FILE HISTORY US 6,538,324

PATENT:	6,538,324
INVENTORS:	Tagami, Masayoshi
	Hayashi, Yoshihiro
TITLE:	Multi-layered wiring layer and method of fabricating the same
APPLICATION NO:	US2000596415A
FILED:	19 JUN 2000
ISSUED:	25 MAR 2003
COMPILED:	22 MAY 2015

	Issue classification	U.S. UTIL	. ITY Patent	Application		PATENT N 6538: 653832	324	
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not extend beyond the expiration date of U.S Patent. No.	Tom Thomas Supervisory patent examiner			1SS	
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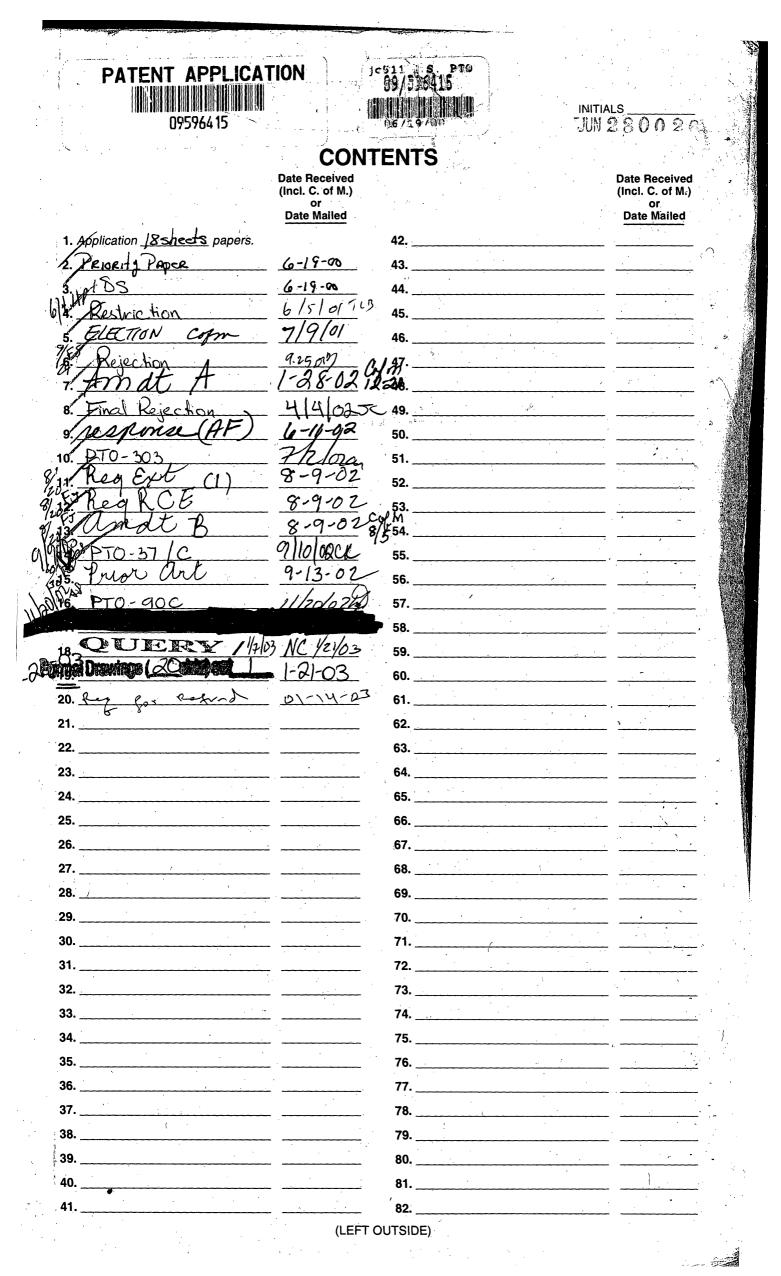
6,538,324

MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

Transaction History

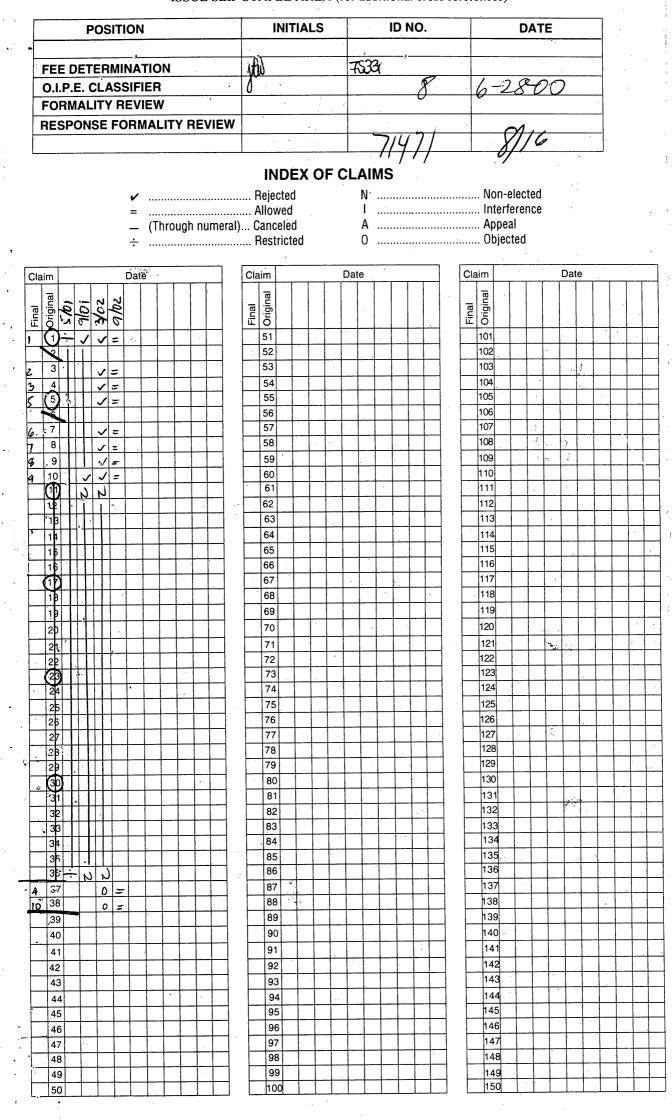
Date	Transaction Description
6/19/2000	Information Disclosure Statement (IDS) Filed
6/19/2000	Information Disclosure Statement (IDS) Filed
	Request for Foreign Priority (Priority Papers May
6/19/2000	Be Included)
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7/10/2000	IFW Scan & PACR Auto Security Review
8/16/2000	Application Dispatched from OIPE
8/16/2000	Correspondence Address Change
9/13/2000	Case Docketed to Examiner in GAU
4/29/2001	Case Docketed to Examiner in GAU
6/4/2001	Restriction/Election Requirement
6/5/2001	Mail Restriction Requirement
7/9/2001	Response to Election / Restriction Filed
7/14/2001	Date Forwarded to Examiner
9/24/2001	Non-Final Rejection
9/25/2001	Mail Non-Final Rejection
1/28/2002	Response after Non-Final Action
2/2/2002	Date Forwarded to Examiner
4/3/2002	Final Rejection
4/4/2002	Mail Final Rejection (PTOL - 326)
6/11/2002	Amendment after Final Rejection
6/25/2002	Date Forwarded to Examiner
7/1/2002	Advisory Action (PTOL-303)
7/2/2002	Mail Advisory Action (PTOL - 303)
8/9/2002	Request for Continued Examination (RCE)
8/9/2002	Request for Extension of Time - Granted
8/9/2002	Workflow - Request for RCE - Begin
8/20/2002	Date Forwarded to Examiner
8/20/2002	Date Forwarded to Examiner
8/20/2002	Disposal for a RCE / CPA / R129

9/9/2002	Notice of Allowance Data Verification Completed
9/9/2002	Case Docketed to Examiner in GAU
9/10/2002	Mail Notice of Allowance
9/13/2002	Information Disclosure Statement (IDS) Filed
9/13/2002	Information Disclosure Statement (IDS) Filed
	Workflow - Informational Disclosure Statement -
9/13/2002	Finish
	Workflow - Informational Disclosure Statement -
9/13/2002	Begin
9/15/2002	Dispatch to Publications
9/17/2002	Receipt into Pubs
9/18/2002	Workflow - File Sent to Contractor
10/11/2002	Receipt into Pubs
11/20/2002	Mail Miscellaneous Communication to Applicant
	Miscellaneous Communication to Applicant - No
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11/21/2002	Receipt into Pubs
12/16/2002	Issue Fee Payment Verified
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	Workflow - Drawings Matched with File at
12/16/2002	Contractor
12/16/2002	Workflow - Drawings Received at Contractor
12/16/2002	Workflow - Drawings Sent to Contractor
12/16/2002	Issue Fee Payment Received
12/30/2002	Application Is Considered Ready for Issue
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1/27/2003	Receipt into Pubs
3/6/2003	Issue Notification Mailed
3/25/2003	Recordation of Patent Grant Mailed
3/25/2003	Patent Issue Date Used in PTA Calculation



