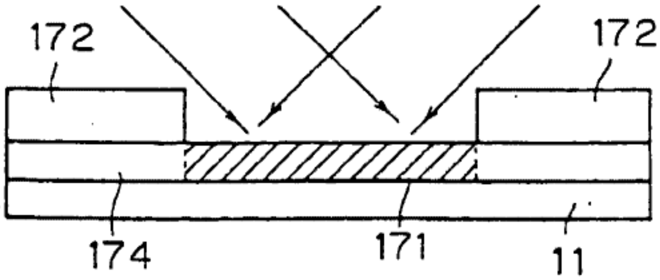


FIG.28

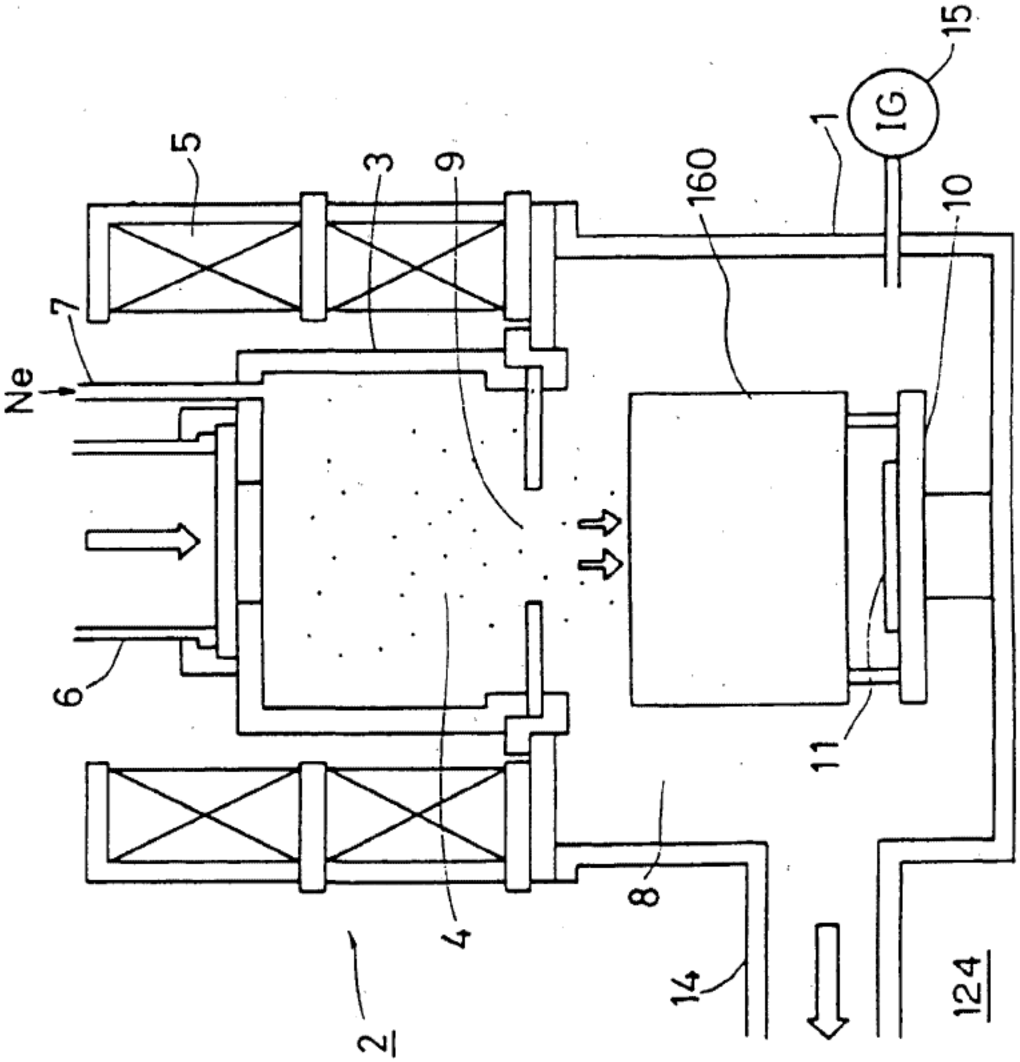


FIG. 29

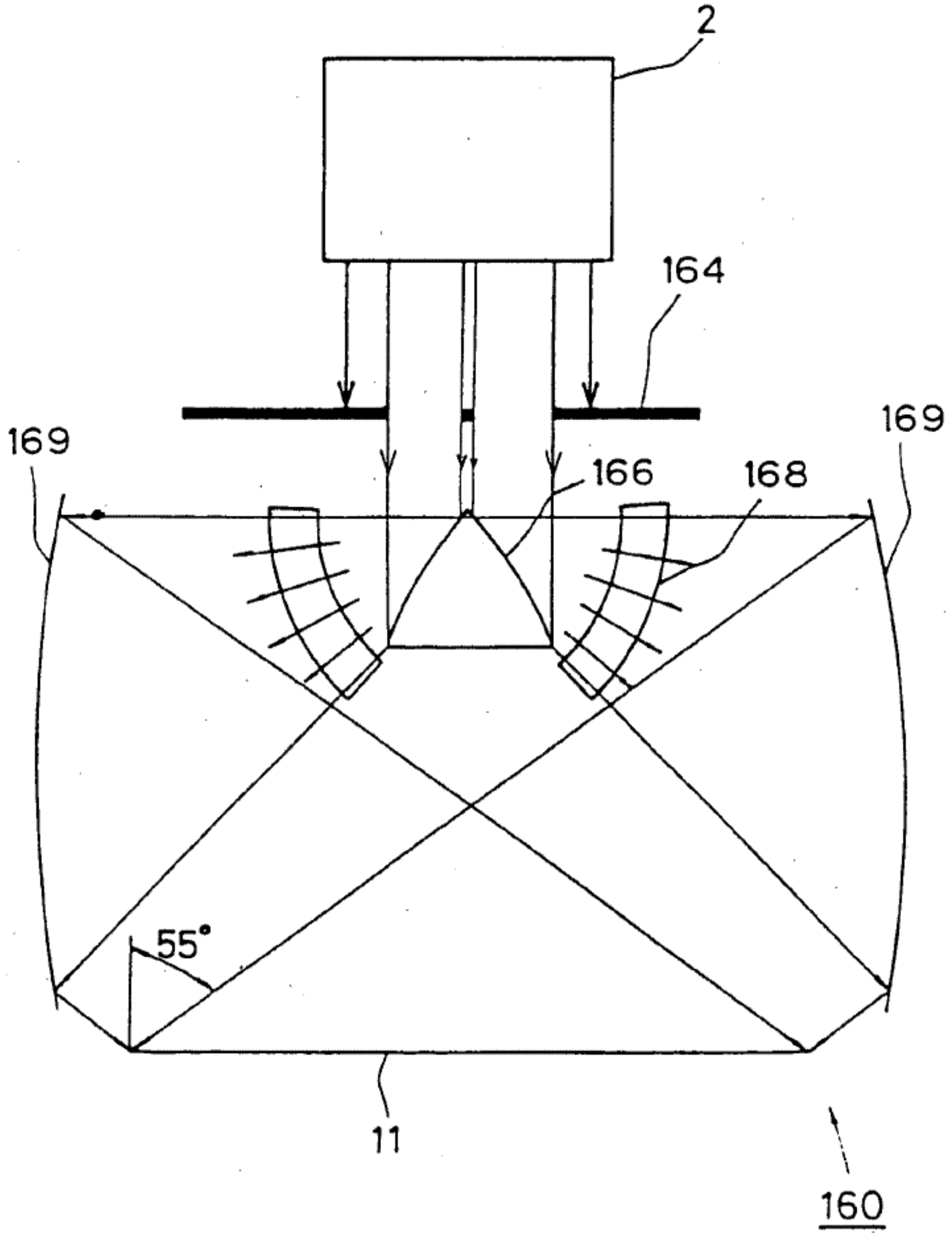


FIG.30

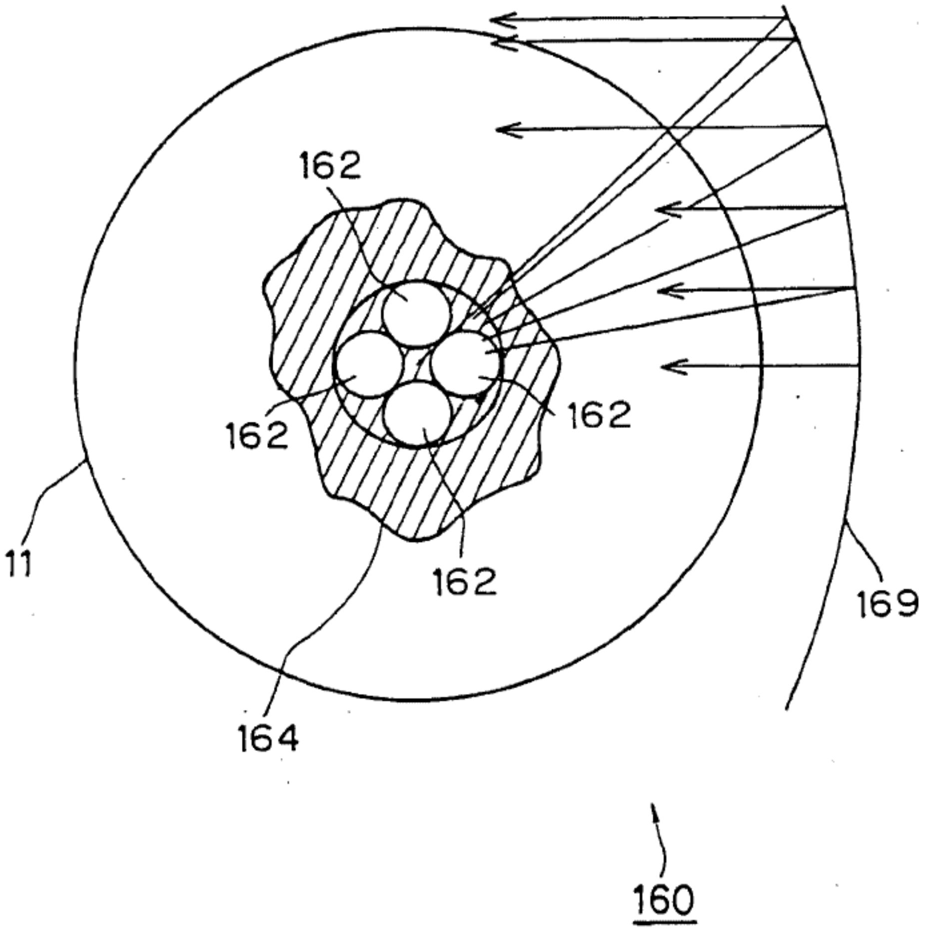


FIG. 31

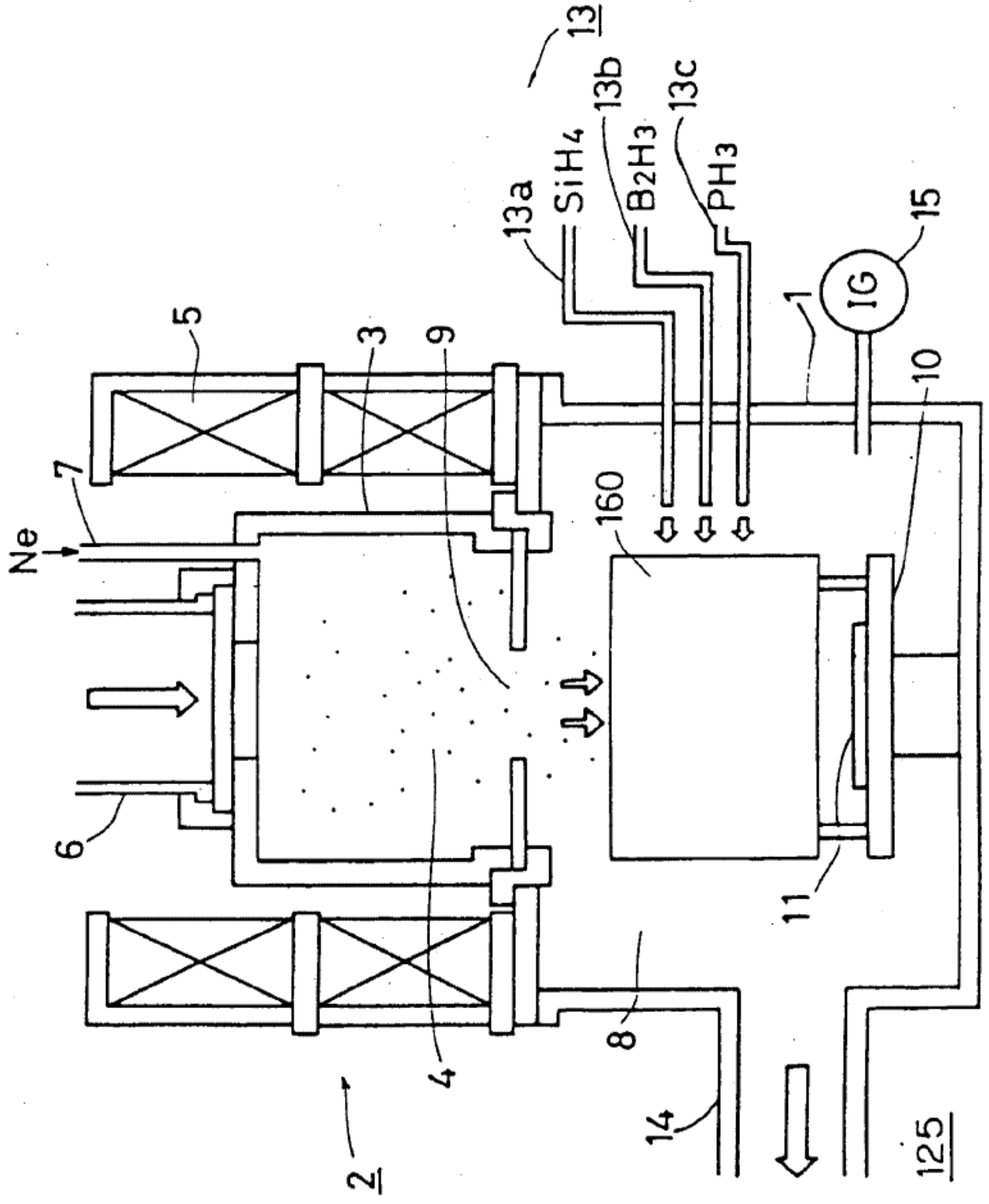


FIG.32

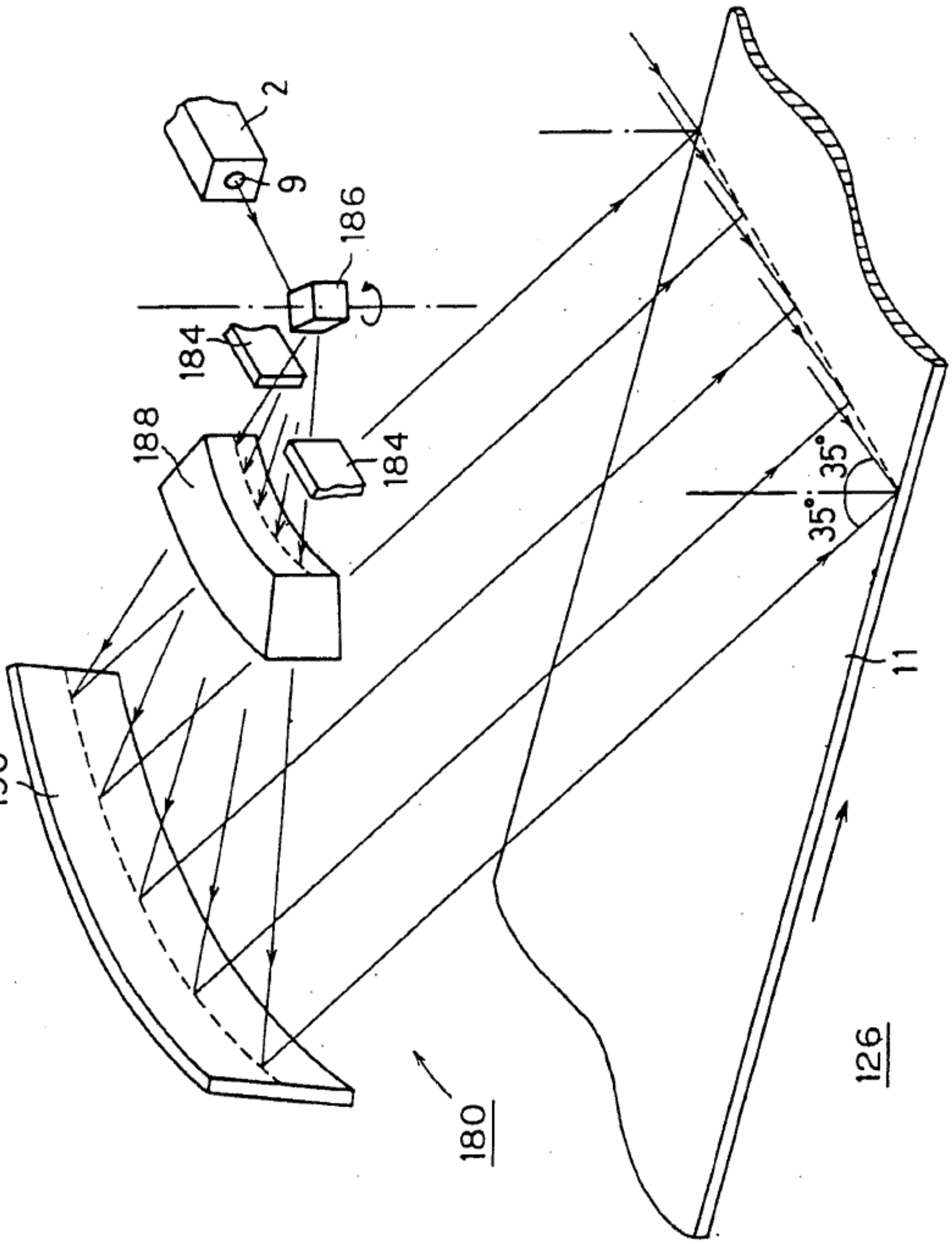


FIG. 33

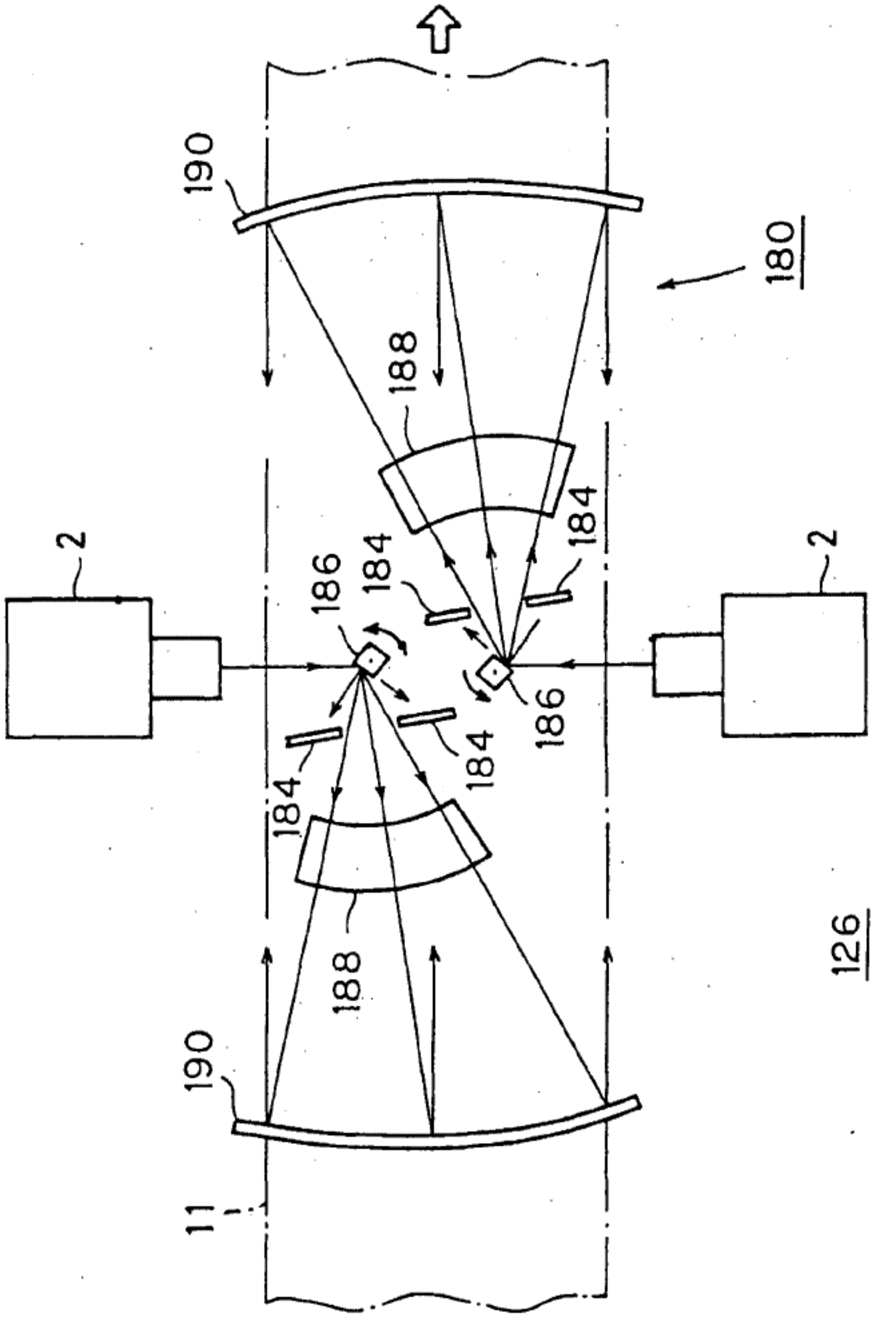


FIG. 34

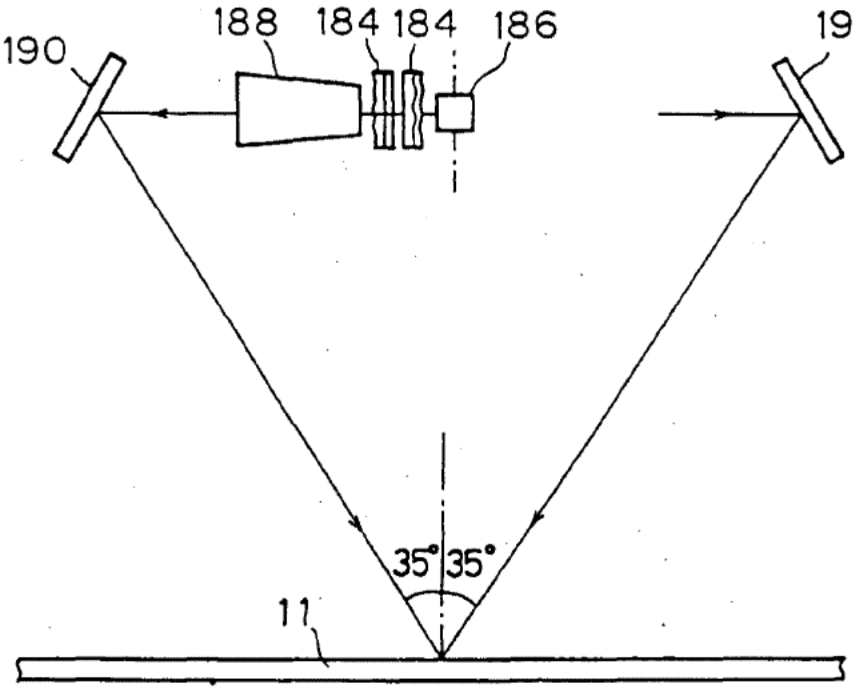


FIG. 35

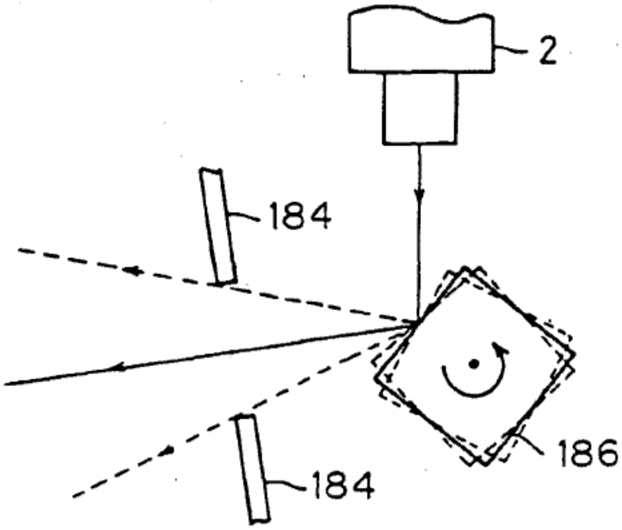


FIG.36

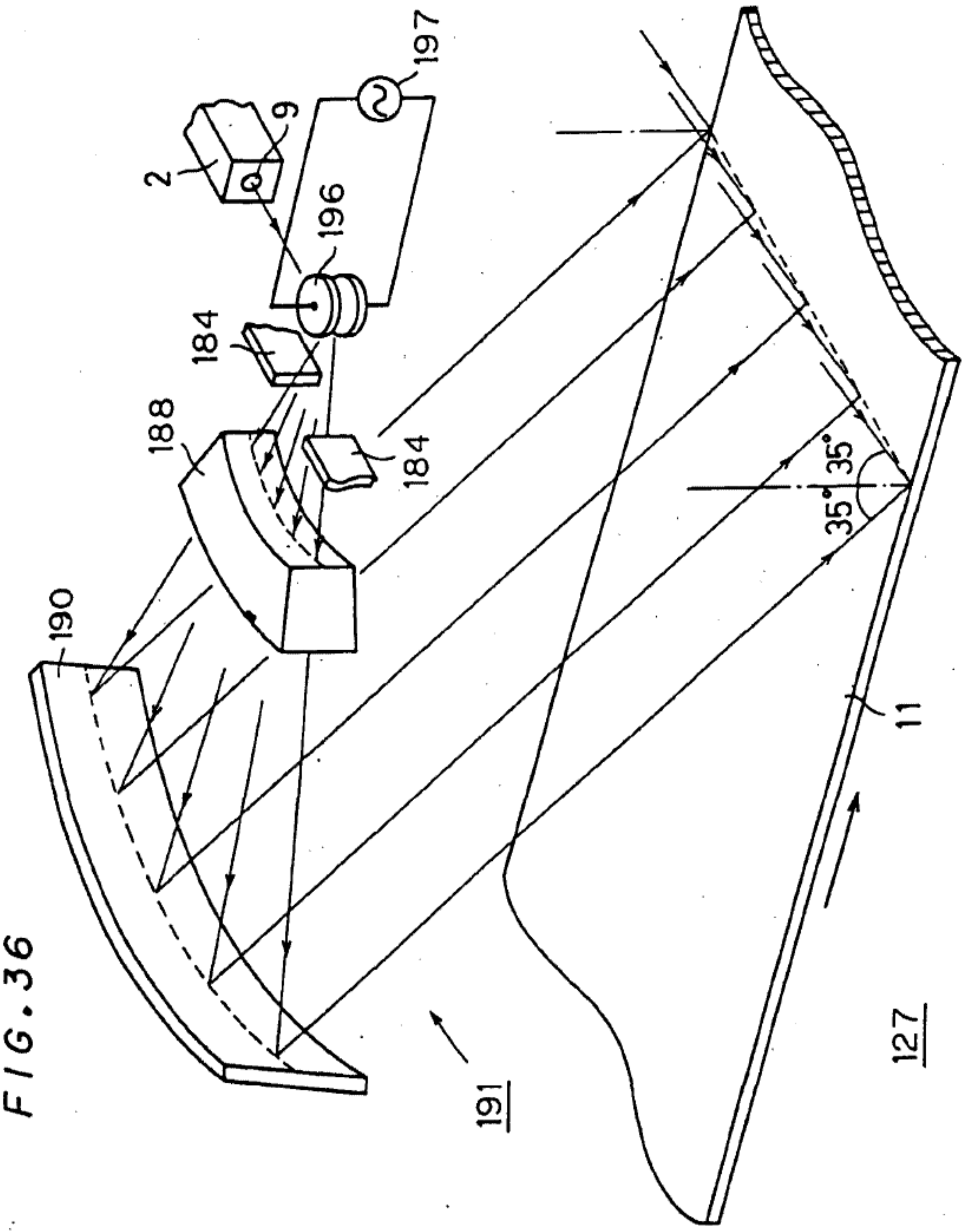


FIG. 37

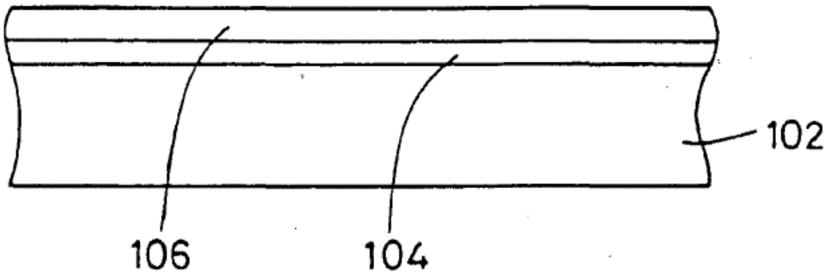


FIG. 38

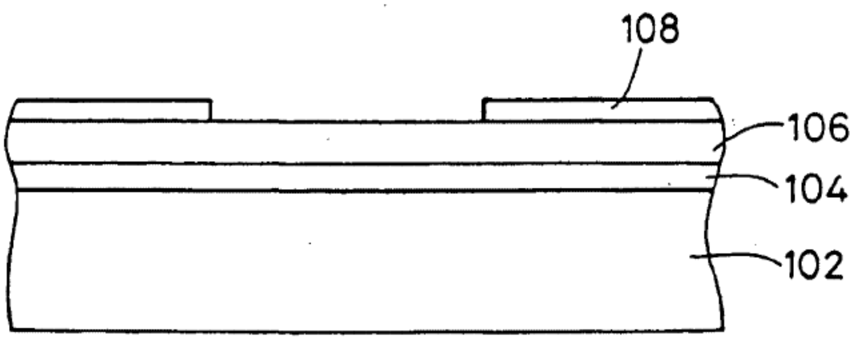


FIG. 39

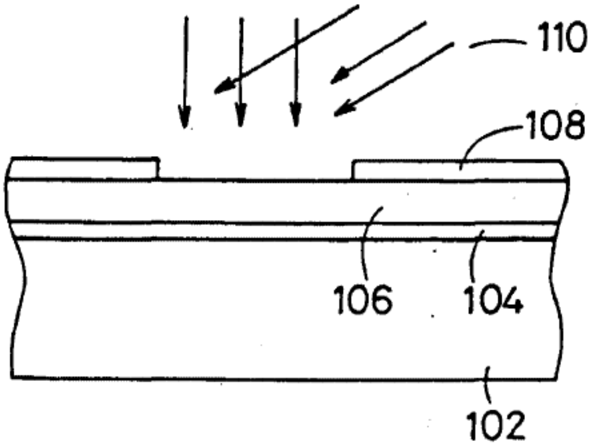


FIG. 40

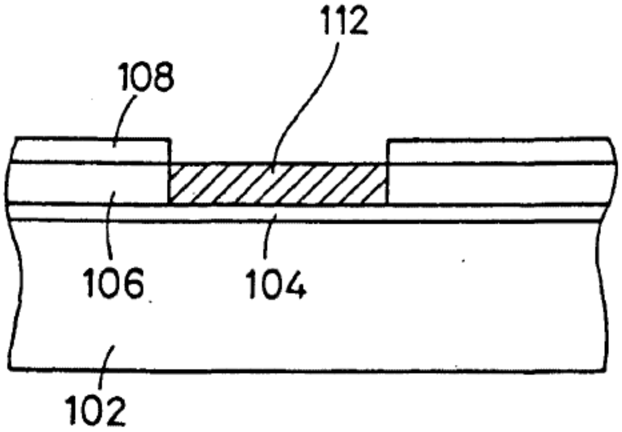


FIG.41

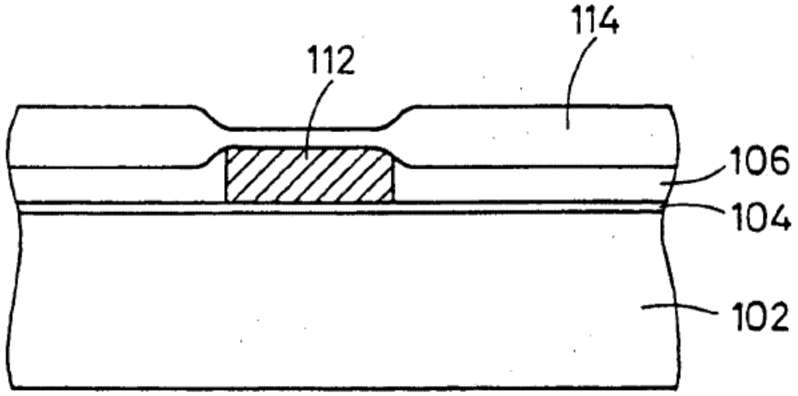


FIG.42

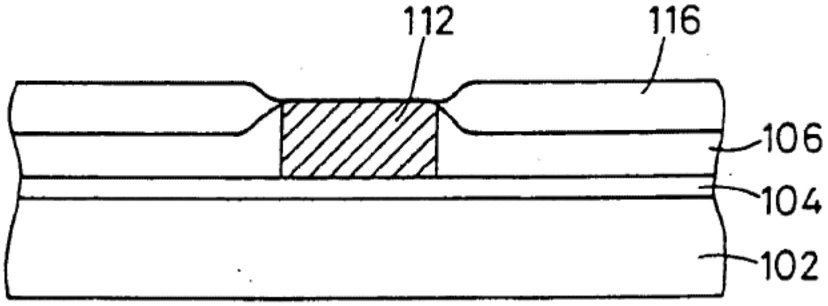


FIG. 43

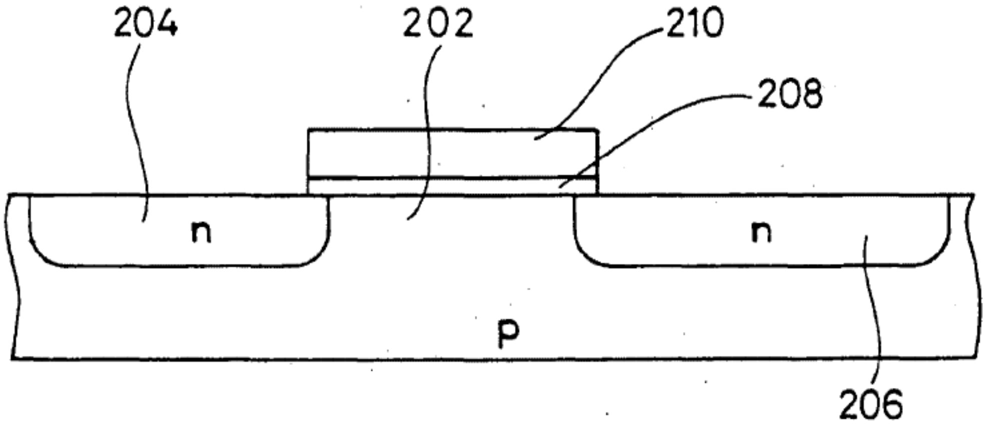


FIG. 44

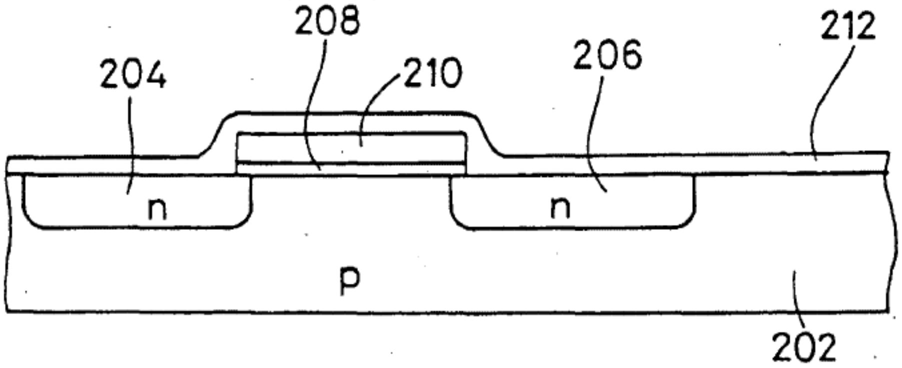


FIG. 45

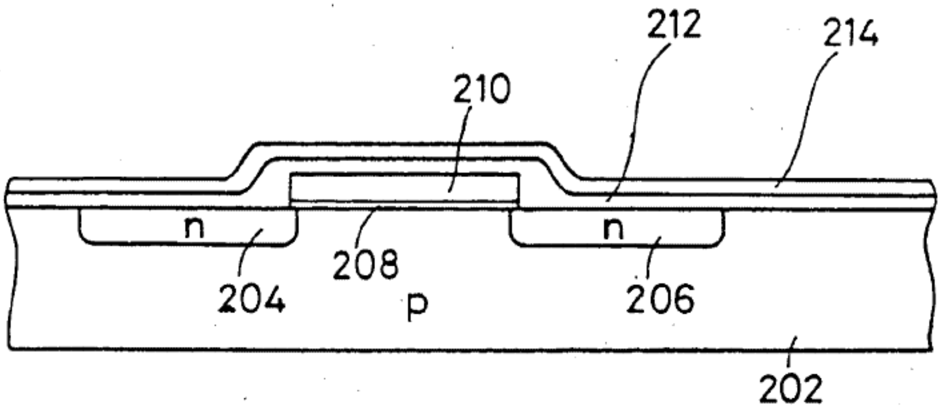
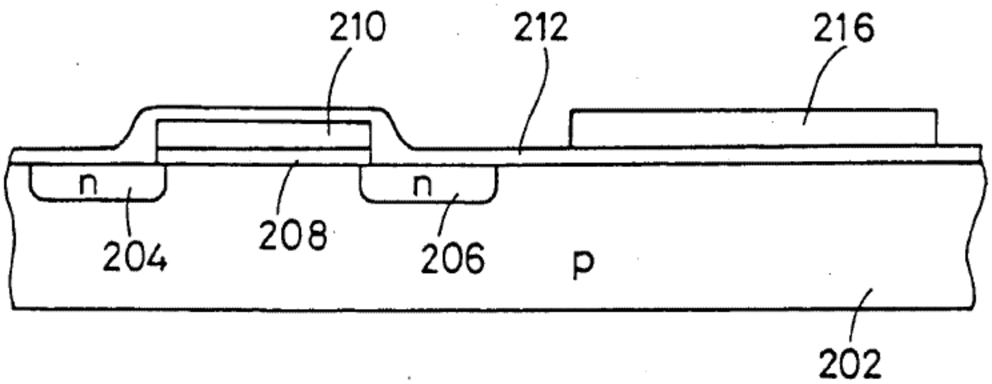


FIG. 46



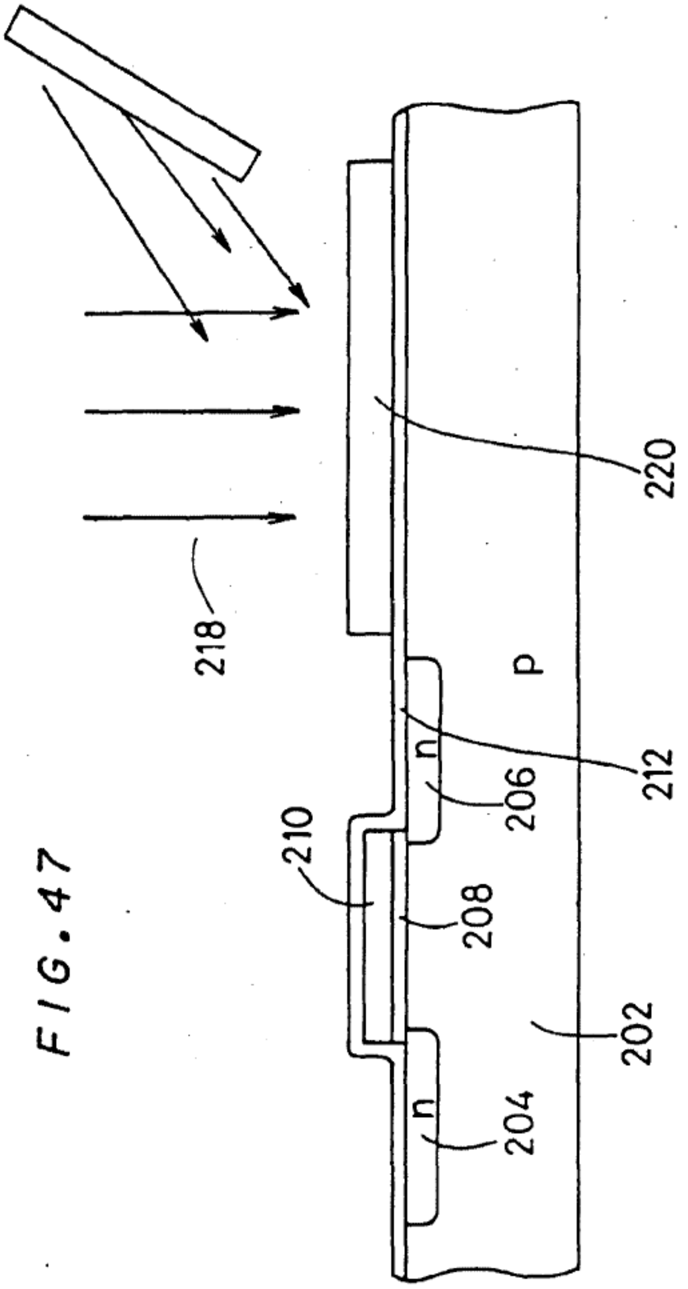


FIG. 47

FIG.48

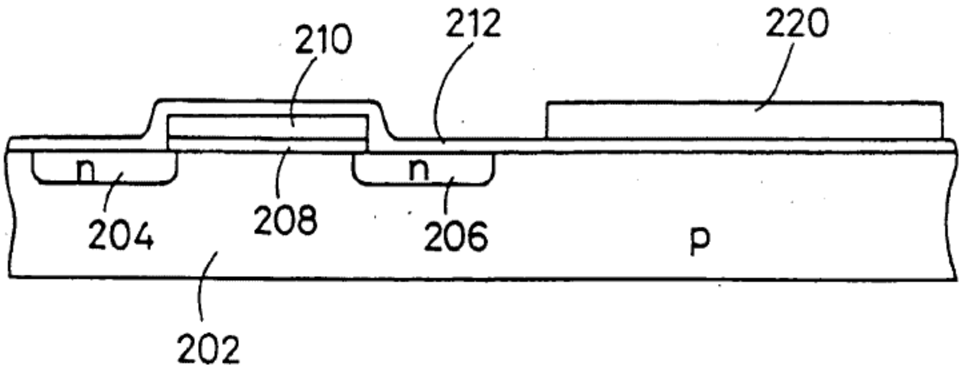

210
212
220
n
n
204
208
206
p
202

FIG.49

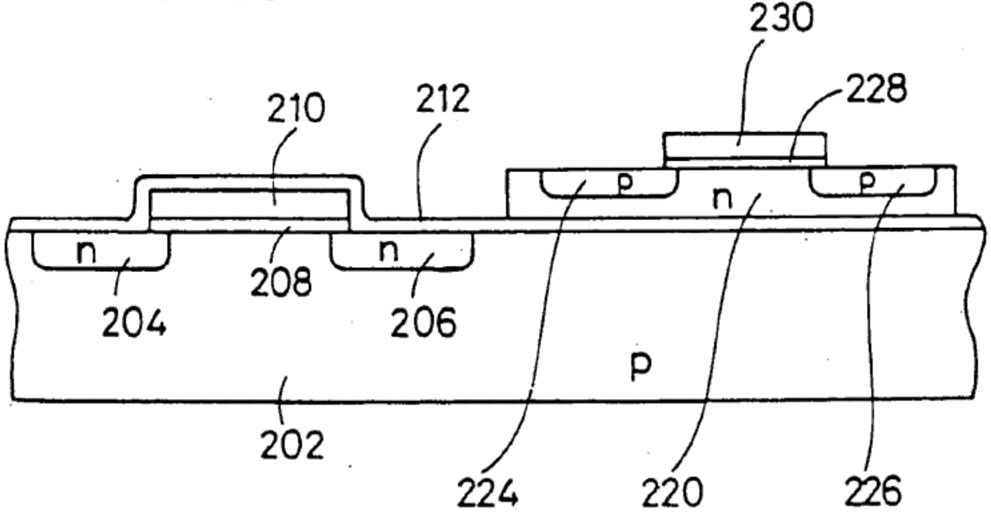

230
228
210
212
p
n
p
n
n
204
208
206
p
202
224
220
226

FIG.50

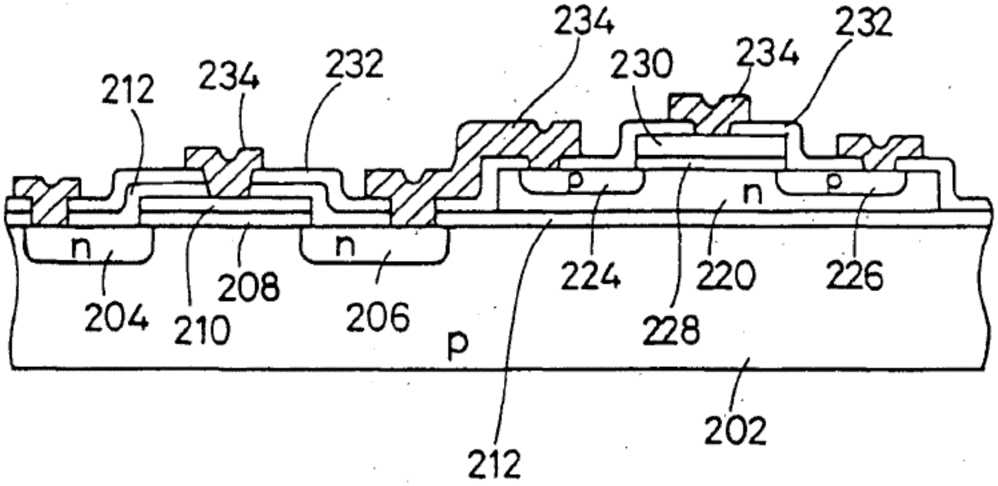

234
232
230
234
212
234
232
p
n
p
n
n
204
210
208
206
p
224
228
220
226
212
202

FIG.51

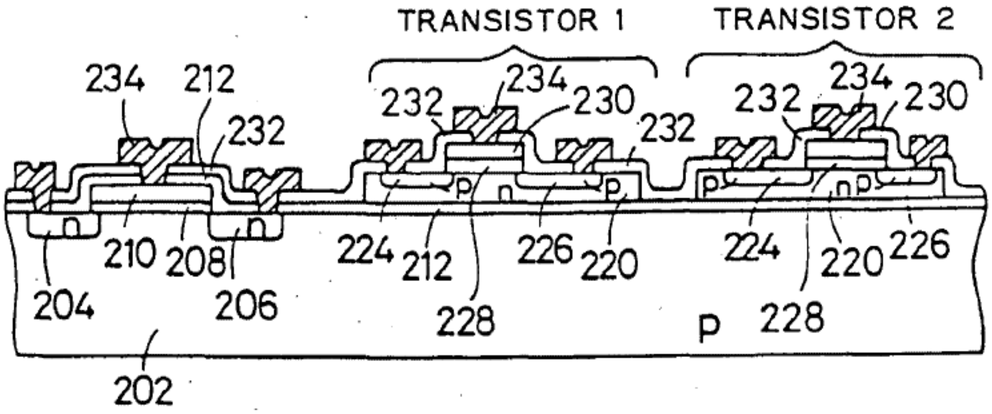

TRANSISTOR 1
TRANSISTOR 2
234
212
232
232
234
230
232
232
234
230
n
n
p
n
p
p
n
p
210
208
224
212
226
220
224
220
226
204
206
228
p
228
202