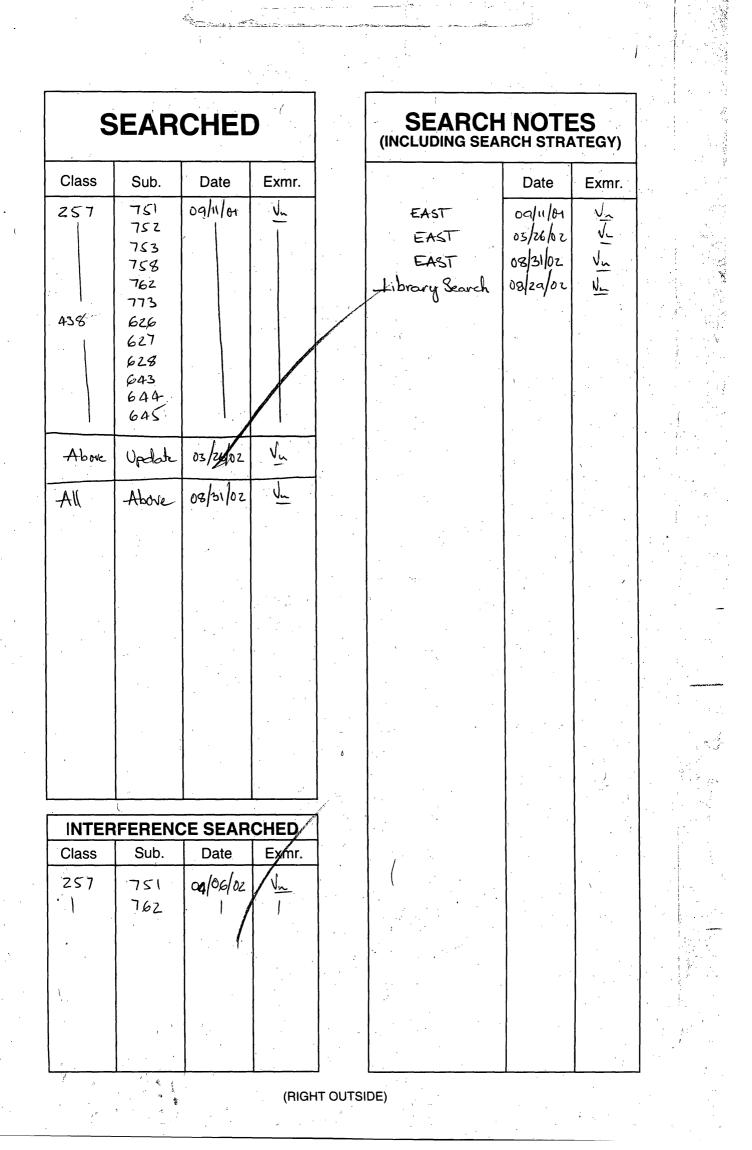
Page 5 of 333

ISSUE SLIP STAPLE AREA (for additional cross references)



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	Туре	Hits	Search Text
1	BRS	949	(amorphous and crystal\$5) with nitride
2	BRS	235	((amorphous and crystal\$5) with nitride) and (barrier or barriers)
3	BRS	633	(amorphous and crystal\$5) with nitride
4	BRS	63	((amorphous and crystal\$5) with nitride) and (barrier or barriers)
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6	BRS	237	(amorphous and crystal\$5) and (((257/751,752,753,753,762,773) or (438/626,627,628,643,644,645)).CCLS.)

09/03/2002, EAST Version: 1.03.0002

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5	USPAT	2002/08/31 13:15			
6	USPAT	2002/09/03 07:36			

09/03/2002, EAST Version: 1.03.0002

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18 S (L7 OR L8) AND L43 16 S L44 NOT ((L38 OR L3y OR L40) OR L30) 125 S (L18 OR L29 OR L37) L44 L45 125 L46 L46 NOT (L44 OR (L38 OR L39 OR L40) OR L30) L47 99 S 90744 S (SECOND OR TOP OR BOTTOM OR UNDER OR OVER)(3A)(FILM OR LAYER####) L48 L49 5 S L47 AND L48 L50 121888 S (L18 OR L35 OR L16 OR L14 OR L11) L51 99 S L47 AND L50 L51 AND (L7 OR L8) L51 AND L7 AND L8 1 52 71 S L53 30 S (L51 AND (H01L021-28 OR H01L021-3205 OR H01L021-768)/IC) NOT L53 L54 0 S L55 (L7 OR L8) AND L50 124 S L56 75 S L53 OR L49 OR (L44 OR (L38 OR L39 OR L40) OR L30) L57 80 S L55 NOT L56 0 S L57 AND (SECOND OR TOP OR BOTTOM)(2A)(FILM OR LAYER####) 38 S L57 AND (FILM OR LAYER####) 0 S L35 AND (L7 OR L8) 1.58 38 S L59 L60 L35 AND (L5 OR L6) L61 31 . S L62 L61 AND (NONCRYST? OR NON CRYST######## OR AMORPHOUS) 0 S L63 5 S 31751 S (NITROGEN OR "N")(2A)(FILM OR LAYER#####) 79 S (L7 OR L8) AND L64 L64 1 65 L48 AND L65 L66 6 S L67 12725 S (NITROGEN OR "N")(2A)DIFFERENT L50 AND L67 L68 2315 S (L5 OR L6) AND L68 L59 OR L66 OR L63 L69 43 S L70 49 S L70 OR L53 OR L49 OR (L44 OR (L38 OR L39 OR L40) OR L30) L71 121 S L69 NOT L71 L72 41 S L73 1 S L48 AND L72 L74 40' S L72 NOT L73 L75 30750 S DOUBLE(2W)LAYER### L76 291 Ś L12 AND L75 10 S L76 AND AMORPHOUS(1A)(FILM OR LAYER###) 6 S L76 AND CRYST########(1A)(FILM OR LAYER###) 0 S L76 AND NONCRYST#########(1A)(FILM OR LAYER###) L77 L78 L79 (L77 OR L78) L80 16 S NITRIDE NITRIDE(W)(MULTILAYER OR LAYER OR FILM OR MULTIPLE) PLU=ON L81 1- RN : 69 TERMS 9 S L81 L82 SEL PLU=ON L81 1- RN : 2457130 S L82 9 S L81 AND L83 1.83 L84 L85 0 S CRYSTAL####### AMORPHOUS DOUBLE LAYER CRYSTAL#######(3A)AMORPHOUS DOUBLE(2W)LAYER L86 0 S L87 72 S 1.88 4 S L12 AND L87 266 S (TAGAMI MASAYOSHI OR HAYASHI YOSHIHIRO)/IN,AU 81642 S (TWO OR DUAL OR DOUBLE OR BI)(W)LAYER OR BILAYER? 1 S L89 AND L90 1.89 L90 L'91 L92 686 S L12 AND L90 43 S (AMORPHOUS OR NONCRYST? OR NON CRYST?) AND L92 19 S L93 AND CRYST? L93 L94 SEL PLU=ON L94 1- RN : L95 67 TERMS 1.96 1859308 S L95 L94 AND L96 L97 19 S 1 S DOUBLE NITRIDE LAYER L98 L99 4 S TWO NITRIDE LAYERS

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03/26/2002, EAST Version: 1.02.0008

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2	BRS	4431	crystal\$5 with nitride
3	BRS	841	(amorphous with nitride) and (crystal\$5 with nitride)
4	BRS	142798	barrier\$1
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09/14/2001, EAST Version: 1.02.0008

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5	USPAT	2001/09/11 09:01		

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(10) Patent No.:

(12) United States Patent

Tagami et al.

(54) MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

- (75) Inventors: Masayoshi Tagami, Tokyo (JP); Yoshihiro Hayashi, Tokyo (JP)
- (73) Assignee: NEC Corporation, Tokyo (JP)
- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.
- Appl. No.: 09/596,415 (21)

Jun. 19, 2000 (22)Filed

Foreign Application Priority Data (30)

Jun. 24, 1999 (JP) 11-214110

- (51) Int. Cl.⁷ H01L 23/48; H01L 23/52
- (52)
- (58) Field of Search 257/751, 752, 257/753, 758, 762, 773; 438/626, 627,
- 628, 643, 644, 645

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Sub 0.25µm Technology, 1998 Symposium on VLSI Technology Digest of Technical Papers, 1998, pp. 22-23.

* cited by examiner

Primary Examiner-Tom Thomas

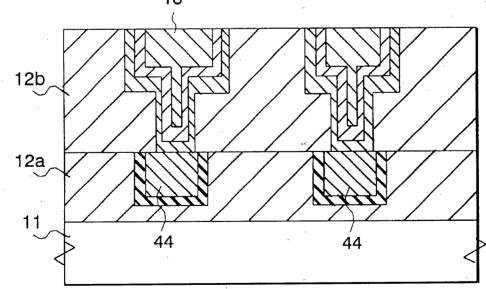
Assistant Examiner-Hung Kim Vu

(74) Attorney, Agent, or Firm-Scully, Scott, Murphy & Presser

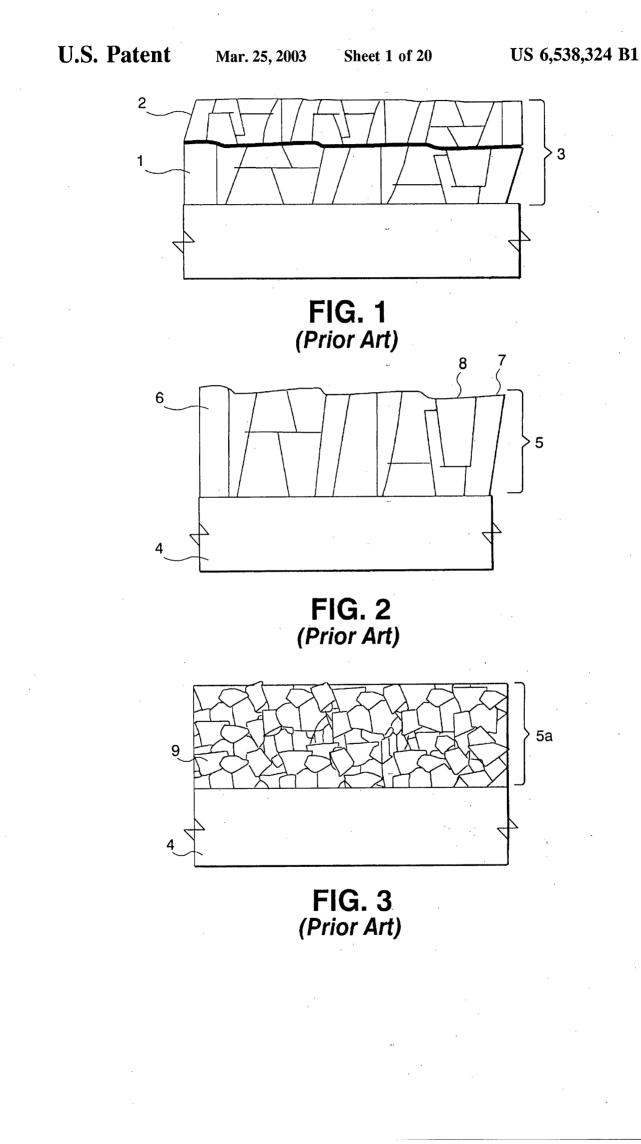
ABSTRACT (57)

There is provided a barrier film preventing diffusion of copper from a copper wiring layer formed on a semicon-ductor substrate. The barrier film has a multi-layered structure of first and second films wherein the first film is composed of crystalline metal containing nitrogen therein, and the second film is composed of amorphous metal nitride. The barrier film is constituted of common metal atomic species. The barrier film prevents copper diffusion from a copper wiring layer into a semiconductor device, and has sufficient adhesion characteristic to both a copper film and an interlayer insulating film.

10 Claims, 20 Drawing Sheets



US 6,538,324 B1 (45) Date of Patent: Mar. 25, 2003



U.S. Patent

Mar. 25, 2003

Sheet 2 of 20

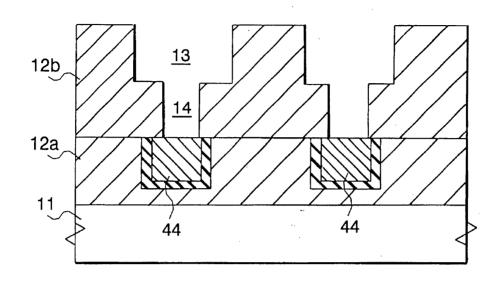


FIG. 4A

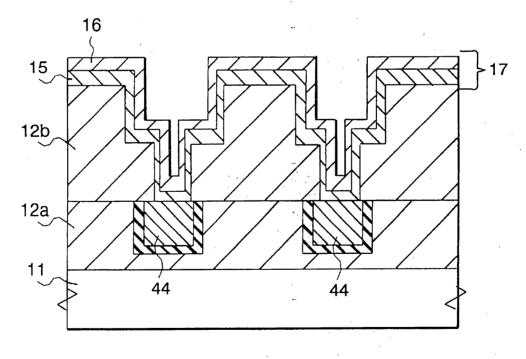


FIG. 4B

Sheet 3 of 20

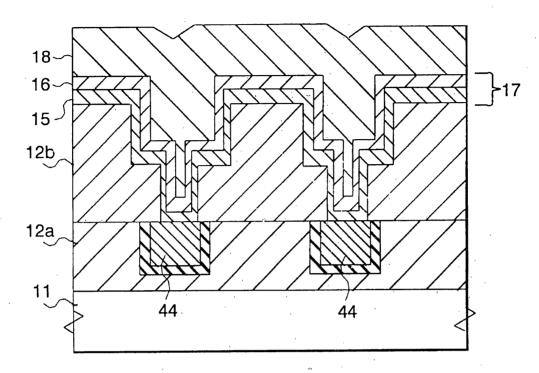


FIG. 4C

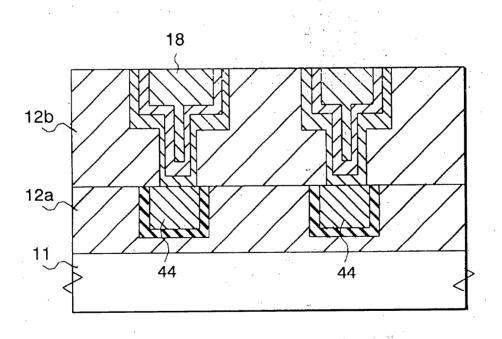
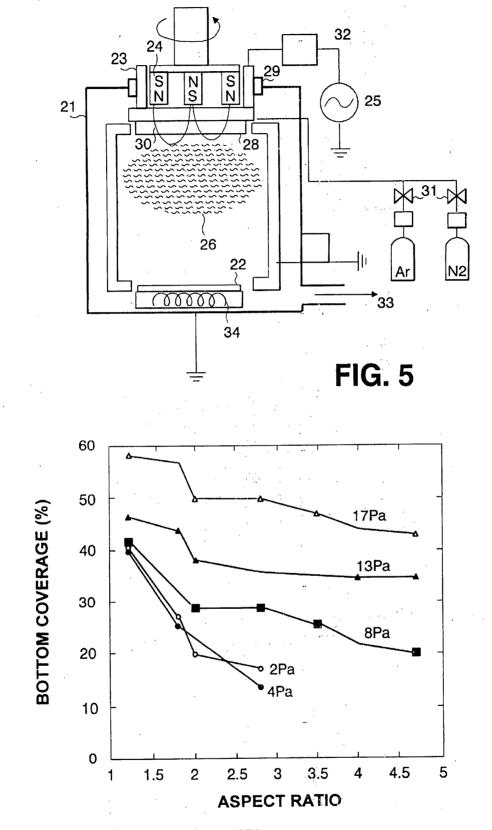


FIG. 4D



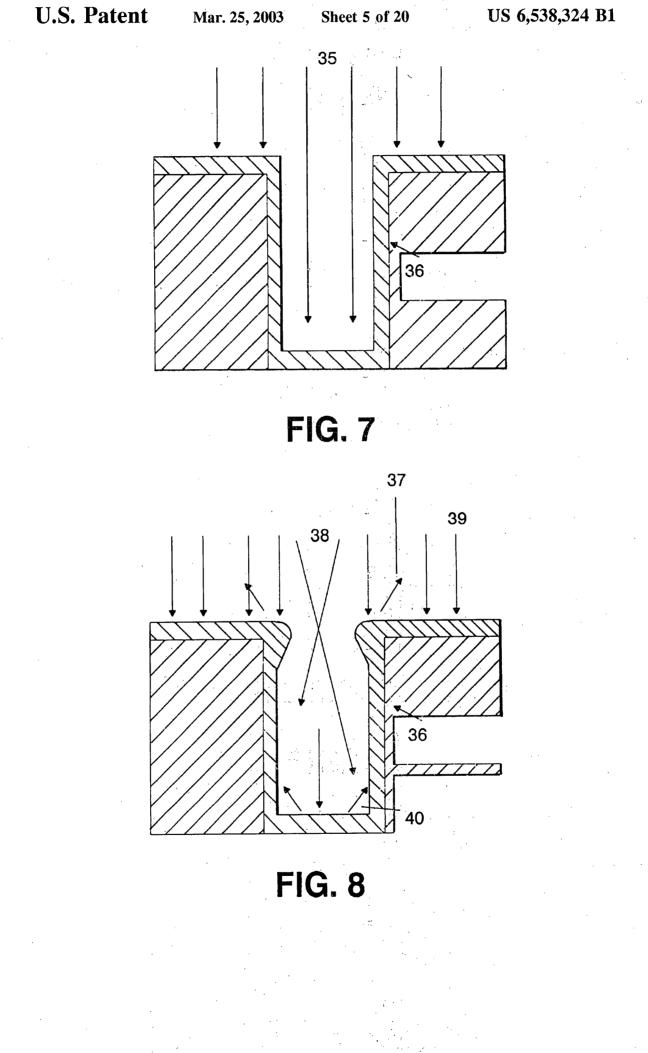
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FIG. 6

U.S. Patent

Mar. 25, 2003

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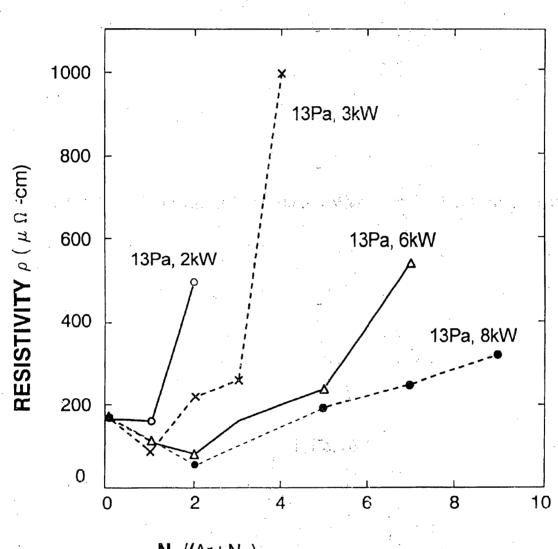
U.S. Patent