FIG.52

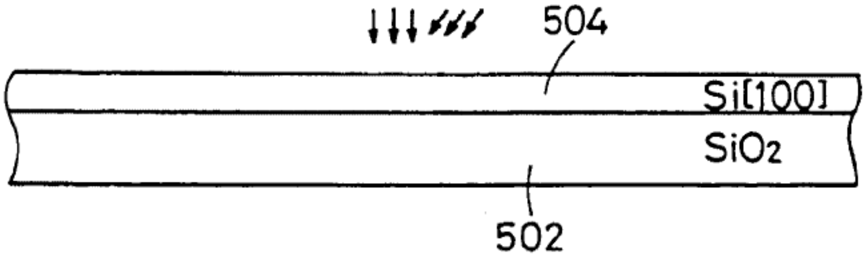

504
Si[100]
SiO2
502

FIG.53

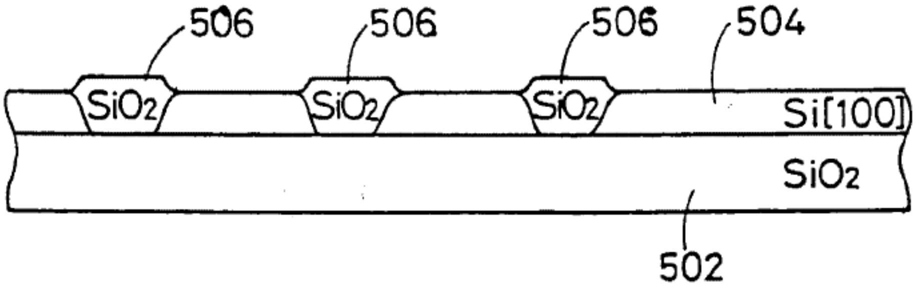

506
506
506
504
SiO2
SiO2
SiO2
Si[100]
SiO2
502

FIG. 54

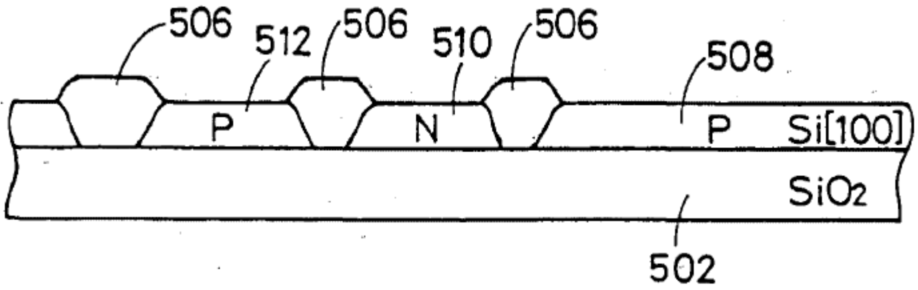

506
512
506
510
506
508
P
N
P
Si[100]
SiO2
502

FIG. 55

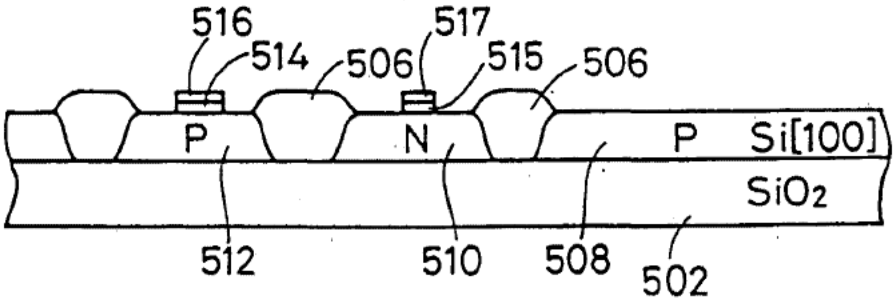

516
514
506
517
515
506
P
N
P
Si[100]
SiO2
512
510
508
502

FIG. 56

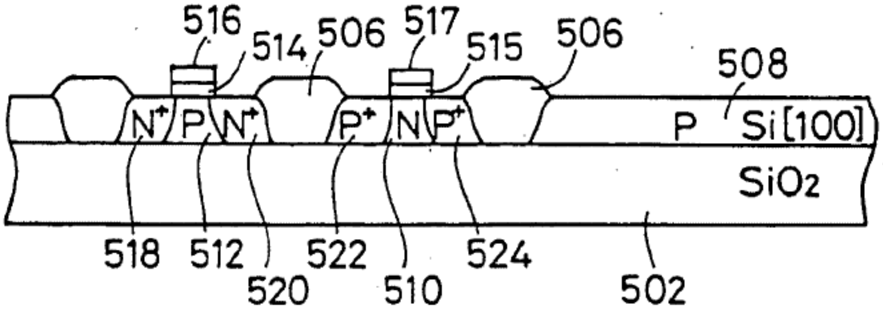

516
514
506
517
515
506
508
N+
P
N+
P+
N
P+
P
Si[100]
SiO2
518
512
520
522
510
524
502

FIG. 57

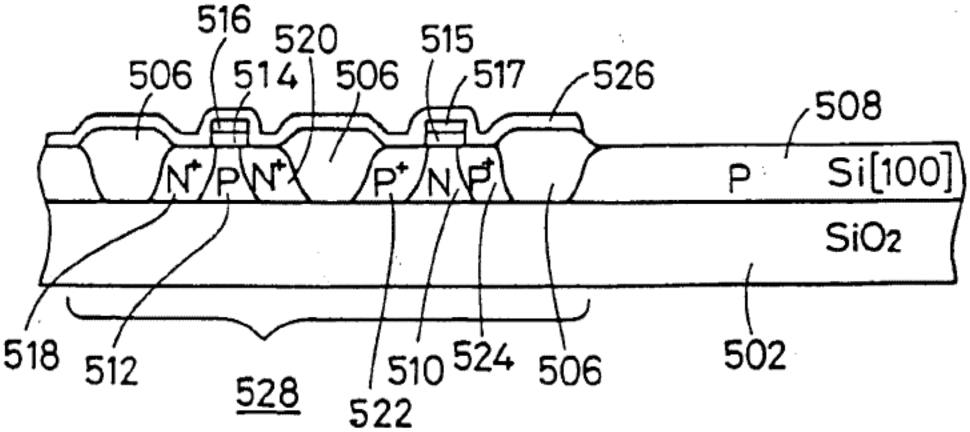

516
520
515
506
514
506
517
526
508
N+
P
N+
P+
N
P+
P
Si[100]
SiO2
518
512
528
522
510
524
506
502

FIG.58

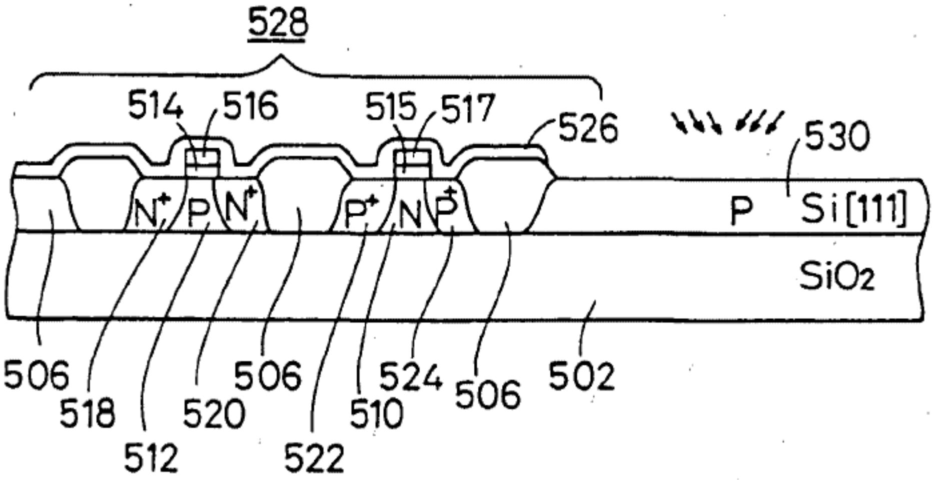

528
514
516
515
517
526
530
N+
P
N+
P+
N
P+
P
Si[111]
SiO2
506
518
512
520
506
522
510
524
506
502

FIG.59

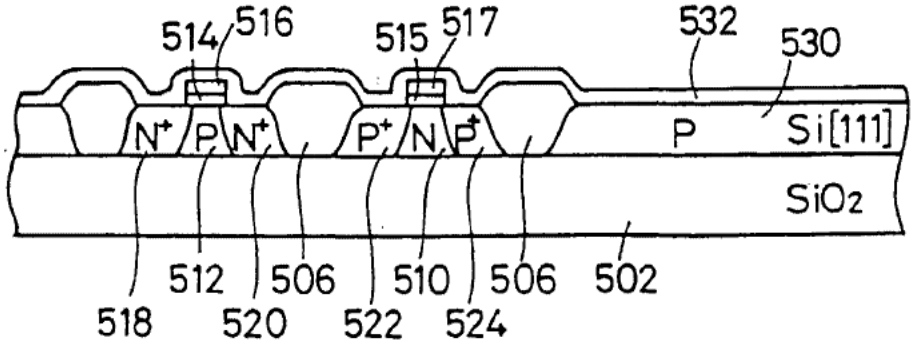

514
516
515
517
532
530
N+
P
N+
P+
N
P+
P
Si[111]
SiO2
518
512
520
506
522
510
524
506
502

FIG.60

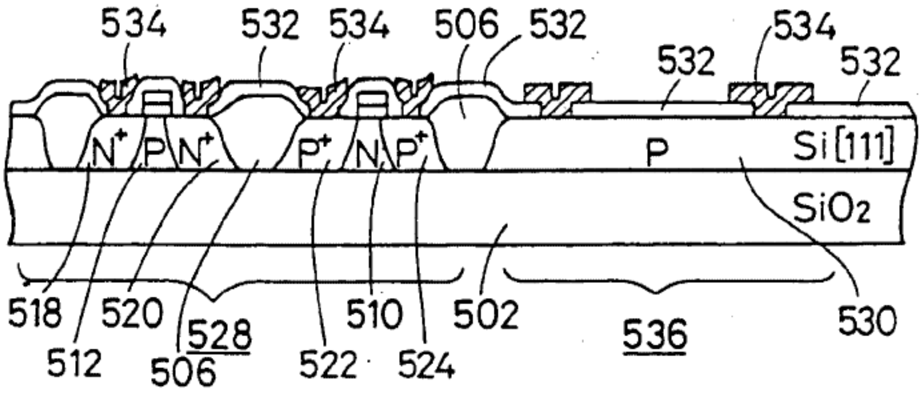

534
532
534
506
532
532
534
532
N+
P
N+
P+
N
P+
P
Si[111]
SiO2
518
520
528
510
502
536
530
512
506
522
524

FIG.61

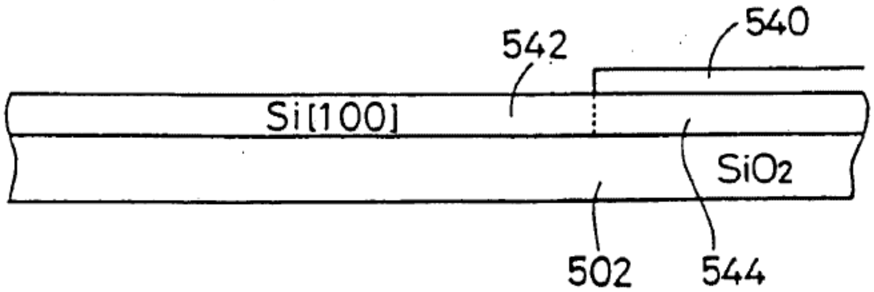

540
542
Si[100]
SiO2
502
544

FIG. 62

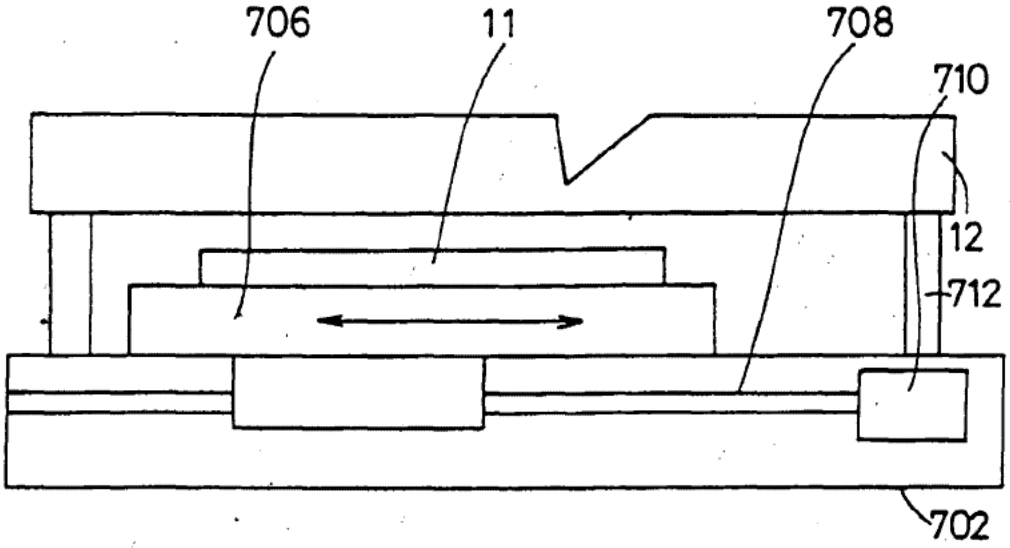


FIG. 63

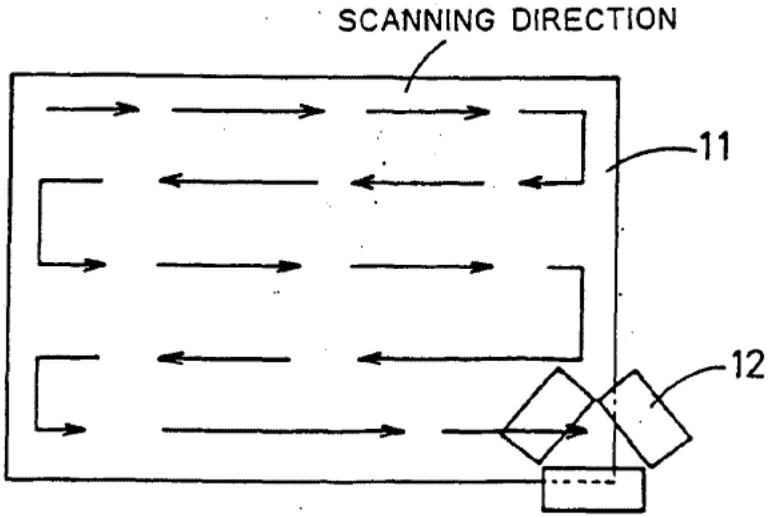


FIG.64

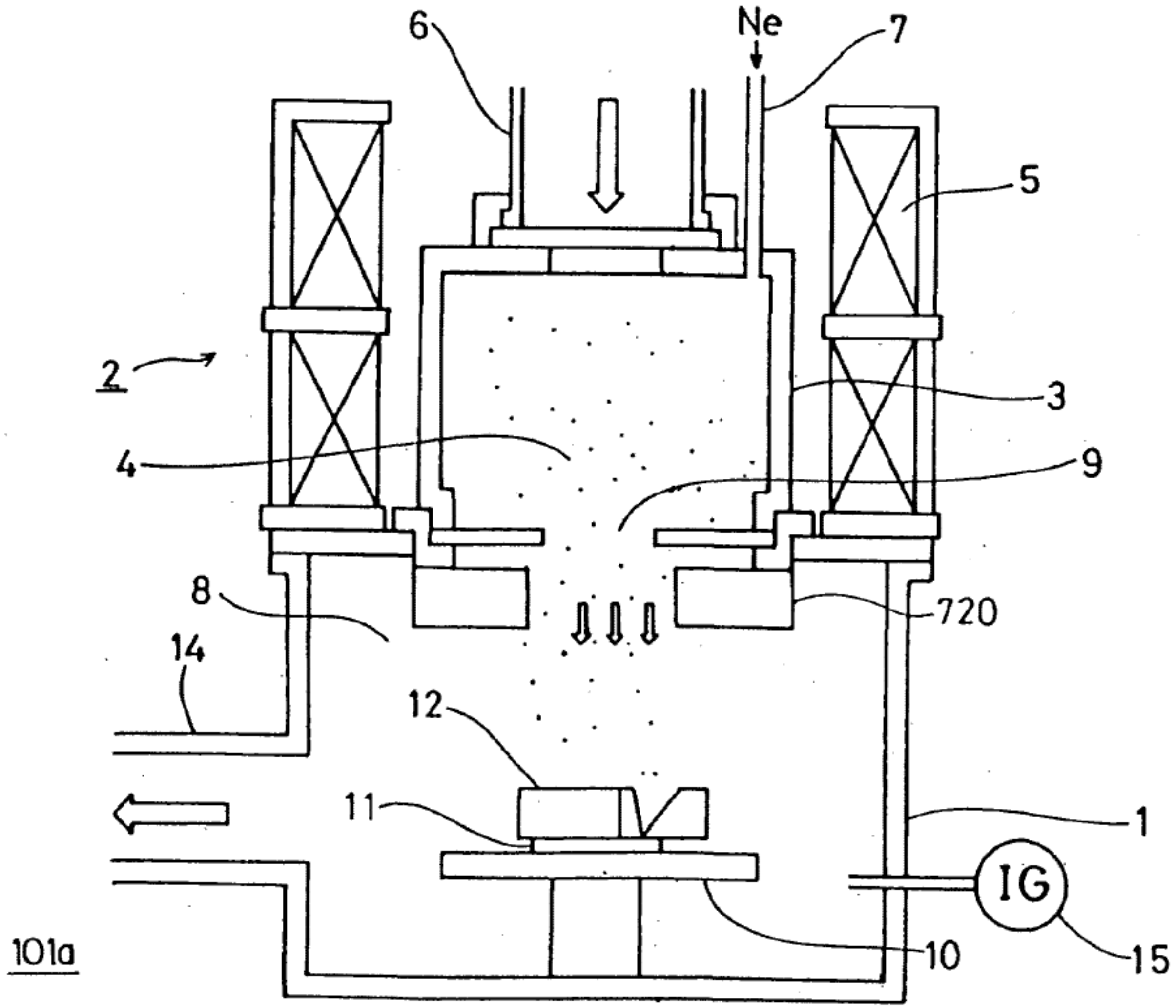


FIG.65

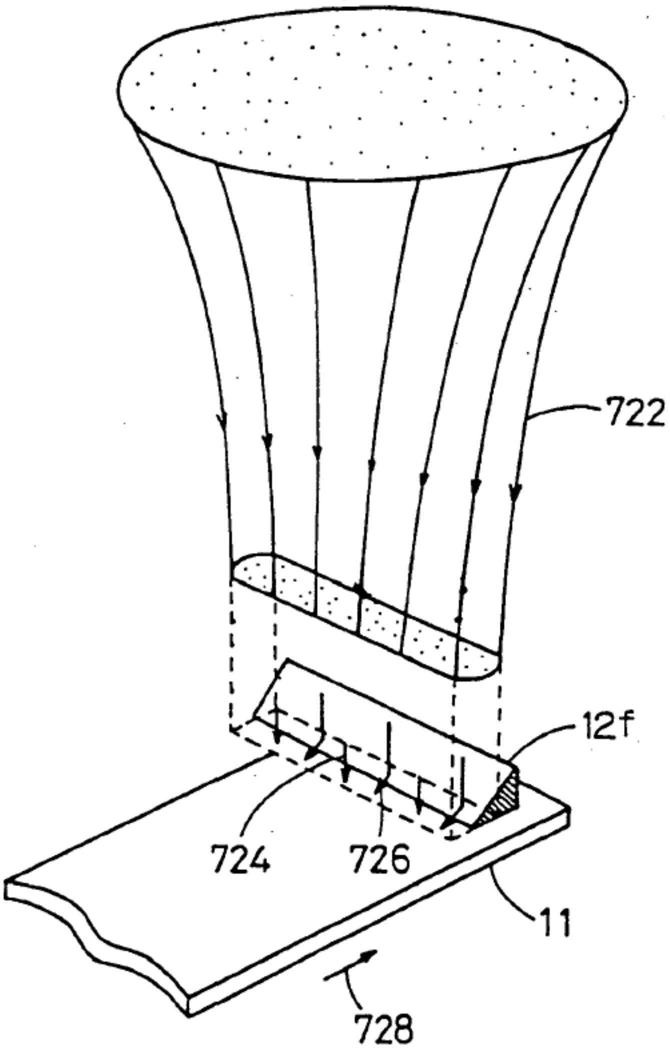


FIG.66

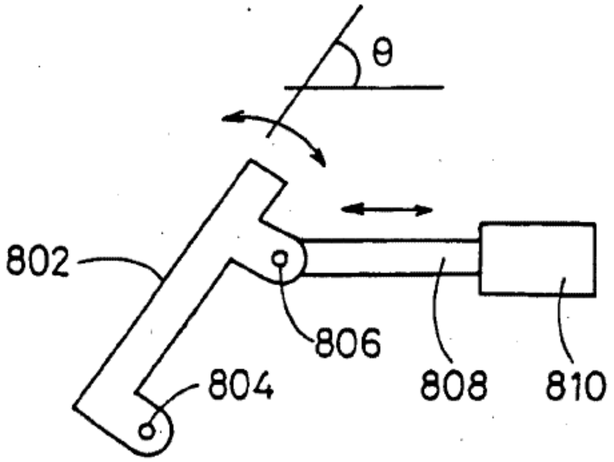


FIG.67

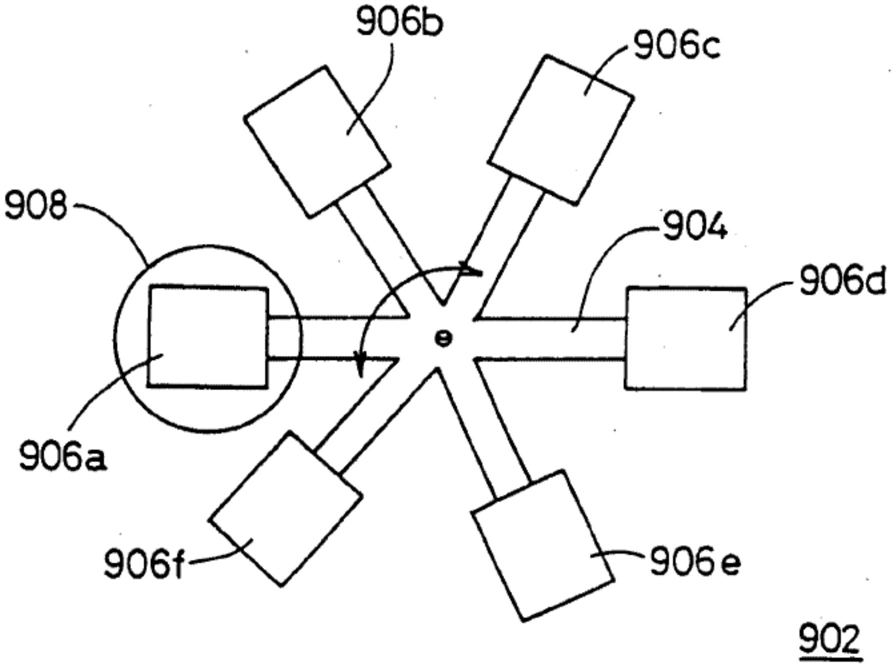


FIG. 68

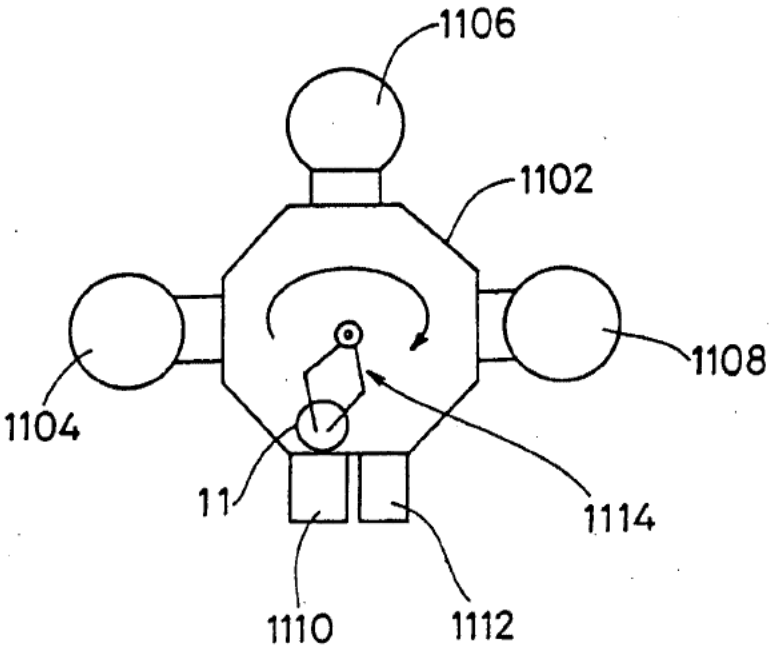


FIG.69

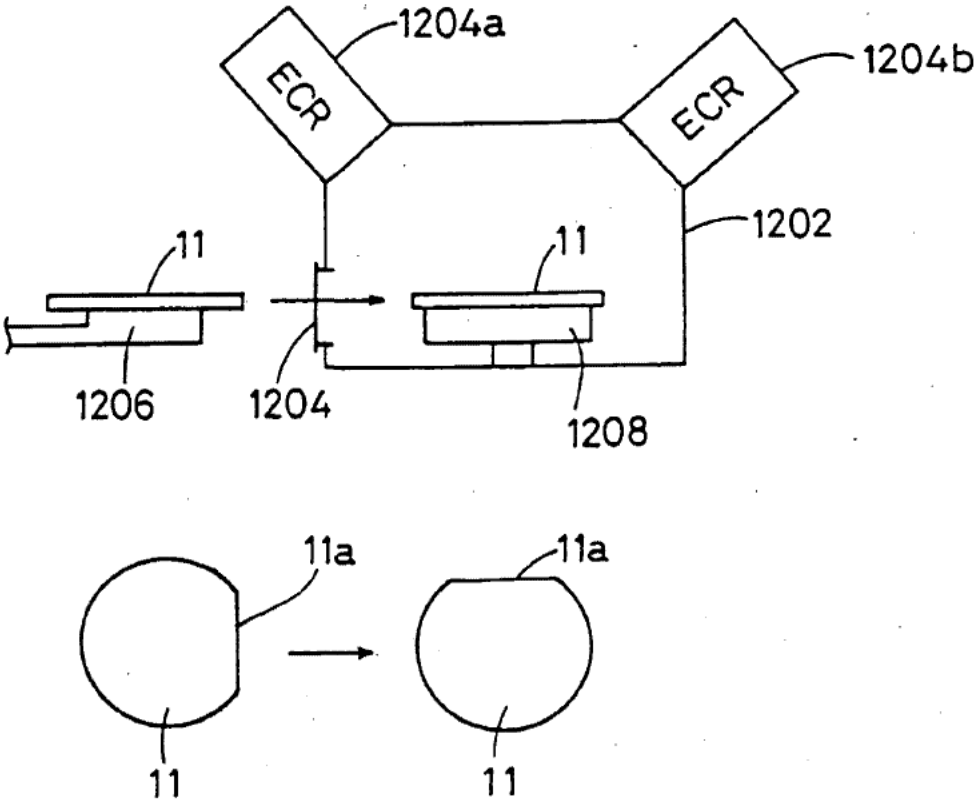


FIG. 70

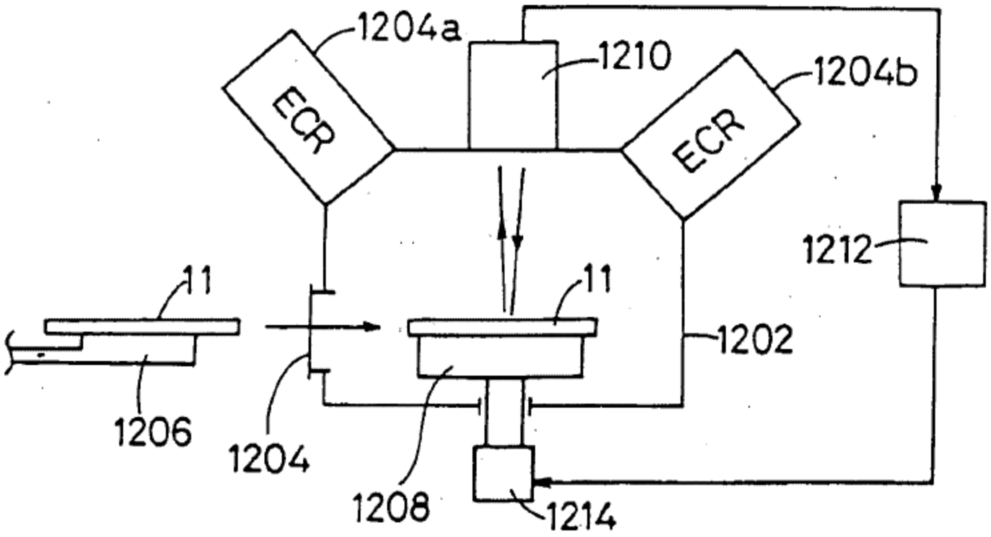

1204a
1210
1204b
ECR
ECR
1212
11
11
1202
1206
1204
1208
1214

FIG. 71

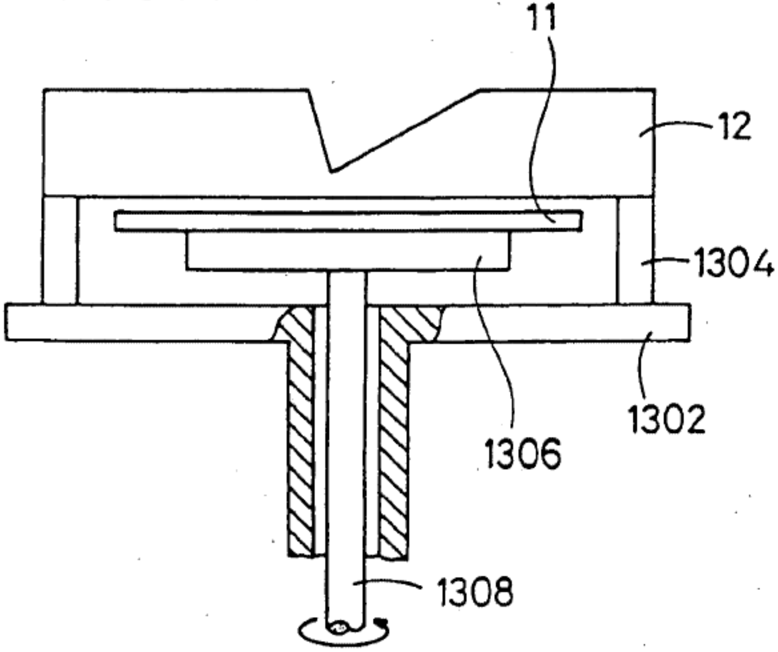

11
12
1304
1306
1302
1308

FIG. 72

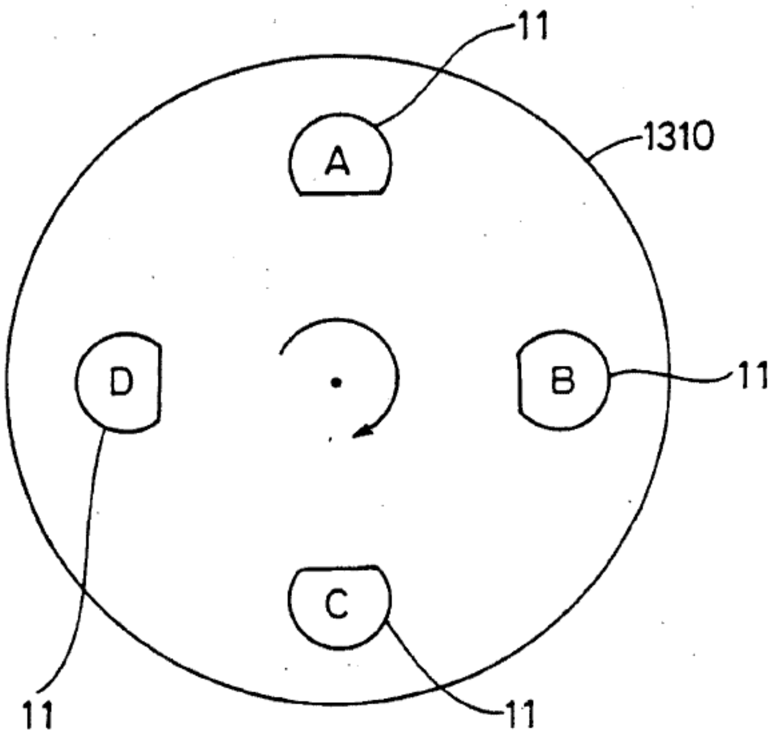
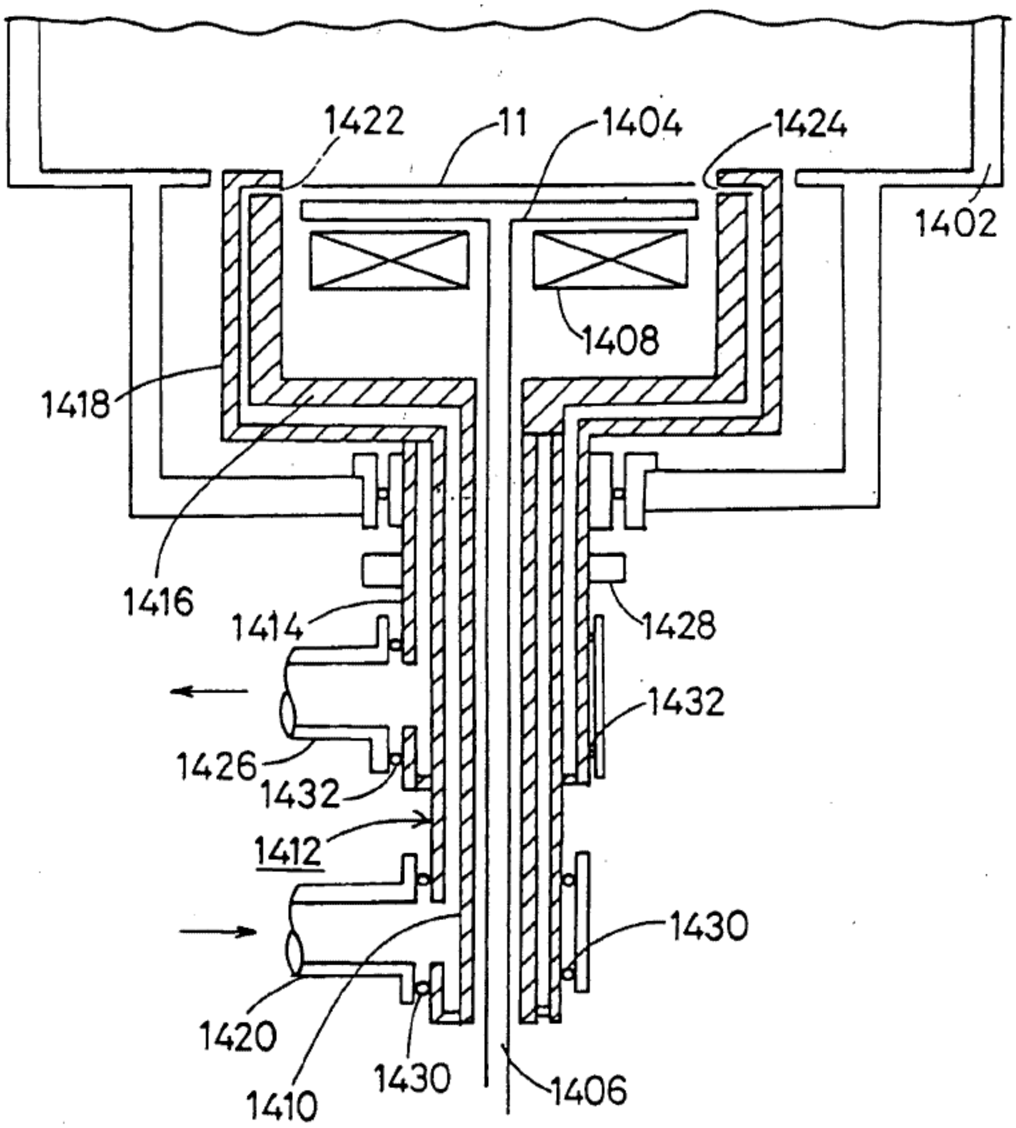


FIG. 73


1422
11
1404
1424
1402
1408
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1414
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1430
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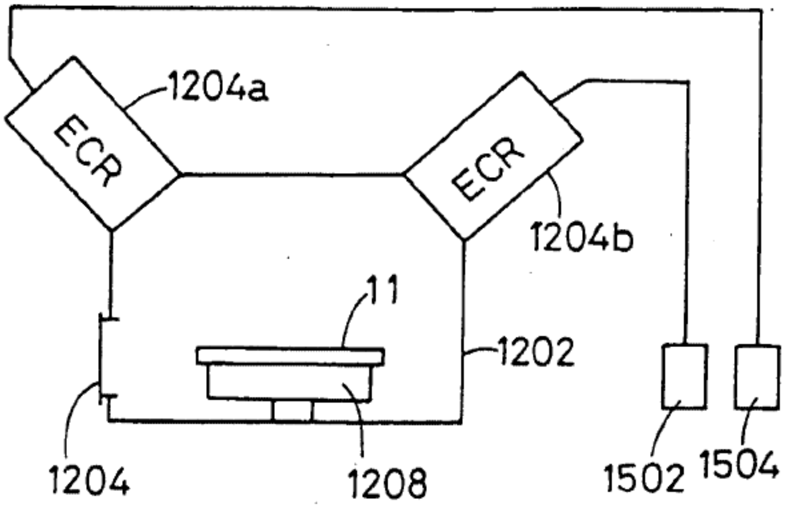
1406

FIG. 74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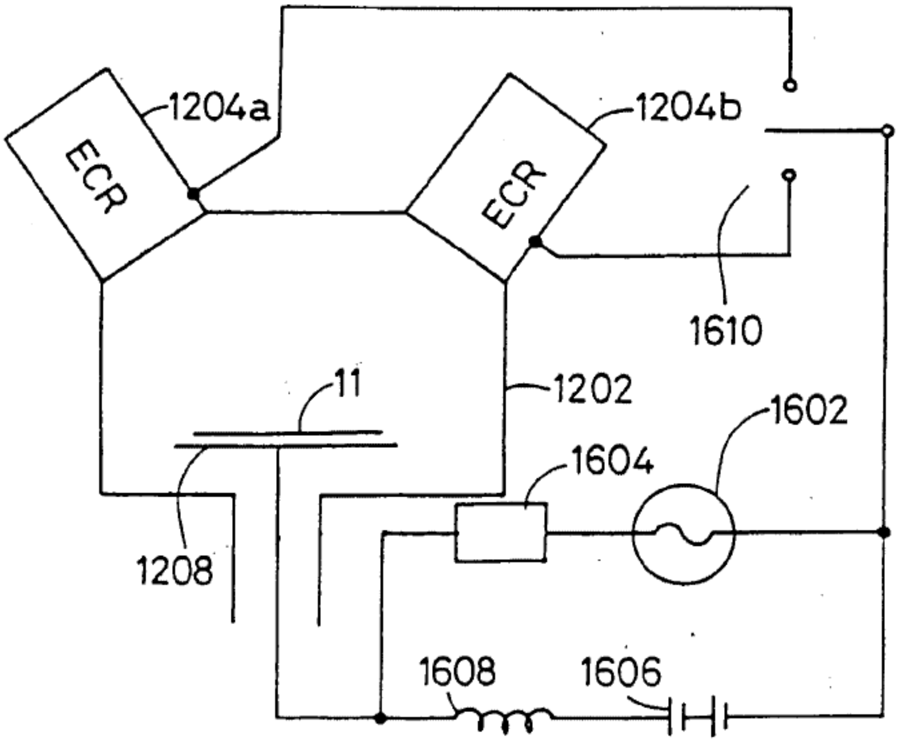
ECR
ECR
1204b
11
1202
1204
1208
1502
1504

FIG. 75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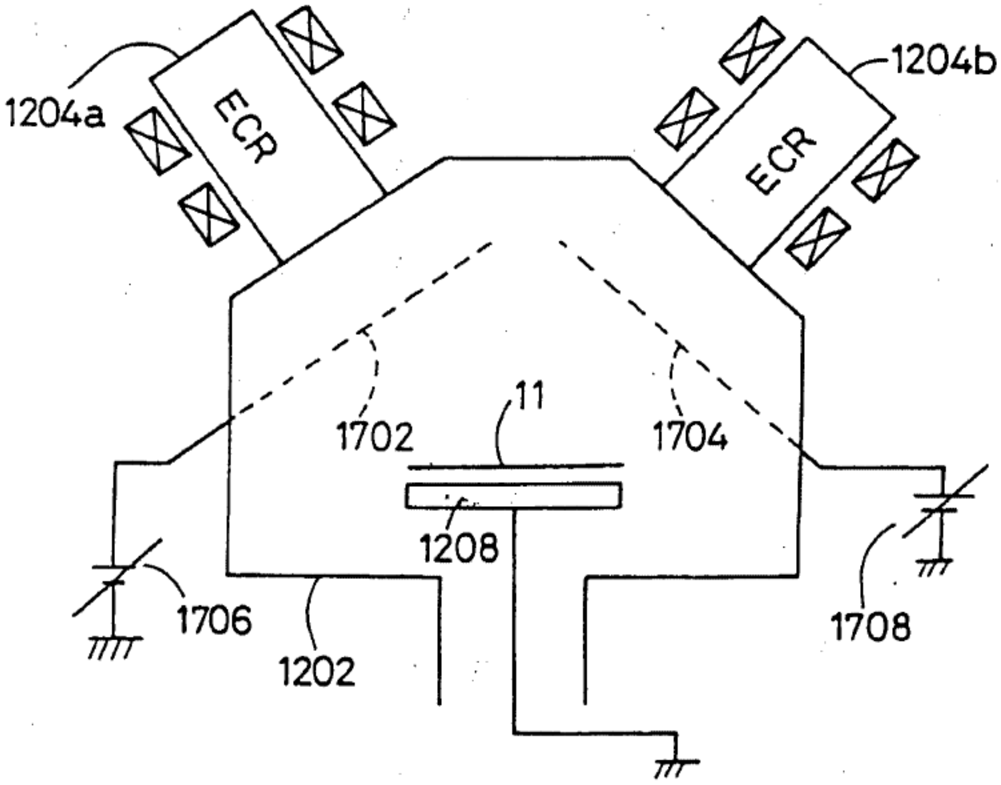
ECR
ECR
1204b
1610
11
1202
1602
1604
1208
1608
1606

FIG.76



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**29.03.1994 JP 58887/94**

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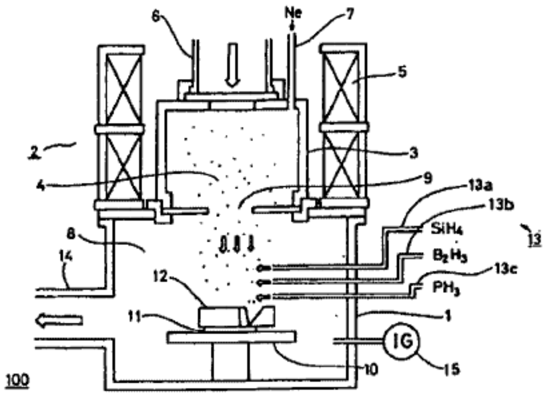
# (54) Method of and apparatus for forming single-crystalline thin film

(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



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2.15.4/3.4

**European Patent Office**

## EUROPEAN SEARCH REPORT

Application Number
EP 94 11 6188

### 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 | PATENT ABSTRACTS OF JAPAN<br>vol. 10, no. 107 (C-341), 22 April 1986<br>& JP 60 235788 A (HITACHI SEISAKUSHO KK), 22 November 1985,<br>* abstract *<br>--- | 1 | C30B23/02 |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 014, no. 543 (C-0783), 30 November 1990<br>& JP 02 229792 A (NIYUURARU SYST:KK), 12 September 1990,<br>* abstract *<br>--- | 1 | |
| L | PATENT ABSTRACTS OF JAPAN<br>vol. 095, no. 003, 28 April 1995<br>& JP 06 340500 A (NIYUURARU SYST:KK), 13 December 1994,<br>*DOCUMENT WHICH MAY THROW DOUBT ON THE PRIORITY CLAIMED*<br>* abstract *<br>----- | | |
| | | | 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

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L : document cited for other reasons

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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.

**PCT**

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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|---|---|---|
| **(51) International Patent Classification** $^7$ **:**<br>**C03C 13/04, H01S 3/06** | **A1** | **(11) International Publication Number:** **WO 00/21898**<br>**(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

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**(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**

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*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 $\mu$m and 1.55 $\mu$m. 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 $Er^{+3}$.

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# OPTICAL FIBER FOR LIGHT AMPLIFIER

## Technical Field

The present invention relates to optical fibers for use in a light amplifier, and more particularly, to an optical fiber for use in a light amplifier which can be used at wavelengths of both 1.3 $\mu$m and 1.55 $\mu$m.

## Background Art

The wavelength of light used in optical communications has been shifted from a wavelength of 1.3 $\mu$m to a wavelength of 1.55 $\mu$m. 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 $\mu$m 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 $\mu$m.

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 $\mu$m 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 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 $\mu$m and 1.55 $\mu$m 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 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 in an optical amplifier, which can be used for both the 1.3 $\mu$m and 1.55 $\mu$m 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.

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 1.55 $\mu$m 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 $\mu$m unfavorably decreased.

Brief Description of the Drawings

FIG. 1 shows the fluorescence emission spectrum at wavelengths of 1.3 $\mu$m and 1.55 $\mu$m 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 $\mu$m is caused by the 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 $\mu$m is caused by the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ 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 $Er^{+3}$ 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;

FIG. 4 shows the fluorescence emission spectrum at the wavelength of 1.3 $\mu$m 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 $\mu$m 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

FIG. 6 shows the fluorescence emission spectrum at the wavelengths of 1.3 $\mu$m and 1.55 $\mu$m 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 $\mu$m is due to the electron transition of $Pr^{3+}$ from the $^1G_4$ level to the $^3H_5$ level, and that at the wavelength of 1.55 $\mu$m 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

The present invention provides an optical fiber for use in a light amplifier, which can be used at wavelengths of both 1.3 $\mu$m and 1.55 $\mu$m, 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 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 $\mu$m and $Er^{+3}$ emits fluorescence at 1.55 $\mu$m. In particular, 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 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.

In order to maximize the light amplification efficiency at both wavelengths of 1.3 $\mu$m and 1.55 $\mu$m, 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 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 (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 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 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.

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).

## 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 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 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)

## 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 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. 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, 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 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 $^4I_{11/2}$ 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

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 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. 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).

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 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 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.

Example 3

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. 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. 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).

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 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.

## 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 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. 1 (d)). The intensify of fluorescence was increased at each wavelength 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 $Er^{+3}$ 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.

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. 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. 1 (e)). The intensify of fluorescence was saturated, i.e., at the maximum level, at each wavelength. Also, the fluorescence lifetime of $Pr^{+3}$ 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 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 $Pr^{+3}$ 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.

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 260°C for 1 hour. After the heating process, the test tube was slowly cooled to room temperature and broken into pieces, resulting in an optical fiber formed of a $Pr^{+3}$ 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 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 (a)).

According to Example 6, it can be understood that both a Ge-GA-S 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 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.

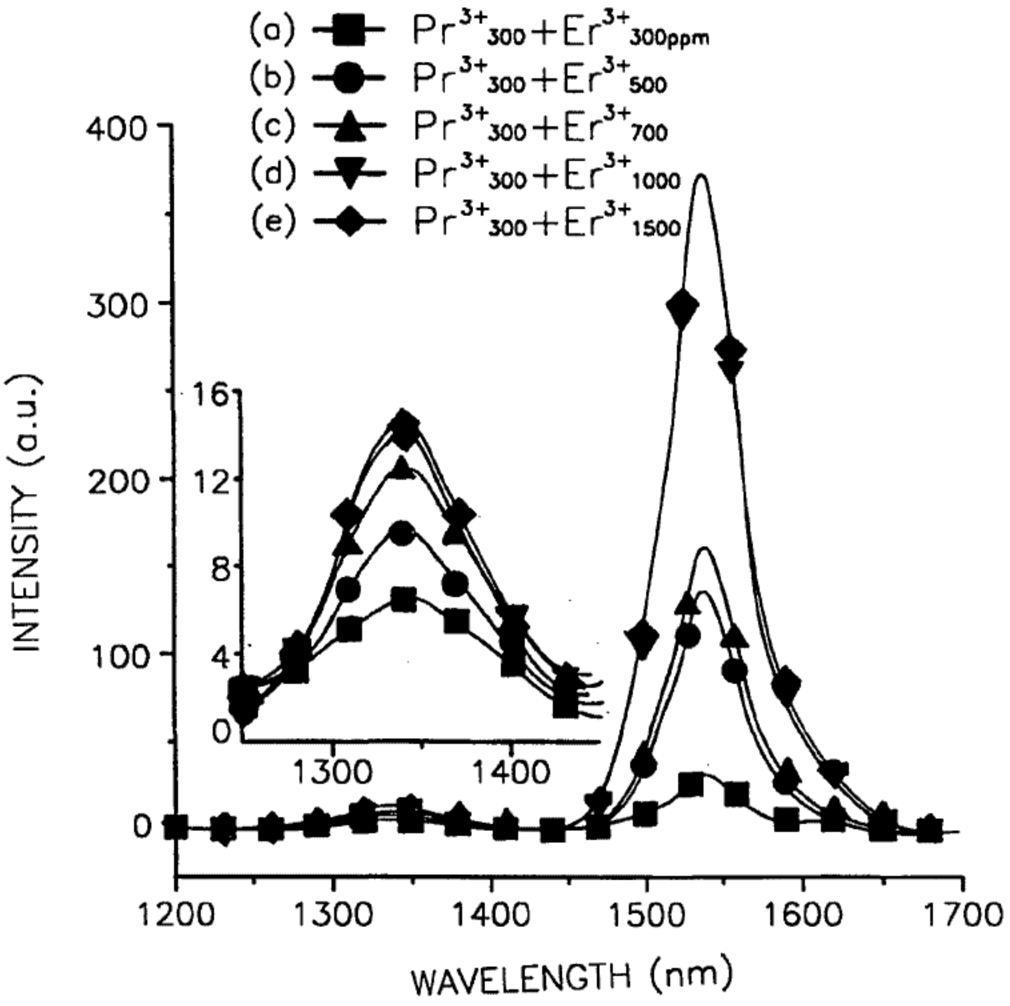
3. The optical fiber of claim 1, wherein the fluoride glass is a ZBLAN glass containing zirconium (Zr), barium (Ba), lanthanum (La), aluminum (Al) and sodium (Na).

4. The optical fiber of claim 1, wherein the mixing weight ratio of $Pr^{+3}$ 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.