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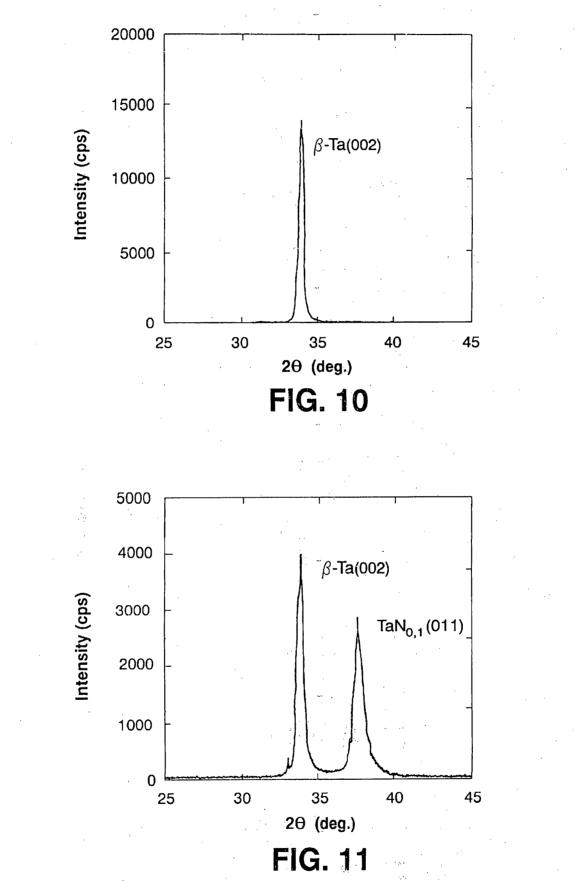
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 $N_2/(Ar+N_2)$ FLOW RATE RATIO (%)

FIG. 9



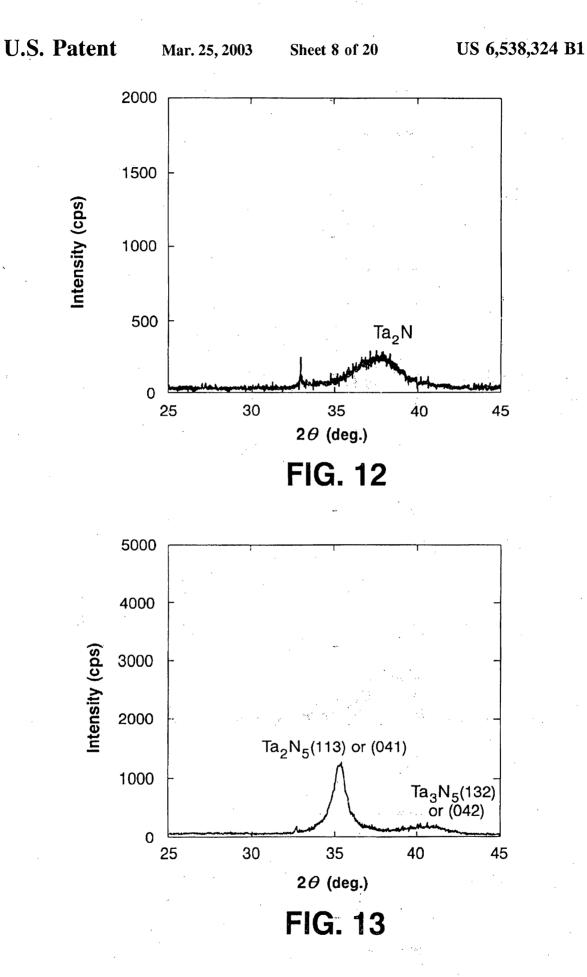


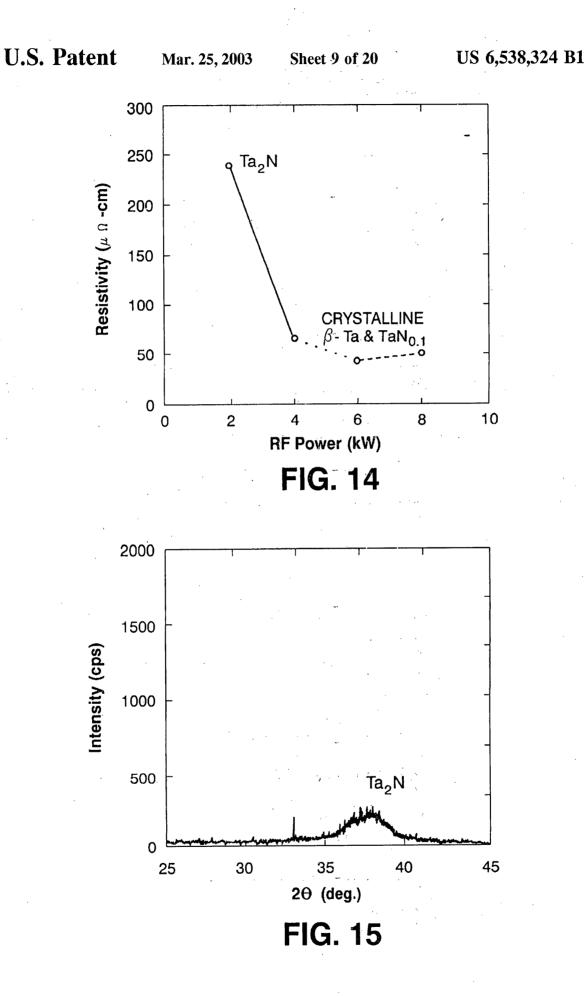


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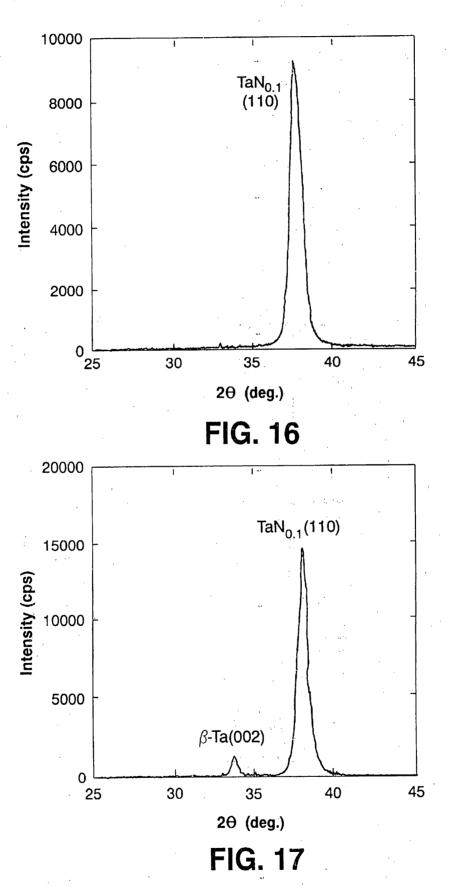