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


(a) ■ $Pr^{3+}_{300}+Er^{3+}_{300ppm}$
(b) ● $Pr^{3+}_{300}+Er^{3+}_{500}$
(c) ▲ $Pr^{3+}_{300}+Er^{3+}_{700}$
(d) ▼ $Pr^{3+}_{300}+Er^{3+}_{1000}$
(e) ◆ $Pr^{3+}_{300}+Er^{3+}_{1500}$
INTENSITY (a.u.)
400
300
200
100
0
16
12
8
4
0
1300
1400
1200
1300
1400
1500
1600
1700
WAVELENGTH (nm)

# FIG. 2

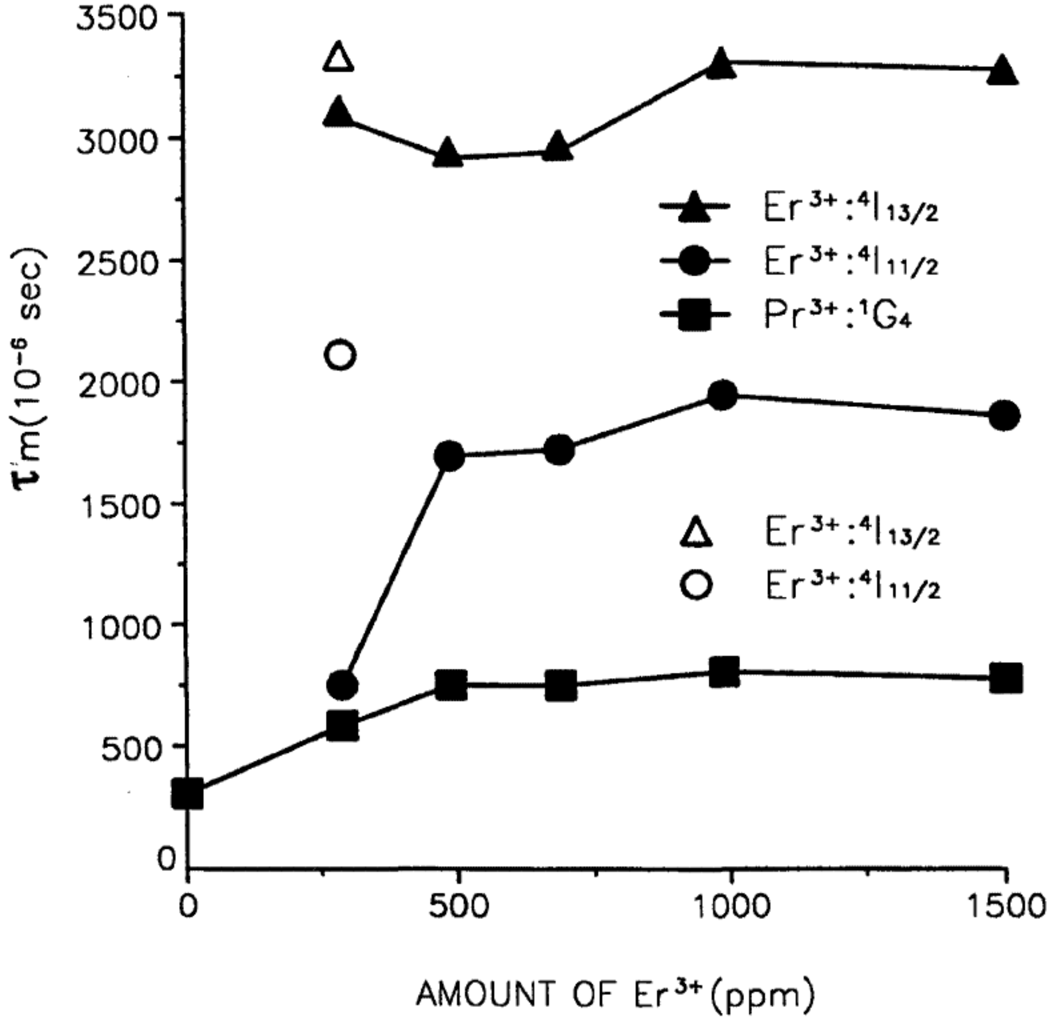

3500
3000
2500
2000
1500
1000
500
0
$\tau_m(10^{-6}$ sec)
0
500
1000
1500
AMOUNT OF $Er^{3+}$(ppm)
▲ $Er^{3+}:{}^4I_{13/2}$
● $Er^{3+}:{}^4I_{11/2}$
■ $Pr^{3+}:{}^1G_4$
△ $Er^{3+}:{}^4I_{13/2}$
○ $Er^{3+}:{}^4I_{11/2}$

**FIG. 3**

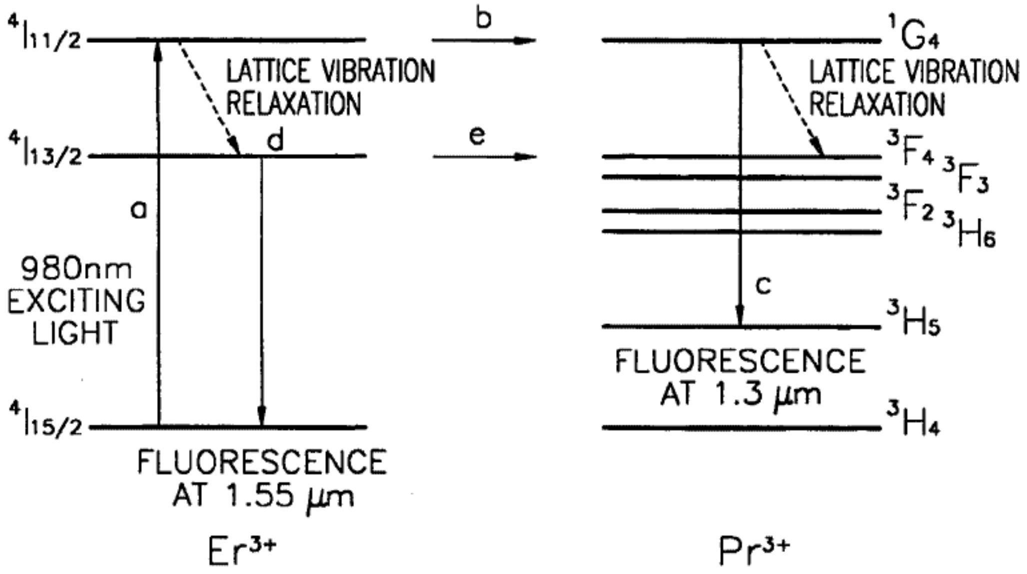

$^4I_{11/2}$
LATTICE VIBRATION RELAXATION
$^4I_{13/2}$
d
a
980nm EXCITING LIGHT
$^4I_{15/2}$
FLUORESCENCE AT 1.55 μm
$Er^{3+}$
b
e
$^1G_4$
LATTICE VIBRATION RELAXATION
$^3F_4$
$^3F_3$
$^3F_2$
$^3H_6$
c
$^3H_5$
FLUORESCENCE AT 1.3 μm
$^3H_4$
$Pr^{3+}$

FIG. 4

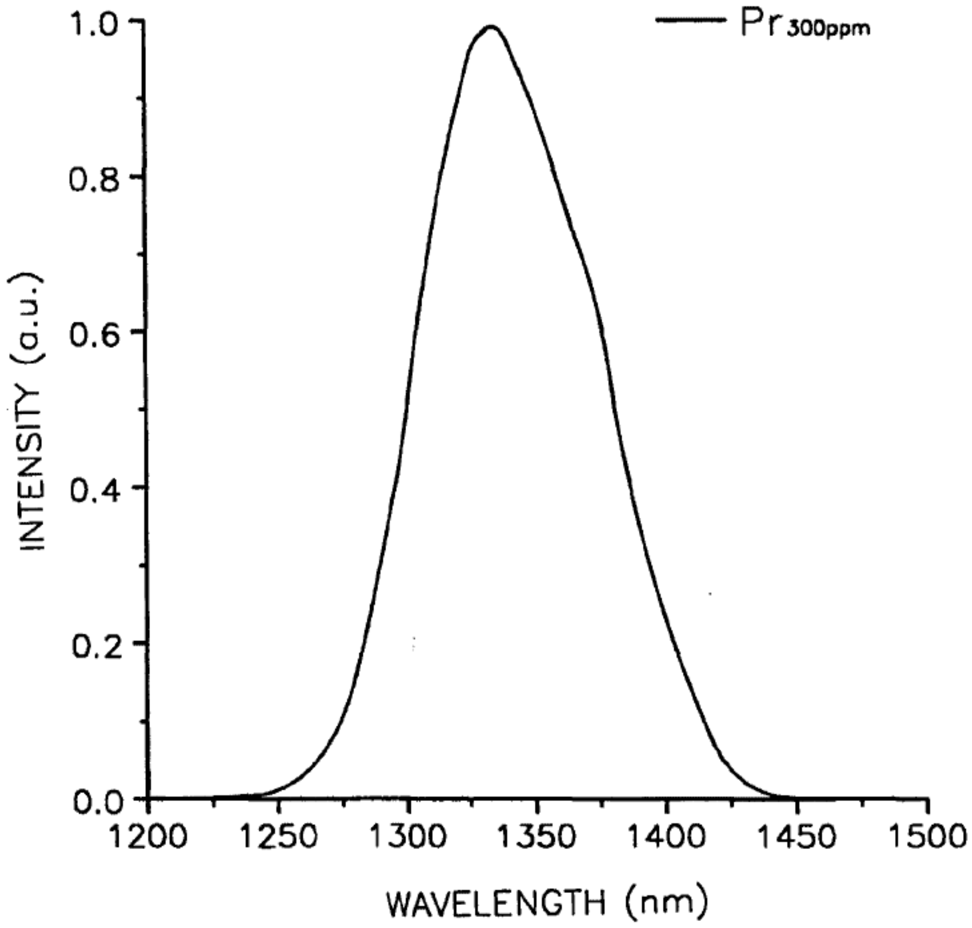

Pr 300ppm
INTENSITY (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
1200
1250
1300
1350
1400
1450
1500
WAVELENGTH (nm)

**FIG. 5**

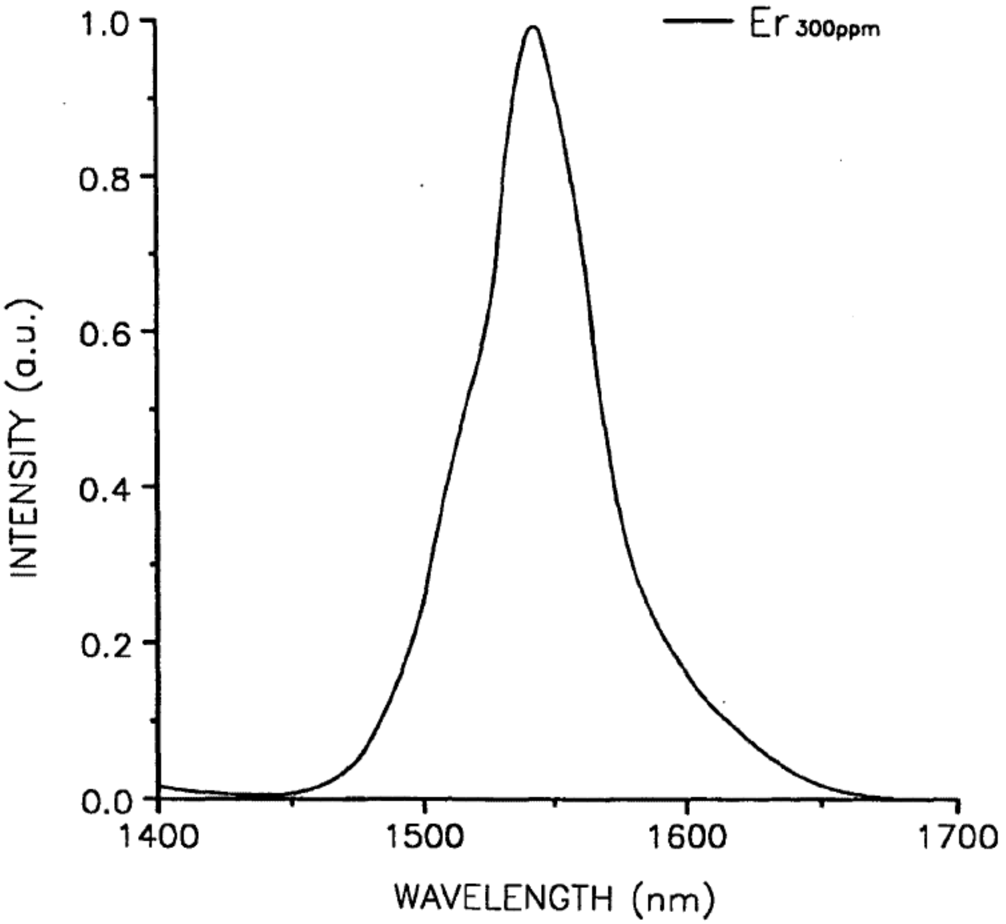
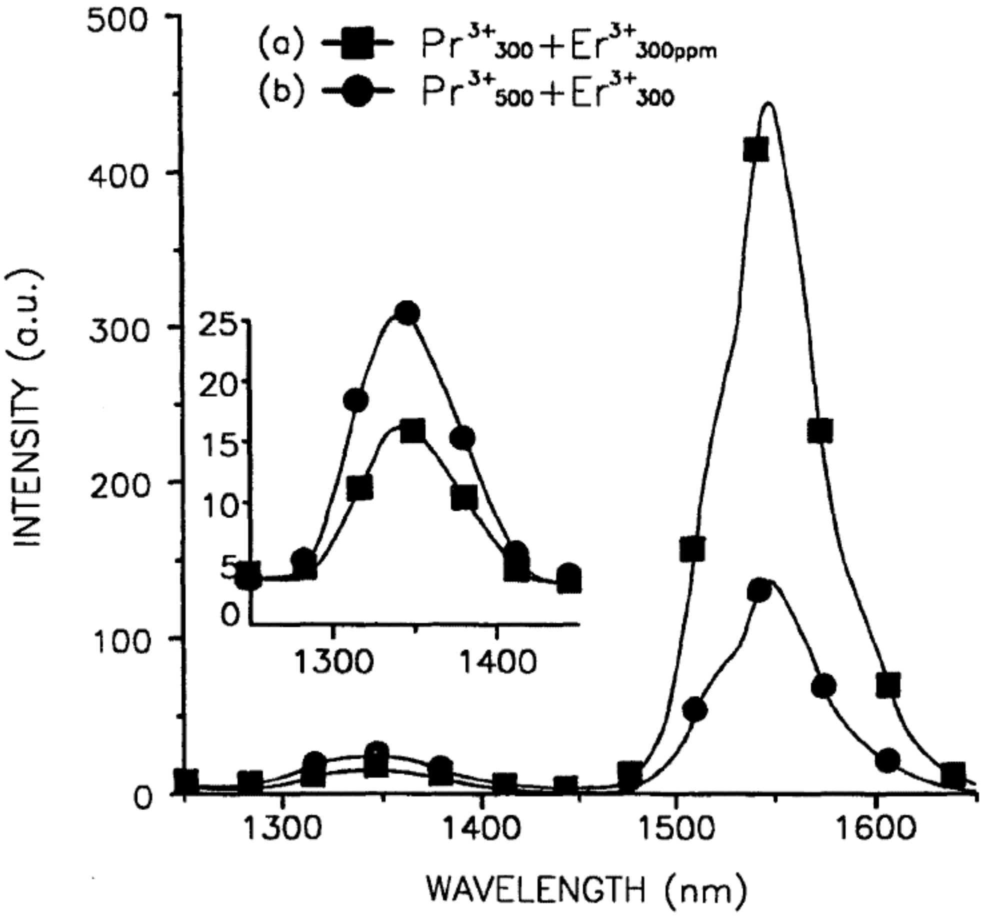

Er 300ppm
1.0
0.8
0.6
0.4
0.2
0.0
INTENSITY (a.u.)
1400
1500
1600
1700
WAVELENGTH (nm)

FIG. 6


(a) ■ $Pr^{3+}_{300}+Er^{3+}_{300ppm}$
(b) ● $Pr^{3+}_{500}+Er^{3+}_{300}$
INTENSITY (a.u.)
0
100
200
300
400
500
WAVELENGTH (nm)
1300
1400
1500
1600
0
5
10
15
20
25
1300
1400

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00609

A. CLASSIFICATION OF SUBJECT MATTER

IPC$^7$: 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)

IPC$^7$: 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.<br>---- | 1 |

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
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| | |
|---|---|
| Date of the actual completion of the international search<br>24 November 1999 (24.11.99) | Date of mailing of the international search report<br>18 February 2000 (18.02.00) |
| Name and mailing adress of the ISA/AT<br>Austrian Patent Office<br>Kohlmarkt 8-10; A-1014 Vienna<br>Facsimile No. 1/53424/200 | Authorized officer<br>Hauswirth<br>Telephone No. 1/53424/136 |

Form PCT/ISA/210 (second sheet) (July 1998)

# 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 |
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| | | DE C0 69223720 | 05-02-1998 |
| | | DE T2 69223720 | 23-04-1998 |
| | | EP A2 535798 | 07-04-1993 |
| | | EP A3 535798 | 15-09-1993 |
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| 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 | |

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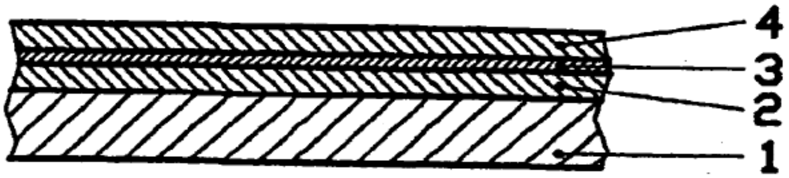
**81476 München (DE)**

# (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



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2.16.7 (HRS)/3.6

## 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 Haakkesche 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 $\Omega_{sq}$. So besitzt beispielsweise eine Schicht mit einer Transmission von 90% und einem Flächenwiderstand von 3 $\Omega_{sq}$ einen Haackeschen Gütefaktor von 0,116 $\Omega^{-1}$. Eine Schicht mit einer Transmission von 80% und einem Flächenwiderstand von 5 $\Omega_{sq}$ besitzt einen Gütefaktor von 0,021 $\Omega^{-1}$.

**[0003]** Eine weitere wichtige Eigenschaft eines solchen Schichtsystems ist seine Ätzbarkeit. Diese hängt von seiner chemischen Zusammensetzung und seiner Dicke ab. Für 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\text{Ohm}^{-1}$.

**[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

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 $\Omega_{sq}$, vorzugsweise 2,5 $\Omega_{sq}$ und geringer auf, bei einem über die Wellenlängen 435, 545 und 610 nm gemittelten Haakkeschen Gütefaktor von grösser als 0,085 $\Omega^{-1}$.

**[0014]** Dabei ist es aus Gründen der Farbneutralität günstig, wenn bei einem Flächenwiderstand von 2,5 $\Omega_{sq}$ 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-Zerstäubung, sondern mit einer gepulsten DC-Zerstäubung oder mit einer AC-überlagerten DC-Zerstäubung 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 $\Omega_{sq}$. |

**[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, 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 $\Omega_{sq}$ 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 $\Omega^{-1}$.

## 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 $\Omega_{sq}$., vorzugsweise < 2,5 $\Omega_{sq}$ und weniger, der mittlere Haackesche Gütefaktor des Schichtsystems für die Wellenlängen 435, 545 und 610 nm ($\Phi_{Tc}=T^{10}/R_s$)>0,085$\Omega^{-1}$beträgt.

2. Schichtsystem nach Anspruch 1, **dadurch gekennzeichnet, dass** bei einem Flächenwiderstand von 2,5 $\Omega_{sq}$ 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.

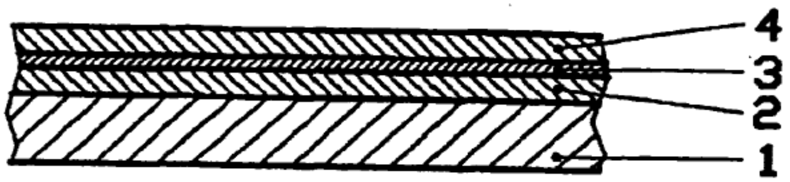
9. Verfahren nach Anspruch 6, 7 und 8, **dadurch gekennzeichnet, dass** die totale Leistungsdichte (AC und DC) im Bereich 1 bis 3 W/cm$^2$, vorzugsweise aber bei 2 bis 2.2 W/cm$^2$ liegt.

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.

Fig.1


4
3
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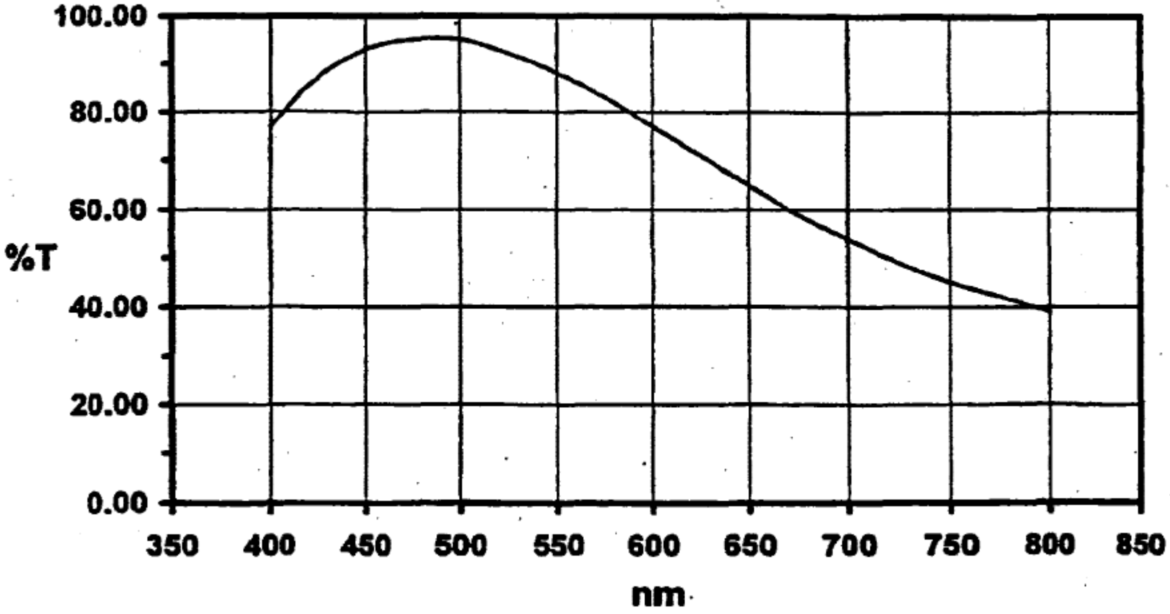
1

Fig.2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850
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**Europäisches Patentamt**

# EUROPÄISCHER TEILRECHERCHENBERICHT

der nach Regel 45 des Europäischen Patentübereinkommens 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)<br>21. Januar 1986 (1986-01-21)<br>* Anspruch 1; Tabelle 3 * | 4 | C03C17/36 |
| X | GB 2 126 256 A (TOYODA CHUO KENKYUSHO KK)<br>21. März 1984 (1984-03-21)<br>* Ansprüche 1-15; Beispiel 1 * | 4-12 | |
| A | DATABASE WPI<br>Section Ch, Week 199015<br>Derwent Publications Ltd., London, GB;<br>Class A32, AN 1990-113453<br>XP002159490<br>& JP 02 066158 A (UNITIKA LTD),<br>6. März 1990 (1990-03-06)<br>* Zusammenfassung * | 4 | |
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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

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EPO FORM 1503 03.82 (P04C09)

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## 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.

## 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 |
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EPO FORM P0461

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

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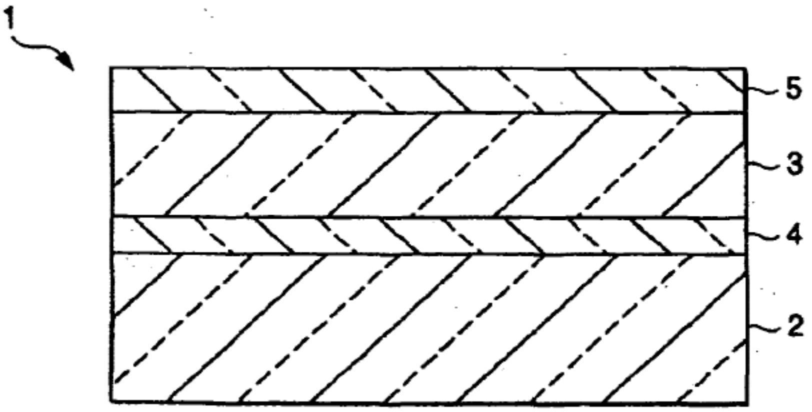
## (54) Multilayer structure and process for producing the same

(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



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## Description

### FIELD OF THE INVENTION

**[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

**[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.

**[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.

**[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.

**[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.

**[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.

**[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.

### 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.

**[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.

**[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

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.

**[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 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 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 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.

**[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)
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.

## 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, 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 regulated 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$_\alpha$ 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 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.
○: Even more reduced adhesion of fouling substances, and the sample looked less white in terms of reflected light.

**[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 ○, which is the best.

## 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.

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 | ○ |
| Sample 2 | $Nb_2O_5$ | 1.0 | 5 | amorphous | 4 | 11 | ○ |
| Sample 3 | $Nb_2O_5$ | 5.0 | 10 | amorphous | 2 | 9 | ○ |
| Sample 4 | $Nb_2O_5$ | 10.0 | 20 | amorphous | 6 | 11 | ○ |

(Notes) Substrate temperature: 230°C
Titanium oxide film thickness: 250 nm

## 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.

## 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.

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 | ○ |
| Sample 6 | $SiO_2$ | 50 | $SiO_2$ | 10 | amorphous | 27 | 7 | ○ |
| Sample 1 | none | | none | | amorphous | 0 | 9 | ○ |

(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<br>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.

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 | ○ |
| Sample 14 | $Nb_2O_5$ | 2.5 | 200 | 250 | amorphous | 9 | 11 | ○ |
| Sample 1 | $Nb_2O_5$ | 2.5 | 230 | 250 | amorphous | 0 | 9 | ○ |
| Sample 15 | $Nb_2O_5$ | 2.5 | 250 | 250 | amorphous | 6 | 9 | ○ |
| Sample 16 | $Nb_2O_5$ | 2.5 | 270 | 250 | amorphous | 9 | 10 | ○ |
| 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.

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

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

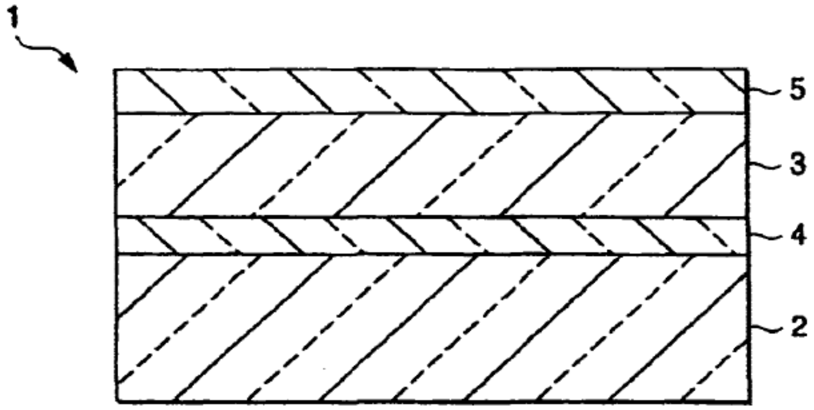

1
5
3
4
2

FIG. 2

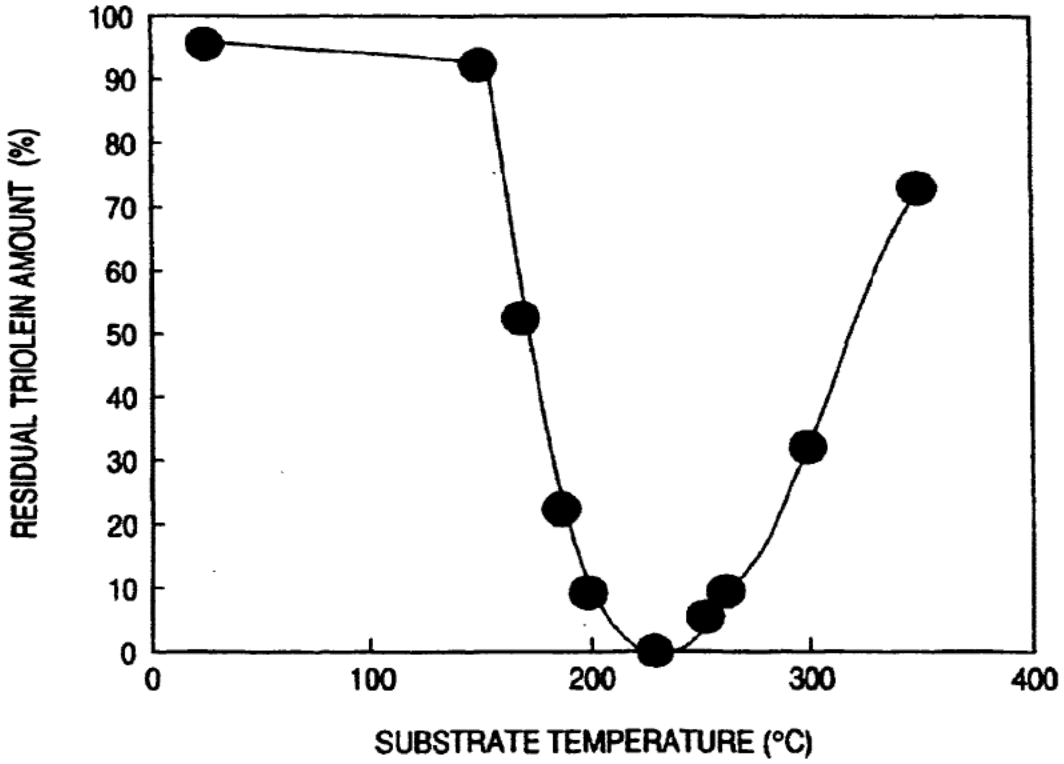
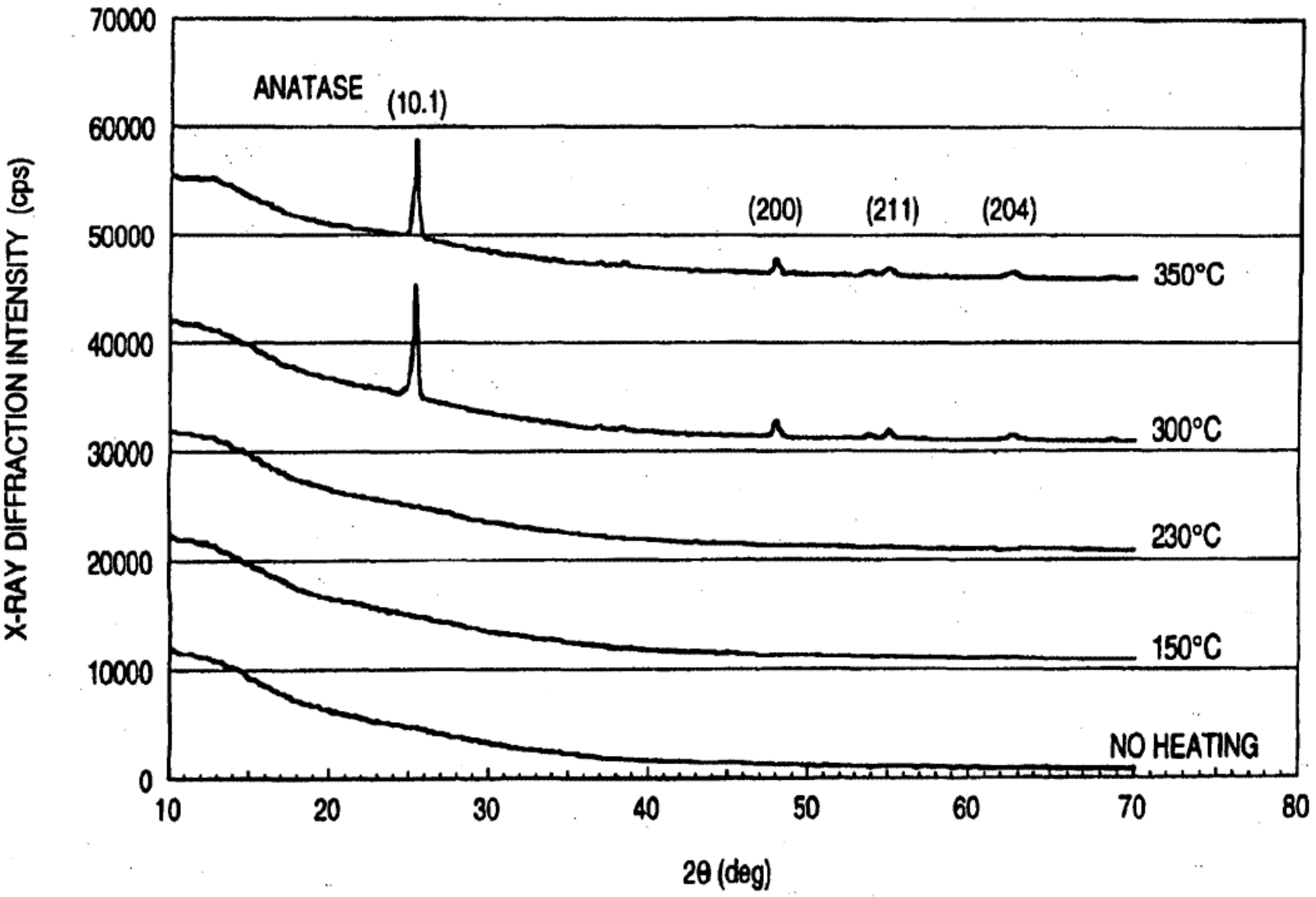

RESIDUAL TRIOLEIN AMOUNT (%)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
SUBSTRATE TEMPERATURE (°C)

FIG. 3



ANATASE
(10.1)
(200)
(211)
(204)
350°C
300°C
230°C
150°C
NO HEATING
X-RAY DIFFRACTION INTENSITY (cps)
70000
60000
50000
40000
30000
20000
10000
0
10
20
30
40
50
60
70
80
2θ (deg)

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<br>Section Ch, Week 199930<br>Derwent Publications Ltd., London, GB;<br>Class D15, AN 1999-352578<br>XP002149112<br>& JP 11 130434 A (BRIDGESTONE CORP),<br>18 May 1999 (1999-05-18)<br>* abstract *<br>--- | | B01J35/00<br>B01J37/34 |
| A | DATABASE WPI<br>Section Ch, Week 199924<br>Derwent Publications Ltd., London, GB;<br>Class D15, AN 1999-283348<br>XP002149113<br>& JP 11 092176 A (BRIDGESTONE CORP),<br>6 April 1999 (1999-04-06)<br>* abstract *<br>--- | | |
| A | DATABASE WPI<br>Section Ch, Week 199901<br>Derwent Publications Ltd., London, GB;<br>Class J04, AN 1999-003984<br>XP002149114<br>& JP 10 278165 A (ASAHI GLASS CO LTD),<br>20 October 1998 (1998-10-20)<br>* abstract *<br>--- | | TECHNICAL FIELDS SEARCHED (Int.Cl.7)<br>B01J |
| A | DATABASE WPI<br>Section Ch, Week 199706<br>Derwent Publications Ltd., London, GB;<br>Class D15, AN 1997-060199<br>XP002149115<br>& JP 08 309204 A (BRIDGESTONE CORP),<br>26 November 1996 (1996-11-26)<br>* abstract *<br>----- | | |

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

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 11 4185

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

⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 639 655 A1**

# ⑫ EUROPEAN PATENT APPLICATION

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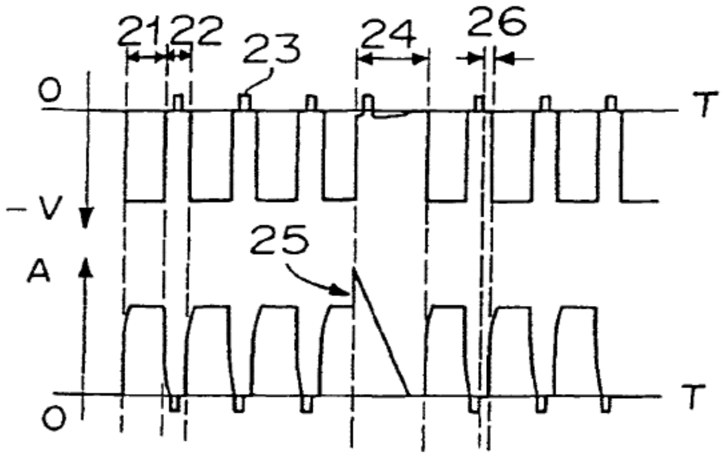
## (54) Method and apparatus for sputtering.

(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 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 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 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.

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 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 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, 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 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.

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 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 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 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 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 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.

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 voltage is in a range of from 10 $\mu$s to 10 ms and a non-application time is in a range of from 10 $\mu$s 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 $\mu$s to 10 ms and an application time of negative voltage and a non-application time is in a range of from 10 $\mu$s to 100 ms.

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).

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.

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 $\omega_A$ (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 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 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.

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.

Formula 1

$$W = \frac{1}{T} \int_0^T V(t)\, I(t)\, dt$$

Formula 2

$$W = \frac{(-V_N)}{a_1 \div b_1} \int_0^{a_1} I(t)\, dt$$

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.

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 $3.0 \times 10^{-3}$ Torr and an effective power value of 2 kW. When a 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 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 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 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

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 $2.0 \times 10^{-3}$ Torr and at an effective power value of 13 kW to deposit a film of $SiO_2$ doped with aluminum on a substrate.

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 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 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

In a vacuum chamber, N-type silicon (phosphorus doped single crystal) having a specific resistance of 1.2 Ω•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 $1 \times 10^{-5}$ Torr. Then, a gas mixture of argon and oxygen was introduced as sputtering gas, and conductance was adjusted so that the pressure is $2 \times 10^{-3}$ Torr.

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.

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.

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

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 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.

## 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 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.

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 |

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.

## EXAMPLE 4

N-type silicon having a specific resistance of 1.2 Ω•cm and a surface area of 160 mm x 40 mm was 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.

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

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.

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.

## 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 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

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 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.

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 |

Table 3

| Ratio of ammonia/silane | 3 | 5 | 10 | 15 |
|---|---|---|---|---|
| Composition (N/si)<br>Amount of out diffused Na (μg/cm$^2$) | 1.27<br>0.047 | 1.36<br>0.038 | 1.49<br>0.056 | 1.56<br>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 × $10^{-5}$ Torr or lower. Then, argon gas containing 1 vol% of oxygen gas was introduced so that gas pressure was 3 × $10^{-3}$ 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.

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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 | $1.9 \times 10^{-4}$ | $1.9 \times 10^{-4}$ | $1.9 \times 10^{-4}$ |
| Specific resistance of ITO film (after film-sputtering for 23 hours) | $4.0 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $1.9 \times 10^{-4}$ |
| 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.

In Comparative Examples, the decrease of the sputtering rate was remarkable by about 40%. The specific resistance is reduced from $1.9 \times 10^{-4}$ Ω•cm (at the initial stage of sputtering) to $4 \times 10^{-4}$ Ω•cm due to the reduction of sputtering rate. Nodules were very rigid and it was necessary to conduct mechanical grinding for cleaning.

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 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 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.

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. 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 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 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 those obtained by the conventional DC sputtering method.

## Claims

1. A sputtering method which 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.

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 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.

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.

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.

FIGURE 1

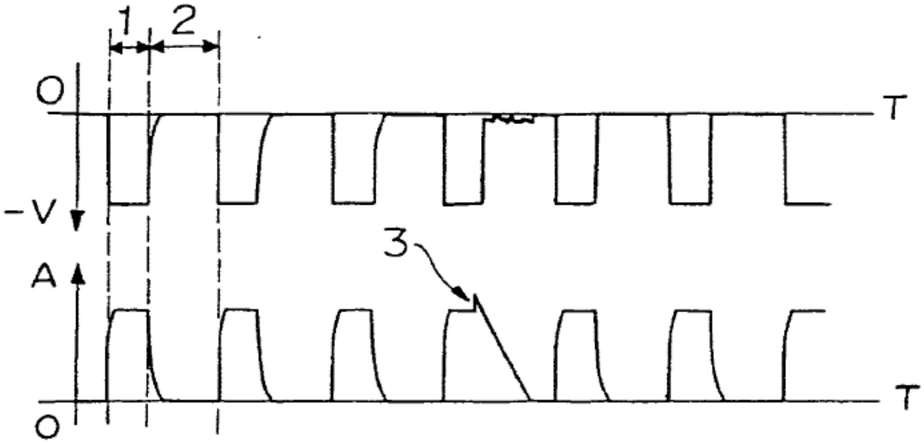


FIGURE 2

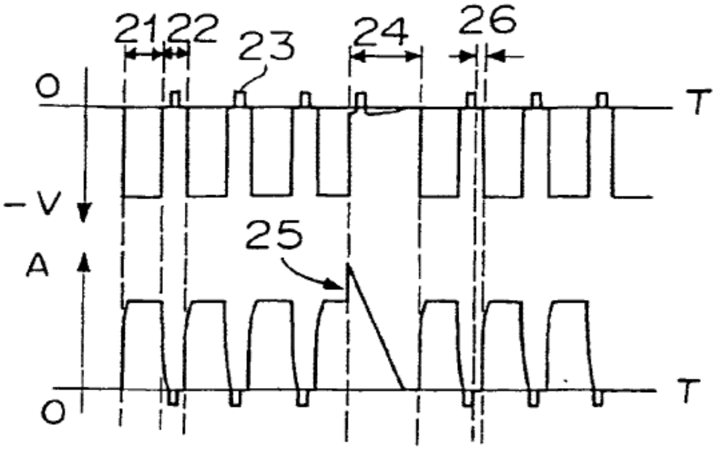


FIGURE 3

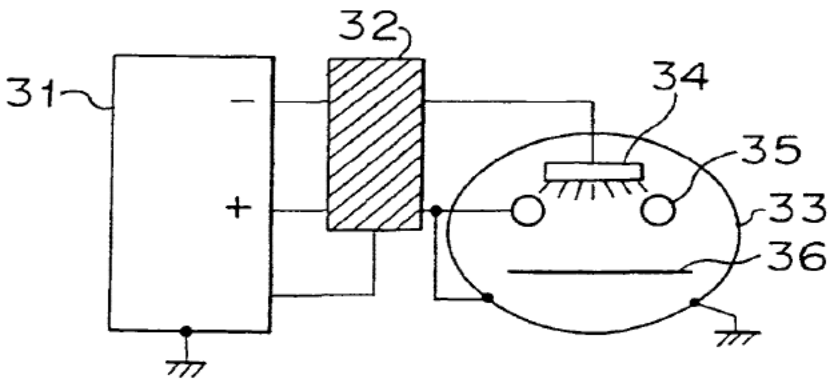


**FIGURE 4**

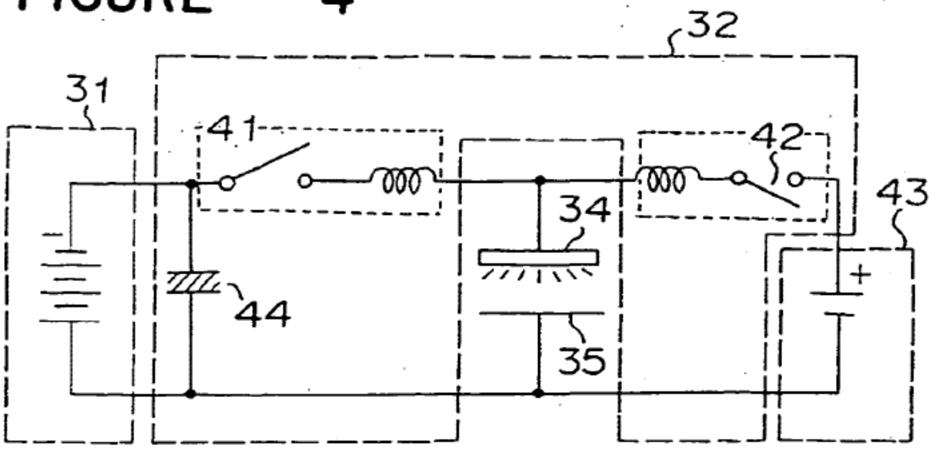


**FIGURE 5**

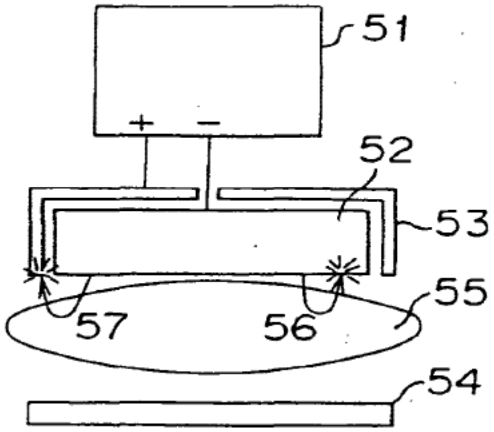


**FIGURE 6**

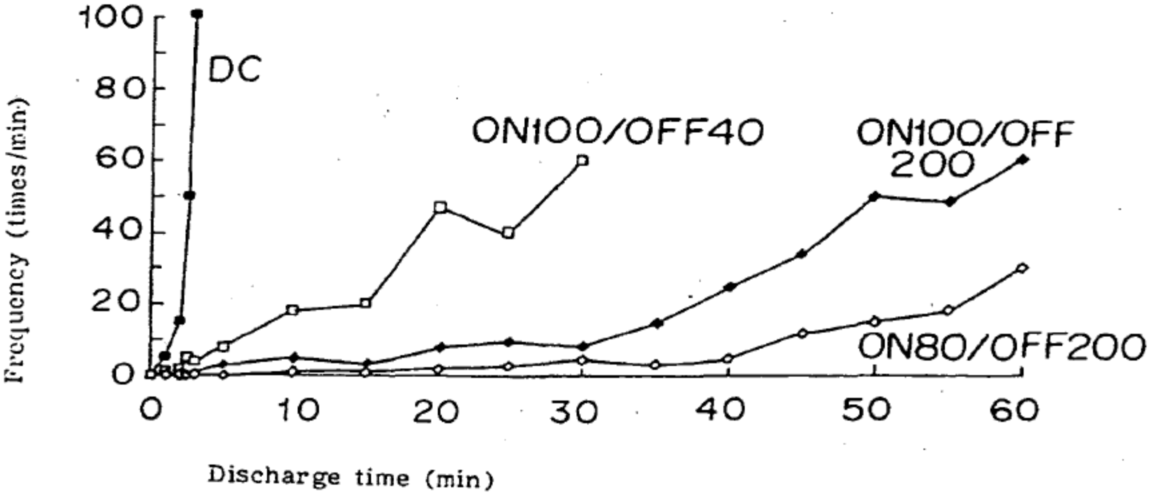


FIGURE 7

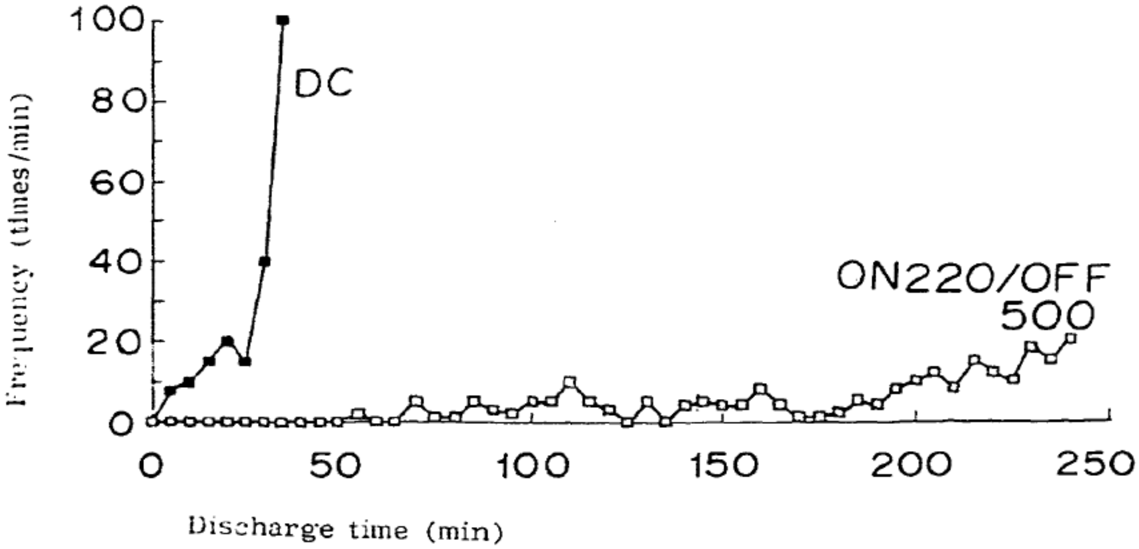


FIGURE 8

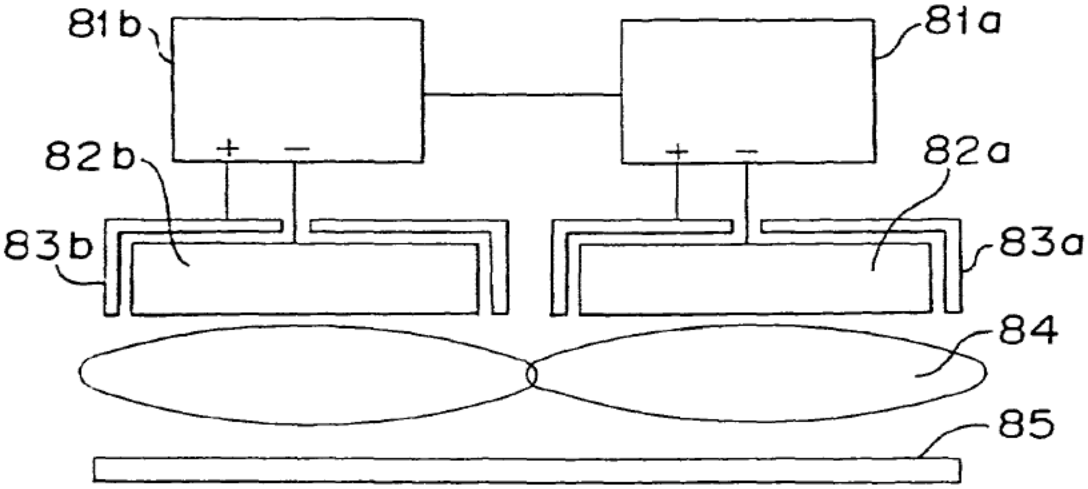


FIGURE 9

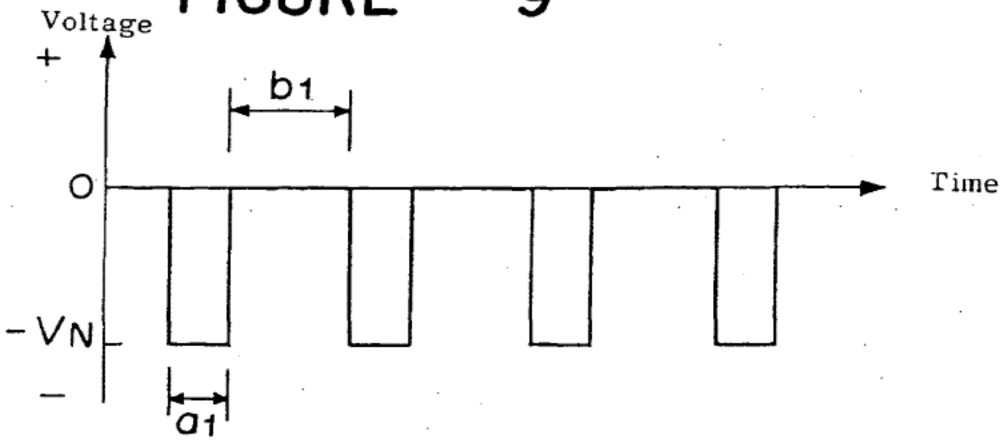


FIGURE 10

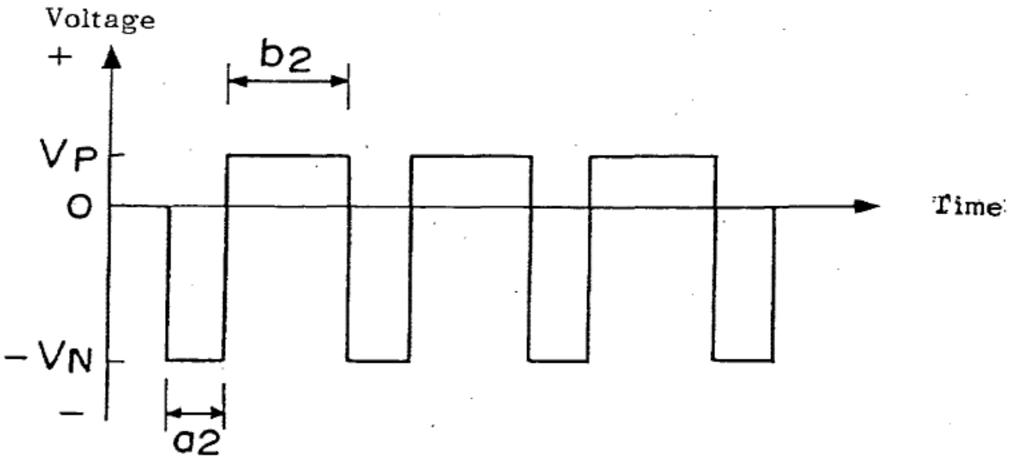
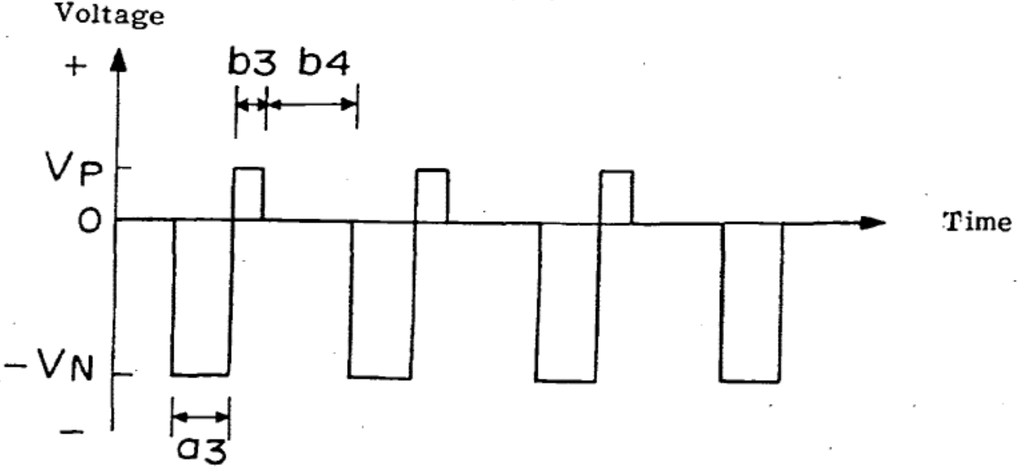


FIGURE 11



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<br>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'<br>* page 180, left column, line 2 - right column, line 2 *<br>--- | 1-19 | C23C14/00<br>C23C14/34<br>H01J37/32 |
| X<br>A | EP-A-0 275 018 (GRUN R) 20 July 1988<br>* column 4, line 40 - line 50; claims 1-4 *<br>--- | 5<br>1-4,6-19 | |
| A | WO-A-87 05053 (QUAZI)<br>* page 28, line 3 - line 12; claim 1 *<br>--- | 1-19 | |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 14, no. 90 (C-0691) 20 February 1990<br>& JP-A-01 301 856 (SHIMADSU CORP) 6 December 1989<br>* abstract *<br>--- | 1-19 | **TECHNICAL FIELDS SEARCHED (Int.Cl.6)**<br>C23C<br>H01J<br>H03J |
| A | CIP 93 PROCEEDINGS, 6 June 1993, FR<br>pages 66 - 68, XP399216<br>B. STAUDER ET AL 'A METHOD FOR SUPRESSING THE HYSTERESIS EFFECT IN REACTIVE SPUTTERING'<br>* page 67, line 9 - line 21 *<br>--- | 1-19 | |
| A | WO-A-91 02103 (THE BOC GROUP INC)<br>* claims 1,2 *<br>----- | 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)

07-27-05

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JUL 2 5 2005
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

Fee only

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/954,182 | Examiner: ESTRADA, Michelle |
| Filed: October 1, 2004 | Confirmation No.: 9873 |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## AMENDMENT AND RESPONSE TO OFFICE ACTION

08/05/2005 TLAWRENC 00000001 060916 10954182
01 FC:1203 360.00 DA
02 FC:1201 1200.00 DA
03 FC:1202 600.00 DA

In reply to the Office Action mailed March 25, 2005, the period of response extended to July 25, 2005, by a one month extension of time and 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 that begins on page 2 of this paper.

**Remarks/Arguments** follow the amendment sections on page 9 of this paper.

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

Application or Docket Number 10954182

## APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | RATE ($) | FEE ($) | | RATE ($) | FEE ($) |
| BASIC FEE (37 CFR 1.16(a), (b), or (c)) | | | | | | | |
| SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | | | | | | | |
| EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | | | | | | | |
| 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 A | 7/25/05 | (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)) | * 61 | Minus | ** 45 | = 16 | x = | | OR | x 50 = | 800 |
| | Independent (37 CFR 1.16(h)) | * 9 | Minus | *** 3 | = 6 | x = | | OR | x 200 = | 1200 |
| | Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | ~~180~~ | | OR | 360 | 360 |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

Paid

| AMENDMENT B | | (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)) | * | 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.