U.S. Patent

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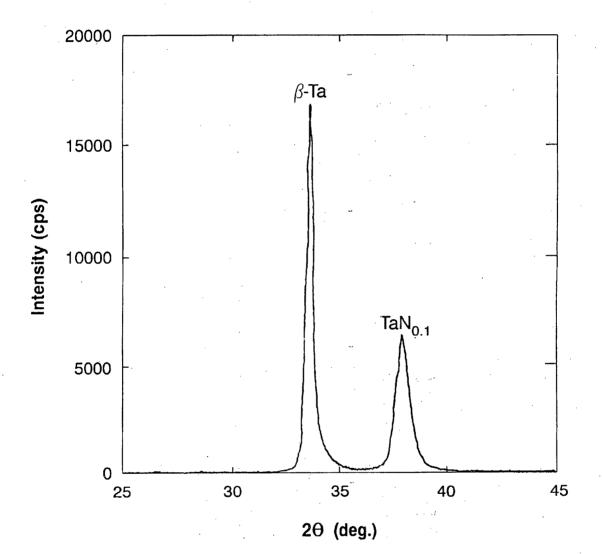
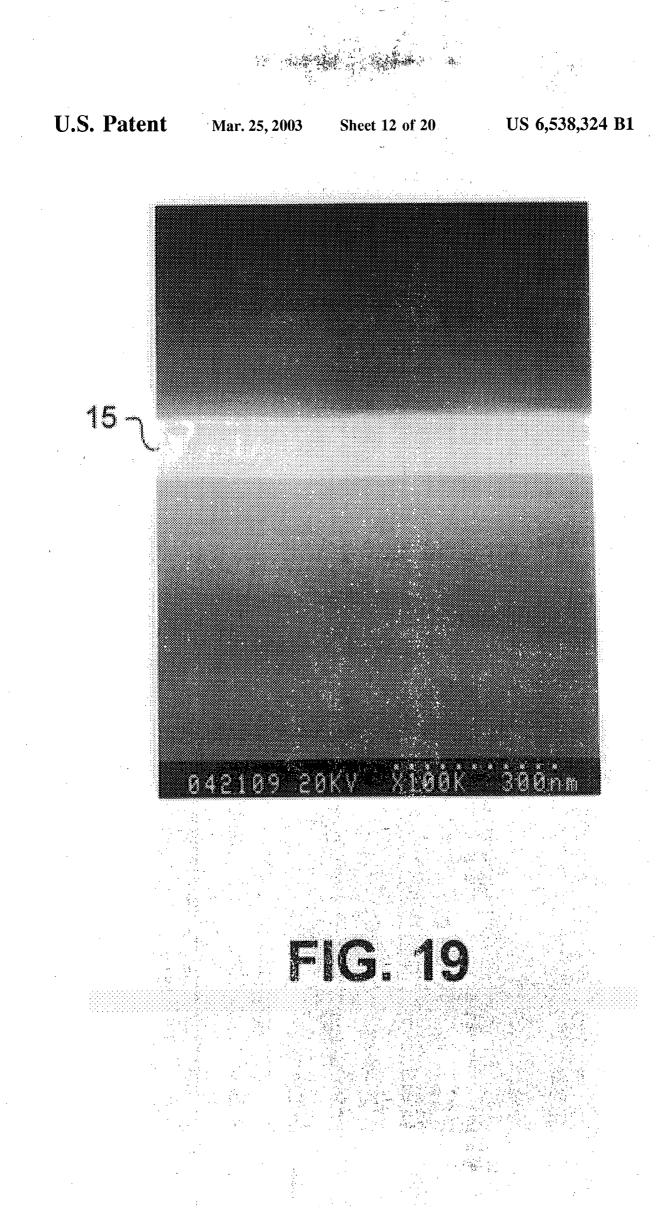
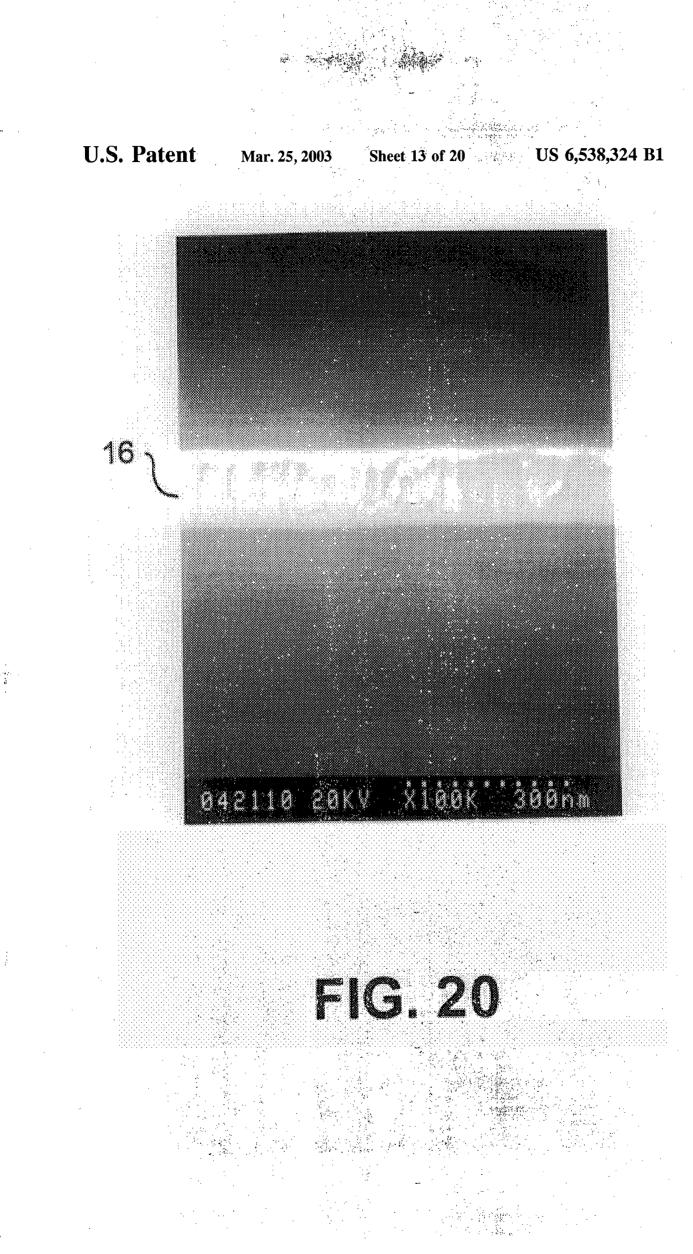


FIG. 18

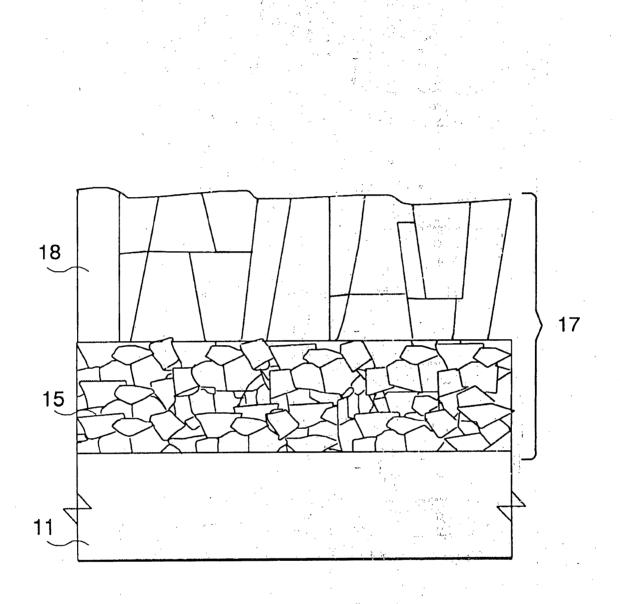
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FIG. 21

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U.S. Patent

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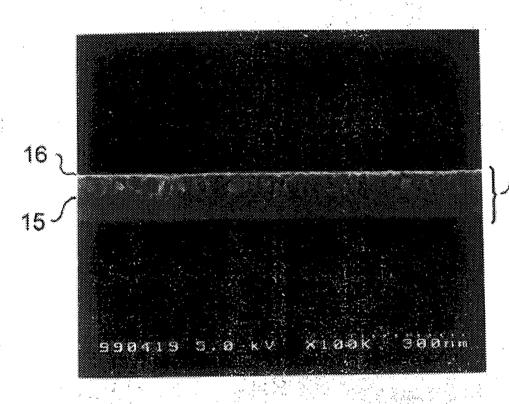
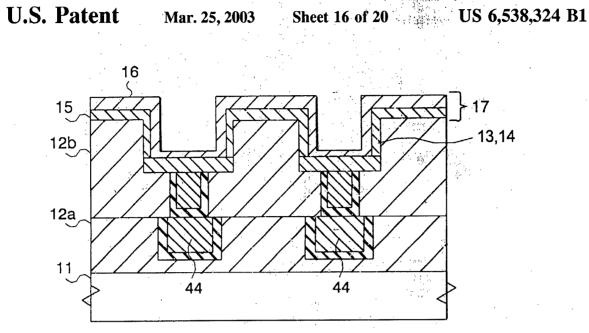


FIG. 22

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FIG. 23

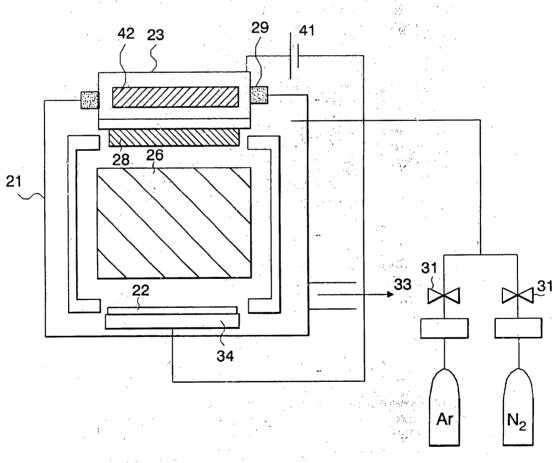
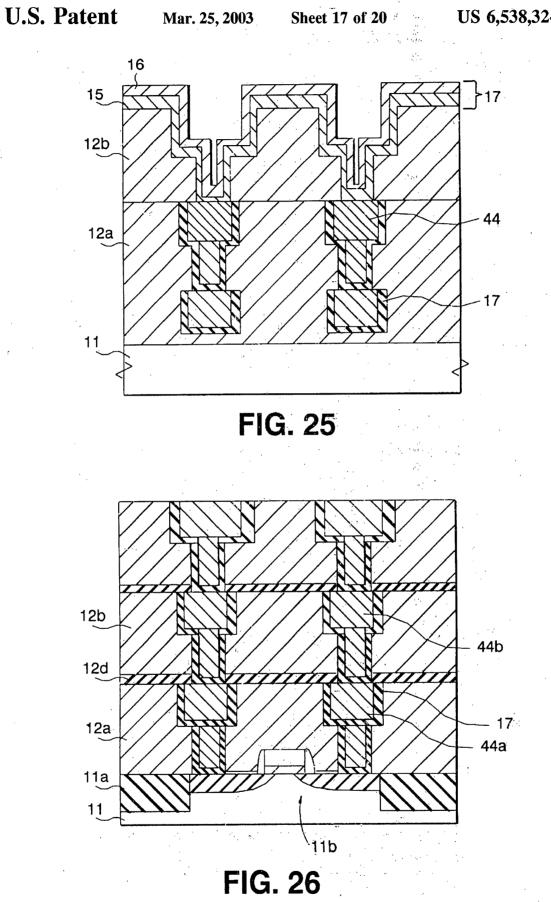