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

Application Number 10954182

Filing Date

Applicant(s)

* May be used for additional claims or amendments

| CLAIMS | AS FILED | | AFTER FIRST AMENDMENT | | AFTER SECOND AMENDMENT | |
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| Total Indep | | | | | | |
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| Total Indep | | | 9 | | | |
| Total Depend | | | 52 | | | |
| Total Claims | | | 61 | | | |

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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. |
|---|---|---|---|---|
| 10/954,182 | 10/01/2004 | Hongmei Zhang | 09140-0016-01000 | 9873 |

22852 7590 10/25/2005

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: 10/25/2005

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

PTO-90C (Rev. 10/03)

|  |  |  |  |
|---|---|---|---|
| **Office Action Summary** | **Application No.**<br>10/954,182 | **Applicant(s)**<br>ZHANG ET AL. | RM |
|  | **Examiner**<br>Michelle Estrada | **Art Unit**<br>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 *25 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) *41-62,64-66 and 68-92* is/are pending in the application.

4a) Of the above claim(s) *64-66,68-84,86 and 90-92* is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *41-62,85 and 87-89* 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 _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

## DETAILED ACTION

Newly submitted claims 64-84, 86 and 90-92 are directed to an invention that is independent or distinct from the invention originally claimed for the following reasons: these claims are directed to an apparatus and the originally examined claims are directed to a process.

Since applicant has received an action on the merits for the originally presented invention, this invention has been constructively elected by original presentation for prosecution on the merits. Accordingly, claims 64-84, 86 and 90-92 are withdrawn from consideration as being directed to a non-elected invention. See 37 CFR 1.142(b) and MPEP § 821.03.

### *Claim Rejections - 35 USC § 112*

The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claims 41-62, 85 and 87-89 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. There is no description in the specification as originally filed of what is a "metallic mode", a "poison mode" and a "transition mode".

Claims 41-62, 85 and 87-89 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the enablement requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention. There is no description of what is a “metallic mode”, a “poison mode” and a “transition mode” as discussed above and therefore insufficient guidance to enable one of ordinary skill in the art to determine suitable conditions to achieve the instant invention.

## *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
Michelle Estrada
Patent Examiner
Art Unit 2823

ME
October 17, 2005

12-23-05

JFW

OIPE
IAP15
DEC 21 2005
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/954,182 | Examiner: ESTRADA, Michelle |
| Filed: October 1, 2004 | Confirmation No.: 9873 |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | |

**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 October 25, 2005, please amend the above-identified application as follows:

**Amendments to the Claims** are reflected in the listing of claims that begins on page 2 of this paper.

**Remarks/Arguments** follow the amendment sections on page 6 of this paper.

## AMENDMENTS TO THE CLAIMS:

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

Claims 1-39 (Canceled).

Claim 40 (Canceled).

Claim 41 (Previously presented): The method of claims 59, 60, or 85, wherein the target is a metallic target and the process gas includes oxygen.

Claim 42 (Previously presented): The method of claims 59, 60, or 85, wherein the target is a metallic target and the process gas includes one or more of a set consisting of $N_2$, $NH_3$, CO, NO, $CO_2$, halide containing gasses.

Claim 43 (Previously presented): The method of claims 59, 60, or 85, wherein the target is a ceramic target.

Claim 44 (Canceled):

Claim 45 (Previously presented): The method of claims 59, 60, or 85, wherein the magnetic field is provided by a moving magnetron.

Claim 46 (Previously presented) The method of claims 59, 60, or 85, further including holding the temperature of the substrate substantially constant.

Claim 47 (Previously presented): The method of claims 59, 60, or 85, wherein the process gas includes a mixture of Oxygen and Argon.

Claim 48 (Previously presented): The method of claims 59, 60, or 85, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

Claim 49 (Previously presented): The method of claims 59, 60, or 85, wherein the process gas further includes nitrogen.

Claim 50 (Previously presented): The method of claims 59, 60, or 85, 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 51 (Previously presented): The method of claims 59, 60, or 85, further including uniformly sweeping the target with a magnetic field.

Claim 52 (Previously presented): The method of claim 51 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 53 (Previously presented): The method of claims 59, 60, or 85, wherein the target is an alloyed target.

Claim 54 (Previously presented): The method of claim 53 wherein the alloyed target includes one or more rare-earth ions.

Claim 55 (Previously presented): The method of claim 53 wherein the alloyed target includes Si and Al.

Claim 56 (Previously presented): The method of claim 53 wherein the alloyed target includes one or more elements taken from a set consisting of Si, Al, Er, Yb, Zn, Ga, Ge, P, As, Sn, Sb, Pb, Ag, Au, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy Ho, Tm, and Lu.

Claim 57 (Previously presented): The method of claim 53 wherein the alloyed target is a tiled target.

Claim 58 (Previously presented): The method of claim 57 wherein each tile of the tiled target is formed by prealloy atomization and hot isostatic pressing of a powder.

Claim 59 (Previously presented): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;
providing pulsed DC power to the target;
providing a magnetic field to the target; and
wherein a material is deposited on the substrate, and
an oxide film is formed by reactive sputtering in metallic mode.

Claim 60 (Previously presented): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;
providing pulsed DC power to the target;
providing a magnetic field to the target; and
wherein a material is deposited on the substrate, and an oxide film is formed by reactive sputtering in poison mode.

Claim 61 (Previously presented): A method of depositing a film on a substrate, comprising:

providing a process gas between a metallic target and a substrate;
providing pulsed DC power to the target;
providing a magnetic field to the target; and
reconditioning a metallic target;
wherein a material is deposited on the substrate.

Claim 62 (Previously presented): The method of claim 61, wherein reconditioning the metallic target includes:

reactive sputtering in the metallic mode and then reactive sputtering in the poison mode.

Claims 63-84 (Canceled).

Claim 85 (Currently amended): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;

providing pulsed DC power to the target;

providing a magnetic field to the target; and

wherein a material is deposited on the substrate, and an oxide film is formed by reactive sputtering in ~~transition mode~~ a mode between a metallic mode and a poison mode.

Claim 86 (Canceled).

Claim 87 (Previously presented): The method according to claims 59, 60, or 85, further comprising:

providing a narrow-band RF filter between the pulsed DC power supply and the target; and

providing an RF bias to the substrate.

Claim 88 (Previously presented): The method according to claim 87, wherein the narrow-band RF filter has a bandwidth of about 100 kHz.

Claim 89 (Previously presented): The method according to claim 87, wherein the RF bias has a frequency of about 2 MHz.

Claims 90-92 (Canceled).

## REMARKS

Claims 41-62, 64-66, and 68-92 are pending in this application. The Examiner has rejected claims 41-62, 85 and 87-89. In this Amendment, claim 85 has been amended and claims 64-84, 86, and 90-92 have been canceled, without prejudice. After entry of this Amendment, claims 41-43, 45-62, 85, and 87-89 will remain pending.

## Claim Objections

The Examiner objected to claims 64-84, 86, and 90-92, indicating they are directed to an invention that is independent or distinct from the invention originally claimed for the following reasons: "these claims are directed to an apparatus and the originally examined claims are directed to a process." The Examiner has withdrawn claims 64-84, 86, and 90-92 from consideration. Accordingly, Applicants have canceled claims 64-84, 86, and 90-92 from this application, without prejudice. Applicants reserve the right to pursue these claims in a separate application.

## Claim Rejections under 35 U.S.C. § 112, first paragraph

The Examiner has rejected claims 41-62, 85, and 87-89 under 35 U.S.C. 112, first paragraph as failing to comply with either of the written description requirement or the enablement requirement.

### *Written Description*

The Examiner states that the claims contain subject matter that is not described in the specification. In particular, the Examiner states that "[t]here is no description in the specification as originally filed of what is a 'metallic mode', a 'poison mode' and a 'transition mode'" Office Action, p. 2. Applicants have amended claim 85 to remove reference to the transition mode. Both the metallic mode and the poison mode are well described in the specification.

The metallic mode is described in the specification, for example, at paragraph [0083], which states:

> 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.

(Originally filed specification, para. 0083, emphasis added).

The poison mode is described in the specification, for example, at paragraph [0079], which states:

> 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.

(Originally filed specification, para. 0079, emphasis added).

As indicated in at least the two paragraphs above, the specification as originally filed included a written description of both the metallic and poison modes of operation. Therefore, Applicants respectfully request that the Examiner remove these rejections based on 37 C.F.R. § 112, first paragraph, for failing to comply with the written description requirement.

*Enablement*

Furthermore, the Examiner rejected claims 41-62, 85, and 87-89 under 35 U.S.C. 112, first paragraph as failing to comply with the enablement requirement. In particular, the Examiner states again that these claims are not enabled because there is no description of "metallic mode," "poison mode," or "transition mode" in the specification as filed. Claim 85 has been amended to remove the terminology "transition mode." As discussed above, at least paragraph [0083] of the originally filed application provides enablement for operation in the "metallic mode" while paragraph [0079] provides enablement for operation in the "poison mode." Consequently, Applicants request that the Examiner remove the rejections of claims 41-62, 85, and 87-89 for failure to comply the enablement requirement of 35 U.S.C. § 112, first paragraph.

## 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.

Date: December 21, 2005

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

**EXPRESS MAIL LABEL NO.**
**EV 758329240 US**

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

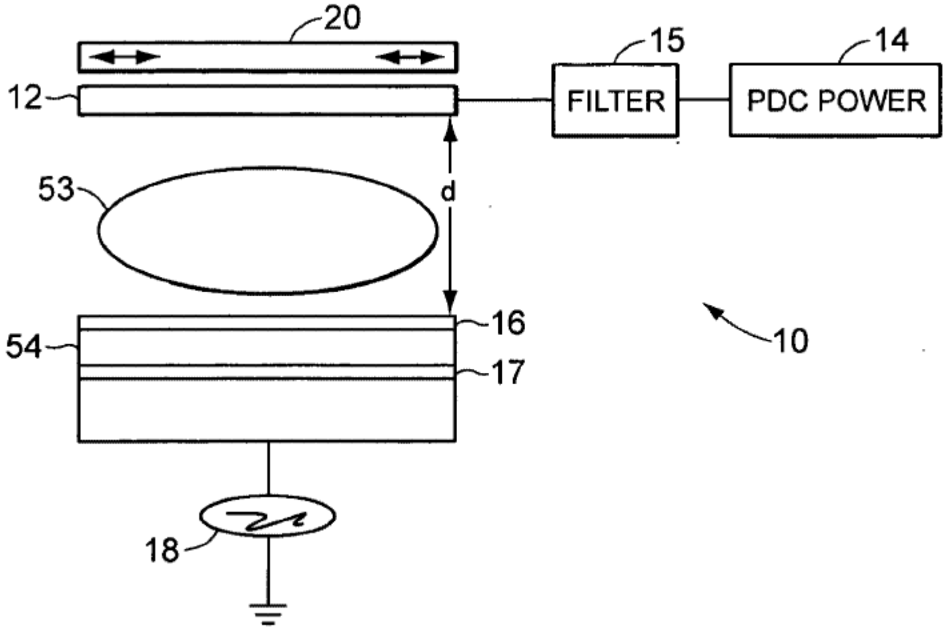

FIG. 1A

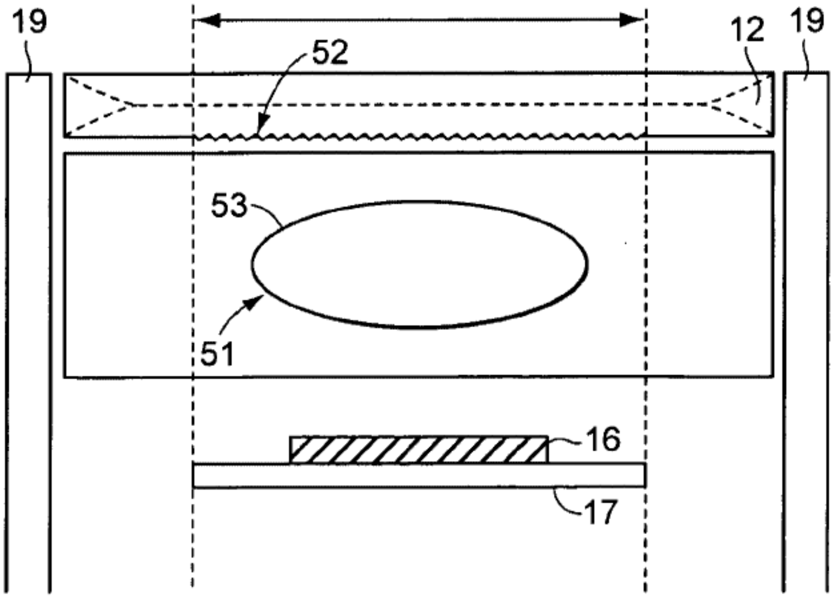

FIG. 1B

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

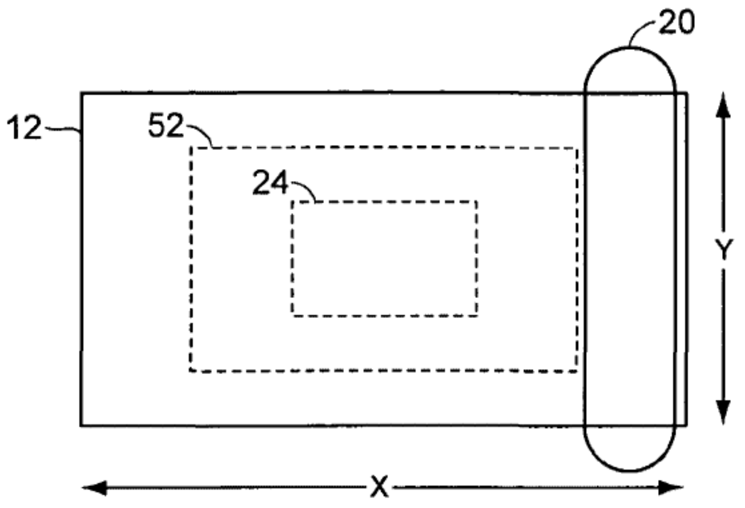

FIG. 2

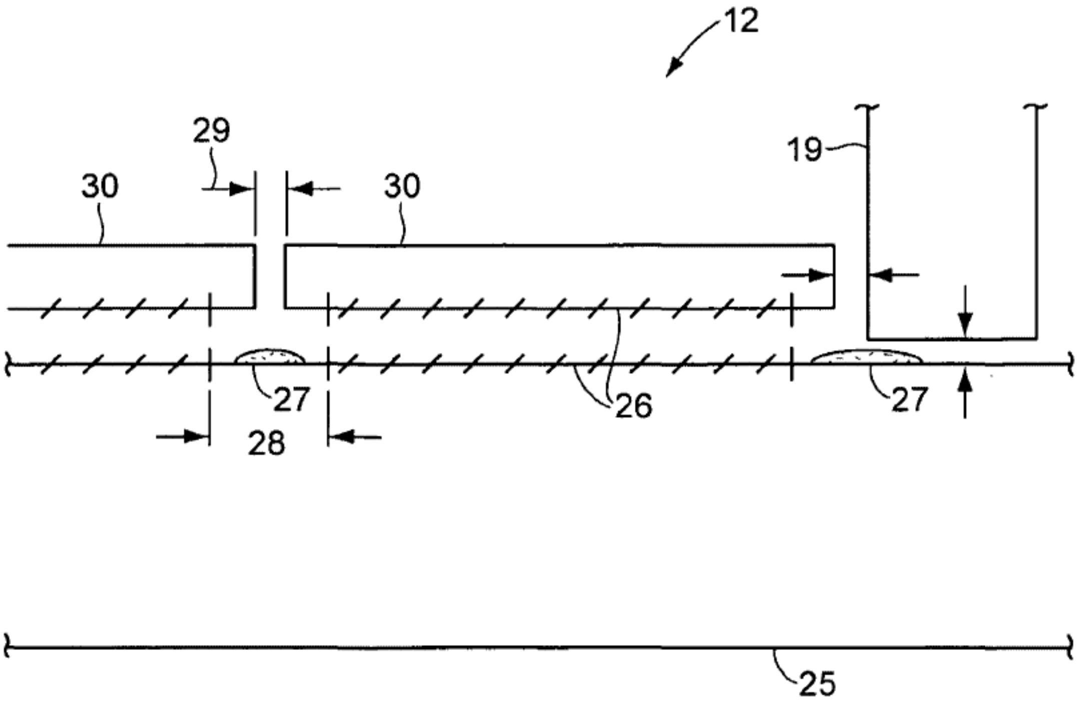

FIG. 3

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

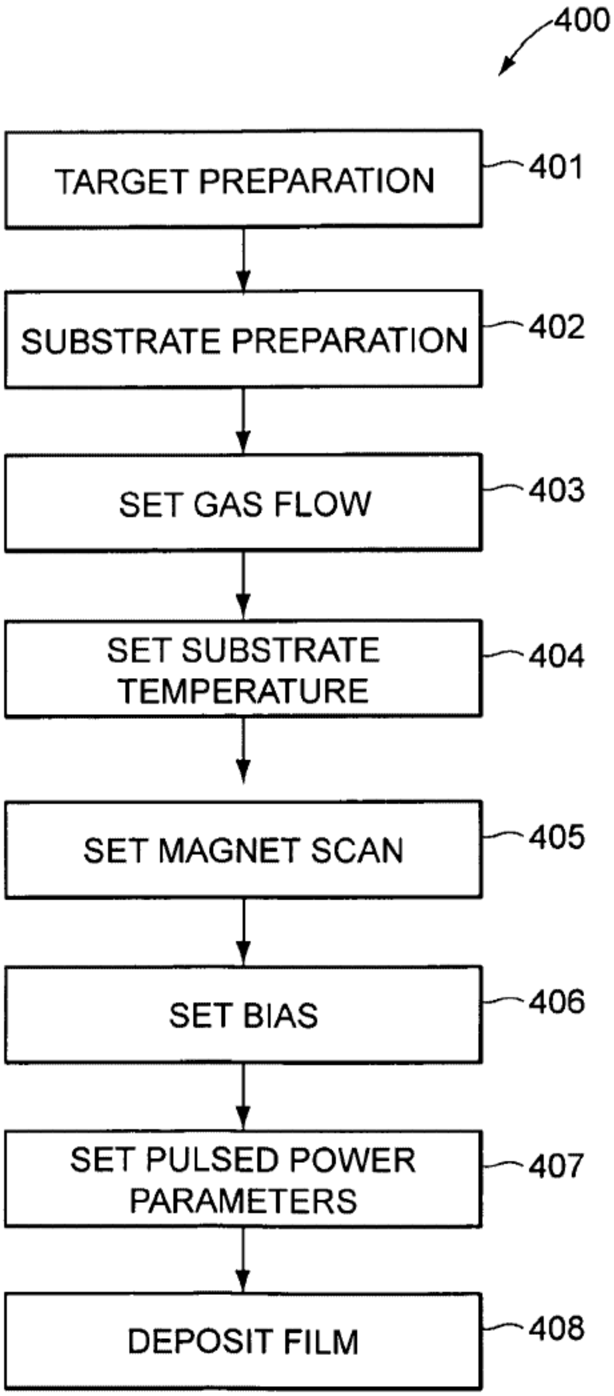

FIG. 4

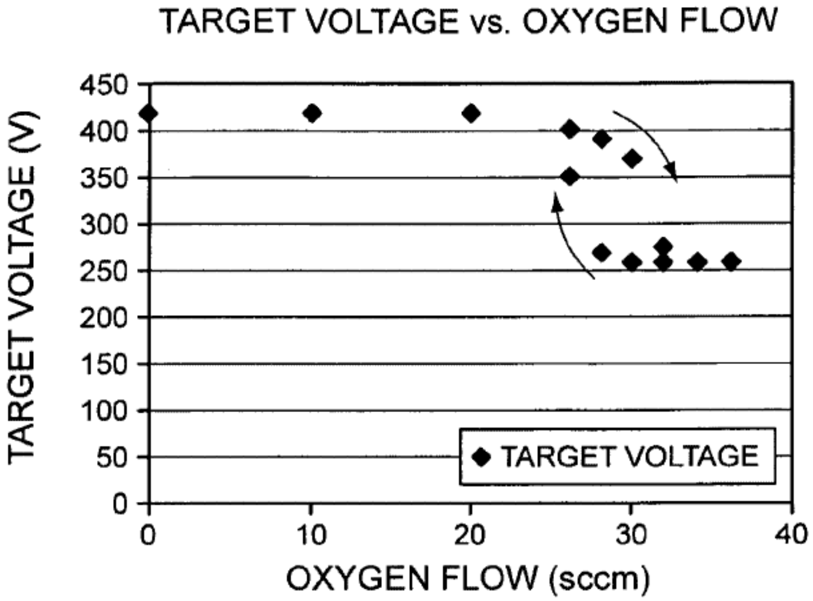
TARGET VOLTAGE vs. OXYGEN FLOW
TARGET VOLTAGE (V)
450
400
350
300
250
200
150
100
50
0
0
10
20
30
40
OXYGEN FLOW (sccm)
◆ TARGET VOLTAGE

FIG. 5

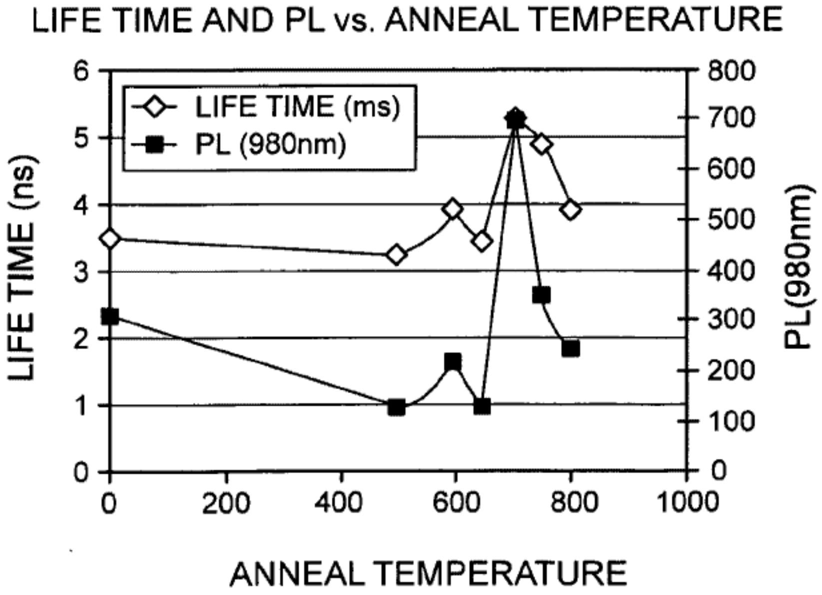
LIFE TIME AND PL vs. ANNEAL TEMPERATURE
LIFE TIME (ns)
6
5
4
3
2
1
0
0
200
400
600
800
1000
ANNEAL TEMPERATURE
800
700
600
500
400
300
200
100
0
PL(980nm)
◇ LIFE TIME (ms)
■ PL (980nm)

FIG. 6

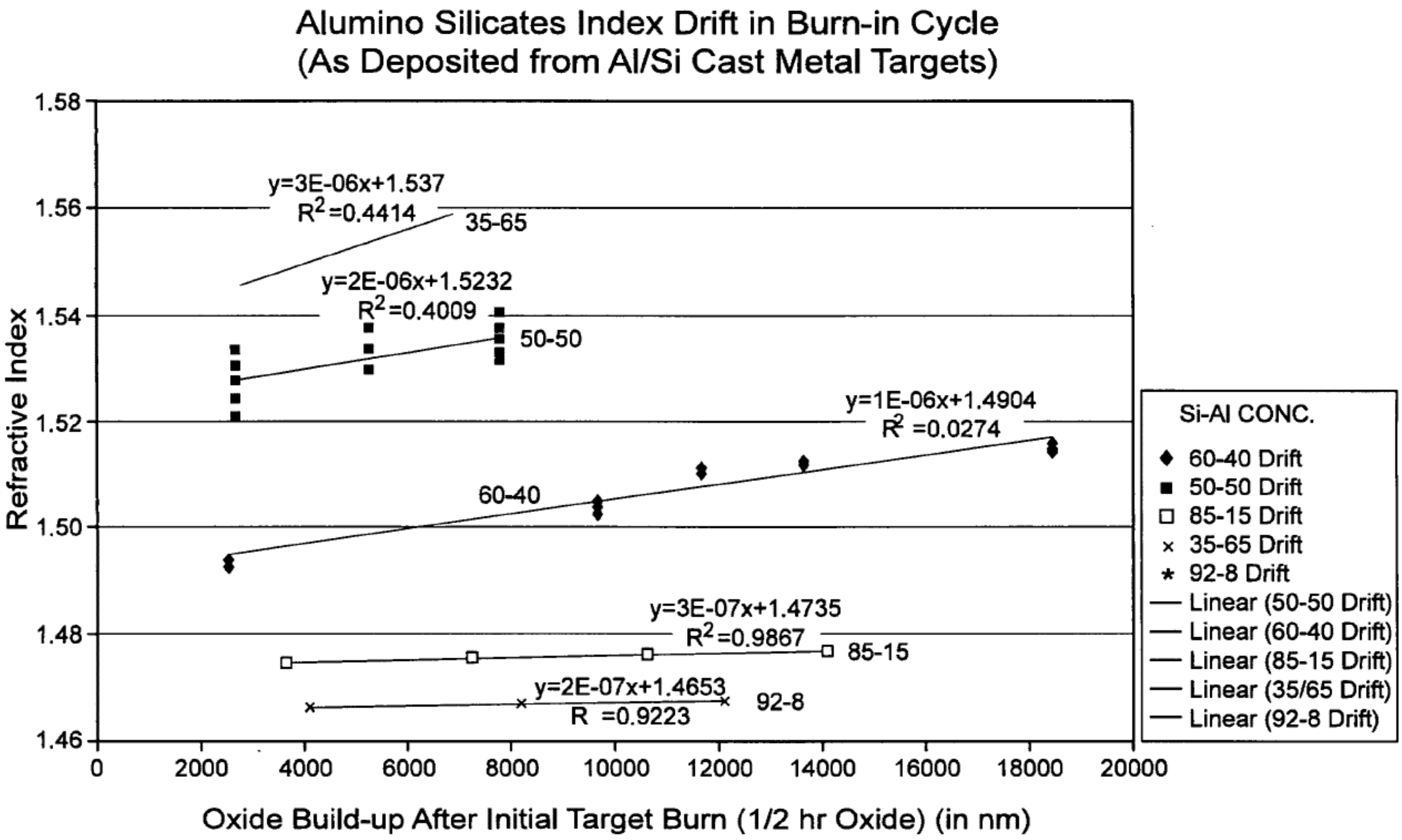

FIG. 7

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

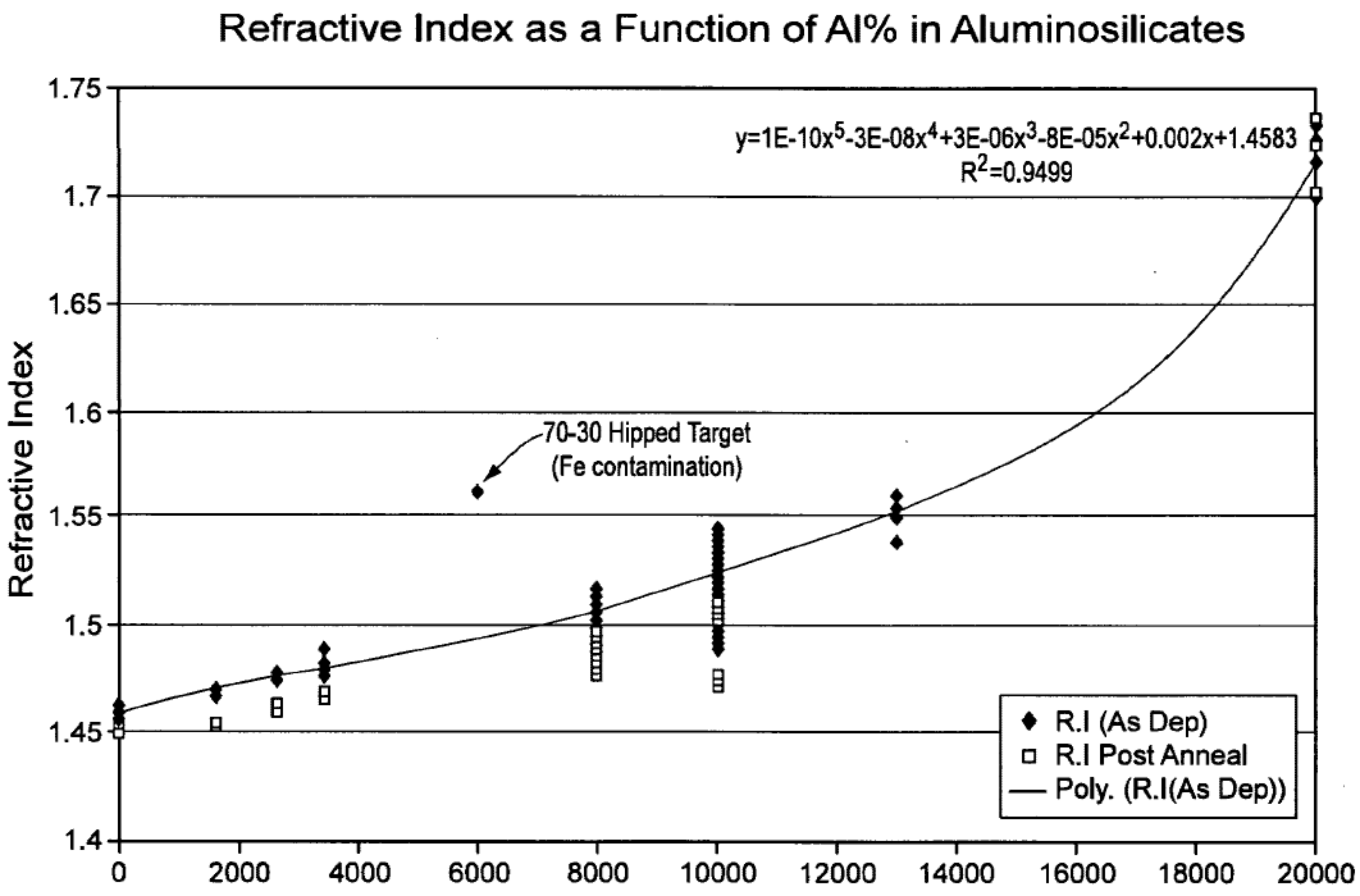

FIG. 8

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
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

7/27

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
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

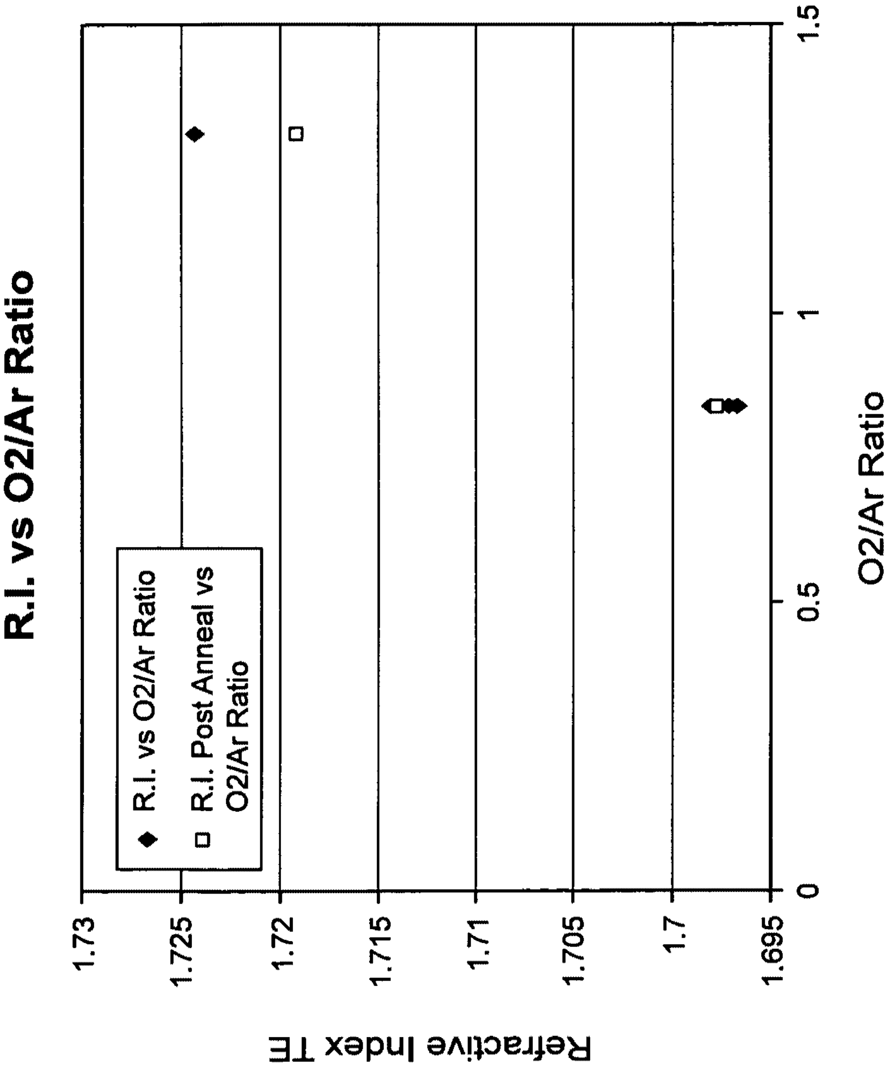
R.I. vs O2/Ar Ratio
◆ R.I. vs O2/Ar Ratio
□ R.I. Post Anneal vs O2/Ar Ratio
Refractive Index TE
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
0.5
1
1.5
O2/Ar Ratio

FIG. 11

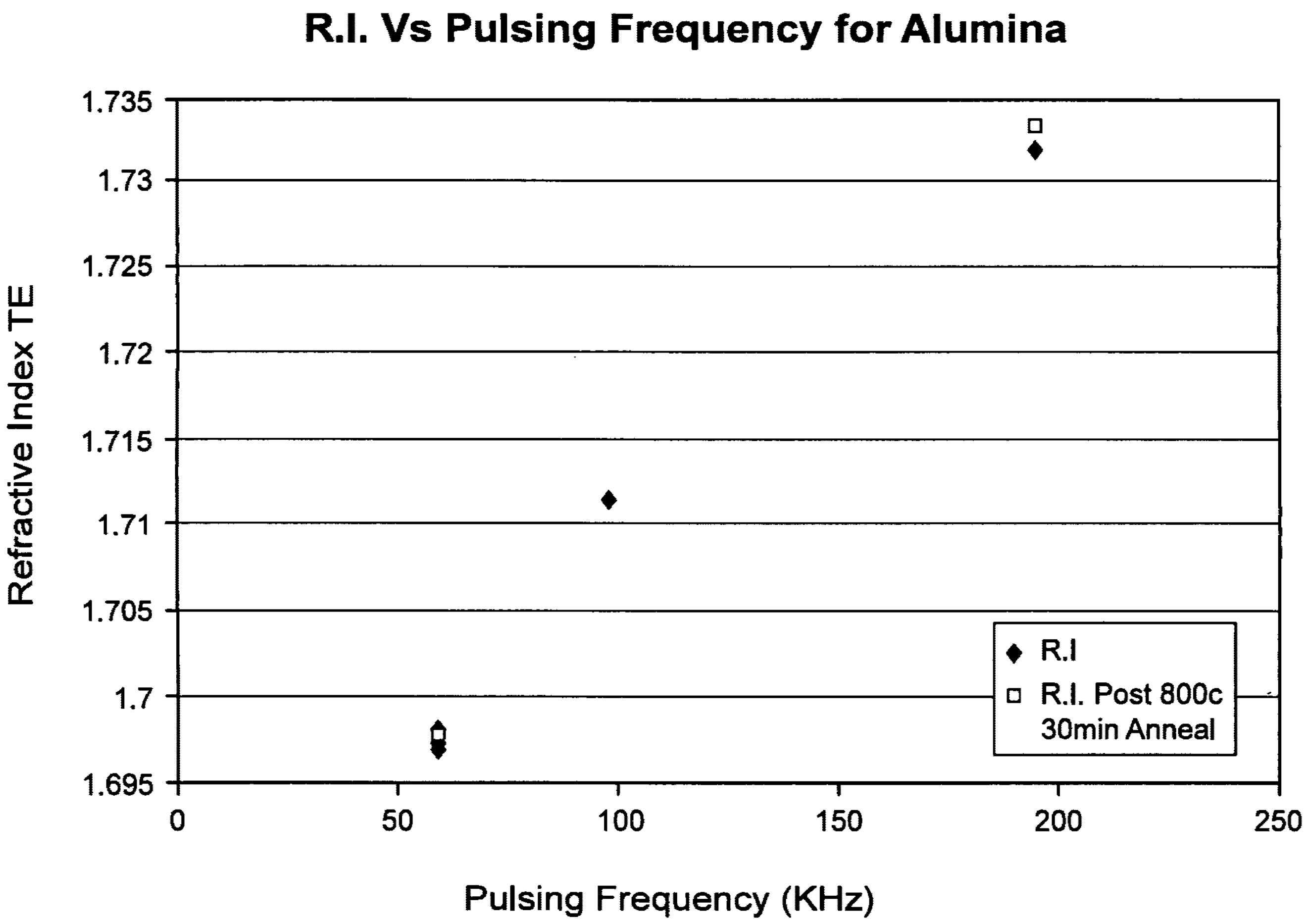

FIG. 12

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

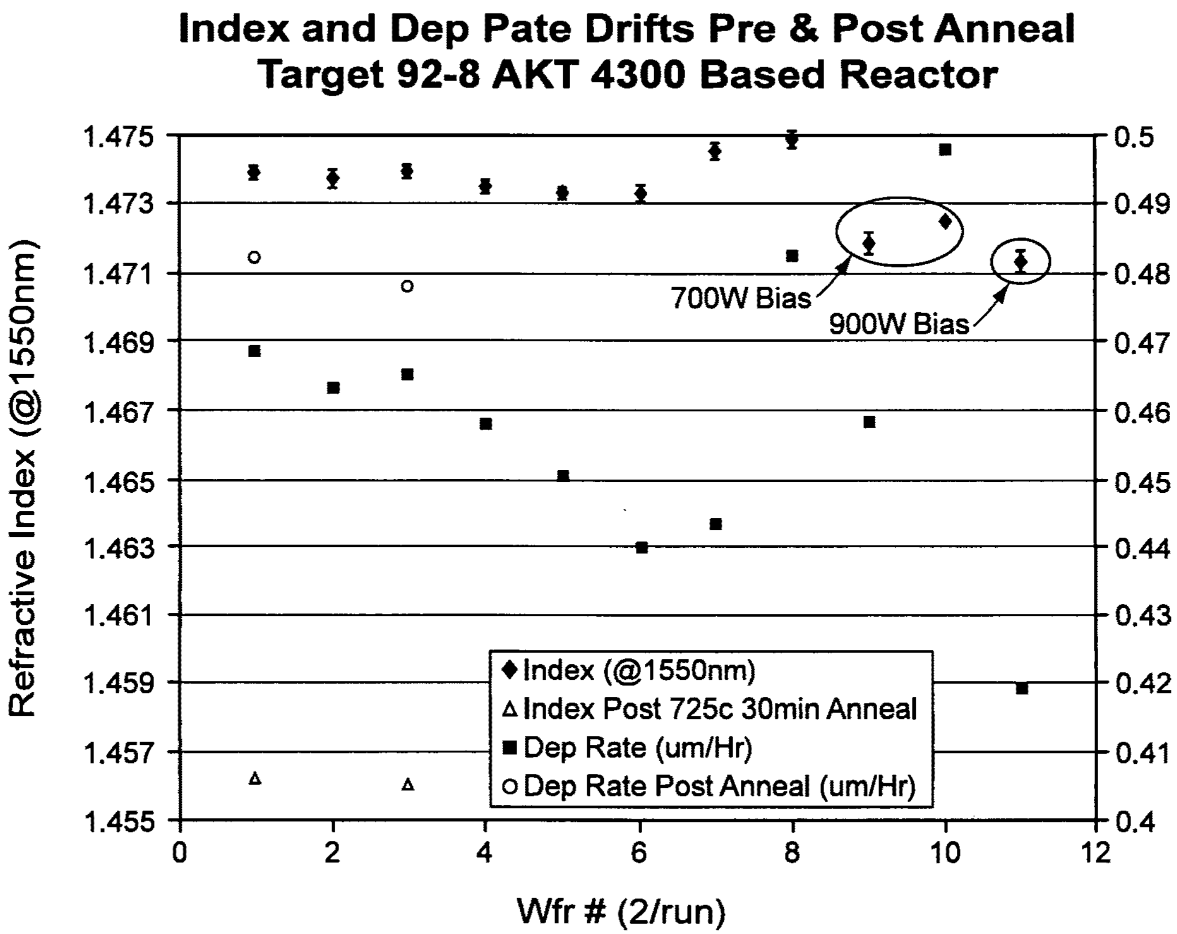

FIG. 13

11/27

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

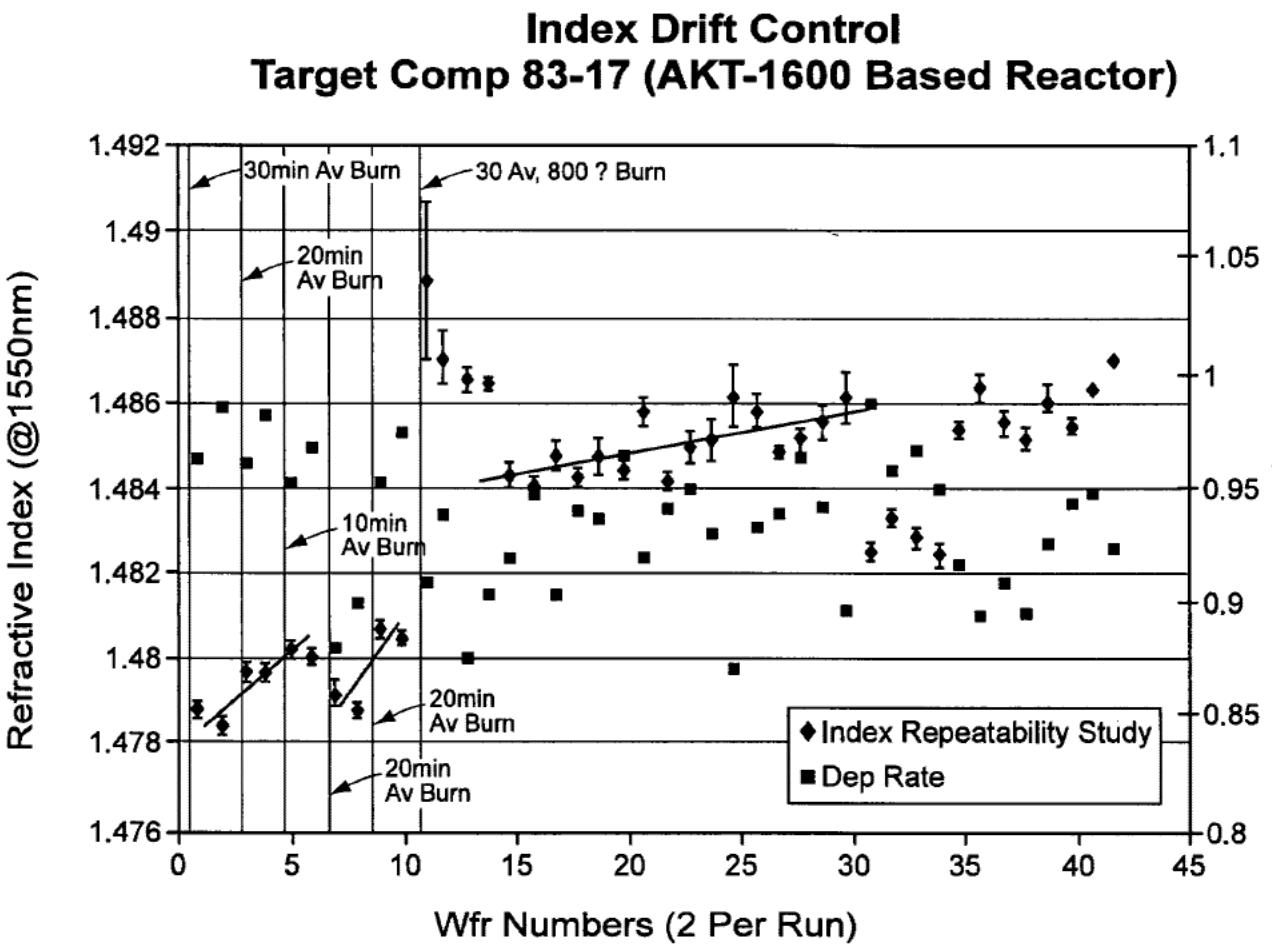
Index Drift Control
Target Comp 83-17 (AKT-1600 Based Reactor)
Refractive Index (@1550nm)
1.492
1.49
1.488
1.486
1.484
1.482
1.48
1.478
1.476
1.1
1.05
1
0.95
0.9
0.85
0.8
0
5
10
15
20
25
30
35
40
45
Wfr Numbers (2 Per Run)
30min Av Burn
20min Av Burn
10min Av Burn
20min Av Burn
20min Av Burn
30 Av, 800 ? Burn
◆ Index Repeatability Study
■ Dep Rate

FIG. 14

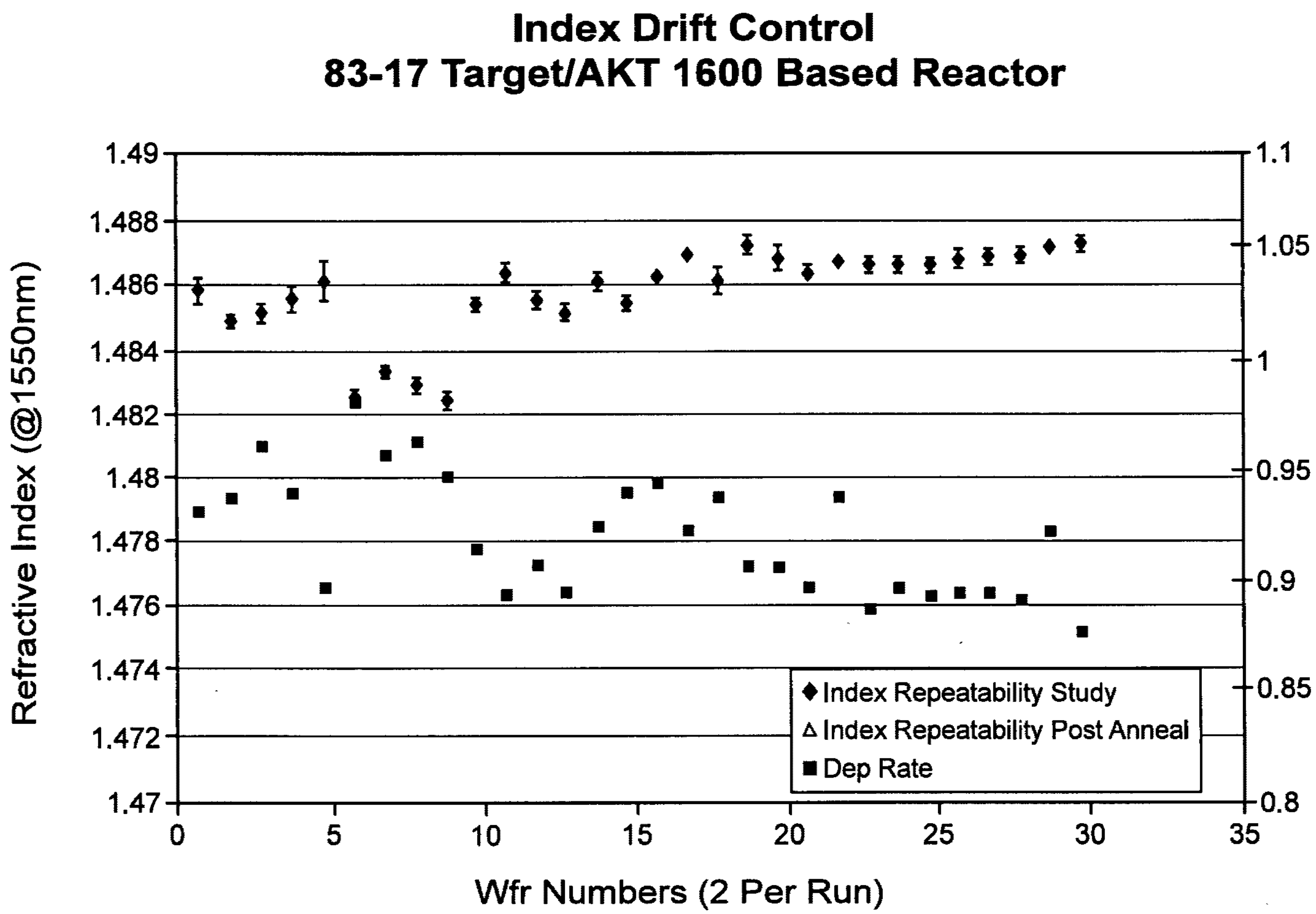

FIG. 15

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

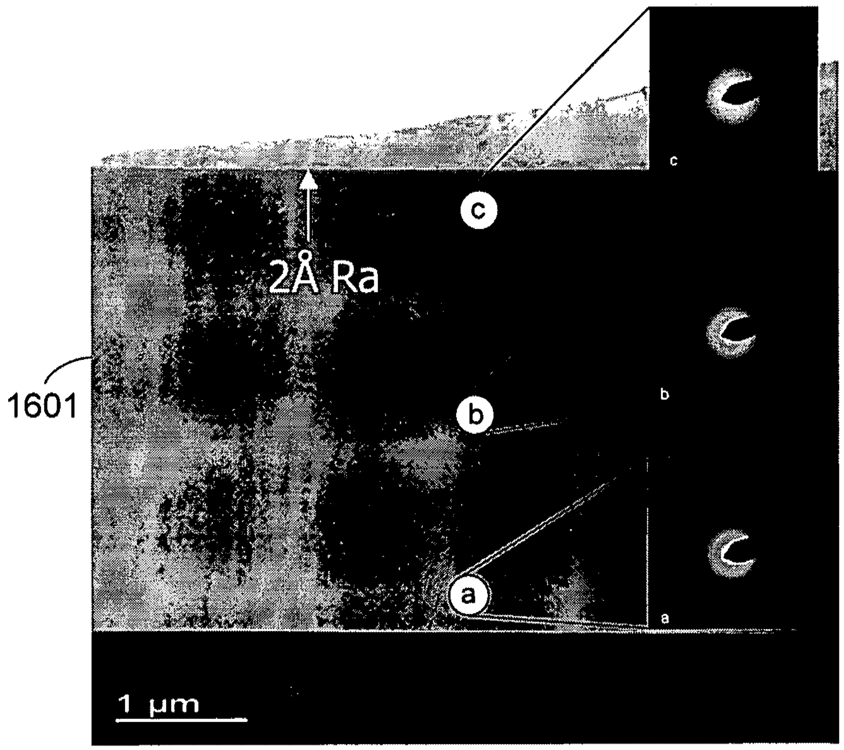

FIG. 16D

FIG. 16C

FIG. 16B

FIG. 16A

SYMMORPHIX PVD ALUMINOSILICATE

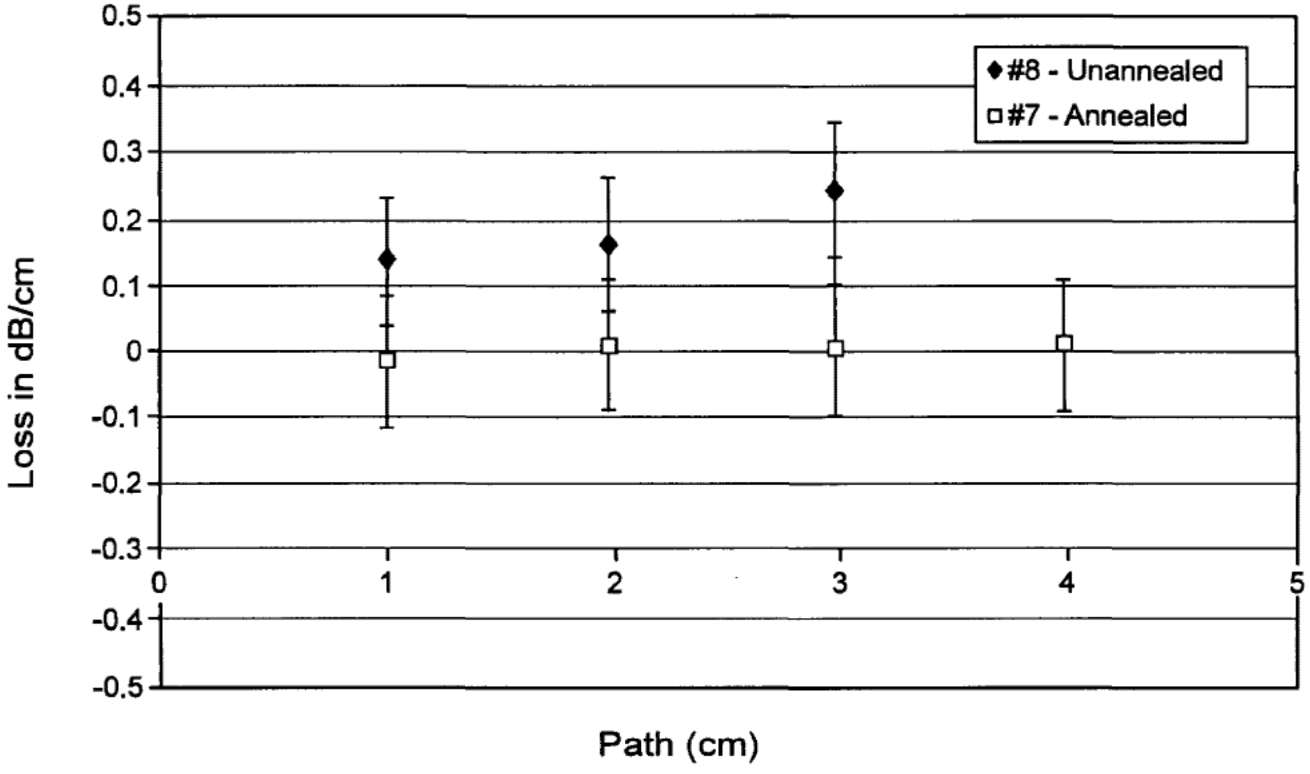
◆ #8 - Unannealed
□ #7 - Annealed
Loss in dB/cm
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
1
2
3
4
5
Path (cm)