FIG. 24





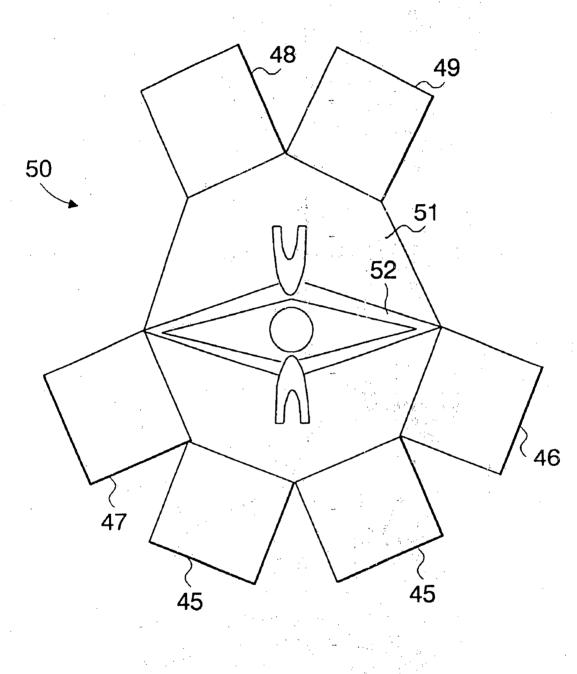
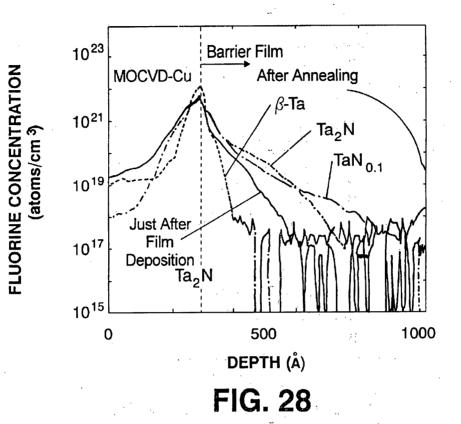


FIG. 27



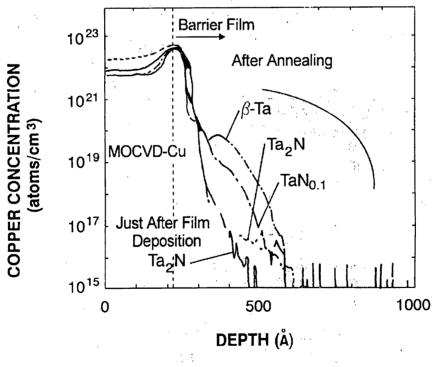
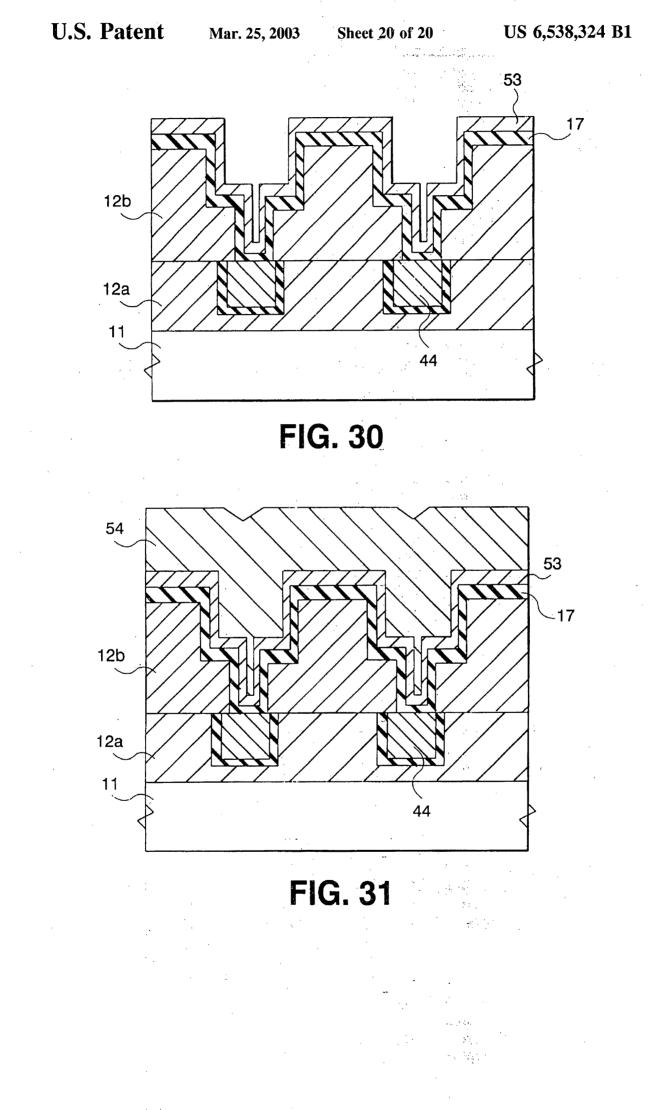


FIG. 29



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MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a semiconductor integrated circuit including a copper wiring layer, and more particularly to a barrier film which prevents copper diffusion from such a copper wiring layer.

2. Description of the Related Art

As a semiconductor device has been designed to be smaller and smaller in size, wiring delay exerts greater influence on a silicon ULSI device. As a result, though a wiring layer has been composed of aluminum, it is necessary to compose a wiring layer of copper in place of aluminum.

Resistivity of copper is equal to about 70% of resistivity of aluminum. However, since copper does not form passive state composed of an oxide film, at a surface thereof, unlike 20 aluminum, copper is more corrosive than aluminum.

In addition, since copper has a high diffusion rate in both silicon (Si) and silicon dioxide (SiO_2) , if copper enters MOSFET formed on a silicon substrate, copper would induce reduction in carrier lifetime.

Hence, it is absolutely necessary for a semiconductor device having a copper wiring layer to have a diffusionbarrier film for preventing diffusion of copper into an interlayer insulating film formed between copper wiring layers. In addition, since such a diffusion-barrier film has to ³⁰ have high adhesion characteristic to both an interlayer insulating film and a copper wiring layer in order to keep reliability in wiring.

Thus, there have been made many suggestions about a structure of a barrier metal layer and a method of fabricating ³⁵ the same, in order to prevent copper diffusion form a copper wiring layer.

For instance, a structure of a barrier metal layer is suggested in the following articles:

(a) Semiconductor World, Nobuyoshi Awaya, February 1998, pp. 91-96 (hereinafter, referred to as Prior Art 1);

(b) Advanced Metallization and Interconnect Systems for ULSI Applications in 1997, Kee-Won Kwon et al.,

- 1998, pp. 711-716 (hereinafter, referred to Prior Art 2); (c) Journal Electrochemical Society, M. T. Wang et al., July 1998, pp. 2538-2545 (hereinafter, referred to as Prior Art 3); and
- (d) 1998 Symposium on VLSI Technology Digest of Technical Papers, D. Denning et al., 1998, pp. 22–23. 50

In addition, a structure of a barrier metal layer and a method of fabricating the same both for preventing copper diffusion is suggested also in Japanese Unexamined Patent Publications 8-139092, 8-274098, 9-64044 and 10-256256, and Japanese Patent Application No. 10-330938. Herein, 55 Japanese Patent Application No. 10-330938 is not published yet, and hence does not constitute prior art to the present invention. However, it is explained in the specification only for better understanding of the present invention. The applicant does not admit that Japanese Patent Application No. 60 10-330938 constitutes prior art to the present invention.

It is quite difficult to dry-etch copper, and hence, a copper wiring layer is formed generally by chemical mechanical polishing (CMP).

Specifically, a copper wiring layer is formed as follows. 65 An insulating film is formed on an underlying copper wiring layer. Then, the insulating film is formed with a

recess and a through-hole reaching the underlying copper wiring layer. Then, a thin diffusion-barrier film is formed on surfaces of the recess and the through-hole therewith such that the recess and the through-hole is completely covered at surfaces thereof with the diffusion-barrier film in order to prevent copper diffusion from uncovered region.

Thereafter, a copper film is deposited filling the recess and the through-hole therewith by CVD or sputtering. Then, the copper film and the diffusion-barrier film are removed in selected regions by CMP. Thus, a copper wiring layer is completed.

As will be obvious to those skilled in the art, the diffusionbarrier film is required to have high coverage as well as capability of preventing copper diffusion and adhesion to copper.

The diffusion-barrier film is composed, for instance, of refractive metal such as tungsten (W), tantalum (Ta) or titanium (Ti), or nitride of such refractive metal such as tungsten nitride (WN), titanium nitride (TiN) or tantalum nitride (TaN).

As explained in Prior Art 2, for instance, a tantalum (Ta) barrier film has high adhesion with a copper film formed on the tantalum barrier film by sputtering, ensuring improvement in crystallinity of the copper film. However, since 25 copper is diffused into the tantalum film, it would be necessary for the tantalum barrier film formed below the copper film, to have a thickness of 50 nm or greater.

Prior Art 4 reports that if a copper film is formed on a tantalum film by CVD, fluorine (F) segregates at an interface between the copper film and TaN, resulting in degradation in adhesion therebetween.