FIG. 17

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

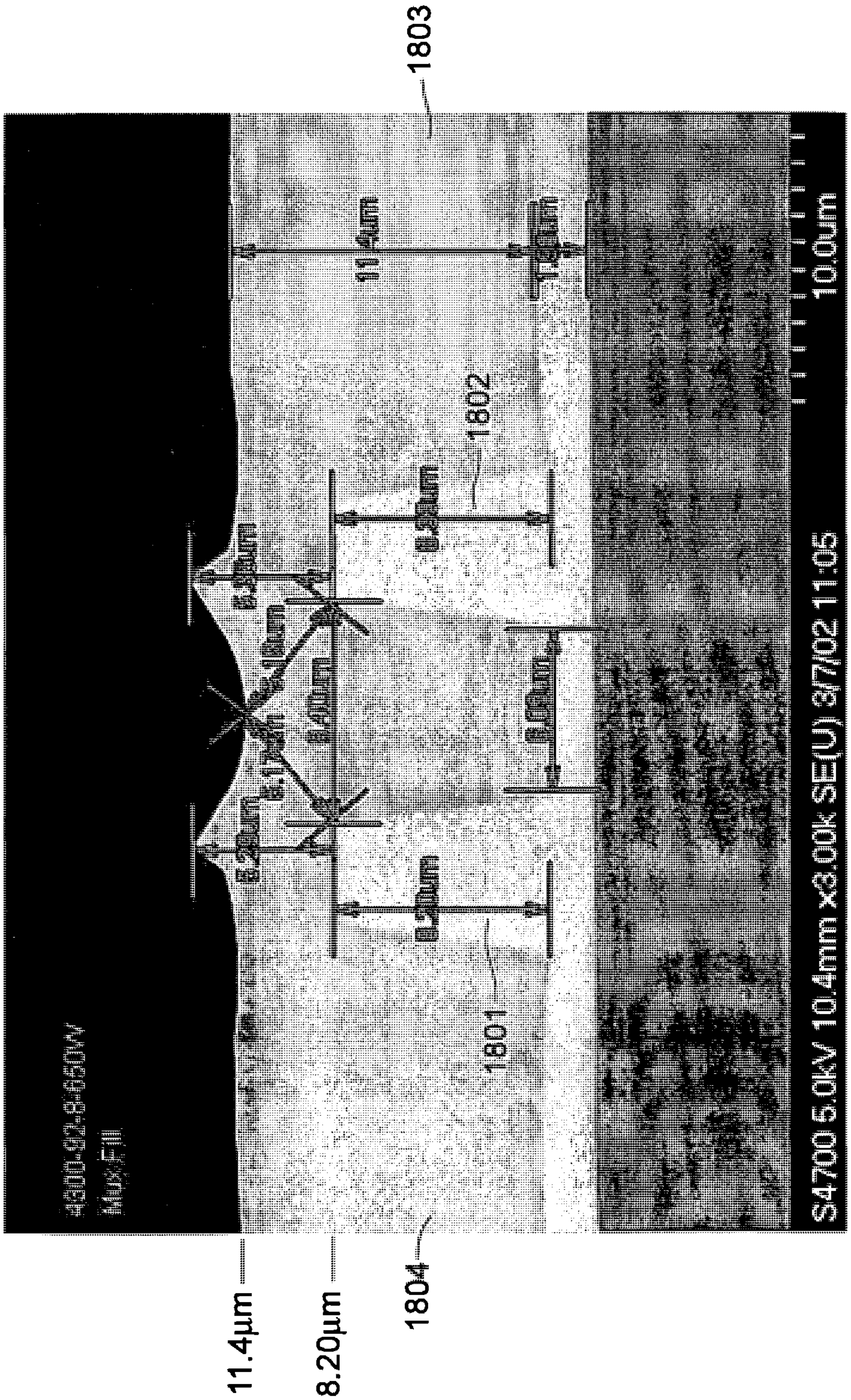

FIG. 18

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REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

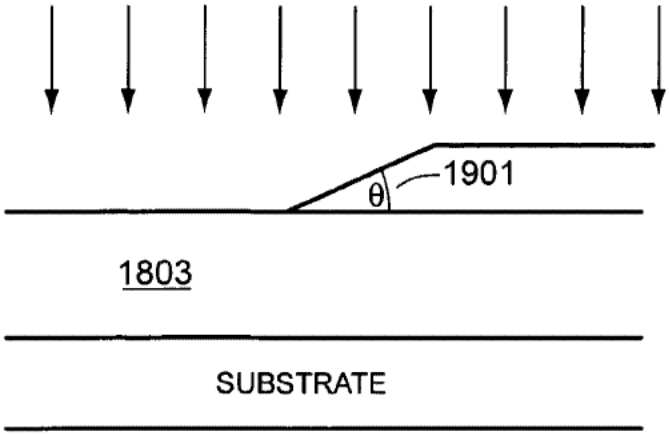

FIG. 19

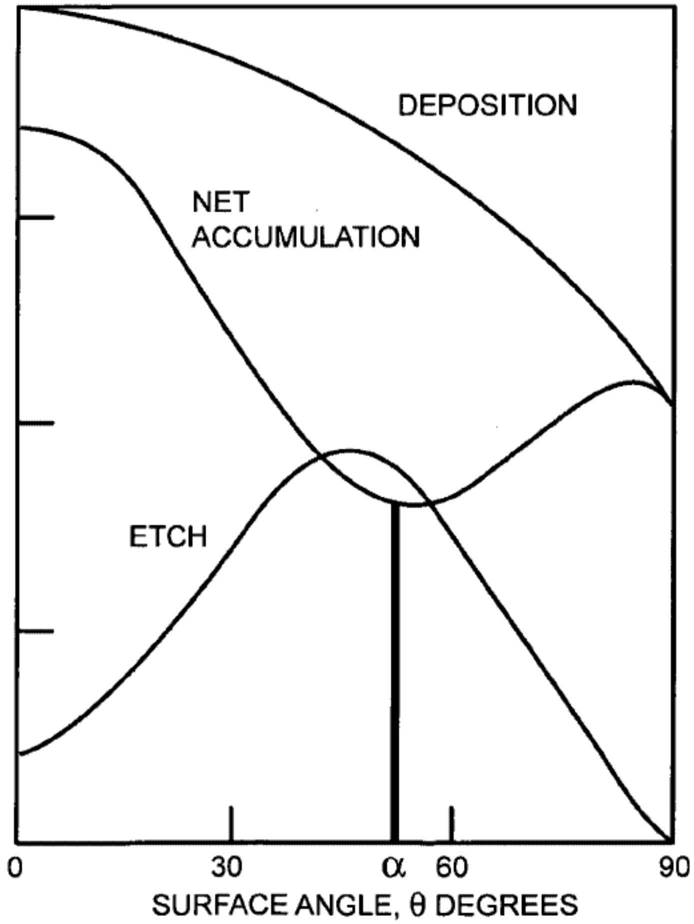

FIG. 20

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

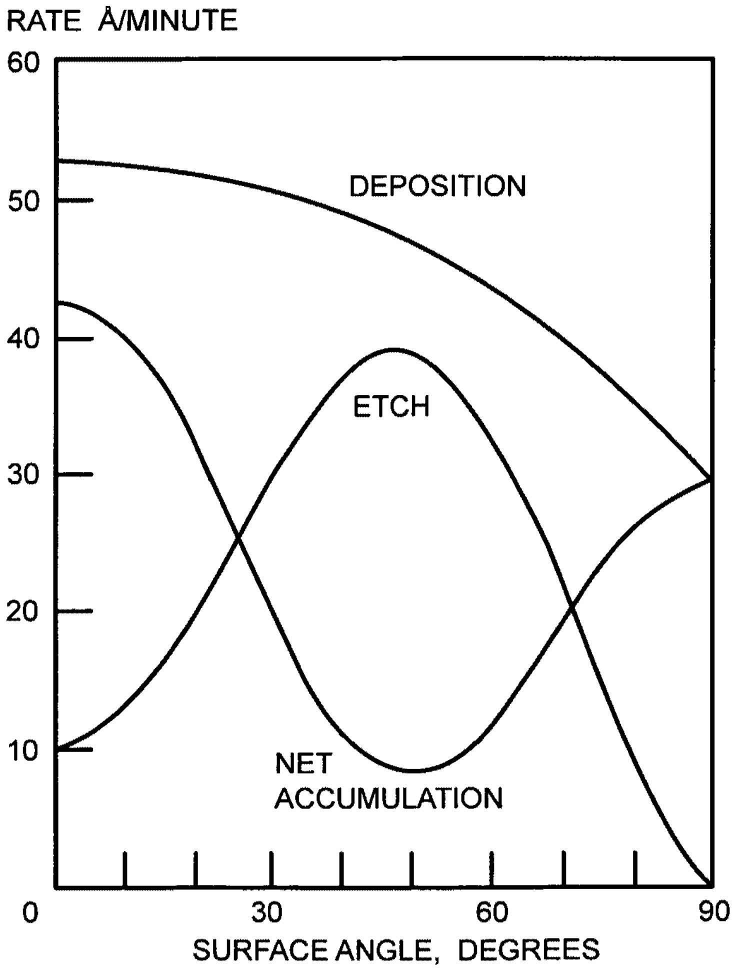

FIG. 21

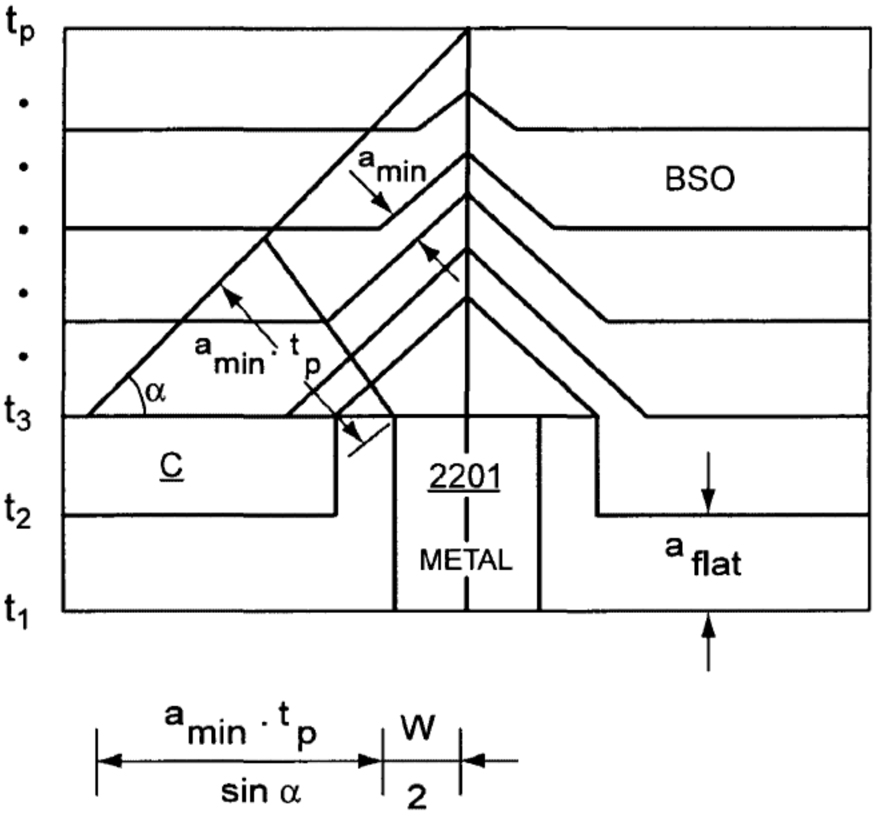
$t_p$
$t_3$
$t_2$
$t_1$
$a_{min}$
BSO
$a_{min} \cdot t_p$
α
C
2201
METAL
$a_{flat}$
$\frac{a_{min} \cdot t_p}{\sin \alpha}$
$\frac{W}{2}$

FIG. 22

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

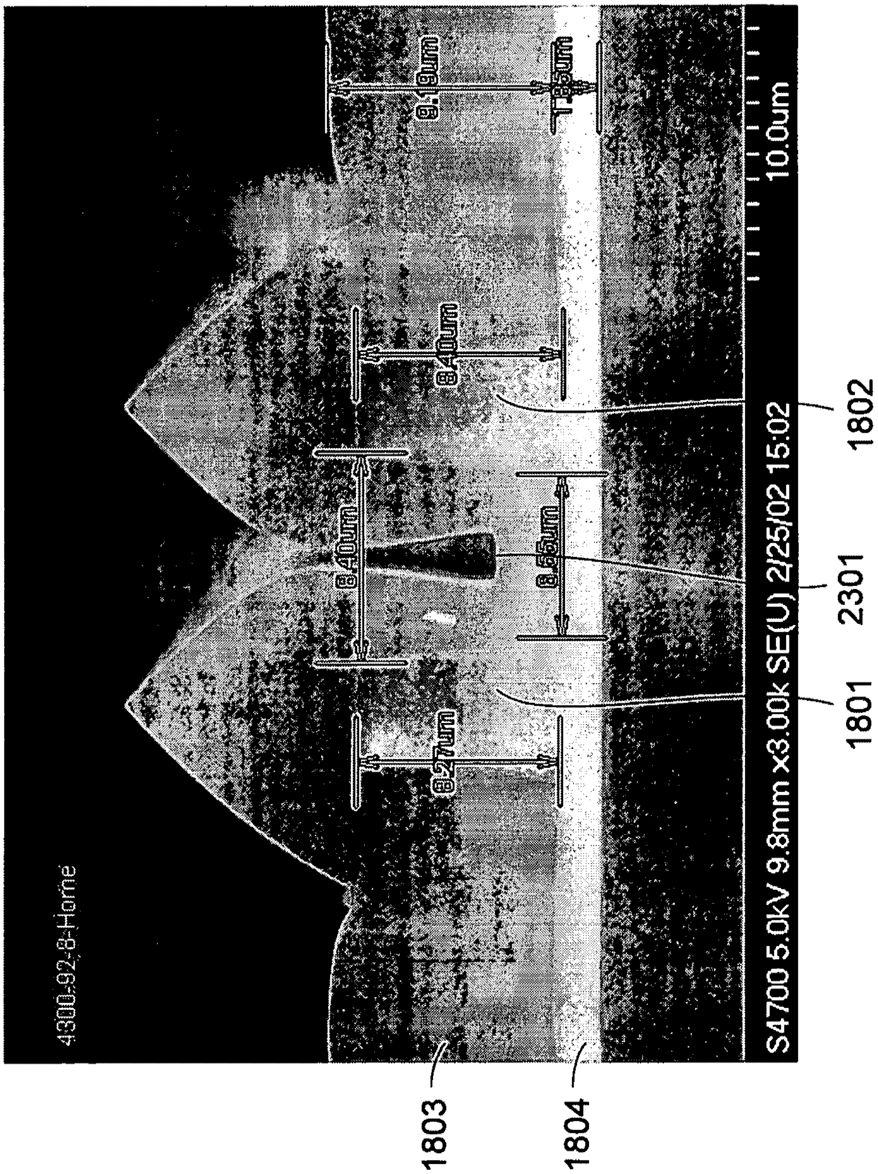

FIG. 23

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REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

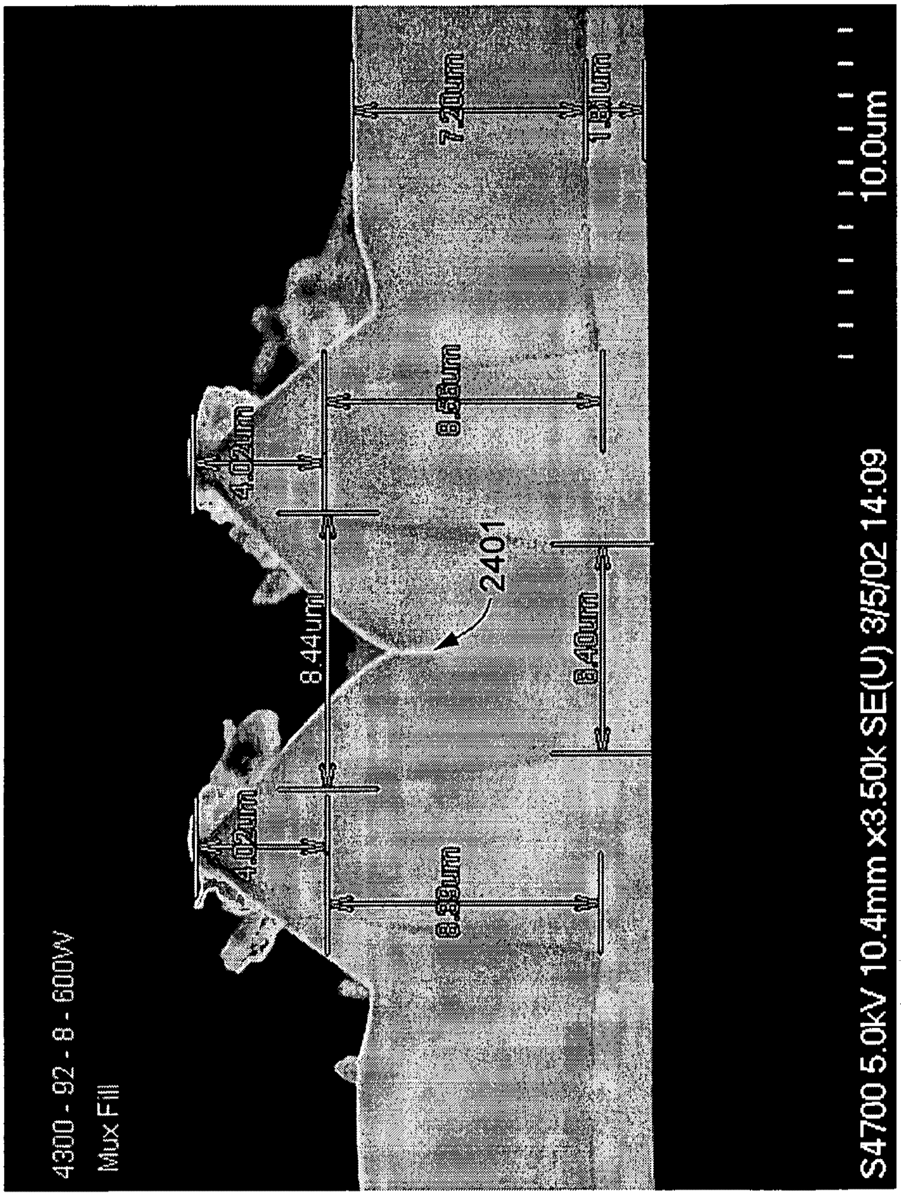

FIG. 24

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REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

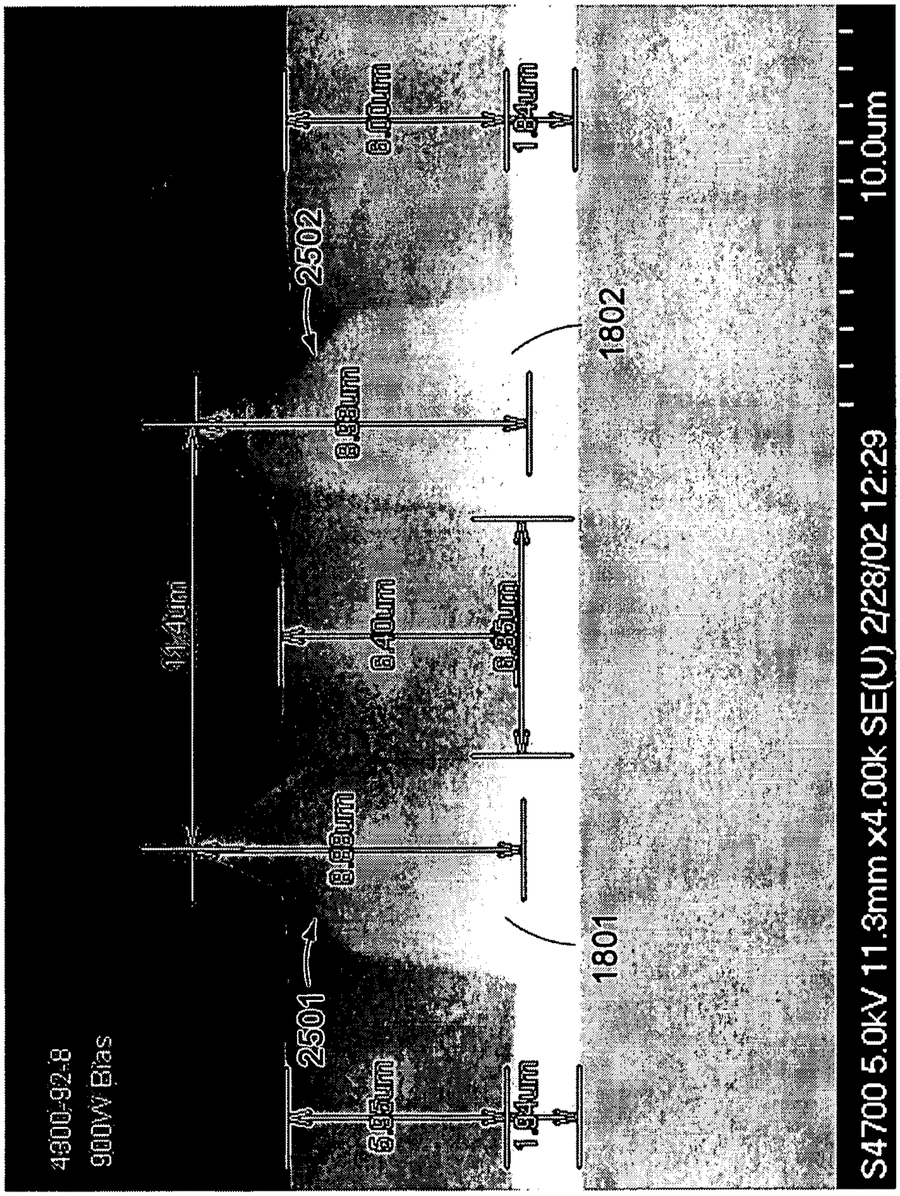

FIG. 25

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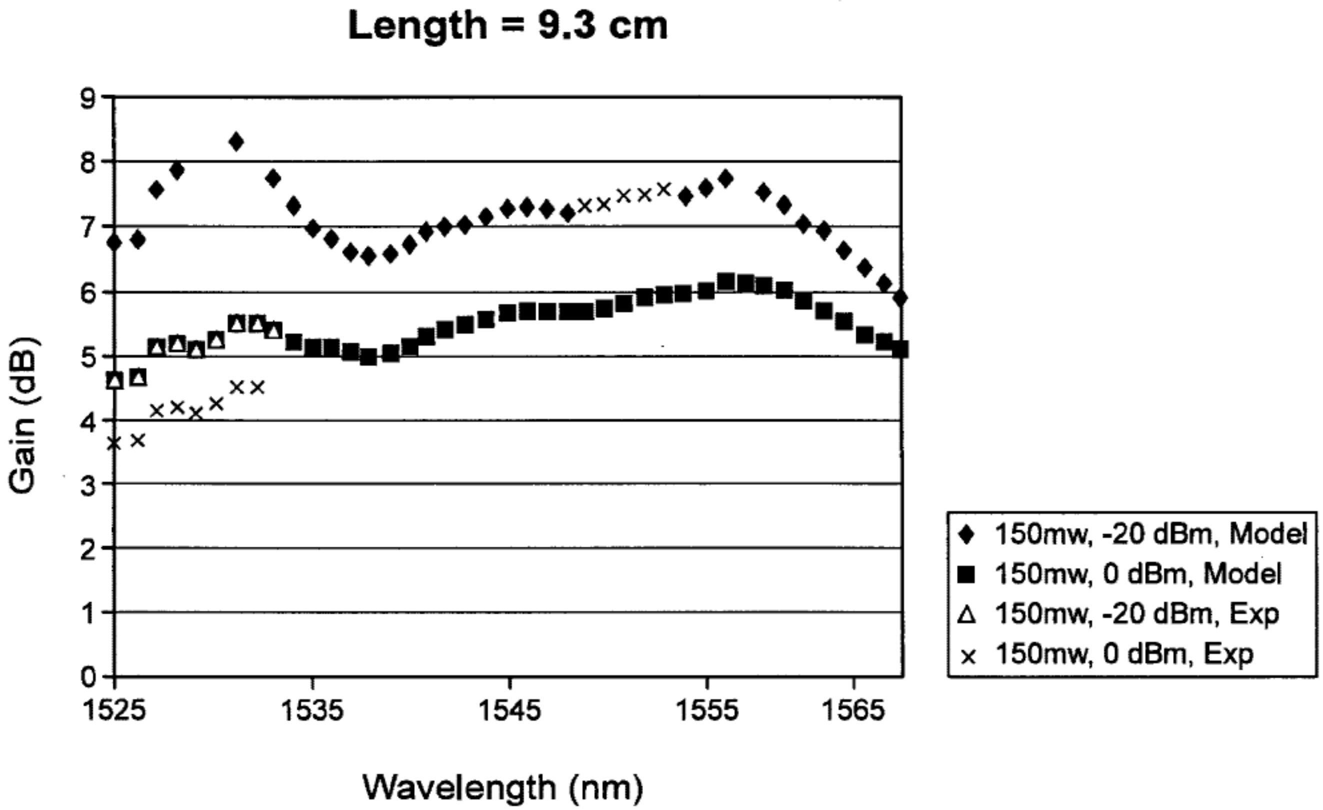
Length = 9.3 cm
Gain (dB)
9
8
7
6
5
4
3
2
1
0
1525
1535
1545
1555
1565
Wavelength (nm)
◆ 150mw, -20 dBm, Model
■ 150mw, 0 dBm, Model
△ 150mw, -20 dBm, Exp
× 150mw, 0 dBm, Exp

FIG. 26

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

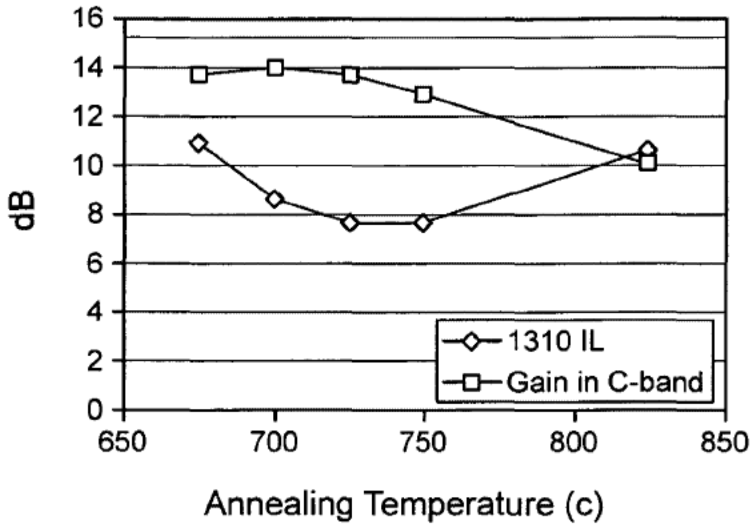

FIG. 27

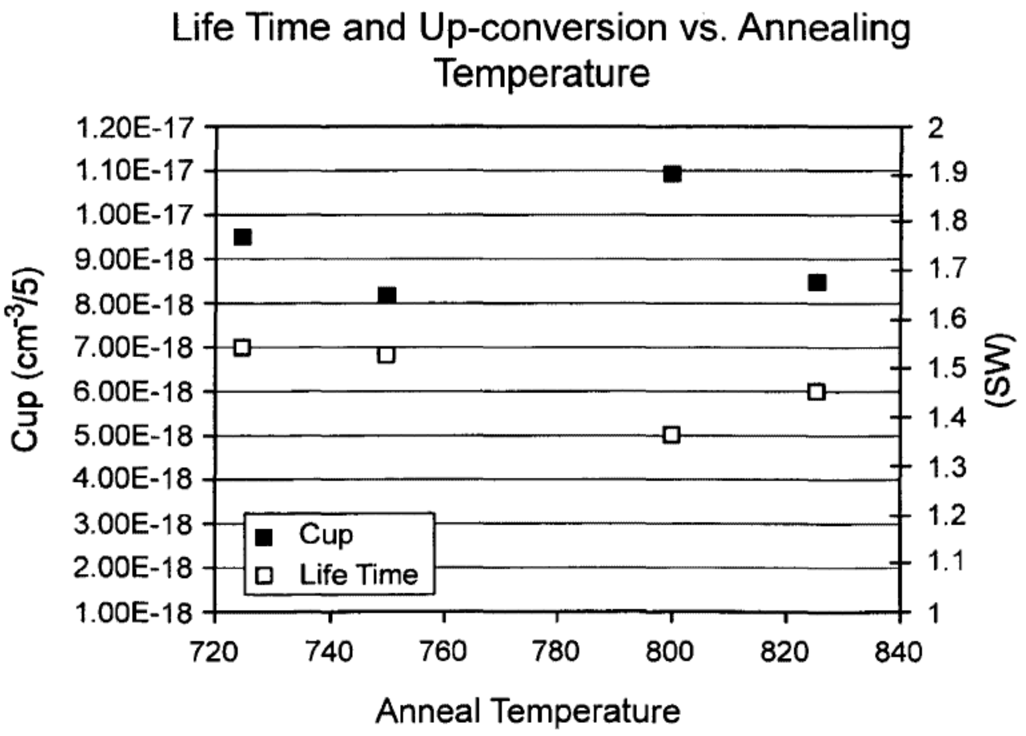

FIG. 28

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

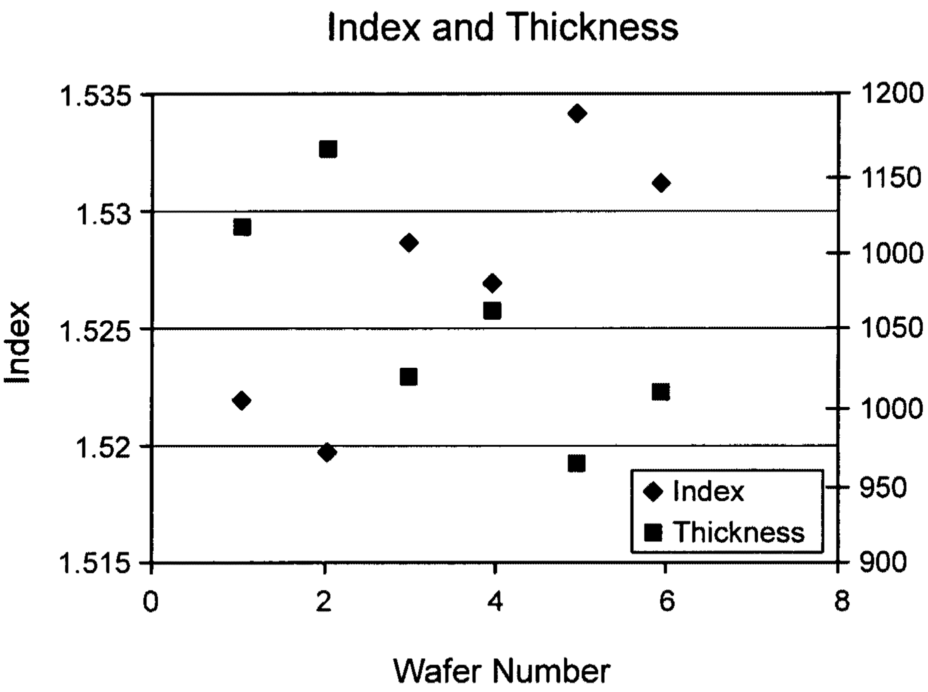

FIG. 29

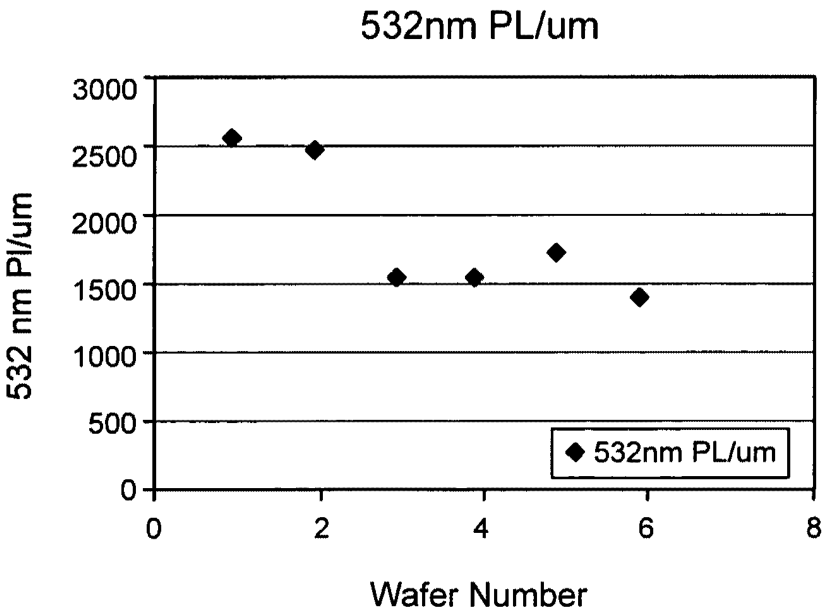

FIG. 30

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

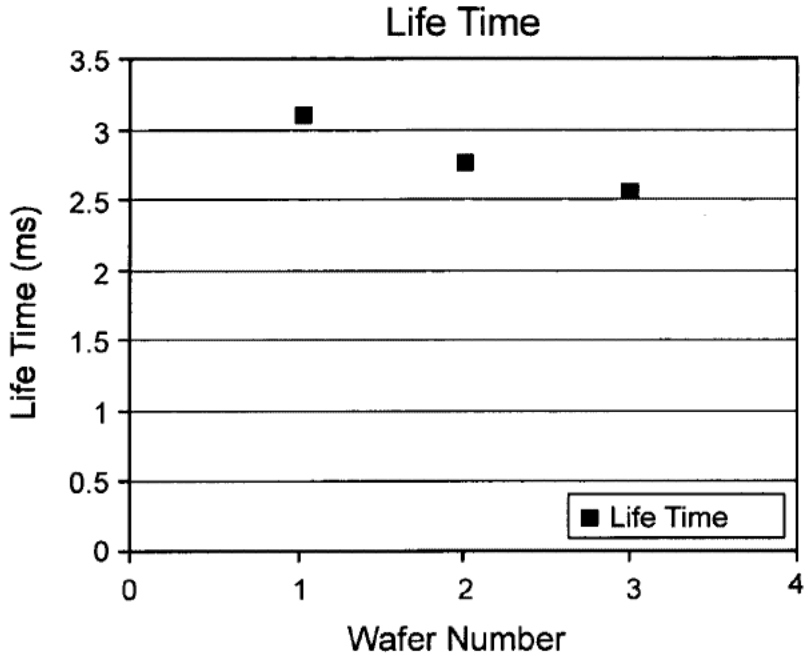

FIG. 31

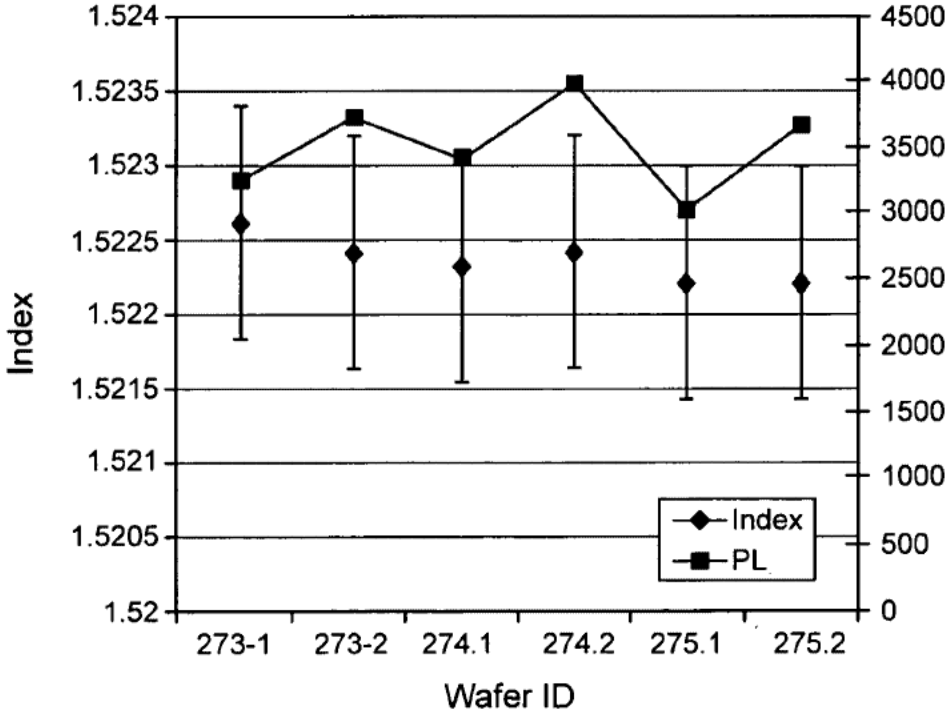

FIG. 32

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

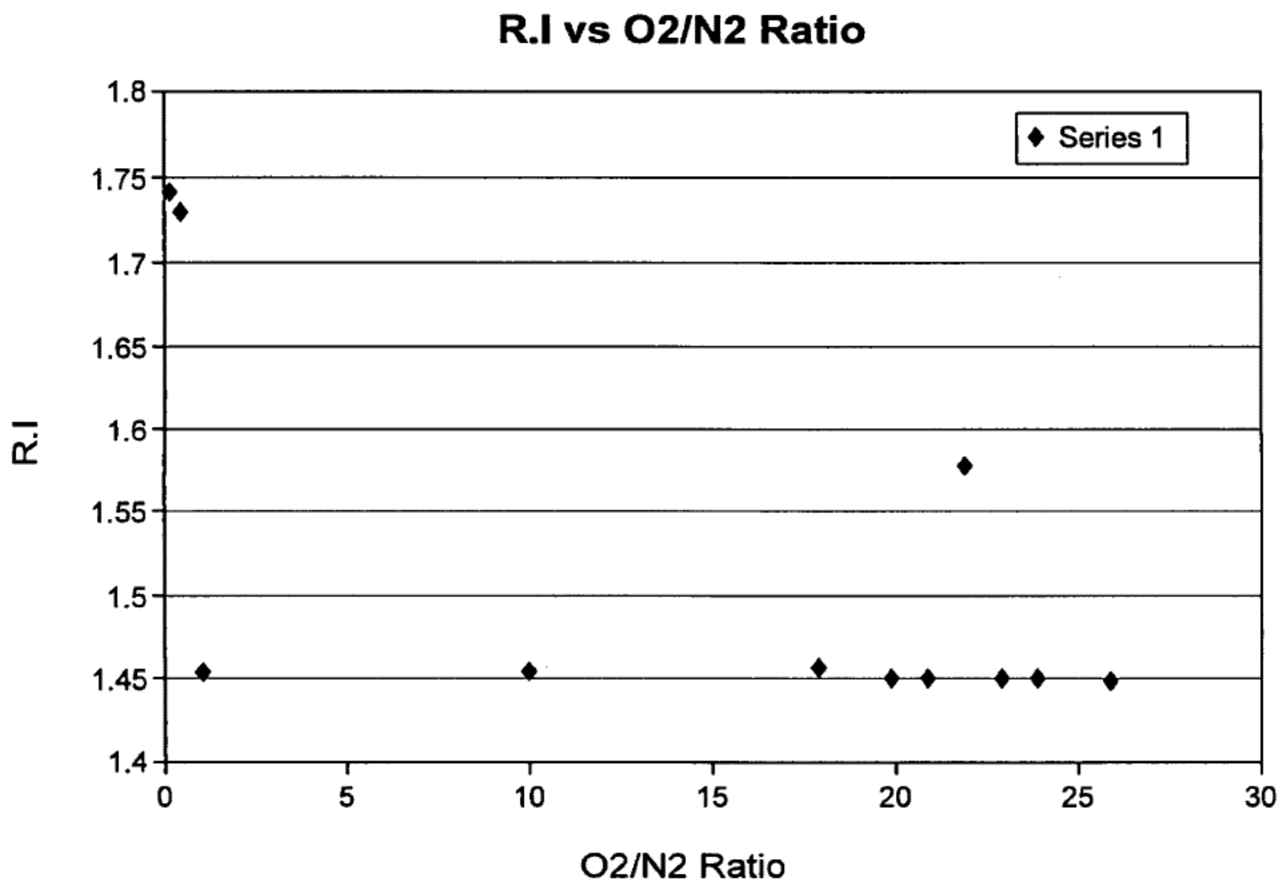

FIG. 33

OIPE IAP15
DEC 2 1 2005
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/954,182 ) Examiner: ESTRADA, Michelle
)
Filed: October 1, 2004 )
) Confirmation No.: 9873
For: BIASED PULSE DC REACTIVE )
SPUTTERING OF OXIDE FILMS )

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## THIRD 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.

12/28/2005 SSITHIB1 00000001 060916 10954182
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 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 21, 2005

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

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**EXPRESS MAIL NO. EV 758329240 US**

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| | | | |
|---|---|---|---|
| Sheet | 1 | of | 1 |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/954,182 |
| *Filing Date* | October 1, 2004 |
| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-01 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>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 2002/0076133 A1 | 06-20-2002 | Li et al. | |
| | | US 5,478,456 | 12-26-1995 | Humpal et al. | |
| | | US 6,846,765 B2 | 01-25-2005 | 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<br>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 4, 2005, in U.S. Application No. 10/101,863 (Attorney Docket No. 09140.0016-00). | |
| | | Office Action issued on August 8, 2005 in U.S. Application 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 March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00). | |
| | | Response to Office Action filed July 25, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00). | |
| | | Office Action issued on October 19, 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.

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

OIPE IAP15
DEC 2 1 2005
PATENT & TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/954,182 ) Examiner: ESTRADA, Michelle
)
Filed: October 1, 2004 )
) Confirmation No.: 9873
For: BIASED PULSE DC REACTIVE )
SPUTTERING OF OXIDE FILMS )

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SUBMISSION OF REPLACEMENT DRAWINGS

Subject to the approval of the Examiner, please replace the drawings in the above-identified application with the twenty-seven (27) sheets of drawings filed herewith (Figures 1A-1B, 2-15, 16A-16D, and 17-33). If the replacement drawings for any reason are not in full compliance with the pertinent statutes and regulations, please so advise the undersigned.

If any fees are necessary for the submission of these formal drawings, please charge our Deposit Account No. 06-0916.

Respectfully submitted,

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

Date: December 21, 2005

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

**EXPRESS MAIL LABEL NO.**
**EV 758329240 US**

# PATENT APPLICATION FEE DETERMINATION RECORD
Effective December 8, 2004

10/954182

## 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 | | ☐ |

* 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 | 150.00 | OR | BASIC FEE | 300.00 |
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |
| TOTAL | | OR | TOTAL | |

## CLAIMS AS AMENDED - PART II

### AMENDMENT A

| 12-21-05 | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA |
|---|---|---|---|---|
| Total | * 31 | Minus | ** 61 | = |
| Independent | * 4 | Minus | *** 9 | = |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM | | | | ☐ |

SMALL ENTITY OR OTHER THAN SMALL ENTITY

| RATE | ADDITIONAL FEE | | RATE | ADDITIONAL FEE |
|---|---|---|---|---|
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |
| 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 | | 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 | | RATE | ADDITIONAL FEE |
|---|---|---|---|---|
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |

**CLAIMS ONLY**

Application Number 10954182

Filing Date

Applicant(s)

* May be used for additional claims or amendments

| CLAIMS | AS FILED Indep | AS FILED Depend | AFTER FIRST AMENDMENT Indep | AFTER FIRST AMENDMENT Depend | AFTER SECOND AMENDMENT Indep | AFTER SECOND AMENDMENT Depend |
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| 43 | | | | ① | | ① |
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| 46 | | | | ① | | ① |
| 47 | | | | ① | | ① |
| 48 | | | | ① | | ① |
| 49 | | | | ① | | ① |
| 50 | | | | ① | | ① |
| Total Indep | | | | | | |
| Total Depend | | | | | | |
| Total Claims | | | | | | |

| | * Indep | * Depend | * Indep | * Depend | * Indep | * Depend |
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| 51 | | | | ① | | ① |
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| 53 | | | | ① | | ① |
| 54 | | | | ① | | ① |
| 55 | | | | ① | | ① |
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| 57 | | | | ① | | ① |
| 58 | | | | ① | | ① |
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| 100 | | | | | | |
| Total Indep | | | 9 | | 4 | |
| Total Depend | | | 52 | | 27 | |
| Total Claims | | | 61 | | 31 | |

03-06-06

IFW

OIPE IAP69
MAR 0 2 2006
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | ) |
| | ) |
| ZHANG, Hongmei et al. | ) Group Art Unit: 2823 |
| | ) |
| Application No.: 10/954,182 | ) Examiner: ESTRADA, Michelle |
| | ) |
| Filed: October 1, 2004 | ) |
| | ) Confirmation No.: 9873 |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | ) ) |

**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.

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: March 2, 2006

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

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PATENT & TRADEMARK OFFICE

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 3 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/954,182 |
| *Filing Date* | October 1, 2004 |
| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-01 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>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 5,909,346 | 06-01-1999 | Malhotra et al. | |
| | | US 5,930,046 | 07-27-1999 | Solberg et al. | |
| | | US 6,000,603 | 12-14-1999 | Koskenmaki et al. | |
| | | US 6,133,670 | 10-17-2000 | Rodgers et al. | |
| | | US 6,242,129 B1 | 06-05-2001 | Johnson | |
| | | US 6,280,875 B1 | 08-28-2001 | Kwak et al. | |
| | | US 6,290,821 B1 | 09-18-2001 | McLeod | |
| | | US 6,356,694 B1 | 03-12-2002 | Weber | |
| | | US 6,376,027 B1 | 04-23-2002 | Lee et al. | |
| | | US 6,632,563 B1 | 10-14-2003 | Krasnov et al. | |
| | | US 6,768,855 B1 | 07-27-2004 | Bakke et al. | |
| | | US 6,683,244 B2 | 01-27-2004 | Fujimori et al. | |
| | | US 6,683,749 B2 | 01-27-2004 | Daby 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. | |

**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<br>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 | Translation[6] |
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| 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.

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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*** | |
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(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.

# 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/80$O_2$ | 244 | 252 | 5.94 | 6.14 |
| 15 | 1.5kw/100w/200khz/2.2µs/300s/20Ar/40$O_2$ | 254 | 263 | 5.7 | 5.9 |
| 17 | 1.5kw/100w/200khz/2.2µs/300s/20Ar/40$O_2$ | 252 | 260 | 5.76 | 5.96 |
| 19 | 1.5kw/100w/200khz/2.2µs/300s/20Ar/36$O_2$ | 254 | 263 | 5.72 | 5.92 |
| 21 | 1.5kw/100w/200khz/2.2µs/300s/20Ar/30$O_2$ | 255 | 268 | 5.76 | 5.9 |
| 1 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 80$O_2$ | 224 | 233 | 4.32 | 4.5 |
| 2 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 36$O_2$ | 231 | 243 | 4.12 | 4.3 |
| 3 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 32$O_2$ | 232 | 242 | 4.12 | 4.28 |
| 4 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 28$O_2$ | 237 | 243 | 4.1 | 4.22 |
| 5 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 24$O_2$ | 233 | 243 | 4.1 | 4.34 |
| 6 | 1kw/100w/200khz/2.2µs/300s/20Ar/ 28$O_2$ | 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.

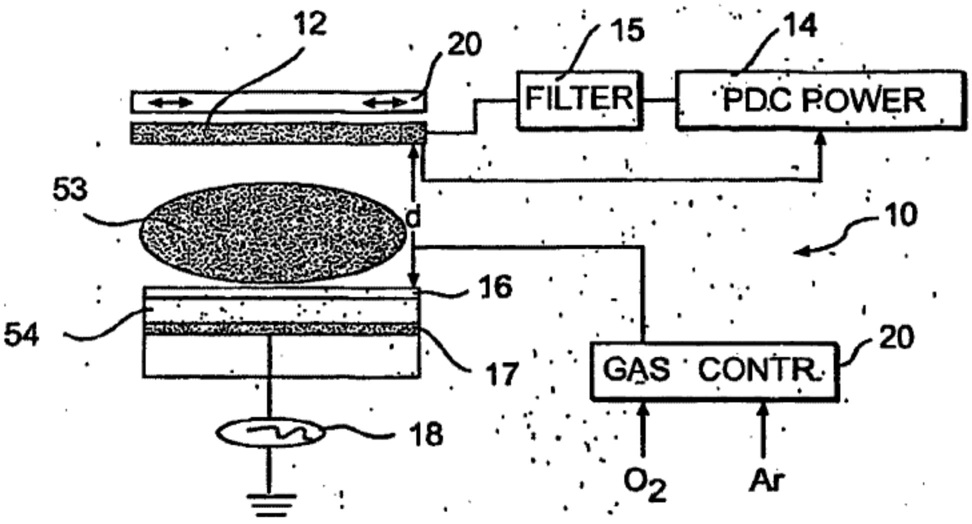

12
20
15
FILTER
14
PDC POWER
53
d
10
16
54
17
GAS CONTR.
20
18
O2
Ar

FIG. 1A

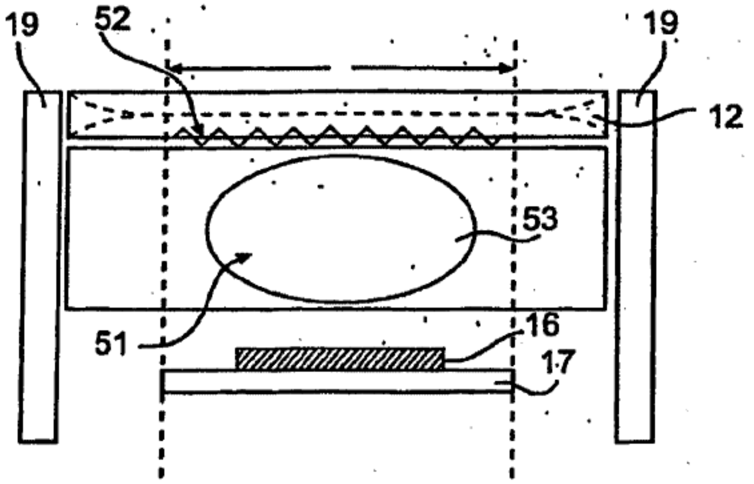

19
52
19
12
53
51
16
17

FIG. 1B

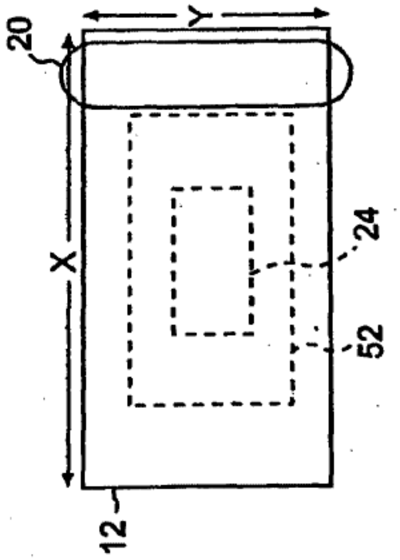
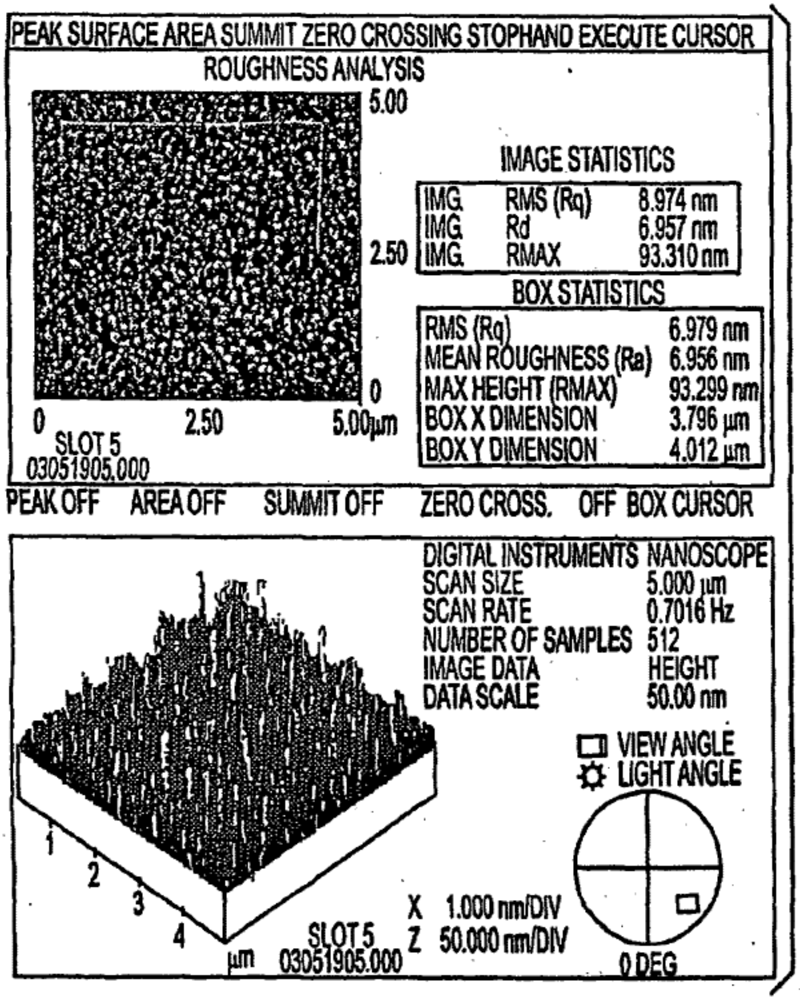


FIG. 2



SLOT 5
03051905.000

IMAGE STATISTICS

| | | |
|---|---|---|
| IMG | RMS (Rq) | 8.974 nm |
| IMG | Rd | 6.957 nm |
| IMG | RMAX | 93.310 nm |

BOX STATISTICS

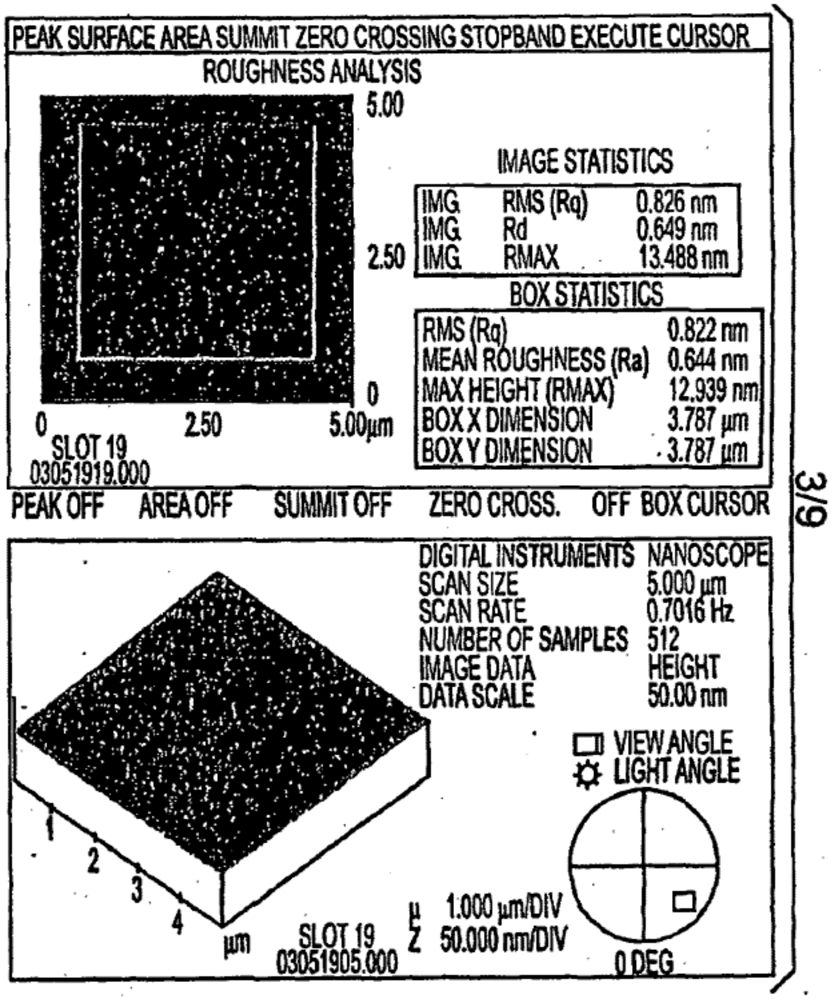
| | |
|---|---|
| RMS (Rq) | 6.979 nm |
| MEAN ROUGHNESS (Ra) | 6.956 nm |
| MAX HEIGHT (RMAX) | 93.299 nm |
| BOX X DIMENSION | 3.796 µm |
| BOX Y DIMENSION | 4.012 µm |

| | |
|---|---|
| DIGITAL INSTRUMENTS | NANOSCOPE |
| SCAN SIZE | 5.000 µm |
| SCAN RATE | 0.7016 Hz |
| NUMBER OF SAMPLES | 512 |
| IMAGE DATA | HEIGHT |
| DATA SCALE | 50.00 nm |

SLOT 5
03051905.000

X 1.000 nm/DIV
Z 50.000 nm/DIV

FIG. 3A



SLOT 19
03051919.000

IMAGE STATISTICS

| | | |
|---|---|---|
| IMG | RMS (Rq) | 0.826 nm |
| IMG | Rd | 0.649 nm |
| IMG | RMAX | 13.488 nm |

BOX STATISTICS

| | |
|---|---|
| RMS (Rq) | 0.822 nm |
| MEAN ROUGHNESS (Ra) | 0.644 nm |
| MAX HEIGHT (RMAX) | 12.939 nm |
| BOX X DIMENSION | 3.787 µm |
| BOX Y DIMENSION | 3.787 µm |

| | |
|---|---|
| DIGITAL INSTRUMENTS | NANOSCOPE |
| SCAN SIZE | 5.000 µm |
| SCAN RATE | 0.7016 Hz |
| NUMBER OF SAMPLES | 512 |
| IMAGE DATA | HEIGHT |
| DATA SCALE | 50.00 nm |

SLOT 19
03051905.000

µ 1.000 µm/DIV
Z 50.000 nm/DIV

FIG. 3B

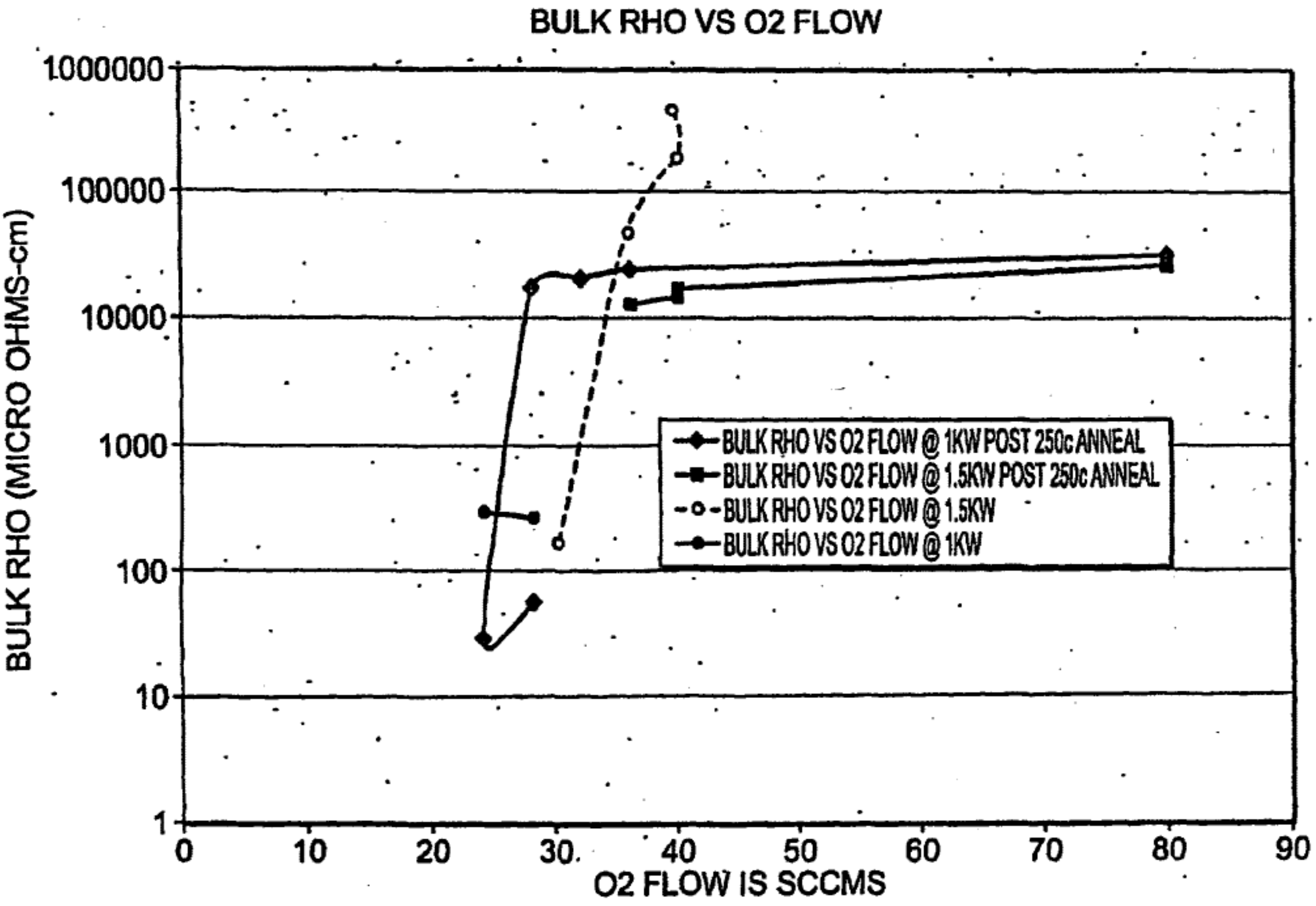

BULK RHO VS O2 FLOW
BULK RHO (MICRO OHMS-cm)
1000000
100000
10000
1000
100
10
1
0
10
20
30
40
50
60
70
80
90
O2 FLOW IS SCCMS
BULK RHO VS O2 FLOW @ 1KW POST 250c ANNEAL
BULK RHO VS O2 FLOW @ 1.5KW POST 250c ANNEAL
BULK RHO VS O2 FLOW @ 1.5KW
BULK RHO VS O2 FLOW @ 1KW

FIG. 4

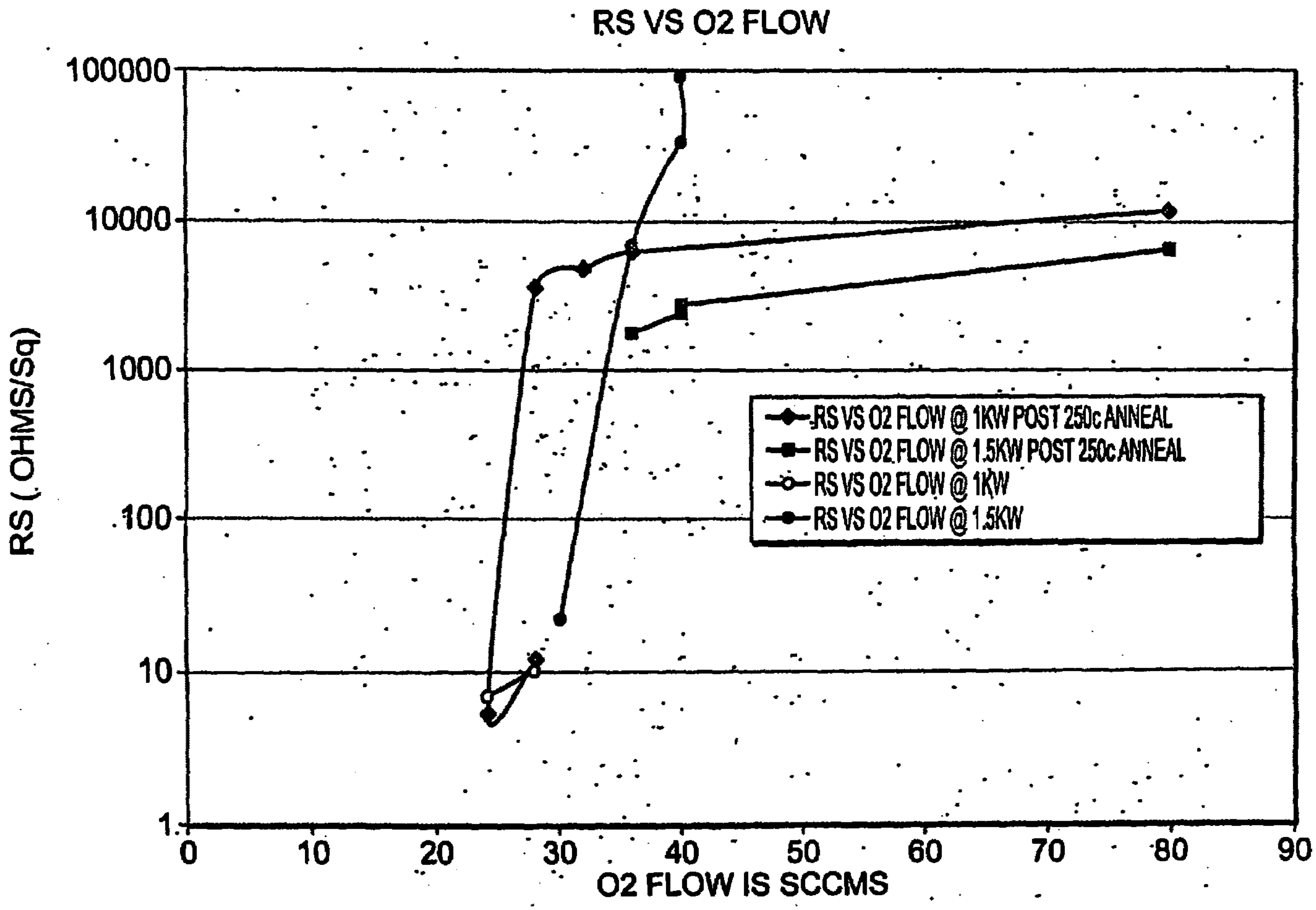

RS VS O2 FLOW
RS ( OHMS/Sq)
100000
10000
1000
100
10
1
0
10
20
30
40
50
60
70
80
90
O2 FLOW IS SCCMS
RS VS O2 FLOW @ 1KW POST 250c ANNEAL
RS VS O2 FLOW @ 1.5KW POST 250c ANNEAL
RS VS O2 FLOW @ 1KW
RS VS O2 FLOW @ 1.5KW

FIG. 5

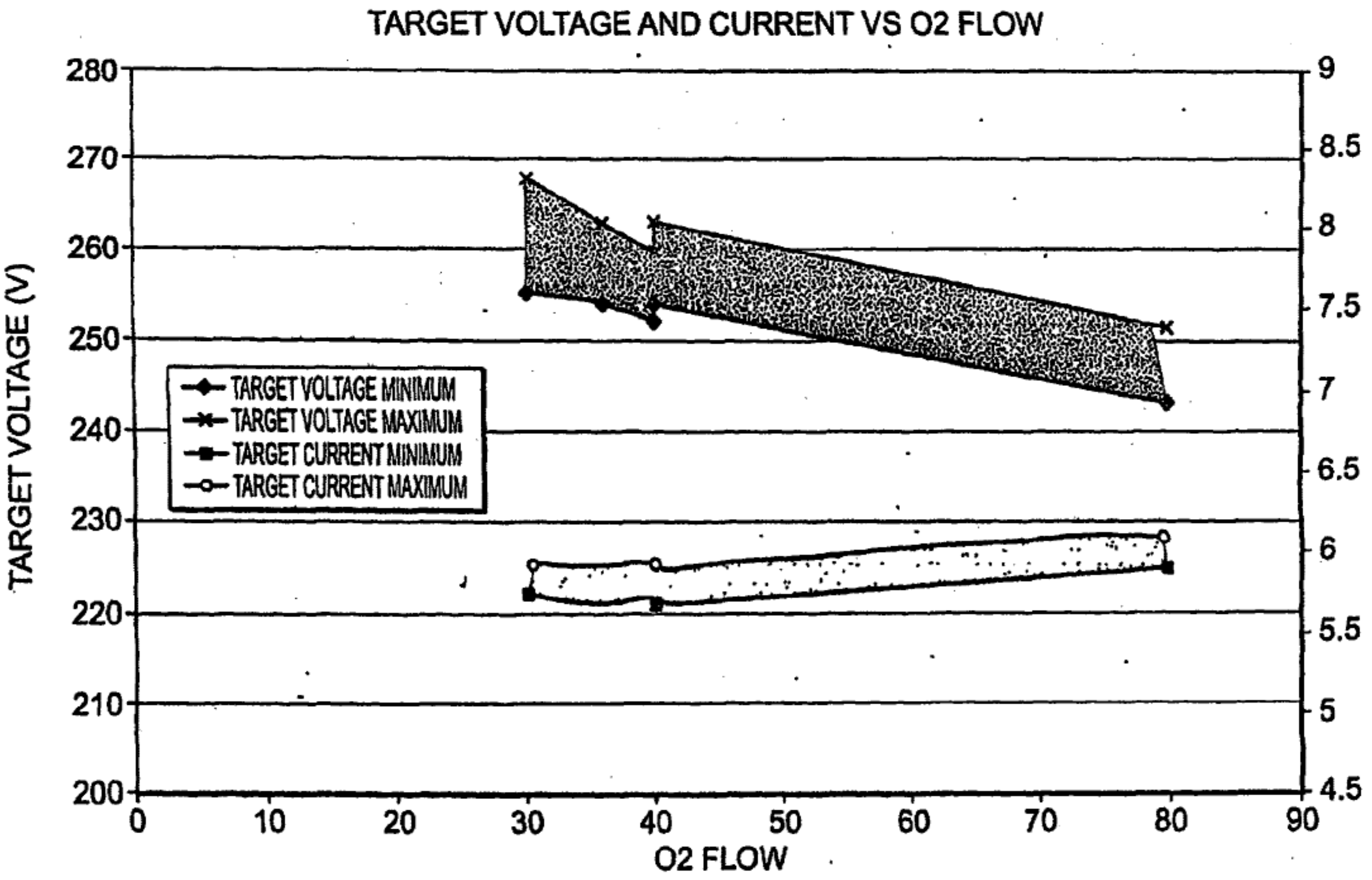

TARGET VOLTAGE AND CURRENT VS O2 FLOW
TARGET VOLTAGE (V)
280
270
260
250
240
230
220
210
200
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
0
10
20
30
40
50
60
70
80
90
O2 FLOW
TARGET VOLTAGE MINIMUM
TARGET VOLTAGE MAXIMUM
TARGET CURRENT MINIMUM
TARGET CURRENT MAXIMUM

FIG. 6

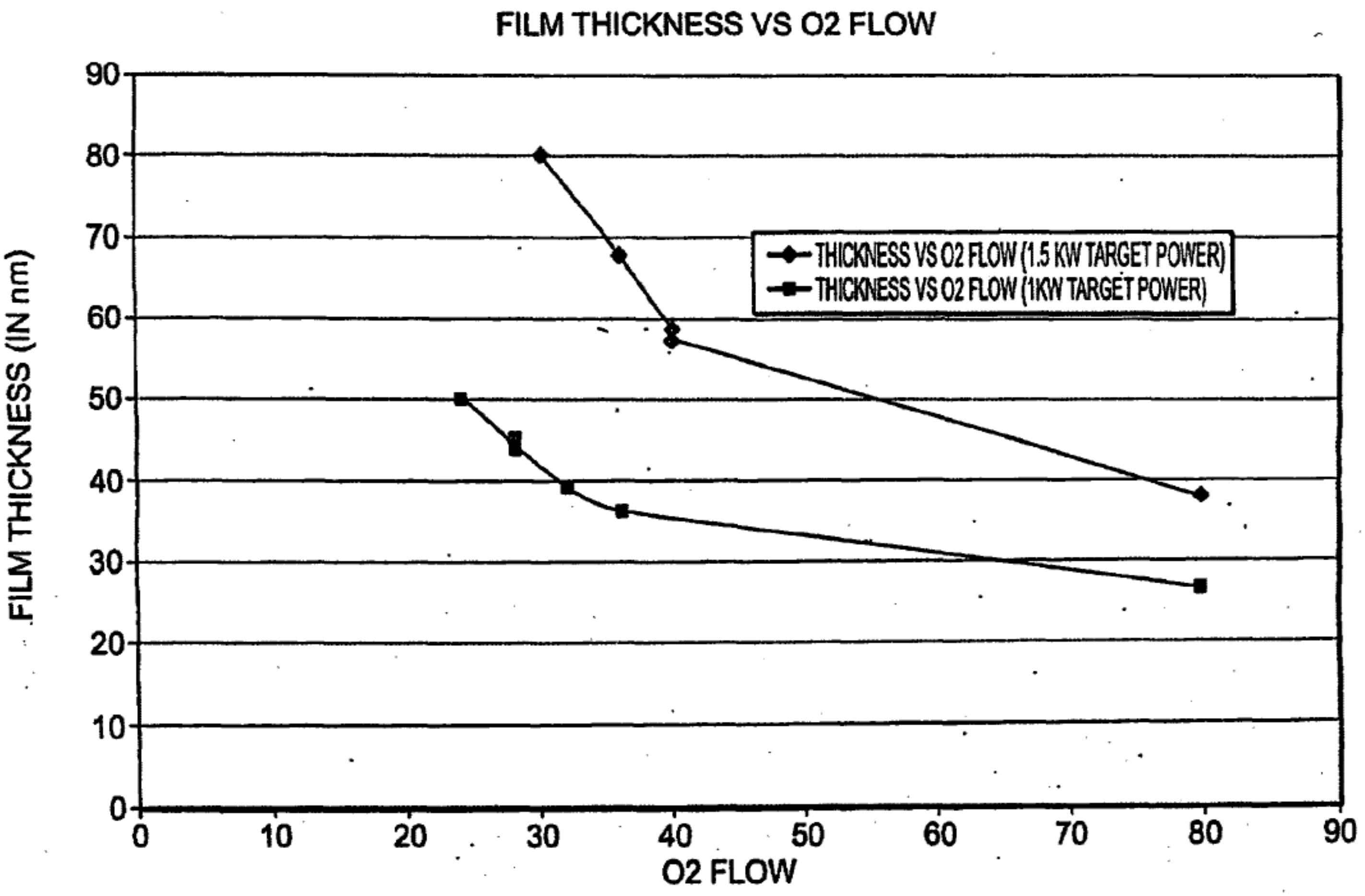

FILM THICKNESS VS O2 FLOW
FILM THICKNESS (IN nm)
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
O2 FLOW
THICKNESS VS O2 FLOW (1.5 KW TARGET POWER)
THICKNESS VS O2 FLOW (1KW TARGET POWER)

FIG. 7

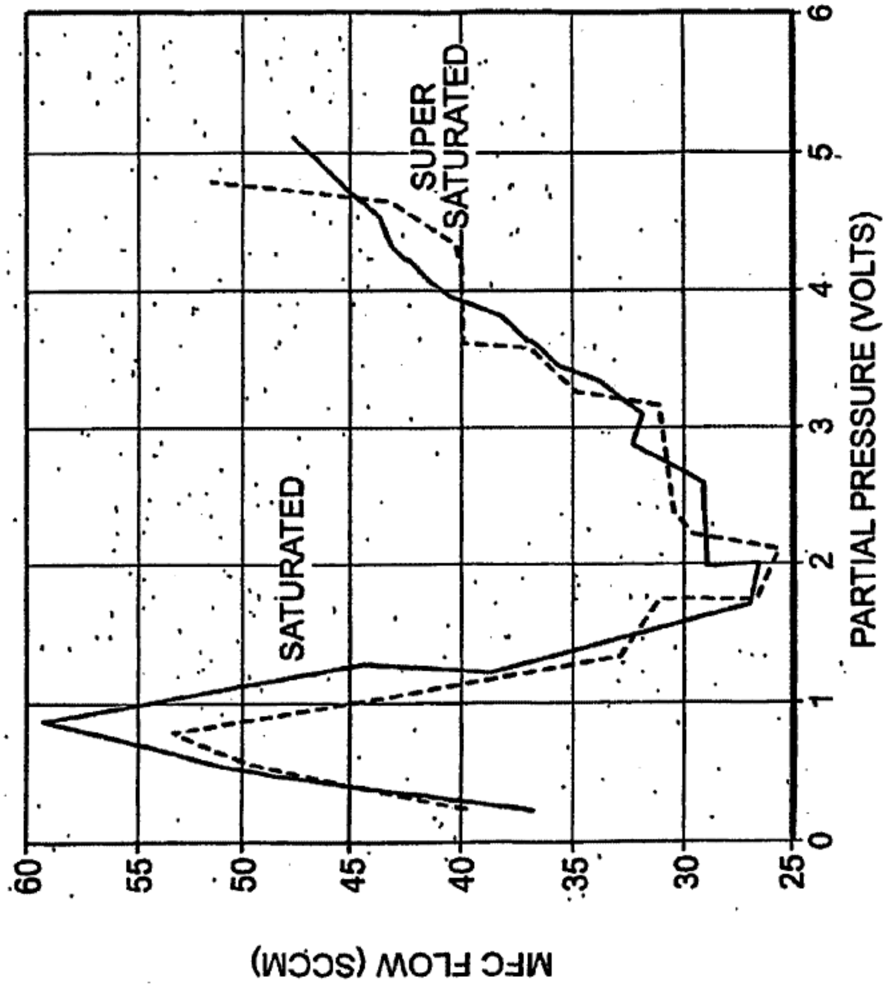

SUPER SATURATED
SATURATED
MFC FLOW (SCCM)
60
55
50
45
40
35
30
25
PARTIAL PRESSURE (VOLTS)
0
1
2
3
4
5
6

FIG. 8

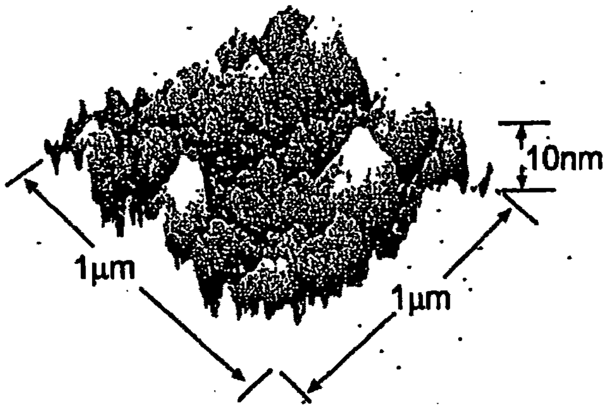


FIG. 9A

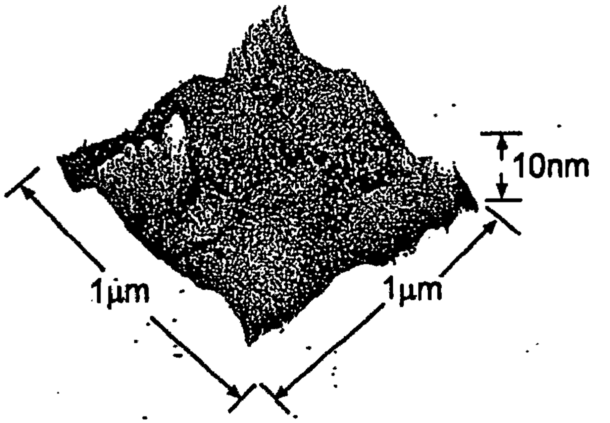


FIG. 9B

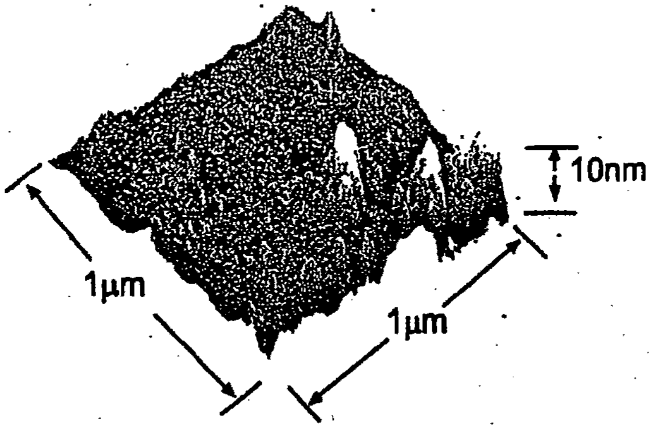


FIG. 9C

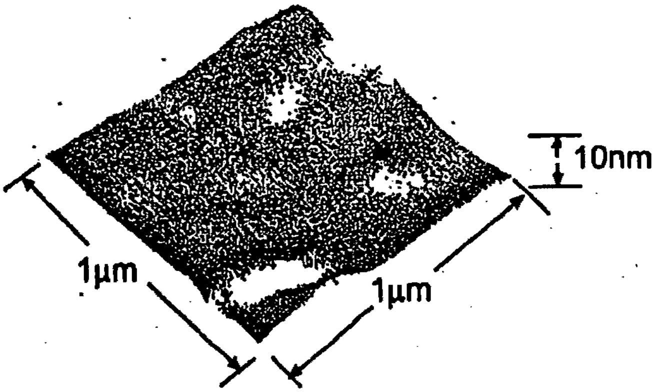


FIG. 9D

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(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).

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(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.

# 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;

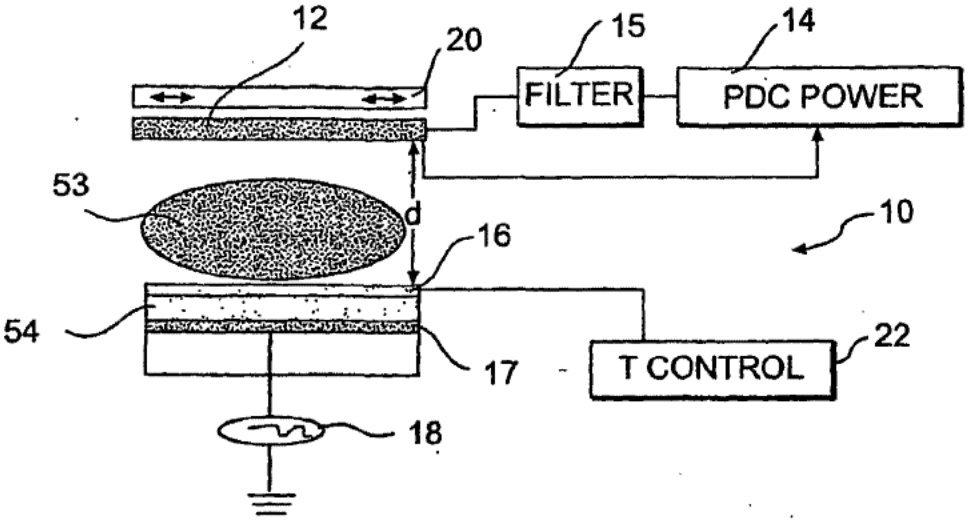
mixing the TiO powder to form a mix;

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.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T CONTROL
18

FIG. 1A

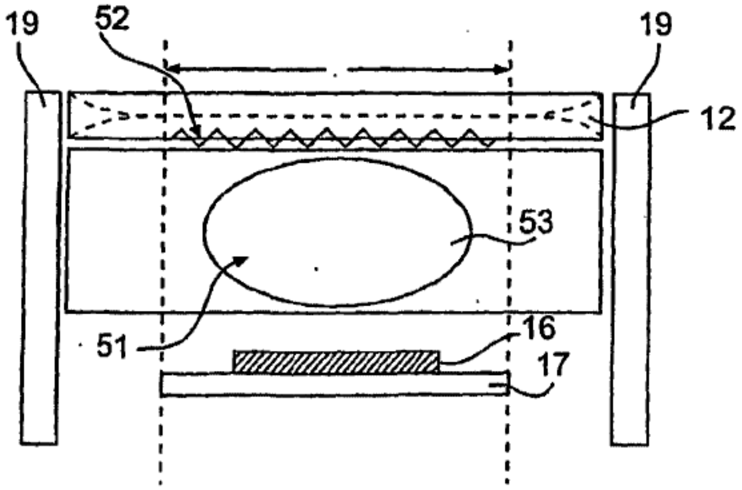
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FIG. 1B

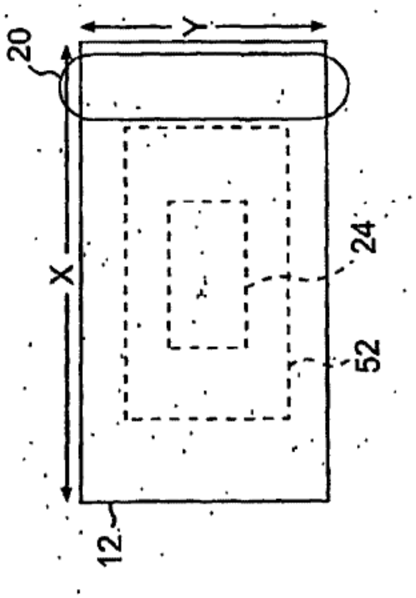


FIG. 2

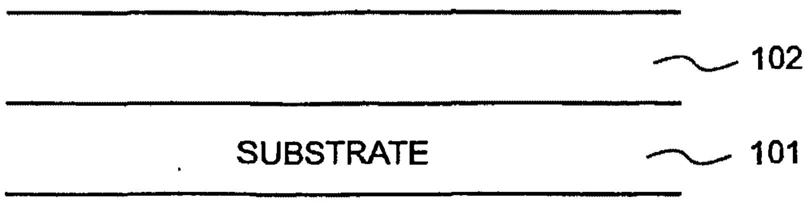


FIG. 3A

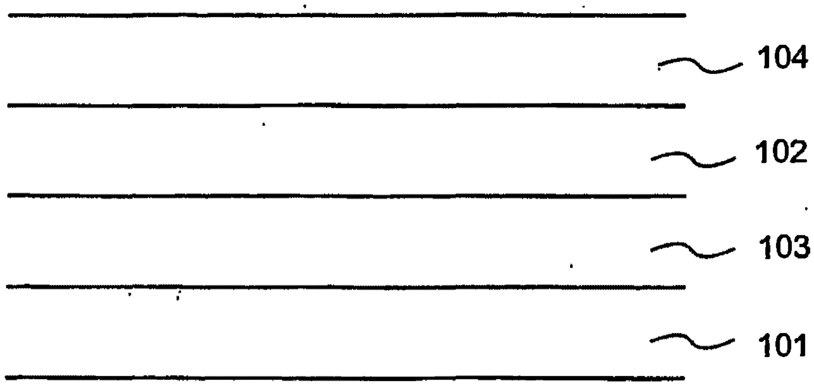


FIG. 3B

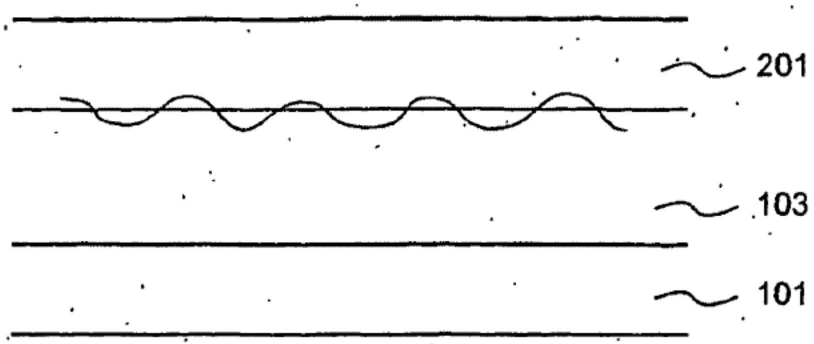


FIG. 4A

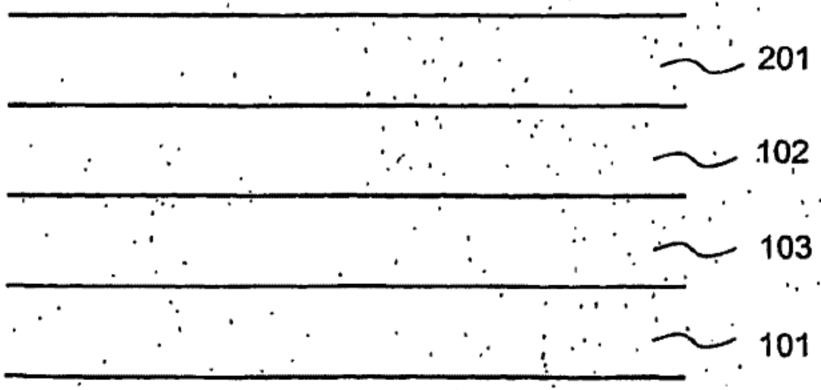


FIG. 4B

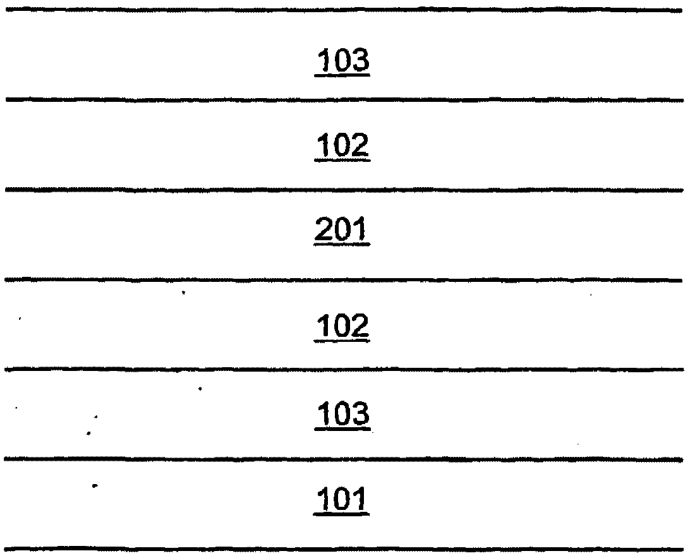


FIG. 5

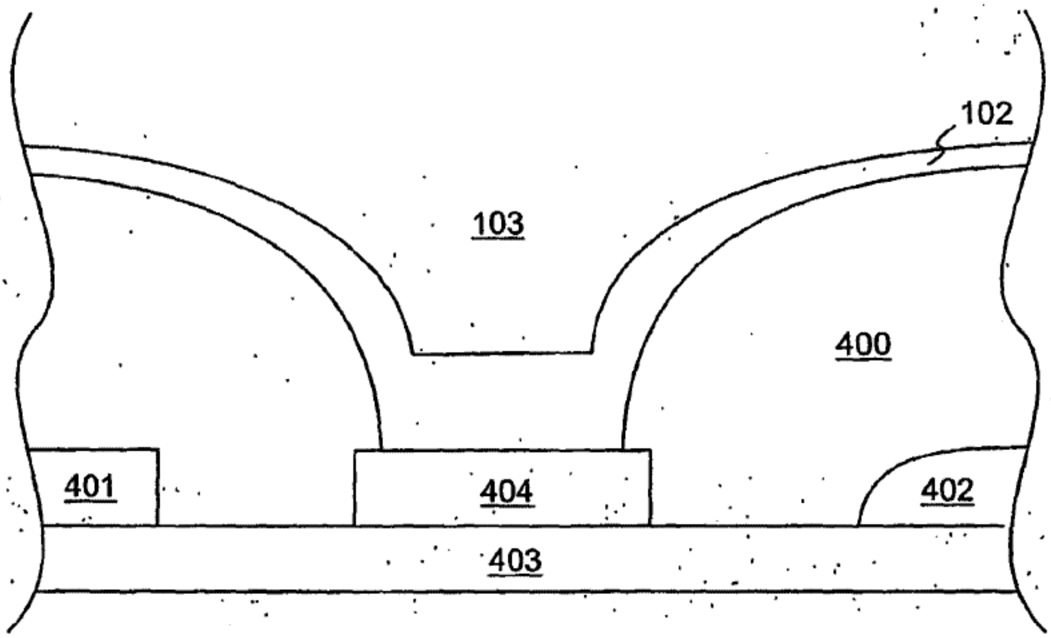


FIG. 6

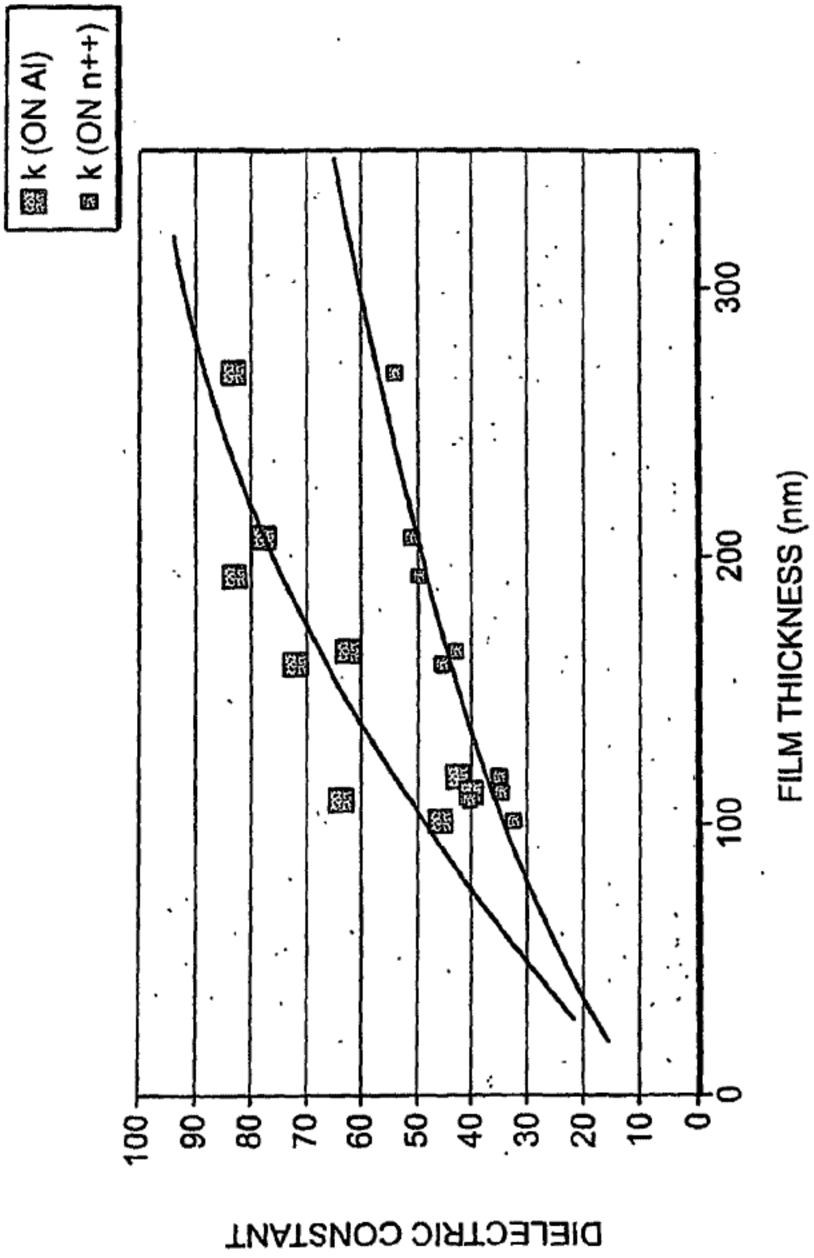
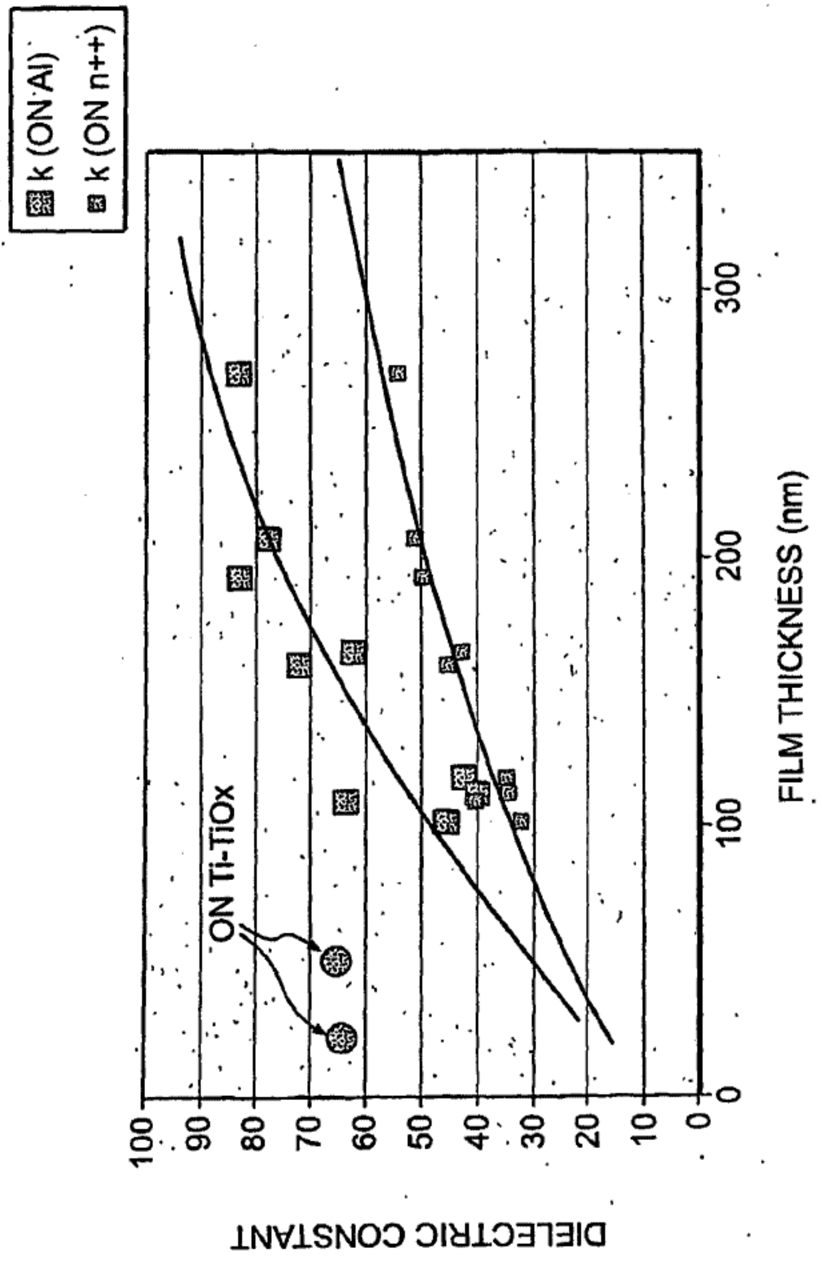

▨ k (ON Al)
▨ k (ON n++)
DIELECTRIC CONSTANT
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
FILM THICKNESS (nm)

*FIG. 7*

7


▨ k (ON Al)
▨ k (ON n++)
ON Ti-TiOx
DIELECTRIC CONSTANT
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20
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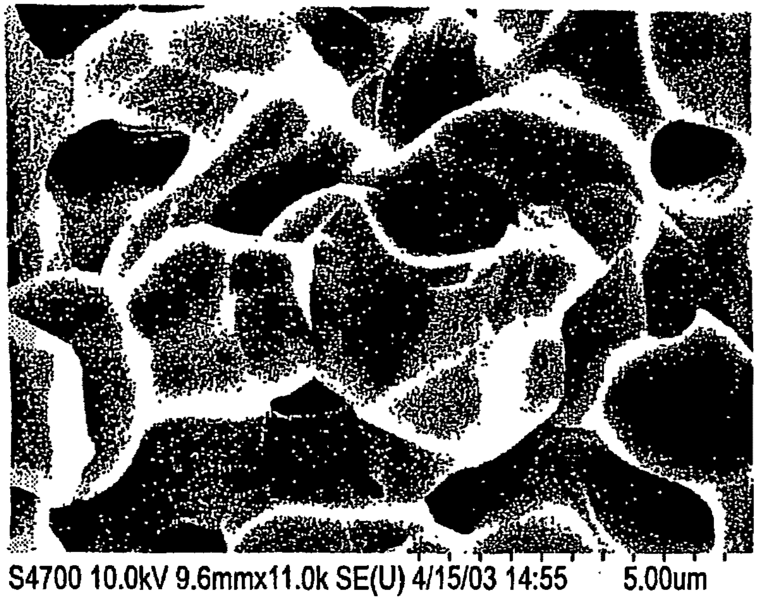
0
0
100
200
300
FILM THICKNESS (nm)