Prior Art 3 reports that a crystalline TaN barrier film oriented in directions of (200) and (111) can prevent copper diffusion more highly than a crystalline Ta barrier film.

As an solution to enhance a characteristic of preventing copper diffusion and adhesion to copper, a multi-layered structure of a metal film and a metal nitride film has been suggested.

For instance, the above-mentioned Japanese Patent Application No. 10-330938 has suggested a method of fabricating a multi-layered barrier film including a titanium film and formed by sputtering.

As illustrated in FIG. 1, in accordance with the suggested method, only an argon gas is introduced into a sputter chamber to thereby form a titanium film 1. Then, a nitrogen gas is introduced into the sputter chamber, and a thin titanium nitride film 2 is formed on the titanium film 1 auxiliarily making use of reaction between titanium and nitrogen. Thus, there is formed a multi-layered barrier structure 3 comprised of the titanium film 1 and the thin titanium nitride film 2.

In the method, a metal oxide film formed on an underlying wiring film is removed by argon plasma prior to carrying out sputtering.

However, the conventional barrier film for preventing copper diffusion is accompanied with the following problems.

The first problem is that it is quite difficult to make a diffusion-barrier film have both a characteristic of preventing copper diffusion and a sufficient adhesive force with copper.

As illustrated in FIG. 2, it is now assumed to form a metal film 5 having a crystallized pillar structure, on a semiconductor substrate 4. In the metal film 5, a lot of grains each comprised of individual crystals, and grain boundaries 7 each defining an interface between the grains 6 exist throughout the metal film 5, that is, from an upper surface to a bottom of the metal film 5. The grain boundaries 7 define paths 8 through which copper is diffused. As a result, the metal film 5 has low barrier characteristic of preventing copper diffusion.

As illustrated in FIG. 3, it is now assumed to form a metal 5 film 5a on a semiconductor substrate 4. If the metal film 5ais composed of metals having small resistivity, such as tungsten (W), titanium (Ti) or tantalum (Ta), the metal film 5 would have a polycrystal structure. As a result, the metal film 5a would have a pillar-like structure similarly to the 10 metal film 5 illustrated in FIG. 2, and accordingly, the metal film 5a would have small barrier characteristic of preventing copper diffusion.

However, it should be noted that if a copper film is formed on a crystalline metal film, such as a β -Ta (002) film as 15 obtained in sputtering of a tantalum film, by sputtering, the copper film would have high adhesion and rich crystal orientation, though a barrier characteristic of preventing copper diffusion would be deteriorated. As a result, the copper film would enhance reliability in copper wiring. 20

In contrast, the metal film 5a illustrated in FIG. 3, which is composed of particles 9 such as amorphous TaN and formed on the semiconductor substrate 4, has small resistivity, specifically in the range of about 200 to 250 $\mu\Omega$ cm, and does not have the paths through which copper is 25 diffused unlike the crystalline metal film 5 illustrated in FIG. 2. As a result, the metal film 5a would have high barrier characteristic of preventing copper diffusion.

However, since a surface of the metal film 5a is amorphous and hence crystal lattice is not uniformly arranged, if 30 a copper film s formed on the amorphous metal film 5a by CVD or sputtering, copper crystallinity and adhesion to copper are degraded.

As mentioned so far, it is quite difficult to form a diffusion-barrier film having a single-layered structure comprised only of a crystalline metal film or an amorphous metal nitride film, and further having high barrier characteristic of preventing copper diffusion and high adhesion to copper.

The second problem is caused when a diffusion-barrier film is designed to have a multi-layered structure in order to avoid the above-mentioned problem of the single-layered diffusion-barrier film.

For instance, if a diffusion-barrier film is designed to have a multi-layered structure comprised of a crystalline metal film having high adhesion to copper and an amorphous 45 metal nitride film having high barrier characteristic, such as TaN, there would be obtained a diffusion-barrier film having high barrier characteristic of preventing copper diffusion and high adhesion to copper.

However, since it was not possible in a conventional 50 method to successively form a crystalline metal film and an amorphous metal nitride film by sputtering, the crystalline metal film and the amorphous metal nitride film had to be separately formed in the same sputtering chamber or be formed in separate sputtering chambers. 55

For instance, the above-mentioned Japanese Patent Application No. 10-330938 has suggested a method including the steps of introducing an argon gas into a sputtering chamber to thereby form a titanium film, and introducing a nitrogen gas into the sputtering chamber to thereby form a titanium 60 nitride film on the titanium film.

However, in accordance with this method, the titanium nitride film cannot be formed until partial pressures of argon and nitrogen become stable by varying a mixture ratio of argon and nitrogen. Hence, it is impossible to enhance a 65 fabrication yield of fabricating a diffusion-barrier film having a multi-layered structure.

4 The third problem relates to coverage of a film formed by sputtering.

In general, when a metal film or a metal nitride film is formed by sputtering, a metal target is sputtered by argon plasma generated by virtue of rotational magnetic field and application of DC bias, and resultingly, a metal film or a metal nitride film is deposited on a substrate located in facing relation to the metal target.

In sputtering, a pressure at which a metal target is sputtered is low, specifically, equal to 1 Pa or smaller. Since metal particles sputtered by argon plasma are radiated randomly to a surface of a substrate, for instance, if the substrate is formed at a surface thereof with a deep recess or hole, it would almost impossible to deposit a metal film such that such a recess or hole is completely covered with the metal film.

In addition, since a sputtering pressure is low, argon plasma could have a low plasma density, and hence, there cannot be expected re-sputtering effect in which a metal film deposited onto a surface of a substrate is sputtered by argon plasma.

In order to enhance coverage of a metal film, there has been suggested collimate sputtering in which a metal plate formed with a lot of through-holes is located between a sputtering target and a substrate, and metal particles are caused to pass through the through-holes to thereby uniform direction of metal particles. In accordance with the collimate sputtering, it is possible to deposit a metal film on a bottom of a recess formed at a surface of a substrate, but it is not possible to deposit a metal film onto an inner sidewall of the recess.

The fourth problem is that a crystalline metal film having high adhesion with a copper film tends to react with atmosphere to thereby a reaction layer at a surface thereof.

sphere to thereby a reaction layer at a surface thereof. Such a reaction layer would much deteriorate adhesion of a metal film with a copper film.

The fifth problem is a copper oxide film is adhered again to a recess or hole.

An oxide film formed on a surface of an underlying wiring metal film is removed by argon plasma prior to deposition of a diffusion-barrier film by sputtering. When an underlying wiring layer is composed of copper, a copper oxide film is scattered by argon sputtering, and as a result, the thus scattered copper oxide is adhered again to a recess or hole formed at a surface of an insulating film.

The sixth problem is that when a copper film is formed on a tantalum film and an amorphous TaN film by CVD, adhesion between the copper film and a diffusion-barrier film is deteriorated.

SUMMARY OF THE INVENTION

In view of the above-mentioned problems in a conventional diffusion-barrier film, it is an object of the present invention to provide a diffusion-barrier film having both a diffusion-barrier characteristic of preventing copper from being diffused into a semiconductor device and high adhesion between a copper film and an interlayer insulating film.

It is also an object of the present invention to provide a multi-layered wiring structure including the abovementioned diffusion-barrier film.

Another object of the present invention is to provide a method of fabricating such the above-mentioned diffusion-barrier film.

A further object of the present invention is to provide a method of fabricating a multi-layered copper wiring layer in which copper is buried above the above-mentioned diffusion-barrier film.

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In one aspect of the present invention, there is provided a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, including a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of common metal atomic species.

It is preferable that the first film is formed on the second film.

It is preferable that the second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

It is preferable that the first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

In another aspect of the present invention, there is provided a multi-layered wiring structure including a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate, the barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of common metal atomic species.

It is preferable that the barrier film covers a recess and a 25 hole formed throughout an insulating film formed on an underlying wiring layer.

It is preferable that the multi-layered wiring structure further includes a copper film formed on the first film.

In still another aspect of the present invention, there is 30 provided a method of forming a diffusion-barrier film by sputtering, including the steps of (a) preparing gas containing nitrogen therein, and (b) varying only power of an electric power source for generating plasma to thereby successively form a diffusion-barrier film having a multilayered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of metal atomic species of sputter target. 40

It is preferable that the gas containing nitrogen therein has a pressure equal to or greater than 5 Pa.

It is preferable that the gas contains nitrogen at 10 volume % or smaller.

It is preferable that the metal atomic species of sputter target is one of tantalum, tungsten, titanium, molybdenum and niobium alone or in combination.

It is preferable that the second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

It is preferable that the first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

There is further provided a method of forming a diffusionbarrier film by RF magnetron sputtering making use of rotational magnetic field and RF power, including the steps 55 of (a) preparing gas containing nitrogen therein, and (b) varying the RF power to thereby successively form a diffusion-barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being 60 composed of amorphous metal nitride, the barrier film being constituted of metal atomic species of sputter target.

There is still further provided a method of forming a diffusion-barrier film by RF magnetron sputtering, including the steps of (a) setting an electric power source for generation plasma to generate power having a first value, to thereby a first film, with a concentration of nitrogen in plasma gas -6

being kept at a constant, and (b) setting the electric power source to generate power having a second value greater than the first value at the moment when the first film is formed by a predetermined thickness, to thereby form a second film on the first film.