FIG. 8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5.00um

FIG. 9A

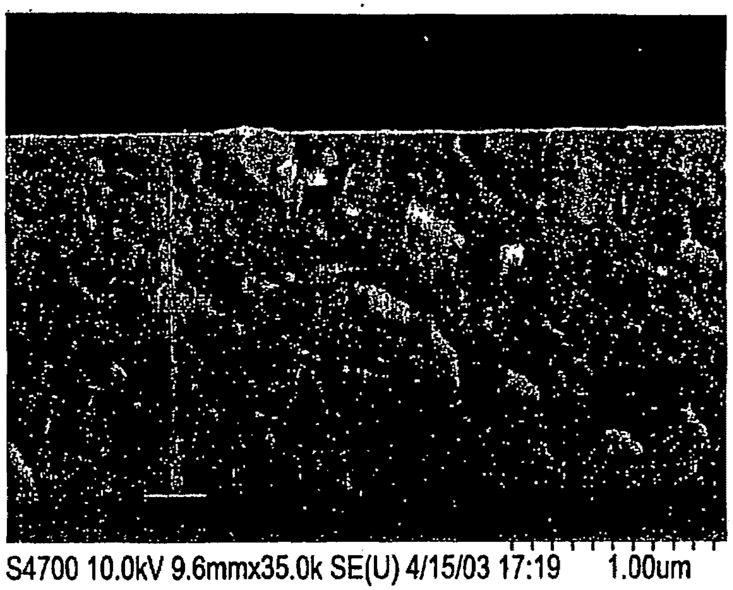
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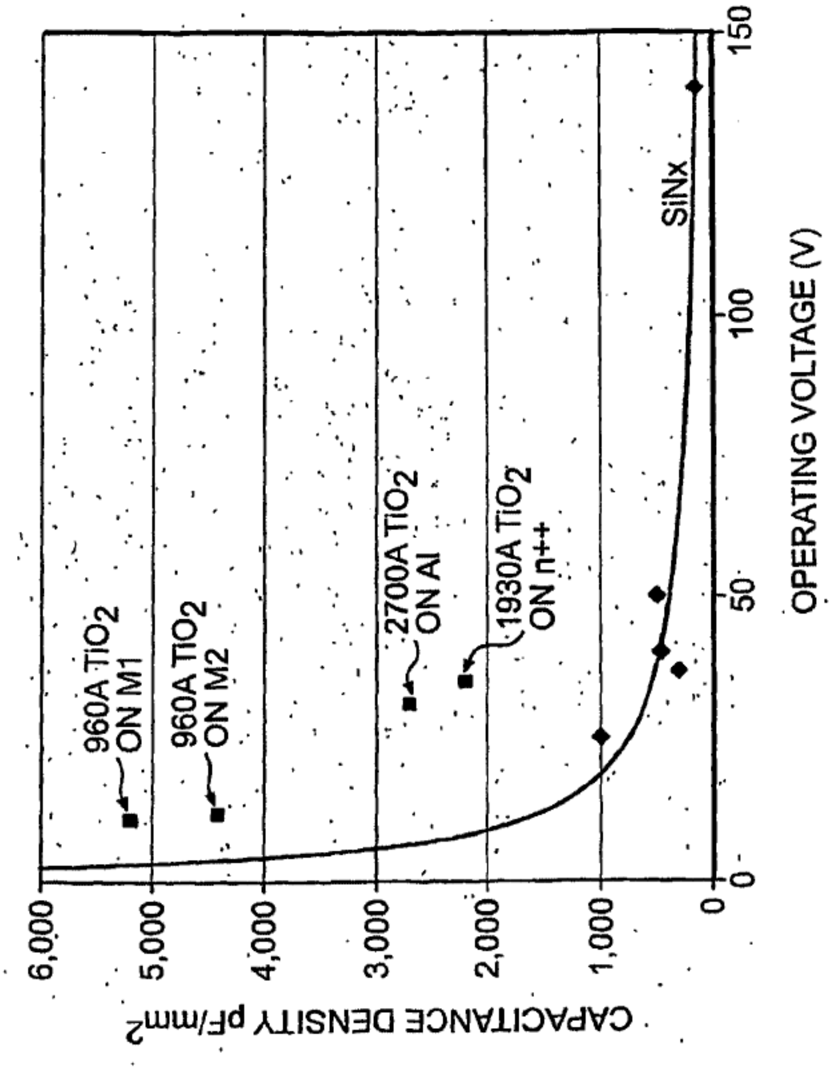
FIG. 9B



CAPACITANCE DENSITY pF/mm²
6,000
5,000
4,000
3,000
2,000
1,000
0
OPERATING VOLTAGE (V)
0
50
100
150
960A TiO₂ ON M1
960A TiO₂ ON M2
2700A TiO₂ ON Al
1930A TiO₂ ON n++
SiNx

FIG. 10

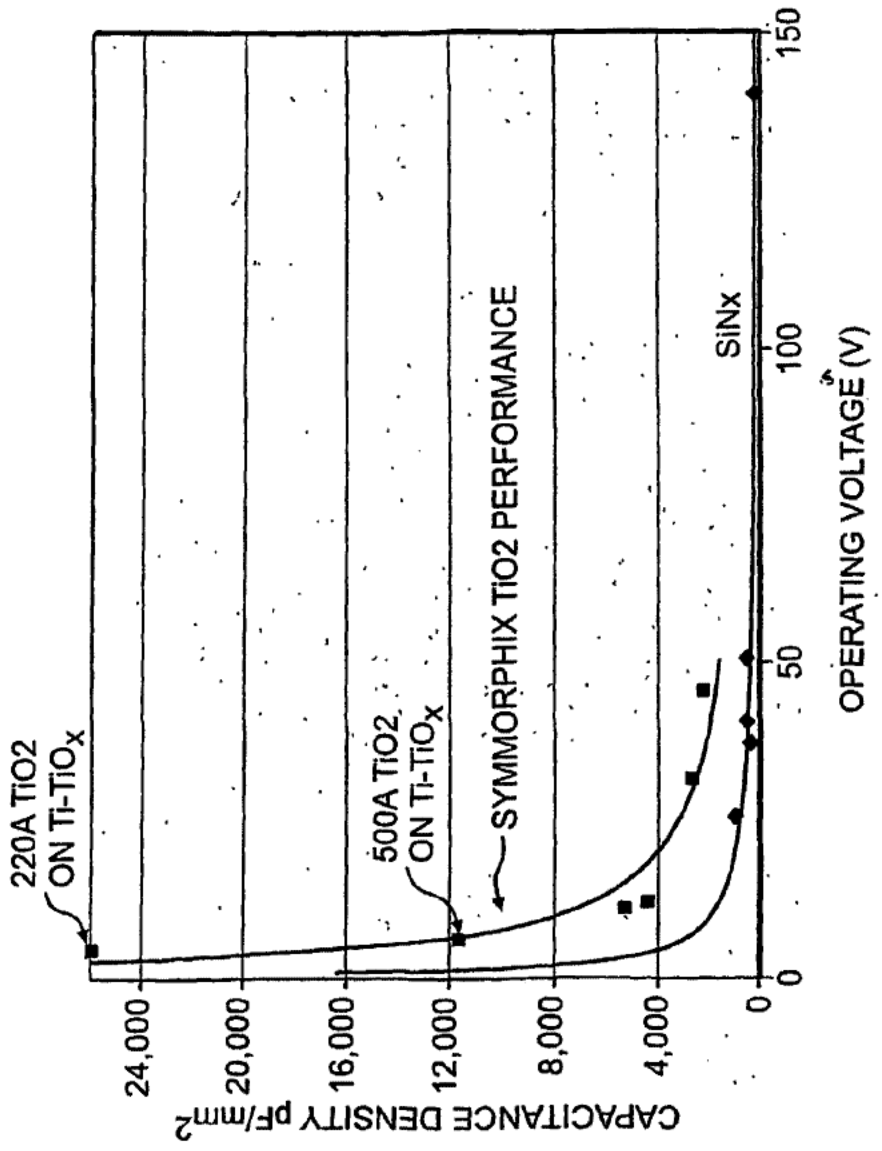

220A TiO2
ON Ti-TiOx
500A TiO2
ON Ti-TiOx
SYMMORPHIX TiO2 PERFORMANCE
SiNx
CAPACITANCE DENSITY pF/mm²
24,000
20,000
16,000
12,000
8,000
4,000
0
0
50
100
150
OPERATING VOLTAGE (V)

FIG. 11

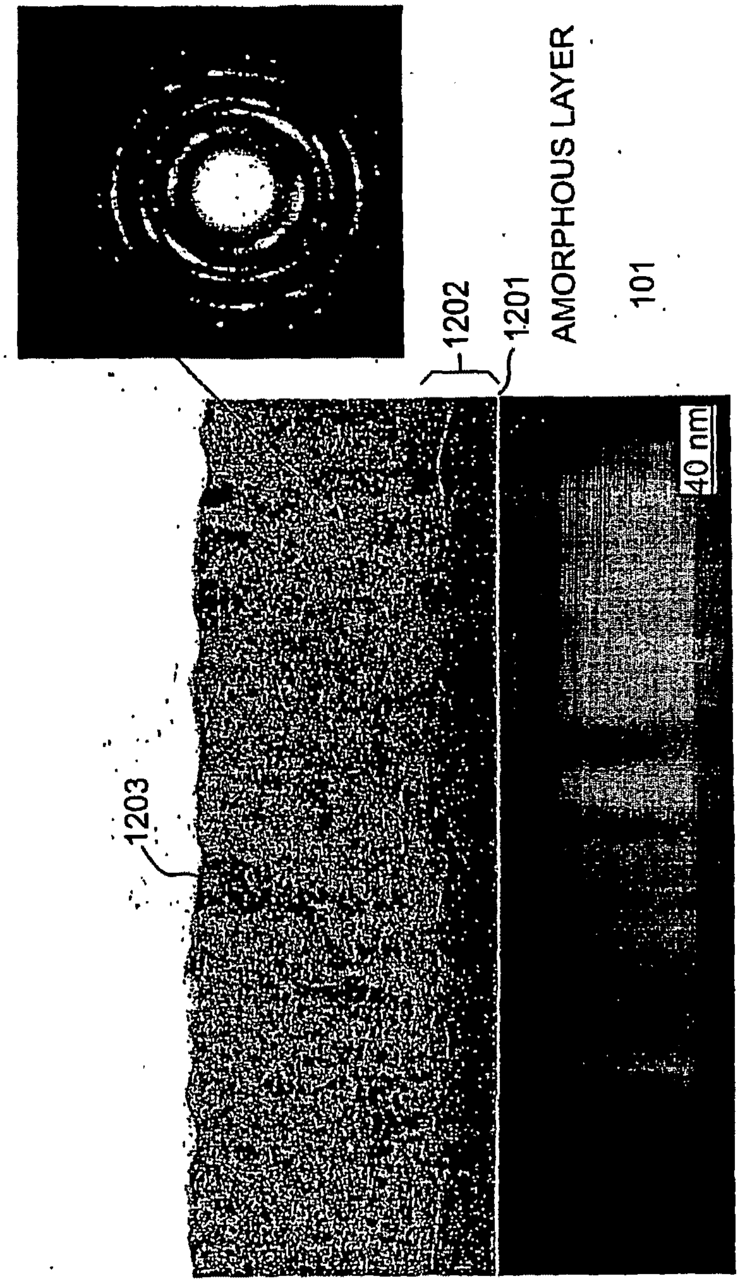


FIG. 12

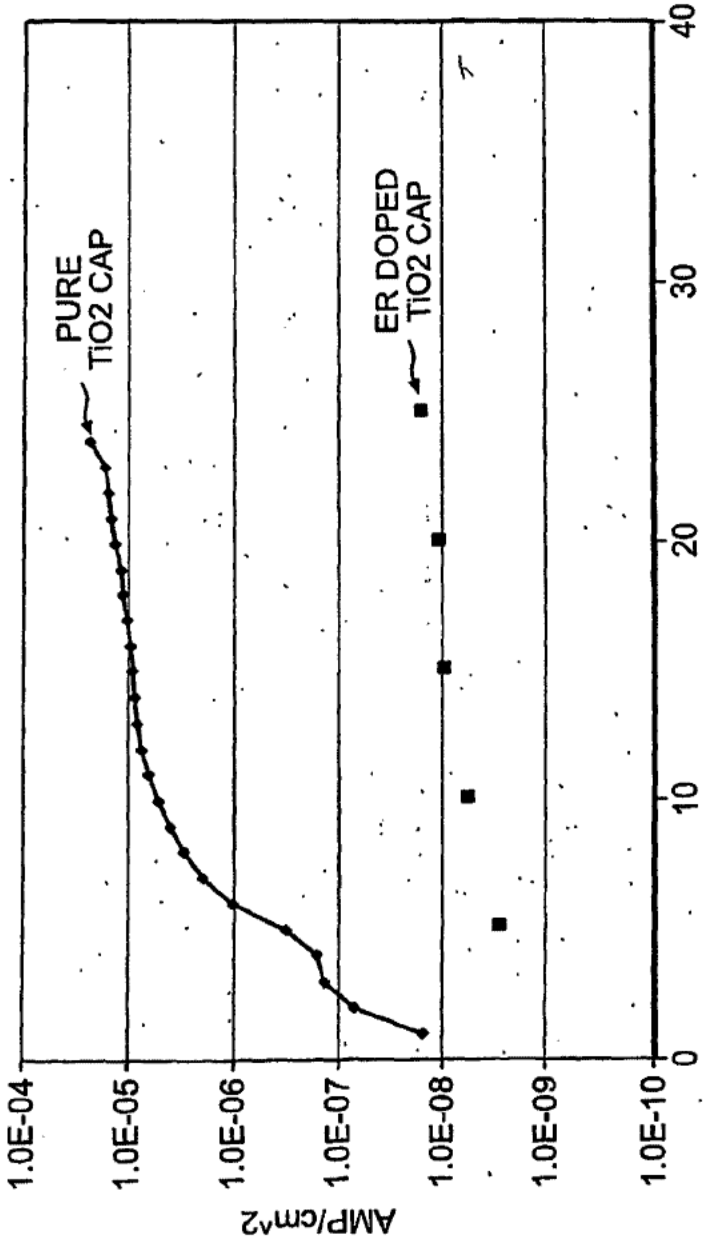
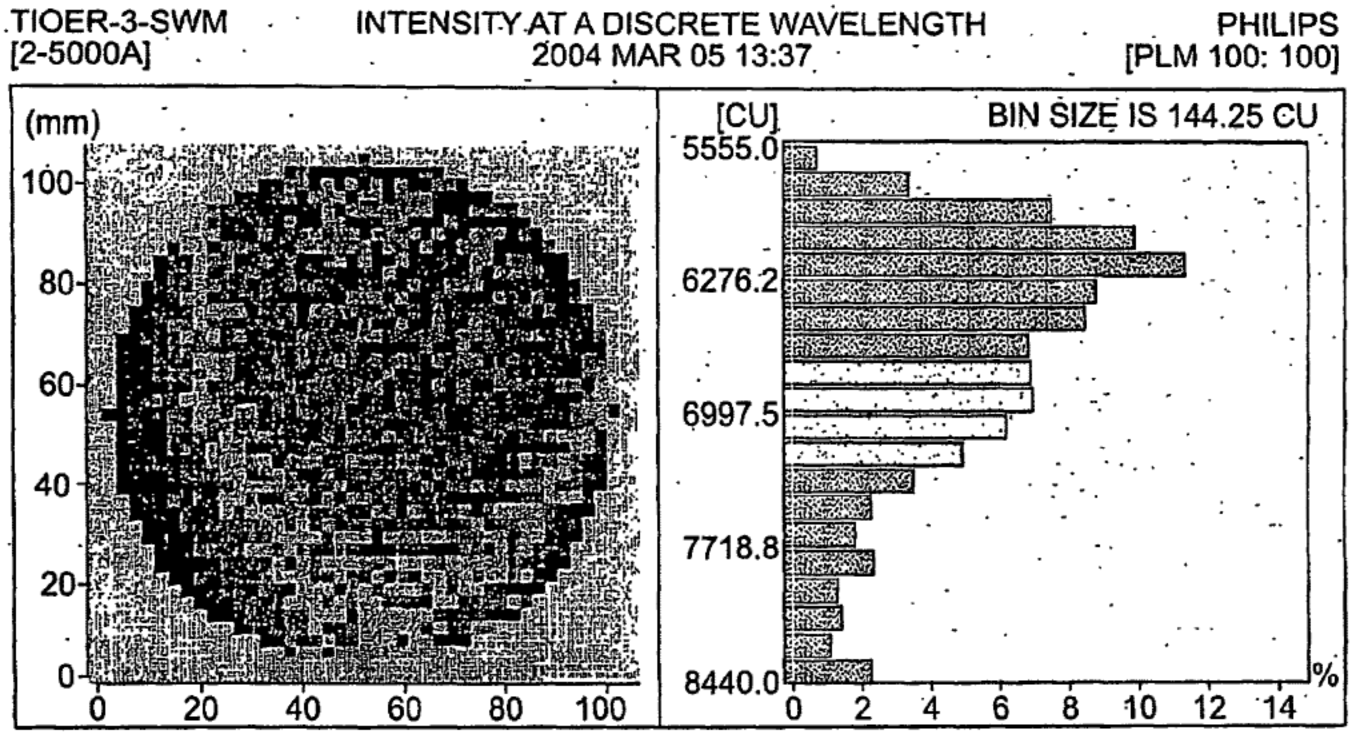

PURE
TiO2 CAP
ER DOPED
TiO2 CAP
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
AMP/cm^2
0
10
20
30
40
V

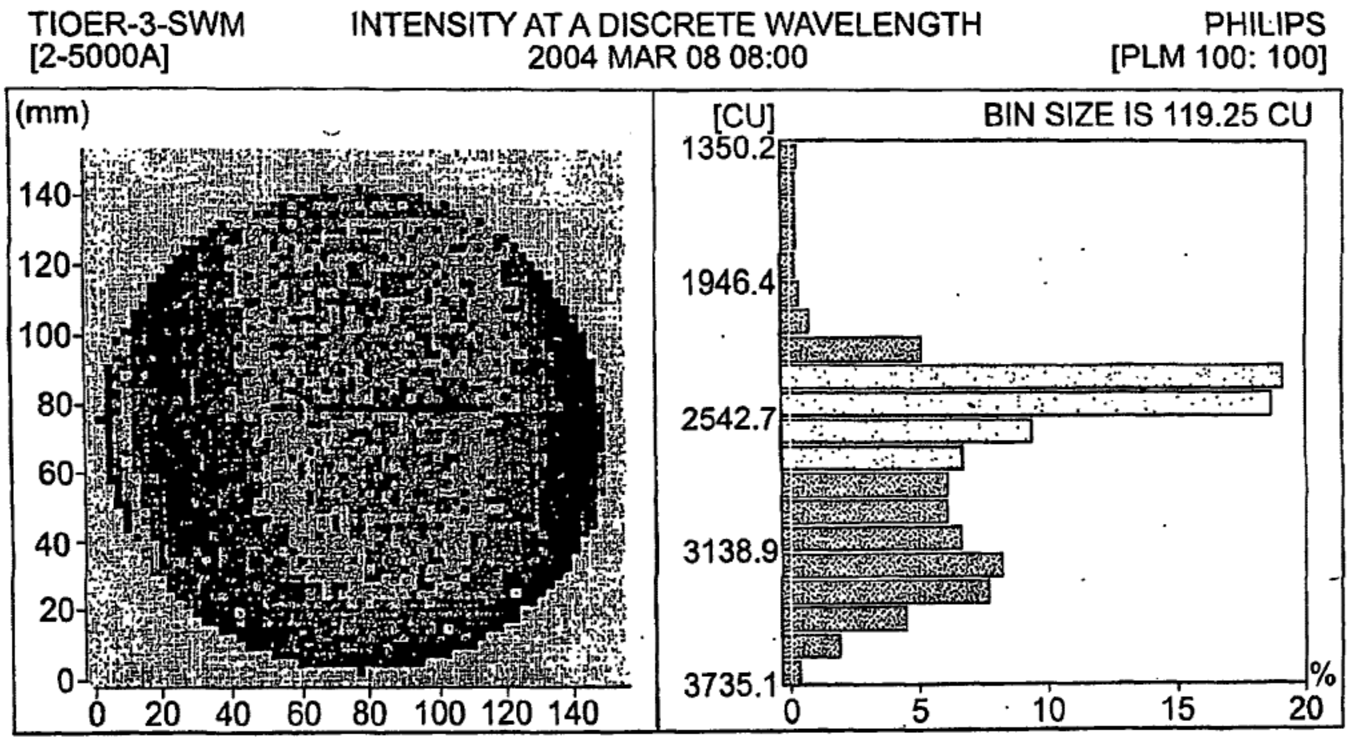
FIG. 13



INTENSITY - AVERAGE (O) : 6669.1 (643.7) CU
- UNIFORMITY : 9.7%
- MEDIAN : 6541.5 CU
- 10% : 5946.4 CU
- 90% : 7607.3 CU
SAMPLE WAVELENGTH : 1530.0 nm

INTENSITY -UNDER ▭ 32.0%
-OVER ☐ 0.0 %

FIG. 14A



INTENSITY - AVERAGE (O) : 2736.0 (382.3) CU
- UNIFORMITY : 14.0 %
- MEDIAN : 2615.1 CU
- 10% : 2330.0 CU
- 90% : 3307.5CU
SAMPLE WAVELENGTH : 1530.0 nm

INTENSITY -UNDER ▨ 34.9%
-OVER ☐ 0.0 %

FIG. 14B

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/954,182 | 10/01/2004 | Hongmei Zhang | 09140-0016-01000 | 9873 |

22852 7590 03/09/2006

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: 03/09/2006

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

| | | | |
|---|---|---|---|
| ***Office Action Summary*** | **Application No.**<br>10/954,182 | **Applicant(s)**<br>ZHANG ET AL. | |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>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 *21 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) *41-43,45-62,85 and 87-89* is/are pending in the application.

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

5)☒ Claim(s) *61,62 and 85* is/are allowed.

6)☒ Claim(s) *41-43 and 45-60* is/are rejected.

7)☒ Claim(s) *87-89* 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 *21 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 *7/25/05,12/21/05*.

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 § 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 45, 47, 49, 51, 52, 59 and 60 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of D'Couto et al. (6,673,716).

Re claims 59 and 60, Smolanoff et al. disclose providing a process gas between the target (16) and a substrate (15); providing pulsed DC power to the target (Col. 5, lines 50-55); providing a magnetic field to the target (Col. 6, lines 1-7); and wherein a material is deposited on the substrate (Col. 5, lines 22-26); and an oxide film is formed by reactive sputtering (Col. 6, lines 15+).

Smolanoff et al. do not disclose wherein the material sputtered is in the metallic mode or in the poison mode.

D'Couto et al. disclose that a material can be sputter neither in the poison mode or metallic mode (Col. 1, line 65-Col. 2, line 20).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and D'Couto et al. to enable the sputtering mode step of Smolanoff et al. to be performed according to the teachings of D'Couto et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed sputtering 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.

Re claim 45, Smolanoff et al. disclose wherein the magnetic field is provided by a moving magnetron (Col. 5, lines 39-49).

Re claim 47, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 22-27).

Re claim 49, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

Re claim 51, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-6).

Re claim 52, Smolanoff et al. disclose wherein 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 41, 42, 46, 48 and 50 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff in view of D'Couto et al. as applied to claims 45, 47, 49, 51, 52, 59 and 60 above, and further in view of Chen et al. (2004/0077161).

Re claim 41, Smolanoff et al. disclose wherein the process gas includes oxygen.

Re claim 42, Smolanoff et al. disclose wherein the process gas includes $N_2$ or $NH_3$.

The combination of Smolanoff et al. and D'Couto et al. does not disclose wherein the target is a metallic target.

Re claims 41 and 42, Chen et al. disclose forming a coating layer in a substrate; applying a magnetic field to a target; wherein the target is a metallic target.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., D'Couto et al. and Chen et al. to enable the target material of Smolanoff et al. to be the same according to the teachings of Chen et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable target materials of the disclosed target of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Re claim 46, Chen et al. disclose further including holding the temperature of the substrate substantially constant (Page 3, Paragraph [0046]).

Re claim 48, Chen et al. disclose wherein the oxygen flow is adjusted by the mass flow controllers; thereby it will adjust the index refraction of the film.

Re claim 50, Chen 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).

Claims 43 and 53-58 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of D'Couto et al. as applied to claims 45, 47, 49, 51, 52, 59 and 60 above, and further in view of Milonopoulou et al. (2003/0175142).

The combination of Smolanoff et al. and D'Couto et al. does not disclose wherein the target is a ceramic target.

Milonopoulou et al. disclose forming a coating layer on a substrate; providing a target (12), which is ceramic (Abstract).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., D'Couto et al. and Chen et al. to enable the target material of Smolanoff et al. to be the same according to the teachings of Milonopoulou et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable target materials of the disclosed target of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Re claim 53, Milonopoulou et al. disclose wherein the target is an alloyed target (Abstract).

Re claim 54, Milonopoulou et al. disclose wherein the alloyed target includes one or more rare earth ions.

Re claim 55, Milonopoulou et al. disclose wherein the alloyed target includes Si and Al.

Re claim 56, Milonopoulou et al. disclose wherein the alloyed target includes one or more elements taken from a set consisting of Si, Al, Er and Yb.

Re claim 57, Milonopoulou et al. disclose wherein the alloyed target is a tiled target.

Re claim 58, Milonopoulou et al. disclose wherein each tiled target is formed by prealloy atomization and hot isostatic pressing of a powder (Page 2, Paragraph [0020]).

### *Allowable Subject Matter*

Claims 87-89 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.

Claims 61, 62 and 85 are 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

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
March 6, 2006

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/954,182
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

1/27

approved

3/6/06

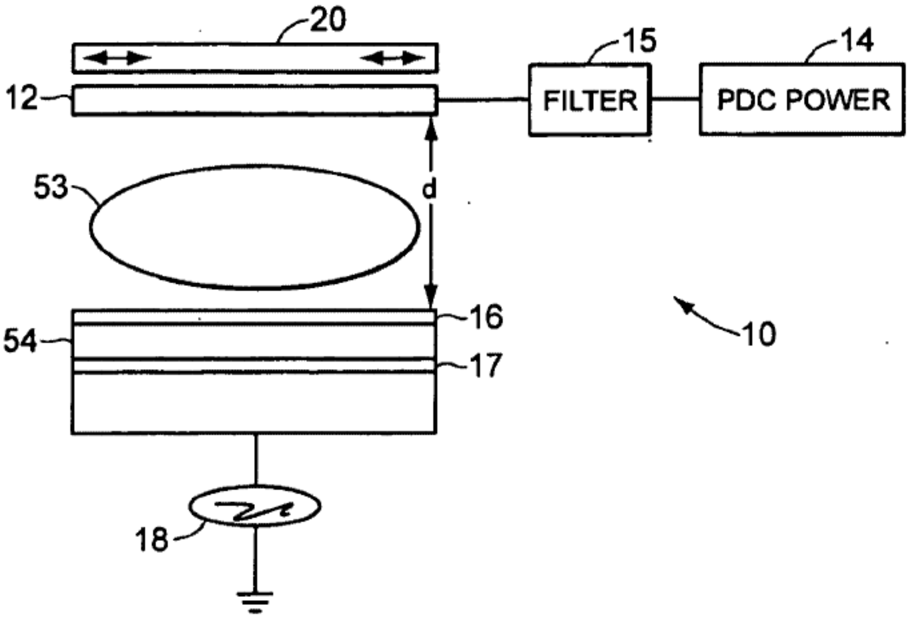

FIG. 1A

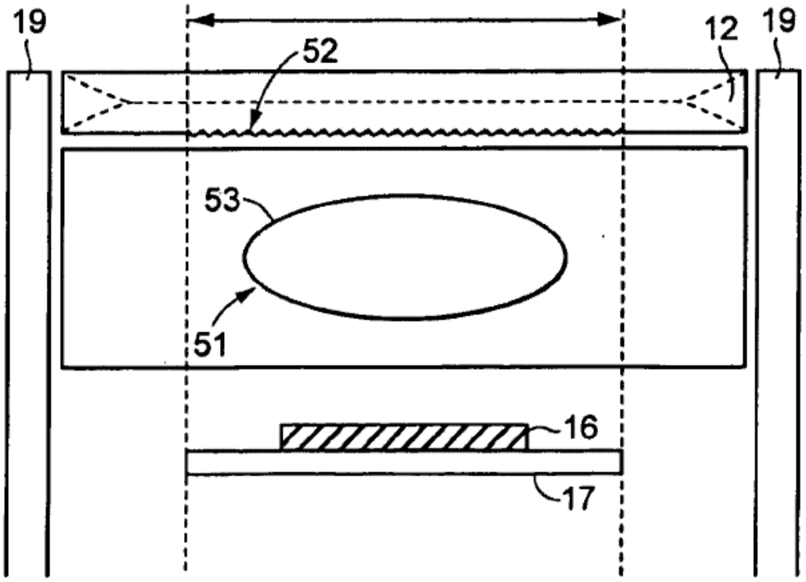

FIG. 1B

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*(Use as many sheets as necessary)*

| | | | |
|---|---|---|---|
| Sheet | 1 | of | 2 |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/954,182 |
| *Filing Date* | October 1, 2004 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-01 |

### U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>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 2003/0141186 A1 | 07-31- 2003 | Wang et al. | |
| | | US 2001/041460 A1 | 11-15-2001 | Wiggins | |
| | | US 2001/0027159 A1 | 10-04-2001 | Kaneyoshi | |
| | | US 6,232,242 | 05-15-2001 | Hata et al. | |
| | | ~~US 6,117,279~~ | ~~09-12-2000~~ | ~~Smolanoff et al.~~ | |
| | | US 5,738,731 (09-00) | 04-04-1998 | Shindo | |
| | | US 5,538,796 | 07-23-1996 | Schaffer | |
| | | US 5,309,302 | ~~03-14-1967~~ 5-3-94 | ~~Heil~~ Vollmann | |
| | | US 5,296,089 | 03-22-1994 | Chen et al. | |
| | | US 5,173,271 | 12-22-1992 | Chen et al. | |
| | | US 4,587,225 | 05-06-1986 | Tsukuma et al. | |
| | | RE 32,449 | 06-30-1987 | Claussen | |

already in 892
Filed 3/25/05

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|---|---|---|---|---|---|---|
| | | ~~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. | | |
| | | JP 7-233469 | 09-05-1995 | Asahi Glass Co, Ltd. | | |
| | | WO 00/21898 A1 | 04/20/2000 | Samsung Electronics Co. | | |

no translation

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 2/27/06 |

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| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Application Number* | 10/954,182 |
| | | | | *Filing Date* | October 1, 2004 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | | | *Examiner Name* | ESTRADA, Michelle |
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|---|---|---|---|
| | | 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. | |
| | | 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. | |
| | | 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. | |
| | | Tukamoto, H. et al., "Electronic Conductivity of $LiCoO_2$ and Its Enhancement by Magnesium Doping," J. Electrochem. Soc., vol. 44, no. 9, pages 3164-3168 (September 1997). | |
| | | 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). | |
| | | 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 dated January 13, 2005, received in Application No. 10/101,863 (Attorney Docket No. 09140.0016-00). | |
| | | Response to office Action filed on June 10, 2005 in U.S. Serial No. 10/101,863 (Attorney Docket No. 09140.0016-00). | |
| | | 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). | |

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|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 2/27/06 |

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| Sheet | 1 | of | 1 |

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| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-01 |

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|---|---|---|---|---|---|
| ME | | US 2002/0076133 A1 | 06-20-2002 | Li et al. | |
| ME | | US 5,478,456 | 12-26-1995 | Humpal et al. | |
| ME | | US 6,846,765 B2 | 01-25-2005 | Imamura et al. | |

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| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>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] |
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|---|---|---|---|
| ME | | 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). | |
| ME | | HOWSON, R.P., "The reactive sputtering of oxides and nitrides," *Pure & Appl. Chem.* *66*(6):1311-1318 (1994). | |
| ME | | Office Action issued September 21, 2005 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01). | |
| ME | | Office Action issued on August 4, 2005, in U.S. Application No. 10/101,863 (Attorney Docket No. 09140.0016-00). | |
| ME | | Office Action issued on August 8, 2005 in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00). | |
| ME | | Office Action issued on October 3, 2005 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00). | |
| 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 filed July 25, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00). | |
| ME | | Office Action issued on October 19, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 2/27/06 |

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.

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| ***Notice of References Cited*** | Application/Control No.<br>10/954,182 | Applicant(s)/Patent Under Reexamination<br>ZHANG ET AL. |
| | Examiner<br>Michelle Estrada | Art Unit<br>2823   Page 1 of 1 |

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| * | A | US-6,673,716 B1 | 01-2004 | D'Couto et al. | 438/656 |
| | B | US- | | | |
| | C | US- | | | |
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| | F | US- | | | |
| | G | US- | | | |
| | H | US- | | | |
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| | K | US- | | | |
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| | M | US- | | | |

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| * | | Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages) |
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*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.

U.S. Patent and Trademark Office
PTO-892 (Rev. 01-2001)

**Notice of References Cited**

Part of Paper No. 20060306

OIPE IAP14
AUG 0 9 2006
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/954,182 | Examiner: ESTRADA, Michelle |
| Filed: October 1, 2004 | |
| | Confirmation No.: 9873 |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | |

**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 9, 2006, the period for response having been extended to August 9, 2006, by a request for extension of two months and authorization for the Commissioner to charge the fee to deposit account, please amend the above-identified application as follows:

**Amendments to the Claims** are reflected in the listing of claims that begins on page 2 of this paper.

**Remarks/Arguments** follow the amendment sections on page 6 of this paper.

## AMENDMENTS TO THE CLAIMS:

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

Claims 1-40 (Canceled).

Claim 41 (Previously presented): The method of claims 59, 60, or 85, wherein the target is a metallic target and the process gas includes oxygen.

Claim 42 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the target is a metallic target and the process gas includes one or more of a set consisting of $N_2$, $NH_3$, CO, NO, $CO_2$, halide containing gasses.

Claim 43 (Currently amended): ~~The method of claims 59, 60, or 85,~~ A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;
providing pulsed DC power to the target through a narrow band-rejection filter;
providing a magnetic field to the target; and
wherein a material is deposited on the substrate,
wherein the target is a ceramic target.

Claim 44 (Canceled).

Claim 45 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the magnetic field is provided by a moving magnetron.

Claim 46 (Currently amended) The method of claims 43, 59, 60, or 85, further including holding the temperature of the substrate substantially constant.

Claim 47 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the process gas includes a mixture of Oxygen and Argon.

Claim 48 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the Oxygen flow is adjusted to adjust the index of refraction of the film.

Claim 49 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the process gas further includes nitrogen.

Claim 50 (Currently amended): The method of claims 43, 59, 60, or 85, 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 51 (Currently amended): The method of claims 43, 59, 60, or 85, further including uniformly sweeping the target with a magnetic field.

Claim 52 (Previously presented): The method of claim 51 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 53 (Currently amended): The method of claims 43, 59, 60, or 85, wherein the target is an alloyed target.

Claim 54 (Previously presented): The method of claim 53 wherein the alloyed target includes one or more rare-earth ions.

Claim 55 (Previously presented): The method of claim 53 wherein the alloyed target includes Si and Al.

Claim 56 (Previously presented): The method of claim 53 wherein the alloyed target includes one or more elements taken from a set consisting of Si, Al, Er, Yb, Zn, Ga, Ge, P, As, Sn, Sb, Pb, Ag, Au, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy Ho, Tm, and Lu.

Claim 57 (Previously presented): The method of claim 53 wherein the alloyed target is a tiled target.

Claim 58 (Previously presented): The method of claim 57 wherein each tile of the tiled target is formed by prealloy atomization and hot isostatic pressing of a powder.

Claim 59 (Currently amended): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;
providing pulsed DC power to the target through a narrow band-rejection filter;
providing a magnetic field to the target; and
wherein a material is deposited on the substrate, and
an oxide film is formed by reactive sputtering in metallic mode.

Claim 60 (Currently amended): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;
providing pulsed DC power to the target through a narrow band-rejection filter;
providing a magnetic field to the target; and
wherein a material is deposited on the substrate, and an oxide film is formed by reactive sputtering in poison mode.

Claim 61 (Previously presented): A method of depositing a film on a substrate, comprising:

providing a process gas between a metallic target and a substrate;
providing pulsed DC power to the target;
providing a magnetic field to the target; and
reconditioning a metallic target;
wherein a material is deposited on the substrate.

Claim 62 (Previously presented): The method of claim 61, wherein reconditioning the metallic target includes:

reactive sputtering in the metallic mode and then reactive sputtering in the poison mode.

Claims 63-84 (Canceled).

Claim 85 (Previously presented): A method of depositing a film on a substrate, comprising:

providing a process gas between a target and a substrate;

providing pulsed DC power to the target;

providing a magnetic field to the target; and

wherein a material is deposited on the substrate, and an oxide film is formed by reactive sputtering in a mode between a metallic mode and a poison mode.

Claim 86 (Canceled).

Claim 87 (Currently amended): The method according to claims 43, 59, 60, or 85, ~~further comprising:~~ wherein the narrow band-rejection filter rejects power at an RF frequency, and further including

~~providing a narrow-band RF filter between the pulsed DC power supply and the target; and~~

providing an RF bias to the substrate at the RF frequency.

Claim 88 (Currently amended): The method according to claim 87, wherein the ~~narrow-band RF~~ narrow band-rejection filter has a bandwidth of about 100 kHz.

Claim 89 (Currently amended): The method according to claim 87, wherein the RF ~~bias has a frequency of~~ frequency is about 2 MHz.

Claims 90-92 (Canceled).

## REMARKS

Claims 41-43, 45-62, 85, and 87-89 are pending in this application. The Examiner has rejected claims 41-43 and 45-60, objected to claims 87-89, and allowed claims 61, 62, and 85. In this Amendment, claims 42, 43, 45-51, 53, 59-60, and 87-89 have been amended. Claim 43 has been amended to be independent. Claims 42, 45-51, 53, and 87 have been amended to adjust their dependency. Claims 87-89 have been further amended for clarity to better claim the invention. Claims 59 and 60 have been amended as described below.

## Claim Rejections under 35 U.S.C. § 103

Claims 45, 47, 49, 51, 52, 59, and 60

The Examiner rejected claims 45, 47, 49, 51, 52, 59, and 60 under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 6,117,279 ("Smolonoff et al.") in view of U.S. Patent No. 6,673,716 ("D'Couto et al.").

In the interest of furthering prosecution, Claims 59 and 60 have been amended to clarify that the pulsed DC power is supplied to the target through "a narrow band-rejection filter." Neither Smolonoff nor D'Couto teach a narrow band-rejection filter between the pulsed-DC power and the target. Further, the band-rejection filter is the subject matter of claim 87, which the Examiner has indicated would be allowable if rewritten in independent form.

Claims 45, 47, 49, 51, and 52 are multiply-dependent claims that depend from claims 43, 59, 60, or 85. The Examiner has indicated that claim 85 is allowable. Claims 59-60 are allowable, as discussed above. Claim 43, which also recites "a narrow band-rejection filter," is allowable over Smolonoff and D'Couto at least for the same reasons as discussed above.

Claims 41, 42, 46, 48, and 50

The Examiner rejected claims 41, 42, 46, 68, and 50 under 35 U.S.C. 103(a) as being unpatentable over Smolonoff et al. in view of D'Couto et al. as applied to claims 45, 47, 49, 51, 52, 59, and 60, and further in view of U.S. Published Application No. 2004/0077161 ("Chen et al.").

As discussed above, claims 43, 59, 60, and 85 are allowable over Smolonoff in view of D'Couto. Chen does not cure the defects in Smolonoff and D'Couto, and therefore claims 43, 59, 60, and 85 are allowable over the combination of Smolonoff, D'Couto, and Chen. Claim 41 is a multiply dependent claim that depends from claims 59, 60, or 85 and is therefore allowable for at least the same reasons as is claims 59, 60, and 85. Claims 42, 46, 48, and 50 are multiple dependent claims that depend from claims 43, 59, 60, or 85 and are therefore allowable for at least the same reasons as is claims 43, 59, 60, and 85.

Claims 43 and 53-58

The Examiner has rejected claims 43 and 53-58 under 35 U.S.C. § 103(a) as being unpatentable over Smolonoff et al. in view of D'Couto et al. as applied to claims 45, 47, 49, 51, 52, 59, and 60 above, and further in view of Milonopoulou et al. (2003/0175142).

As an initial matter, Milonopoulou can not be considered prior art to the present application. Milonopoulou was co-filed on March 16, 2002 along with the parent application of the present application (U.S. Application No. 10/101,863). These two applications cross-reference each other and are incorporated by reference one into the other. Milonopoulou is incorporated into the present application in Paragraph [0048], as amended in the preliminary amendment filed with the present continuation application on September 30, 2004. The parent of the present application is incorporated by reference in Paragraph [0039] of Milonopoulou.

As discussed above, claims 43, 59, and 60 are allowable over the combination of Smolonoff and D'Couto. Claims 53-58 depend from claims 43, 59, 60, and 85 and are therefore allowable for at least the same reasons as is claims 43, 59, 60, and 85.

## Allowable Subject Matter

The Examiner objected to claims 87-89 as being independent 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. The Examiner has further indicated that claims 61, 62, and 85 are allowed.

Subject matter from claim 87 has been incorporated in independent claims 43, 59, and 60. Current claims 87-89 are multiply dependent and depend from claims 43, 59, 60, or 85. Claims 87-89, therefore, are allowable for at least the same reasons as are claims 43, 59, 60, and 85.

## 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.

Date: August 9, 2006

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

**EXPRESS MAIL LABEL NO.**
**EV 901562545 US**

08-14-06

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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/954,182 ) Examiner: ESTRADA, Michelle
)
Filed: October 1, 2004 )
) Confirmation No.: 9873
For: BIASED PULSE DC REACTIVE )
SPUTTERING OF OXIDE FILMS )

**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 March 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.

08/14/2006 MBLANCO 00000010 060916 10954182

01 FC:1252 450.00 DA

Date: August 9, 2006

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

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PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/954,182 | Examiner: ESTRADA, Michelle |
| Filed: October 1, 2004 | |
| | Confirmation No.: 9873 |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## FIFTH 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.

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 9, 2006

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

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | ***Complete if Known*** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Application Number* | 10/954,182 |
| | | | | *Filing Date* | October 1, 2004 |
| | | | | *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* | 9140.0016-01 |

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## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>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 |
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| Examiner Signature | | Date Considered | |

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|---|---|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | **Complete if Known** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Application Number* | 10/954,182 |
| | | | | *Filing Date* | October 1, 2004 |
| | | | | *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* | 9140.0016-01 |

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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

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| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>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] |
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| | | WO 2006/063308 A2 | 06/15/2006 | Symmorphix, Inc. | | |

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| 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] |
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|---|---|---|---|
| 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 901562545 US**

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

## INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 3 | of | 3 |
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| Complete if Known | |
|---|---|
| *Application Number* | 10/954,182 |
| *Filing Date* | October 1, 2004 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-01 |

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| | | 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). | |
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| | | Notice of Allowance mailed August 6, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140.0002-01). | |
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| Examiner Signature | | Date Considered | |

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# POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

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# POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

[Pulvermetallurgisches Verfahren zur Herstellung von Targets]

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## 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.

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**TITLE:** High purity, dense targets for cathodic sputtering - produced from rare earth and transition metals iron, cobalt and/or nickel in inert atmos., etc.

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**PATENT-ASSIGNEE:** DEGUSSA AG[DEGS]

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**BASIC-ABSTRACT:**

High-purity, mechanically stable and dense targets are produced for cathodic sputtering and vaporisation systems from rare earths and the transition metals Fe, Co and/or Ni from powder mixts, under the effect of pressure and temp., in inert atmos. or vacuum. High-purity, low-O powders or chips are mfd. from pre-alloyed rare earths with the corresp. transition metal (s). Chips are mfd. under inert atmos.,

while powders are produced by atomisation of the pre-alloyed material,having relatively low m.pt.

ADVANTAGE - Prod. has low proportion and fine distribution of brittle phases, with lowest possible 02 content.

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|---|---|
| **CHOSEN-DRAWING:** | Dwg.0/0 |
| **TITLE-TERMS:** | HIGH PURE DENSE TARGET CATHODE SPUTTER PRODUCE RARE EARTH TRANSITION METAL IRON COBALT NICKEL INERT ATMOSPHERE |

**DERWENT-CLASS:** M13 M22 P53 U11

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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

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## 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 werden. 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.

# Conducting transparent coatings and method for their production

| | |
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| **Publication date:** | 2001-04-18 |
| **Inventor:** | STOLLENWERK JOHANNES PROF DR (DE);<br>KOEPPEL ANDREAS (DE); BENDER MARCUS (DE) |
| **Applicant:** | BPS ALZENAU GMBH (DE) |
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- US4565719
- GB2126256
- GB2344600
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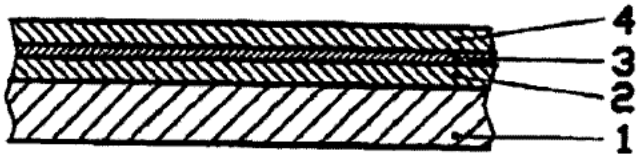
- JP2066158

**Report a data error here**

Abstract of **EP1092689**

Conducting transparent layer system comprises a silver layer (3) between two oxide layers (2, 4) on a substrate (1) and has a quantity coefficient of more than 0.0855 Ohm <-1> for the wavelengths 435, 545 and 610 nm at a flat resistance Rs of less than 2.9 preferably less than 2.5 Ohm sq. An Independent claim is also included for a process for the production of a conducting transparent layer system comprising applying the second oxide layer (4) using a pulsed direct current (DC) sputtering process or an alternating current (AC)-superimposed DC sputtering process.

Fig.1



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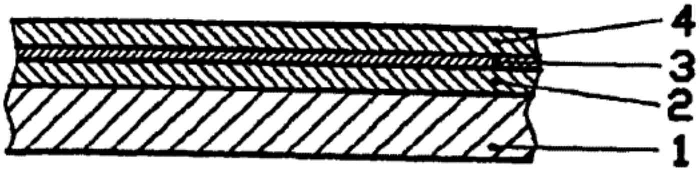
## (54) Leitende transparente Schichten und Verfahren zu ihrer Herstellung

(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



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## 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 Haakkesche 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 $\Omega_{sq}$. So besitzt beispielsweise eine Schicht mit einer Transmission von 90% und einem Flächenwiderstand von 3 $\Omega_{sq}$ einen Haackeschen Gütefaktor von 0,116 $\Omega^{-1}$. Eine Schicht mit einer Transmission von 80% und einem Flächenwiderstand von 5 $\Omega_{sq}$ besitzt einer Gütefaktor von 0,021 $\Omega^{-1}$.

**[0003]** Eine weitere wichtige Eigenschaft eines solchen Schichtsystems ist seine Ätzbarkeit. Diese hängt von seiner chemischen Zusammensetzung und seiner Dicke ab. Für 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\Omega_{sq}$ 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 $\text{Ohm}^{-1}$.

**[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

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 $\Omega_{sq}$, vorzugsweise 2,5 $\Omega_{sq}$ und geringer auf, bei einem über die Wellenlängen 435, 545 und 610 nm gemittelten Haakkeschen Gütefaktor von grösser als 0,085 $\Omega^{-1}$.

**[0014]** Dabei ist es aus Gründen der Farbneutralität günstig, wenn bei einem Flächenwiderstand von 2,5 $\Omega_{sq}$ 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 Zerstäubung, sondern mit einer gepulsten DC-Zerstäubung oder mit einer AC-überlagerten DC-Zerstäubung 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 $\Omega_{sq}$. |

**[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, 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 $\Omega_{sq}$ 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 $\Omega^{-1}$.

## 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 $< 2{,}9\ \Omega_{sq}$., vorzugsweise $< 2{,}5\ \Omega_{sq}$ und weniger, der mittlere Haackesche Gütefaktor des Schichtsystems für die Wellenlängen 435, 545 und 610 nm $(\Phi_{Tc}=T^{10}/R_s)>0{,}085\Omega^{-1}$ beträgt.

2. Schichtsystem nach Anspruch 1, **dadurch gekennzeichnet, dass** bei einem Flächenwiderstand von 2,5 $\Omega_{sq}$ 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.

Fig.1

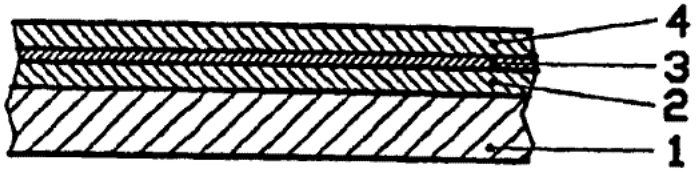
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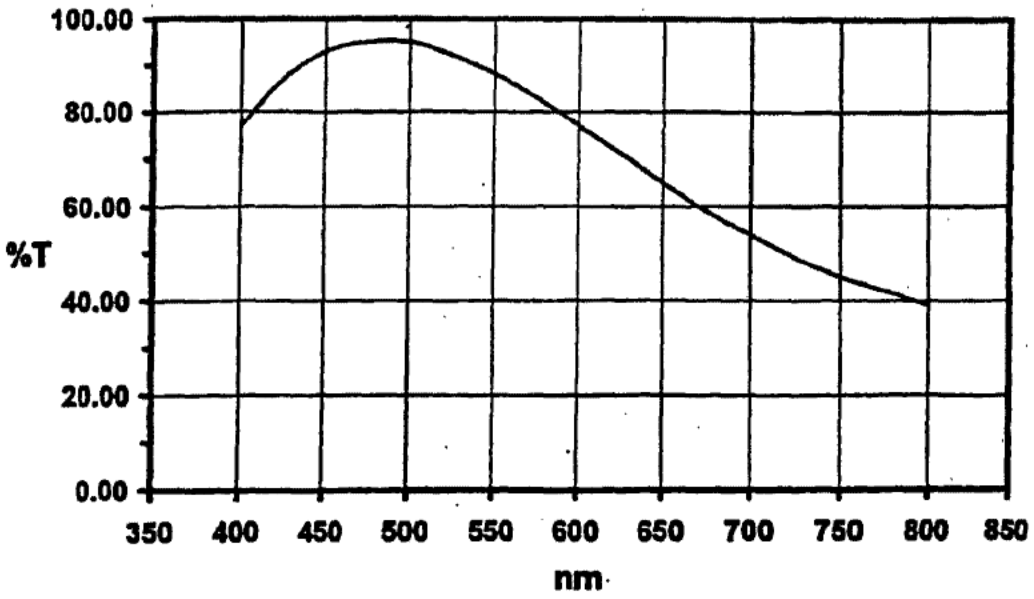
Fig.2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**Europäisches Patentamt**

# 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)<br>21. Januar 1986 (1986-01-21)<br>* Anspruch 1; Tabelle 3 *<br>--- | 4 | C03C17/36 |
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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

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## 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.
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# 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

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EPO FORM P0461

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

## MACHINE-ASSISTED TRANSLATION (MAT):

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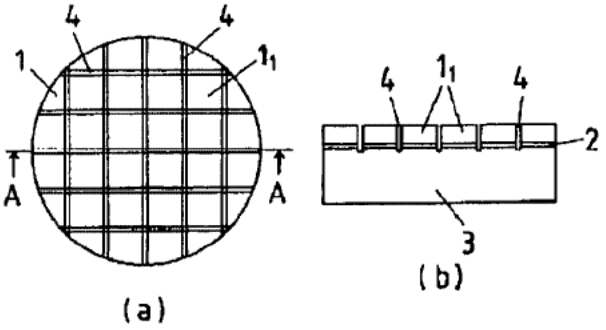
| (57)【要約】 | **(57)[ABSTRACT OF THE DISCLOSURE]** |
| 【目的】<br>ターゲット材の加熱による割れを防止すること。 | **[PURPOSE]**<br>Prevent the crack by heat of a target material. |
| 【構成】<br>所要の元素を含むターゲット材１はボンディング材２によってバッキングプレート３に固着されている。ターゲット材１にスリ割り溝（或いは切り込み、カッティングによる溝）４を設け、ターゲット材１を多数の小区画$1_1$に分割する。ターゲット材の厚さ方向位置での伸びの差等が小さくなり、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]**<br>The target material 1 containing a required element adheres to the backing plate 3 by the bonding material 2.<br>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 $1_1$.<br>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.<br>It is sufficient to bond on a backing plate the fragment of the target material made beforehand. |



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| 【特許請求の範囲】 | **[CLAIMS]** |
| 【請求項１】<br>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]**<br>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】<br>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]**<br>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】<br>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]**<br>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】<br>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]**<br>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 |

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】

**[PROBLEM TO BE SOLVED BY THE INVENTION]**

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。

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】

**[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。

This invention aims to provide the sputter target which prevents the crack of a target material by heating by the plasma or an ion.

【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]**

| | |
|---|---|
| 【実施例】 | **[EXAMPLES]** |
| 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。 | With reference to drawing, it demonstrates the Example of this design.<br>FIG. 1 (a), (b) is the front elevation of the sputter target by offset rate form, and sectional drawing in the A-A.<br>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.<br>If the offset rate slot 4 is formed in the target material part at least, it is enough.<br>However, FIG.1(b) shows what has reached even the backing plate 3. |
| 【０００８】 | **[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。 | FIG. 2 (a), (b) is the front elevation and sectional drawing in an A-A of the sputter target of tile sticking form.<br>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】 | **[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 | 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 |

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.

| | |
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| 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】 | **[ADVANTAGE OF THE INVENTION]** |
| 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。 | 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】 | **[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。 | 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】 | **[FIG. 1]** |
| 本発明の実施例の正面図及び断面図である。 | It is the front elevation and sectional drawing of an Example of this invention. |
| 【図２】 | **[FIG. 2]** |
| 他の実施例の正面図及び断面図である。 | It is the front elevation and sectional drawing of another Example. |

| | |
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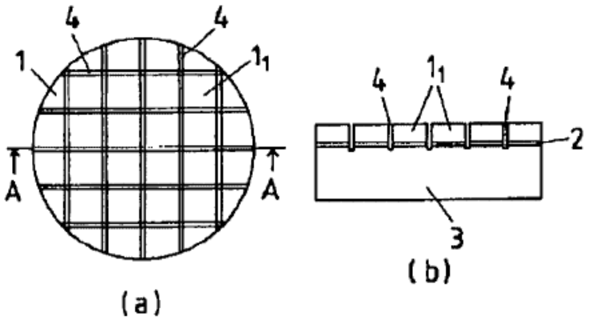
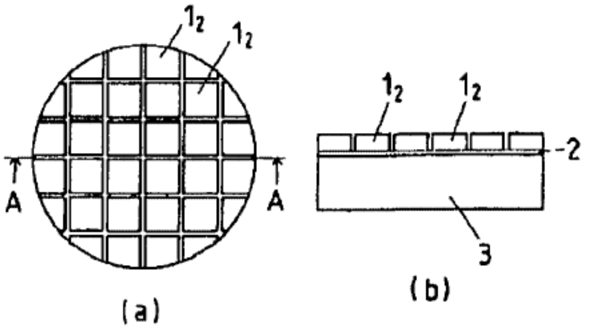
| **【図３】** | **[FIG. 3]** |
| 更に他の実施例の正面図及び断面図である。 | Furthermore, it is the front elevation and sectional drawing of another Example. |
| **【図４】** | **[FIG. 4]** |
| 従来のスパッタ・ターゲットの正面図及び断面図である。 | It is the front elevation and sectional drawing of a sputter target of the past. |
| **【符号の説明】** | **[DESCRIPTION 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 |

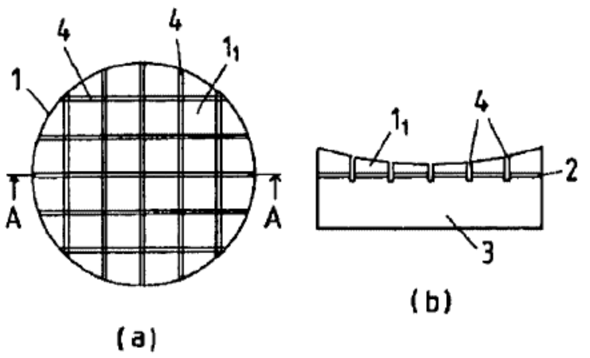
【図１】 **[FIG. 1]**



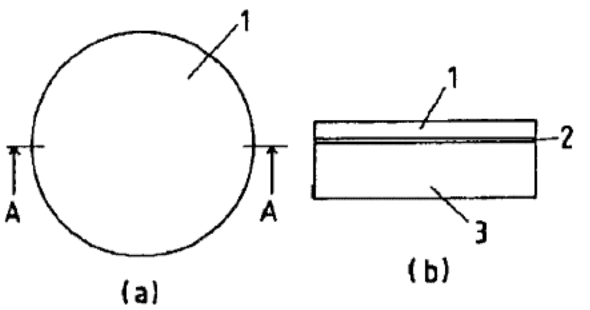
【図２】 **[FIG. 2]**



【図3】 **[FIG. 3]**



【図4】 **[FIG. 4]**



## THOMSON SCIENTIFIC TERMS AND CONDITIONS

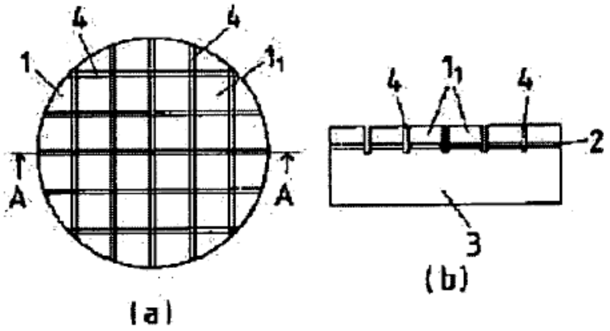
# SPUTTERING TARGET

| | |
|---|---|
| **Publication number:** | JP5230642 |
| **Publication date:** | 1993-09-07 |
| **Inventor:** | BABA TAKASHI; TAKEYAMA KUNIHIKO |
| **Applicant:** | NISSIN HIGH VOLTAGE CO LTD |
| **Classification:** | |
| **- international:** | ***C23C14/34; H01J37/08; H01J37/30;*** **C23C14/34; H01J37/08; H01J37/30;** (IPC1-7): C23C14/34; H01J37/08; H01J37/30 |
| **- european:** | |
| **Application number:** | JP19920069981 19920221 |
| **Priority number(s):** | JP19920069981 19920221 |

**Report a data error here**

Abstract of **JP5230642**

PURPOSE:To prevent the cracks of a target material caused by heating. CONSTITUTION:A target material 1 contg. required elements is fixed to a backing plate 3 by a bonding material 2. The target material 1 is provided with slit grooves (or grooves by notching or grooves by cutting) 4, and the target material 1 is divided into many small divisions 11. The difference of the elongation in the position in the thickness direction of the target material or the like are reduced, by which the cracks of the target material can be prevented. The small pieces of the target material which has previously been made may be adhered to the backing plate.



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(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 |
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| Ｃ２３Ｃ | 14/34 | | 8414−4K | | |
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(21)出願番号　特願平4－69981

(22)出願日　平成４年(1992)２月21日

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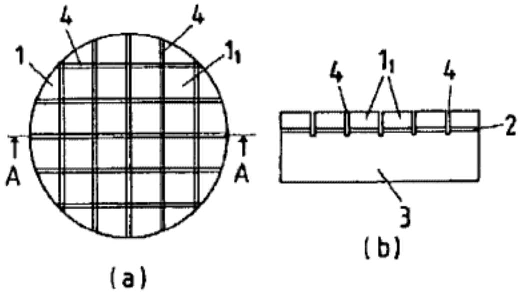
## (54)【発明の名称】　スパッタ・ターゲット

(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。



【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。

【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。

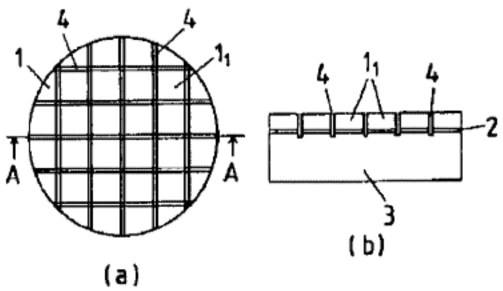
【図３】更に他の実施例の正面図及び断面図である。

【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】

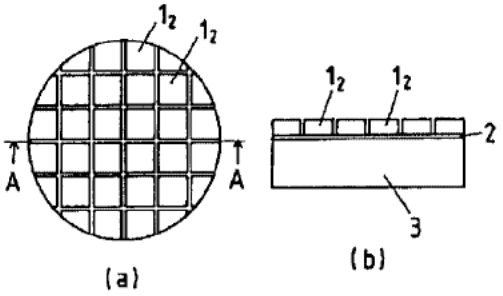
$1, 1_1, 1_2$　ターゲット材
2　ボンディング材
3　バッキングプレート
4　スリ割り溝

【図１】



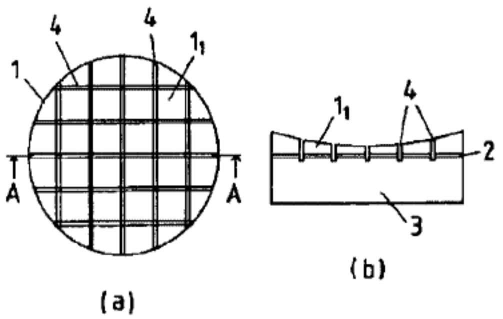
(a)　(b)

【図２】



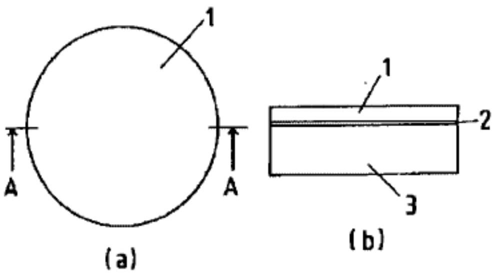
(a)　(b)

【図３】



(a)　(b)

【図４】



(a)　(b)

(19) JAPANESE PATENT OFFICE

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(22) Date of filing: **14.02.94**

(71) Applicant: **ULVAC JAPAN LTD**

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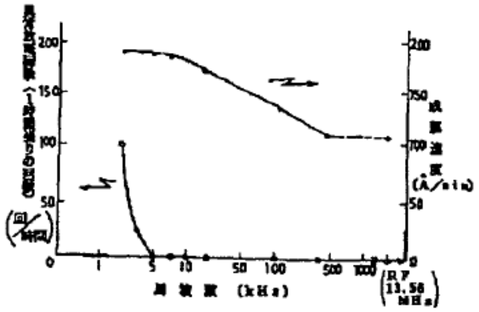
# (54) SPUTTERING METHOD AND DEVICE THEREFOR

(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.



(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 | | |

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(22)出願日　平成6年(1994)2月14日

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(74)代理人　弁理士　北村　欣一　（外2名）

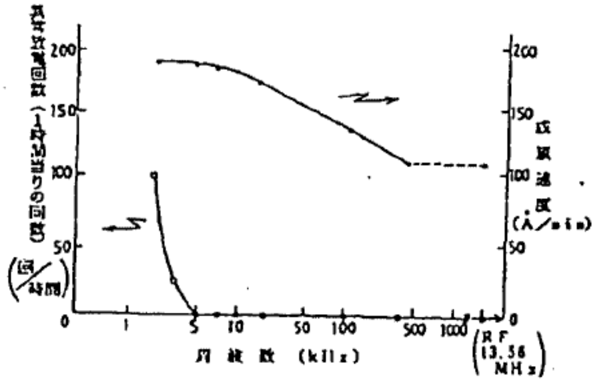
最終頁に続く

(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 $6.7\times10^{-4}$Pa（ $5\times10^{-6}$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 $6.7\times10^{-1}$Pa（ $5\times10^{-3}$ 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。

【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 $6.7\times10^{-1}$ Ｐａ（$5\times10^{-3}$ 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 $6.7\times10^{-1}$ Ｐａ（$5\times10^{-3}$ 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。

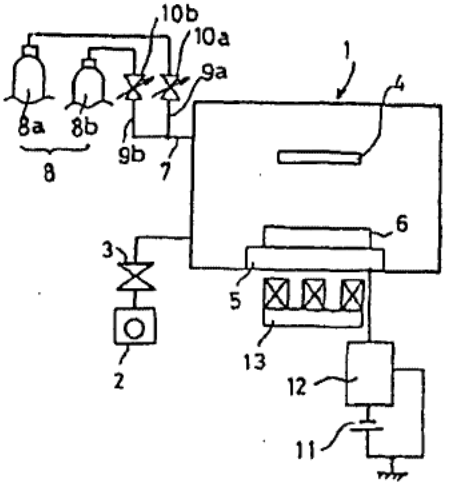
【図３】　本発明スパッタ方法の１実施例における成膜時の周波数と異常放電回数との関係、並びに周波数と成膜速度との関係を示す特性線図。

【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。

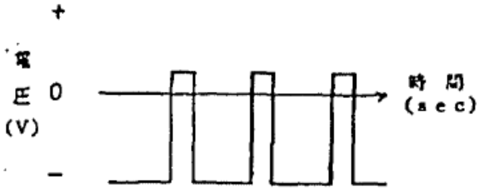
【符号の説明】

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。

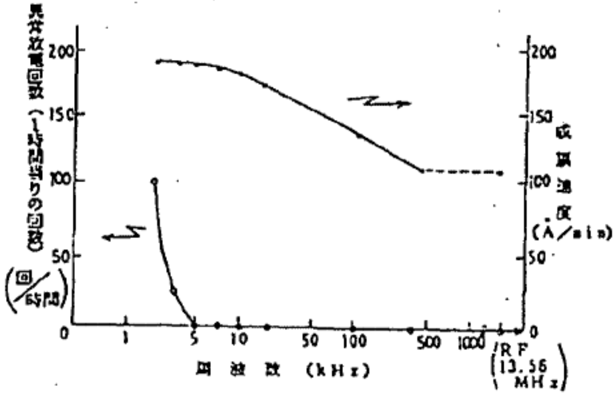
【図1】



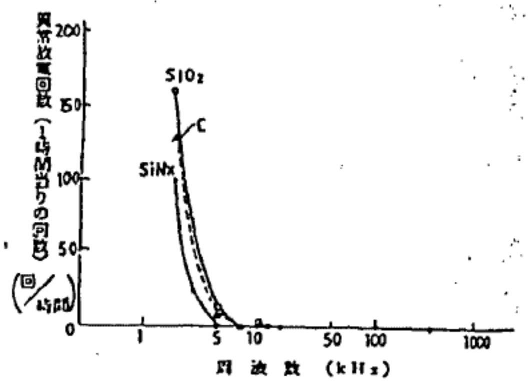
【図2】



【図3】



【図4】



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フロントページの続き

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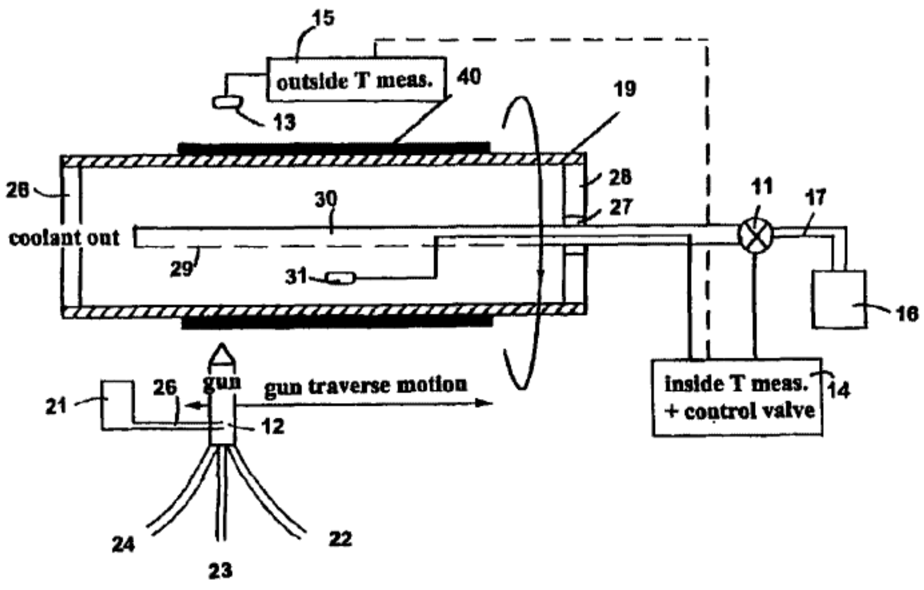

**(57) Abstract**

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.

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# 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 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

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 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 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, 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 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 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 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 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 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.

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.

## 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, 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 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 $15 \times 10^{-6}$ Ohm.m, more preferably lower than $10 \times 10^{-6}$ and most preferably less than $5 \times 10^{-6}$ Ohm.m. Values below $1 \times 10^{-6}$ 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.

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.

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 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 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 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 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 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 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 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 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 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 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 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 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 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.

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

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 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 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 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 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 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 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.

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 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 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 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 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 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 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 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 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 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 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, 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, 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 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 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 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 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 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 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 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.

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 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 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 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 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 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 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 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 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 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 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.

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 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 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 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 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 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 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.

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 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 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 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 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 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.

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 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 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 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 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 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 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.

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

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.

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.

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 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 x $10^{-6}$ Ohm.m, more preferably lower than 10 x $10^{-6}$ and most preferably less than 5 x $10^{-6}$ 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.

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 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.

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 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 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 material to that of the unused material.

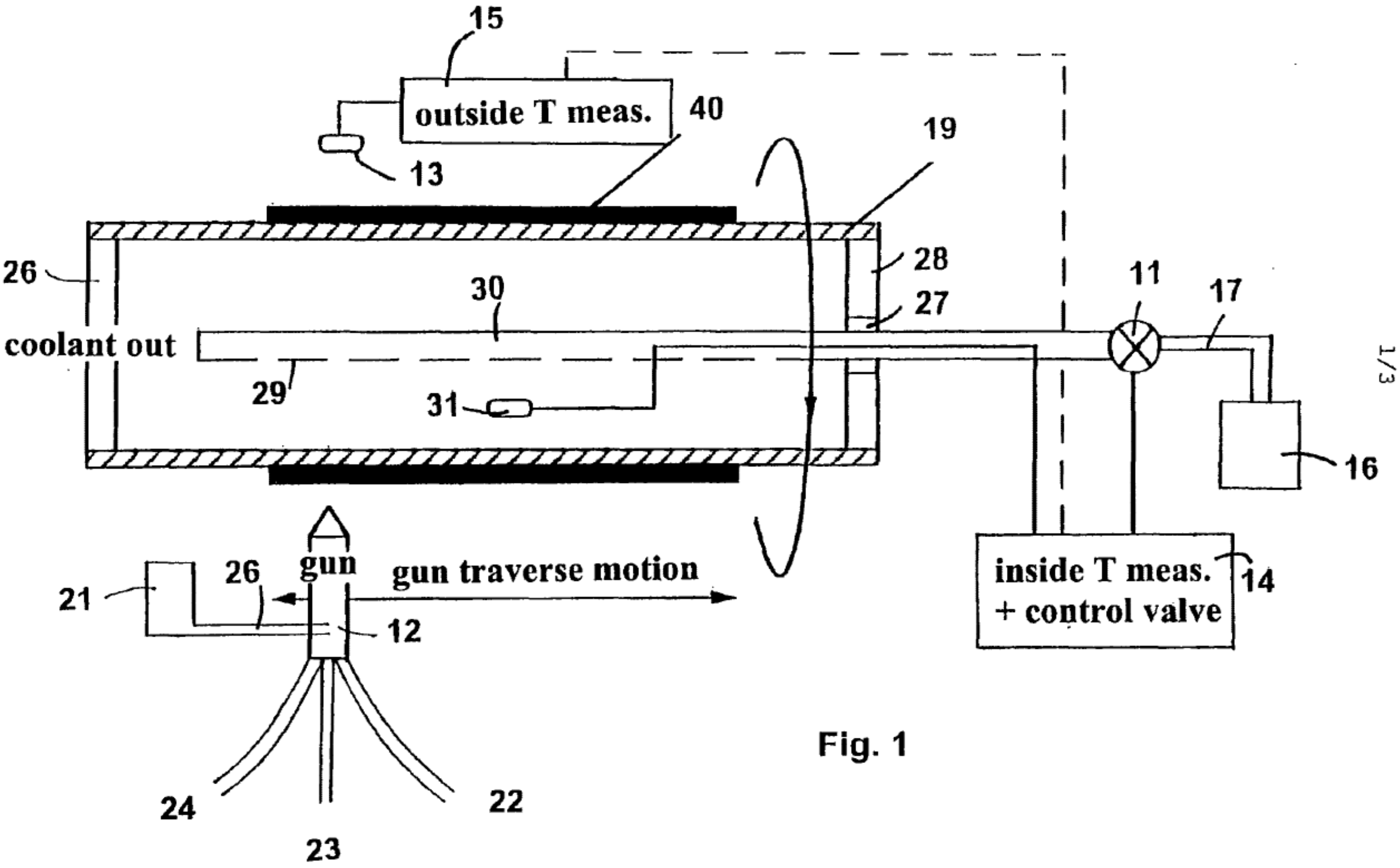
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Fig. 1

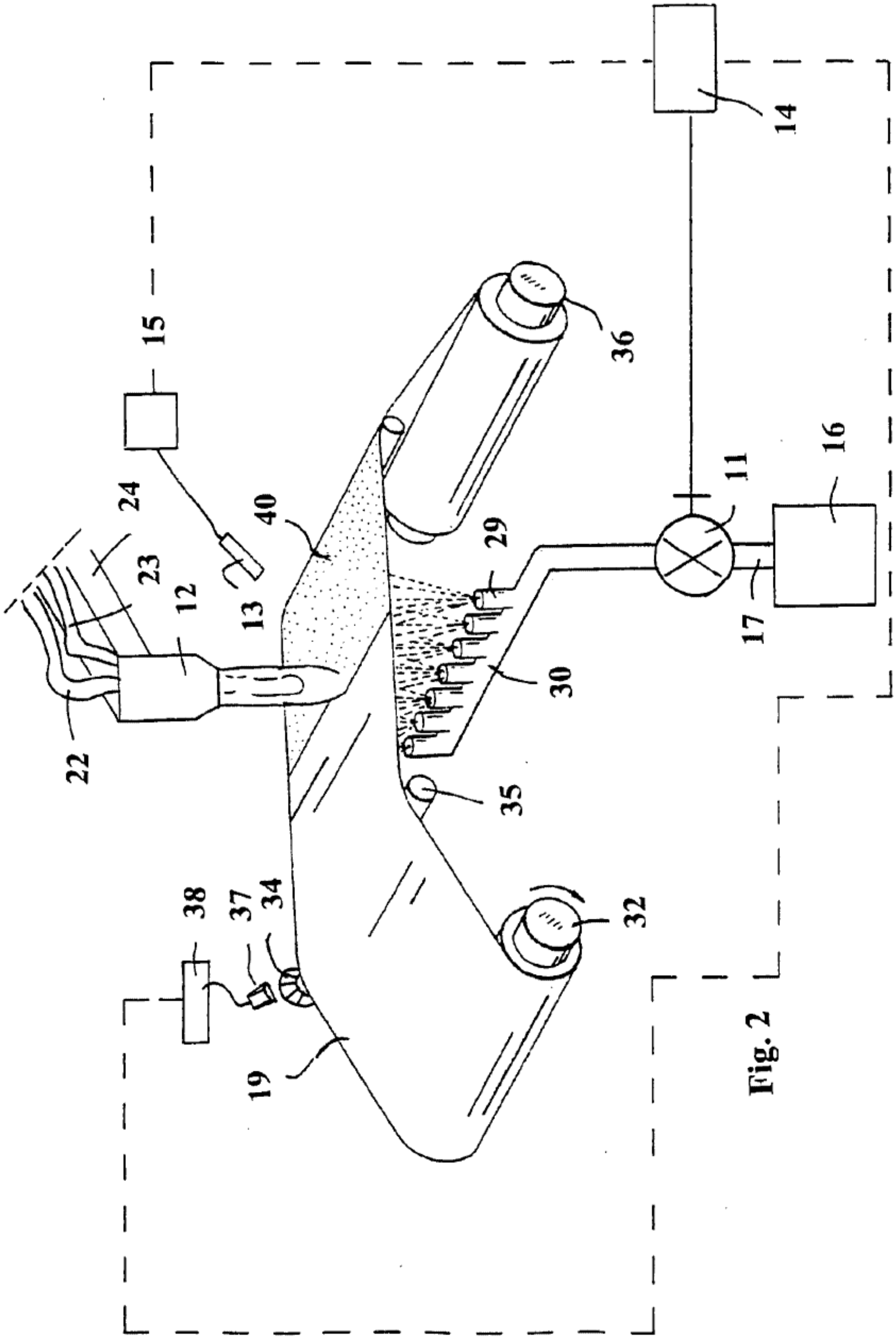

Fig. 2

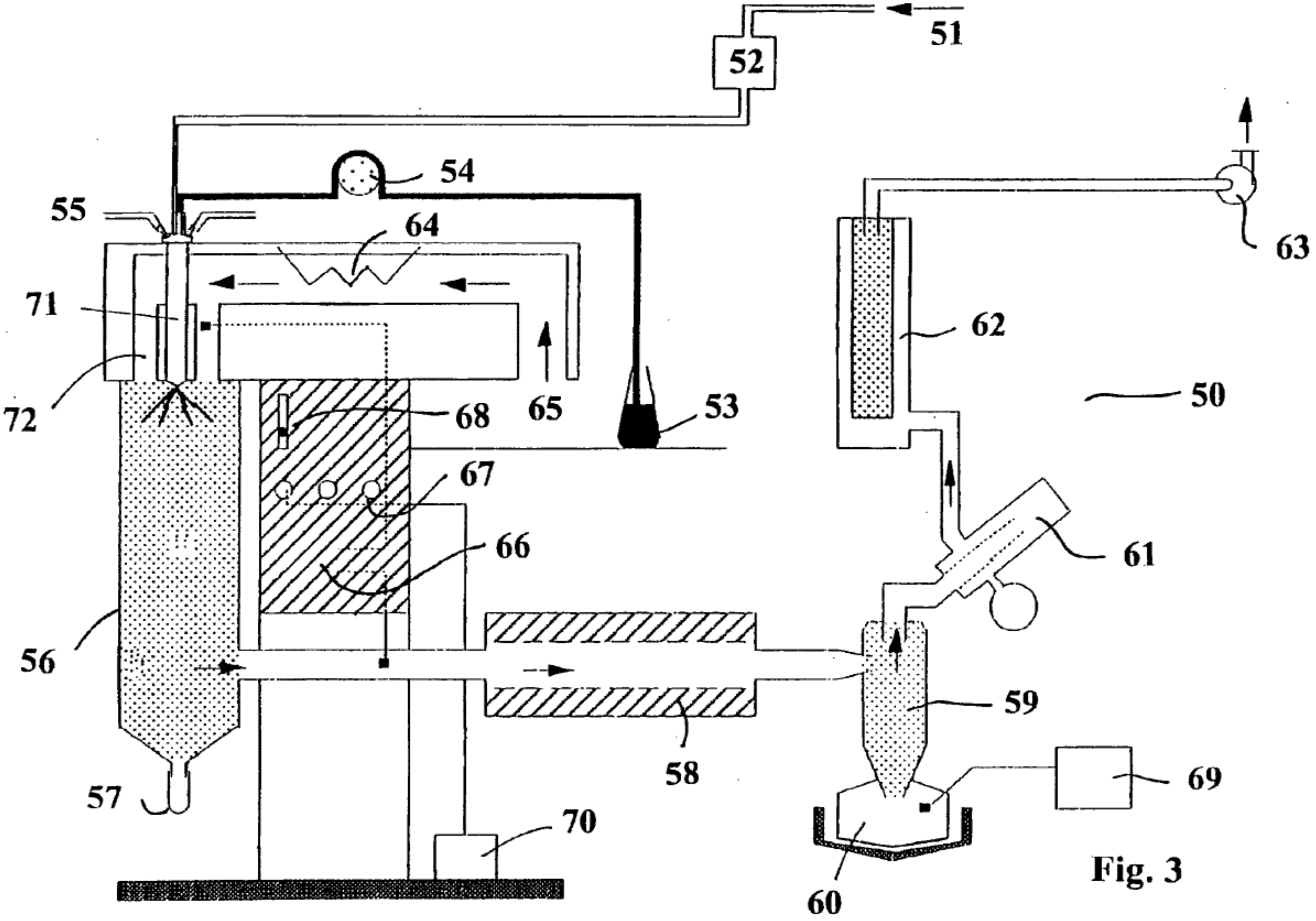

Fig. 3

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/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)<br>23 March 1993 (1993-03-23)<br>cited in the application<br>column 3, line 52 - column 4, line 16<br>--- | 1-5,<br>10-14 |
| X | EP 0 330 196 A (PERKIN ELMER CORP)<br>30 August 1989 (1989-08-30)<br>page 5, line 20 - line 25; claims 1,8<br>--- | 1,2,10,<br>12-14 |
| X | CH 648 358 A (CASTOLIN SA)<br>15 March 1985 (1985-03-15)<br>claim 1<br>--- | 1,10,<br>12-14 |
| X | DD 277 471 A (MANSFELD KOMBINAT W PIECK VEB) 4 April 1990 (1990-04-04)<br>page 2, line 21 - line 23<br>---<br>-/-- | 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<br>9 September 1999 | Date of mailing of the international search report<br>16/09/1999 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Patterson, A |

## 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)<br>21 November 1991 (1991-11-21)<br>the whole document<br>--- | 15,16 |
| A | EP 0 377 073 A (MITSUBISHI METAL CORP)<br>11 July 1990 (1990-07-11)<br>page 3, line 41 - line 57; table 2<br>page 7, line 7 - line 23; table 4<br>----- | 5-8 |

2

## INTERNATIONAL SEARCH REPORT

ernational 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. ☒ 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. ☒ 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.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

## 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 |
|---|---|---|---|---|---|
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| EP 0330196 | A | 30-08-1989 | CN 1036286 | A | 11-10-1989 |
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| CH 648358 | A | 15-03-1985 | NONE | | |
| DD 277471 | A | 04-04-1990 | NONE | | |
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| | | | KR 9507087 | B | 30-06-1995 |
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| | | | KR 9507088 | B | 30-06-1995 |

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**PCT**

**(10) International Publication Number**
**WO 2006/063308 A2**

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*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

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**(25) Filing Language:** English

**(26) Publication Language:** English

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| | | |
|---|---|---|
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| 60/651,363 | 8 February 2005 (08.02.2005) | US |

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**(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).

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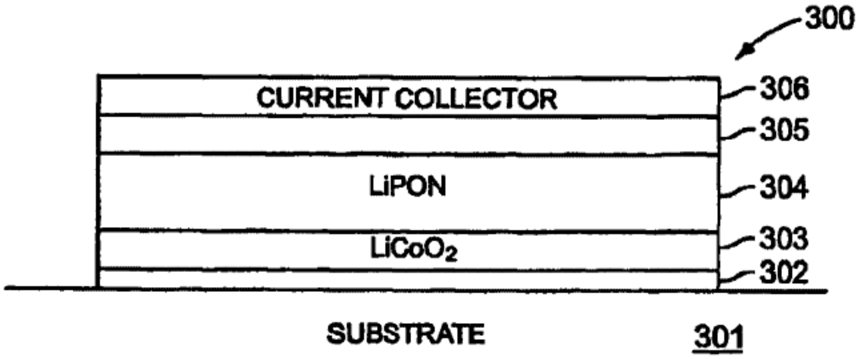
**(54) Title:** DEPOSITION OF LICoO2



**(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

# 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.

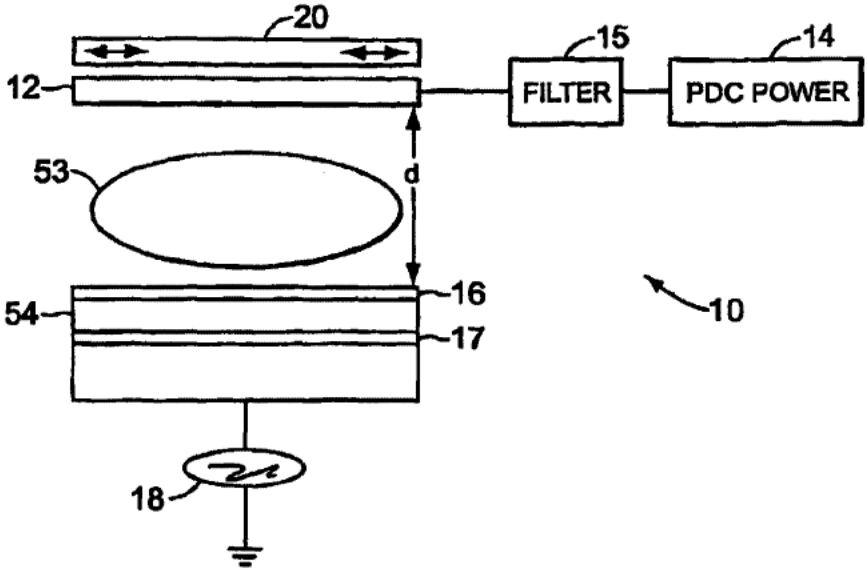

20
15
14
12
FILTER
PDC POWER
53
d
16
54
17
10
18

FIG. 1A

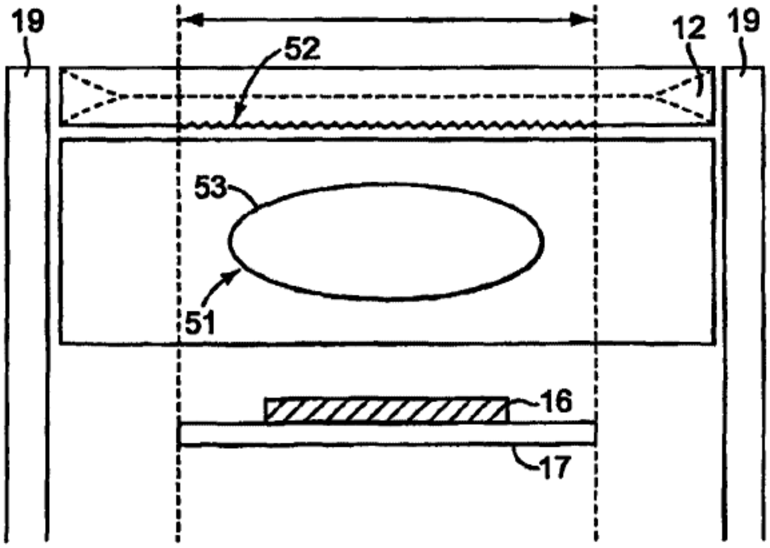

19
12
19
52
53
51
16
17

FIG. 1B

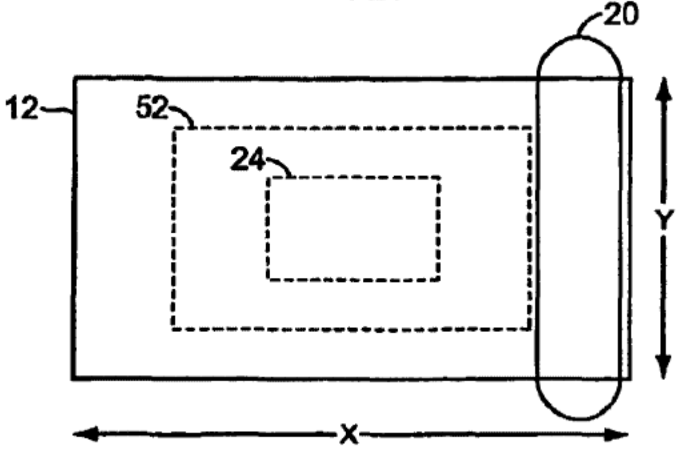


FIG. 2

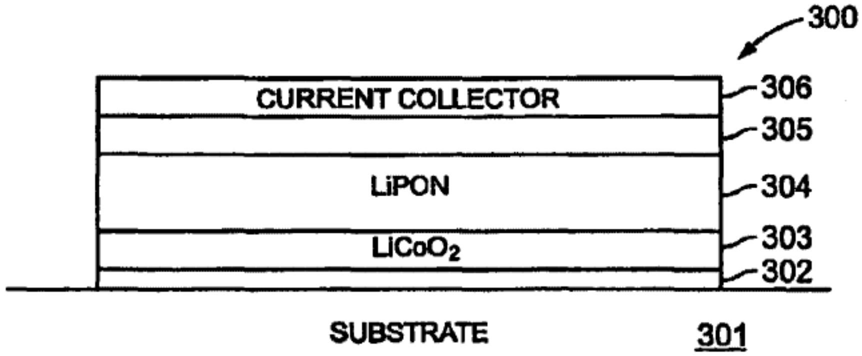


FIG. 3

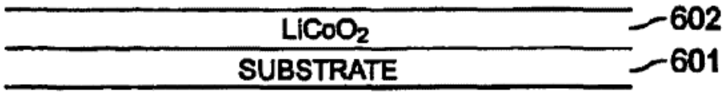


FIG. 6A

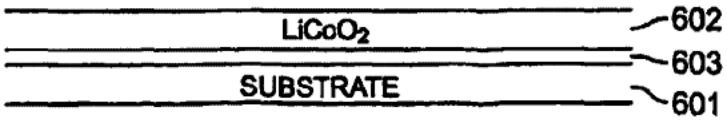


FIG. 6B

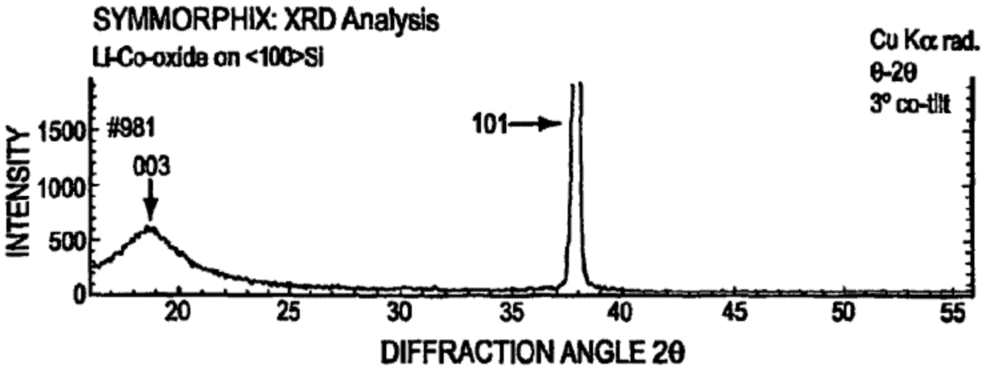

SYMMORPHIX: XRD Analysis
Li-Co-oxide on <100>Si
Cu Kα rad.
θ-2θ
3° co-tilt
#981
003
101
INTENSITY
1500
1000
500
0
20
25
30
35
40
45
50
55
DIFFRACTION ANGLE 2θ

FIG. 4A

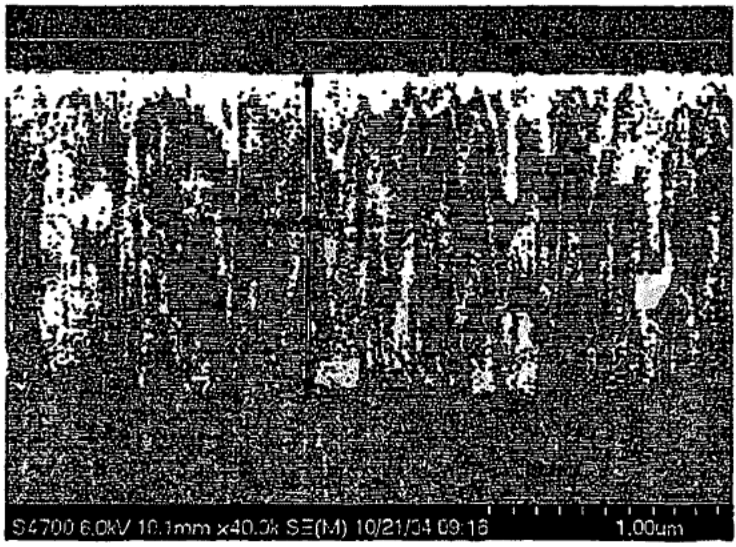

S4700 6.0kV 10.1mm x40.0k SE(M) 10/21/04 09:16
1.00um

FIG. 4B

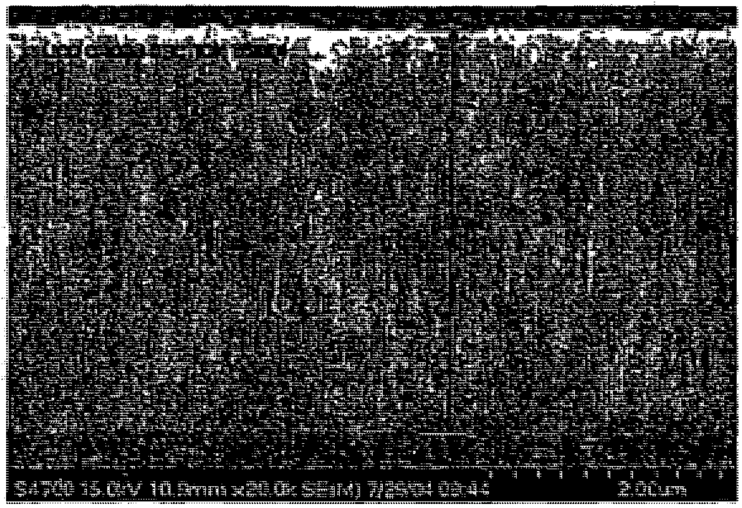

S4700 15.0kV 10.8mm x20.0k SE(M) 7/23/04 09:45
2.00um

FIG. 5A

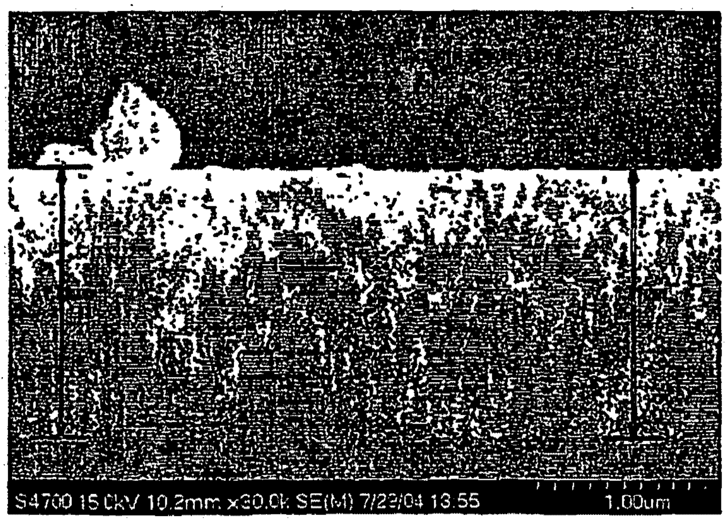

S4700 15.0kV 10.2mm x30.0k SE(M) 7/23/04 13:55
1.00um

FIG. 5B

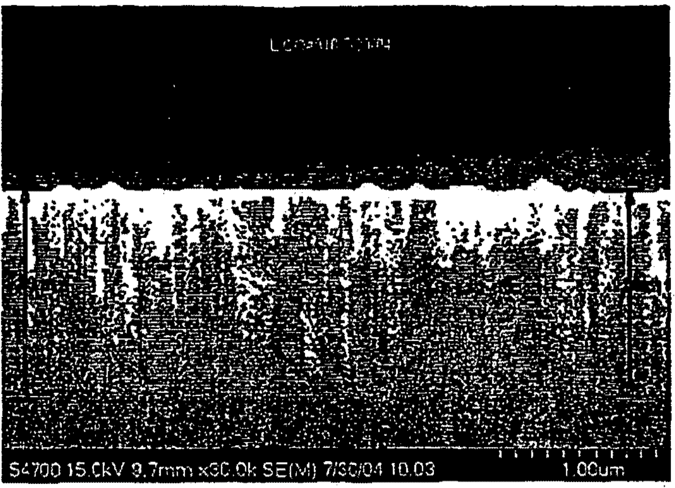

S4700 15.0kV 9.7mm x30.0k SE(M) 7/30/04 10.03
1.00um

FIG. 5C

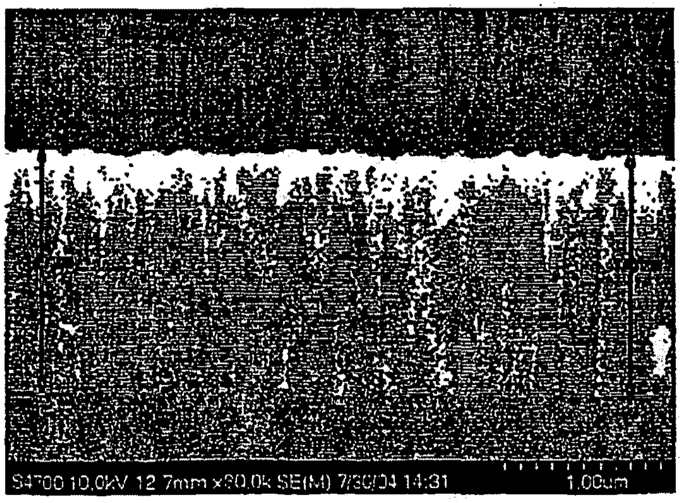

S4700 10.0kV 12.7mm x60.0k SE(M) 7/30/04 14:31
1.00um

FIG. 5D


S4700 10.0kV 12.5mm x30.0k SE(M) 6/2/04 09:27
1.00um

FIG. 5E

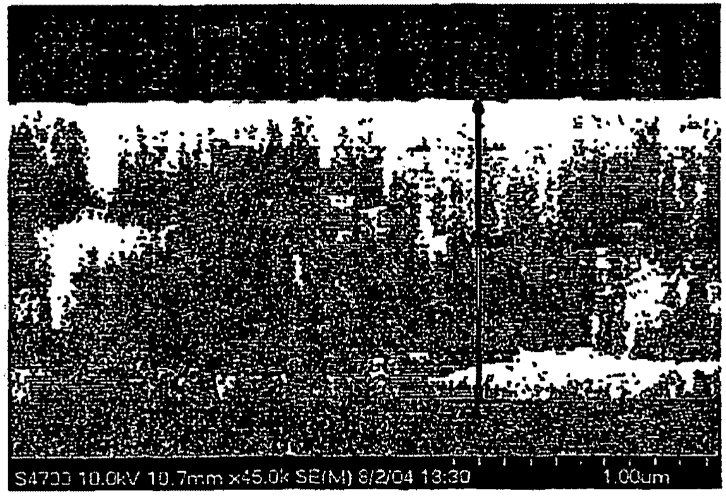

S4700 10.0kV 10.7mm x45.0k SE(M) 6/2/04 13:30
1.00um

FIG. 5F

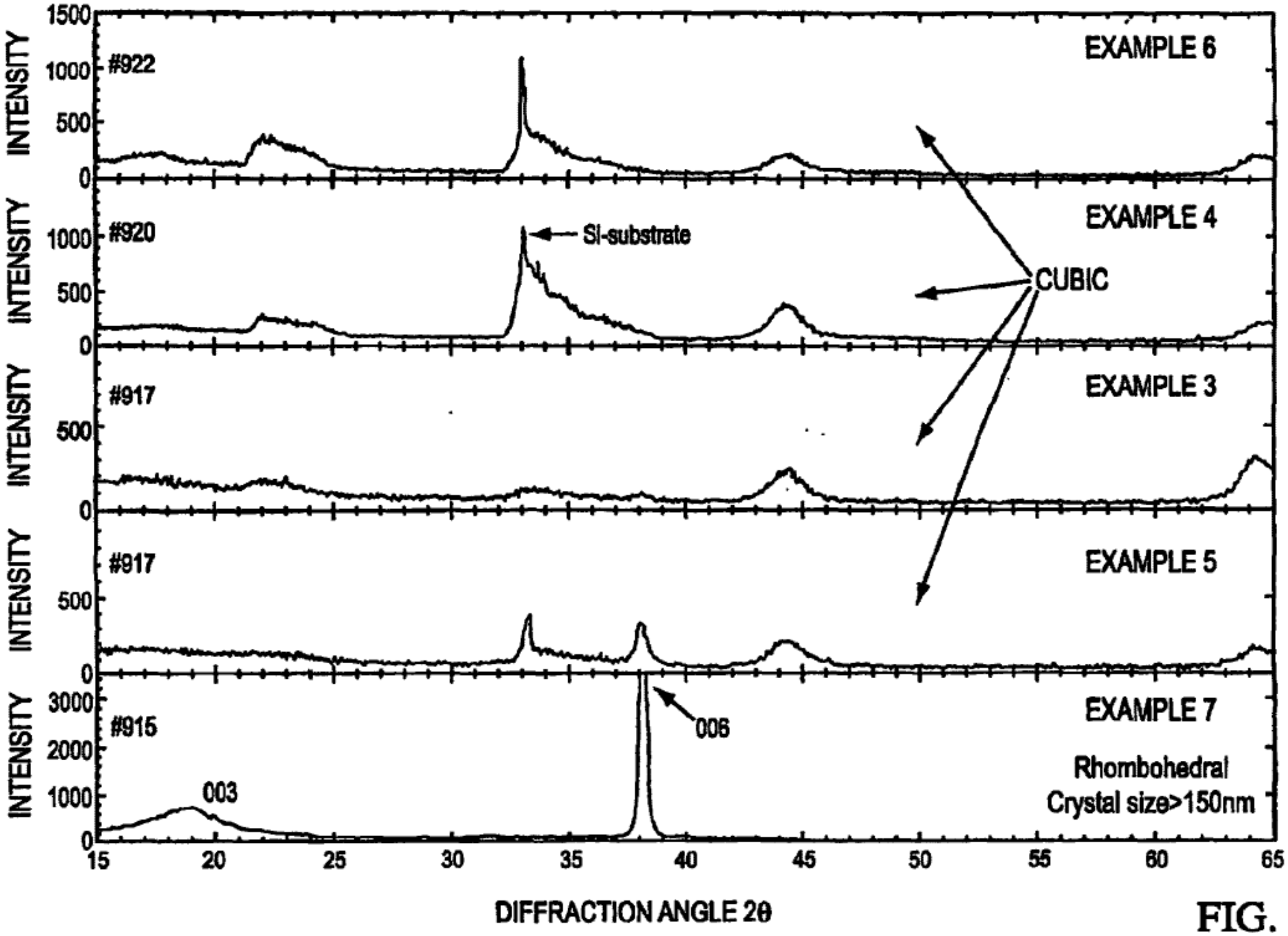

INTENSITY
1500
1000
500
0
#922
EXAMPLE 6
#920
Si-substrate
EXAMPLE 4
CUBIC
#917
EXAMPLE 3
#917
EXAMPLE 5
3000
2000
#915
003
006
EXAMPLE 7
Rhombohedral
Crystal size>150nm
15
20
25
30
35
40
45
50
55
60
65
DIFFRACTION ANGLE 2θ

FIG. 5G

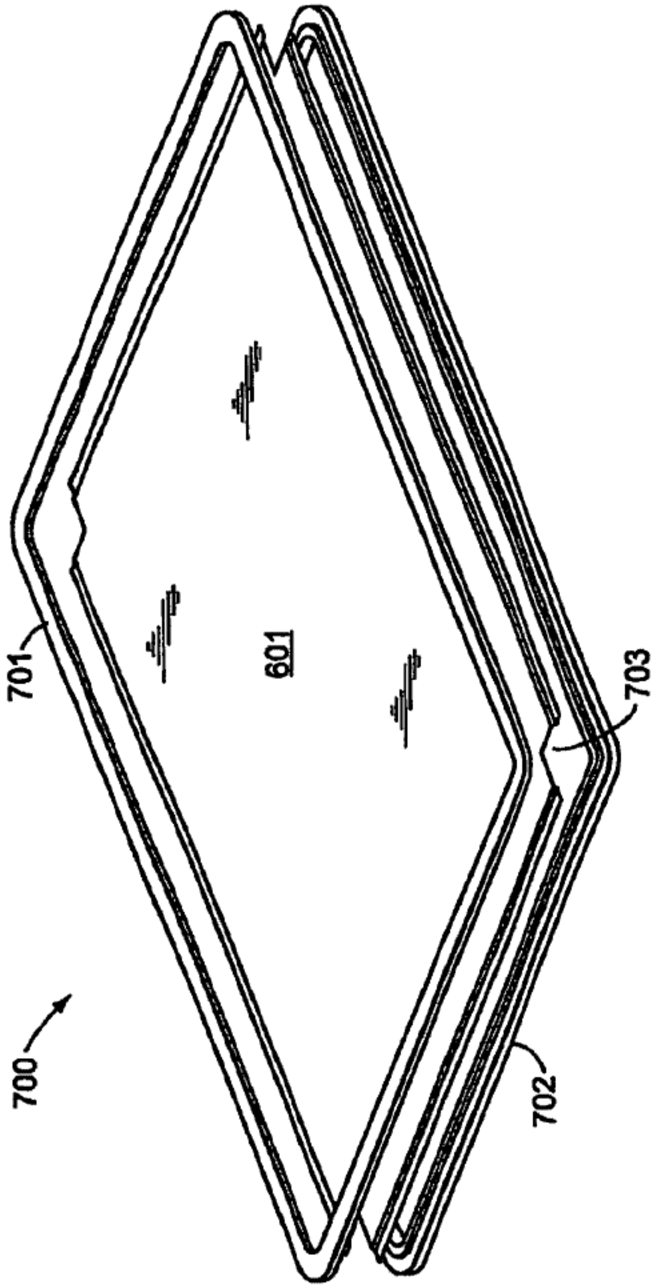


FIG. 7A