It is preferable that the first film is composed of amorphous metal nitride, and the second film is composed of crystalline metal containing nitrogen therein.

There is yet further provided a method of forming a copper wiring film, including the steps of (a) radiating plasma of argon containing hydrogen therein, to a recess or hole formed at an insulating film formed on a semiconductor substrate, (b) forming a diffusion-barrier film to cover the recess or hole therewith without exposing to atmosphere, the diffusion-barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, and (c) forming a copper film on the diffusion-barrier film without exposing to atmosphere.

It is preferable that the diffusion-barrier film is formed by sputtering.

It is preferable that the copper film is formed in vacuum. It is preferable that the copper film is formed by thermal chemical vapor deposition in which thermal dismutation in a complex of organic metal is utilized.

It is preferable that the copper film is formed by sputtering in which copper target is used.

The advantages obtained by the aforementioned present invention will be described hereinbelow.

In the diffusion-barrier film in accordance with the present invention, a copper film makes direct contact with a crystalline metal film containing nitrogen therein, ensuring high adhesion therebetween and high crystallinity of a copper film.

In addition, since the metal film contains nitrogen therein, copper diffusion into a semiconductor device can be prevented more effectively than a metal film having pure crystals.

In the diffusion-barrier film in accordance with the present invention, an amorphous metal film containing nitrogen therein lies under a crystalline metal film containing nitrogen therein. Hence, it is possible to effectively prevent copper diffusion, and to ensure high adhesion with an underlying insulating film such as a silicon dioxide film. That is, by forming a copper wiring layer on the diffusionbarrier film in accordance with the present invention, it is possible to not only ensure high crystallinity and high adhesion of a copper wiring layer, but also to prevent copper diffusion.

The method in accordance with the present invention makes it possible to successively form a diffusion-barrier film having a multi-layered structure of first and second films, by varying only power of an electric power source for generating plasma in sputtering in which gas containing nitrogen therein is employed. Herein, the first film is composed of crystalline metal containing nitrogen therein, and the second film is composed of amorphous metal nitride. The barrier film is constituted of metal atomic species of sputter target.

Specifically, an electric power source for generating plasma is first set to generate relatively low power with a concentration of nitrogen in plasma gas being kept constant. A film is formed in such a condition. Target metal makes sufficient reaction with nitrogen, and resultingly, an amorphous metal nitride film is formed. Immediately after the formation of the amorphous metal nitride film, the electric power source is set to generate relatively high power to thereby form a film without allowing sufficient time for reaction between nitrogen and target metal. As a result, there 5 is obtained a crystalline metal film containing nitrogen therein.

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Thus, it is possible to successively form a diffusionbarrier film in the same chamber, wherein the diffusionbarrier film has a multi-layered structure including a crys- ¹⁰ talline metal film containing nitrogen therein and an amorphous metal nitride film.

The method of fabricating a diffusion-barrier film employs RF magnetron sputtering in which rotational magnetic field and RF power are utilized. Since the method ¹⁵ makes it possible to carry out sputtering where a nitrogencontaining gas has a pressure equal to or greater than 5 Pa, plasma density of argon which is a main constituent of sputtering gas can be enhanced, and thus, there can be obtained coverage for entirely covering a recess or hole ²⁰ formed at a surface of a substrate, with the diffusion-barrier film.

The method of fabricating a diffusion-barrier film, in accordance with the present invention, includes the step of radiating plasma of argon containing hydrogen therein, to a²⁵ recess or hole formed at an insulating film formed on a semiconductor substrate. This step reduces a copper oxide film formed on a surface of an underlying copper wiring layer, to thereby turn copper oxide back to copper, ensuring remarkable reduction in re-sputtering of a copper oxide film to a surface of a recess or hole formed at a surface of an insulating film.³⁰

Then, a diffusion-barrier film is formed to cover the recess or hole therewith without exposing to atmosphere, wherein ³⁵ the diffusion-barrier film has a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride. Then, a thin copper film is formed on the diffusion-barrier film in vacuum. As a result, there is obtained a multi-layered structure comprised of the diffusion-barrier film and the copper wiring film without a metal oxide layer being sandwiched therebetween.

The above and other objects and advantageous features of 45 the present invention will be made apparent from the following description made with reference to the accompanying drawings, in which like reference characters designate the same or similar parts throughout the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a conventional copper wiring structure.

FIG. 2 is a cross-sectional view of another conventional copper wiring structure.

FIG. 3 is a cross-sectional view of still another conventional copper wiring structure.

FIG. 4A is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the first step of a method of fabricating $_{60}$ the same.

FIG. 4B is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the second step of a method of fabricating the same.

FIG. 4C is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present

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invention, illustrating the third step of a method of fabricating the same.

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FIG. 4D is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the fourth step of a method of fabricating the same.

FIG. 5 illustrates a high-pressure RF magnetron sputtering apparatus used in the first embodiment.

FIG. 6 is a graph showing coverage characteristic of a tantalum film in high-pressure RF magnetron sputtering.

FIGS. 7 and 8 are cross-sectional views of a recess covered with a tantalum film in high-pressure RF magnetron sputtering.

FIG. 9 is a graph showing a relation among a ratio of a nitrogen gas in a mixture gas introduced into a chamber, RF power, and resistivity of a film formed by sputtering.

FIGS. 10 to 18 are graphs each showing film quality and characteristics of TaN and Ta films in high-pressure RF magnetron sputtering.

FIGS. 19 and 20 are photographs of a film formed by high-pressure RF magnetron sputtering which photograph is taken by means of a scanning electron microscopy (SEM).

FIG. 21 is a cross-sectional view of a diffusion-barrier film formed by high-pressure RF magnetron sputtering which barrier-diffusion film is comprised of a crystalline Ta film containing nitrogen in solid solution and an amorphous metal TaN film.

FIG. 22 is a photograph of a film formed by high-pressure RF magnetron sputtering which photograph is taken by means of a scanning electron microscopy (SEM).

FIG. 23 is a cross-sectional view of a diffusion-barrier film covering a recess therewith.

FIG. 24 illustrates a DC magnetron sputtering apparatus used in the fourth embodiment.

FIG. 25 is a cross-sectional view of a diffusion-barrier film covering a recess formed at a surface of an insulating film formed above a lower wiring layer.

FIG. 26 is a cross-sectional view of a diffusion-barrier film covering a recess formed at a surface of an insulating film formed above lower wiring layers.

FIG. 27 is a plan view of a cluster apparatus used for forming a copper wiring layer.

FIG. 28 is a graph showing a diffusion profile of fluorine into a diffusion-barrier film.

FIG. 29 is a graph showing a diffusion profile of copper into a diffusion-barrier film.

FIG. 30 is a cross-sectional view of a copper wiring structure in accordance with the seventh embodiment.

FIG. 31 is a cross-sectional view of a copper wiring structure in accordance with the seventh embodiment.

DESCRIPTION OF THE PREFERRED

EMBODIMENTS

Preferred embodiments in accordance with the present invention will be explained hereinbelow with reference to drawings.

A method of fabricating a diffusion-barrier film in accordance with the preferred embodiment is explained hereinbelow with reference to FIGS. 4A to 4D.

As illustrated in FIG. 4A, a first insulating film 12a is formed on a semiconductor substrate 11, and a second insulating film 12b is formed on the first insulating film 12a. A copper wiring layer 44 is buried in the first insulating film 12*a*. The second insulating film 12*b* is formed at a surface thereof with recesses 13 in each of which a wiring is to be formed. Holes 14 reach the first insulating film 12a from a bottom of each of the recesses 13.

First, the semiconductor substrate 11 is exposed to argon plasma containing hydrogen therein, in a first chamber.

Then, the semiconductor substrate 11 is transferred in vacuum to a second chamber, and a film is formed on the semiconductor substrate 11 in a nitrogen-containing gas by sputtering in which a sputtering target is composed of ¹⁰ refractive metal.

First, an electric power source for generating plasma is set to generate relatively low power with a concentration of nitrogen in plasma gas being kept constant. As a result, the target metal makes sufficient reaction with nitrogen, and an amorphous metal nitride film 15 is deposited over a surface of the second insulating film 12b, as illustrated in FIG. 4B.

Then, immediately after the formation of the amorphous metal nitride film 15, the electric power source is set to 20 generate relatively high power to thereby form a film without allowing sufficient time for reaction between nitrogen and the target metal. As a result, a crystalline metal film 16 containing nitrogen therein is formed on the amorphous metal nitride film 15.

Thus, as illustrated in FIG. 4B, it is possible to successively and effectively fabricate the diffusion-barrier film 17 having a multi-layered structure, on both an inner sidewall and a bottom of the recesses 13 and the holes 14 in the same chamber. By setting a sputtering pressure sufficiently high 30 while deposition of the diffusion-barrier film 17 by sputtering, it would be possible to enhance coverage of the diffusion-barrier film 17.

Thereafter, the semiconductor substrate 11 is transferred into a third chamber in vacuum. Then, a copper film 18 is ³⁵ deposited over the diffusion-barrier film 17 in vacuum in the third chamber to thereby completely fill the recesses 13 and the holes 14 with the copper film 18, as illustrated in FIG. 4C. Since the crystal metal film 16 containing nitrogen therein is exposed outside and the semiconductor substrate ⁴⁰ 11 is transferred in vacuum, an oxide film is not formed at a surface of the crystal metal film 16.

Then, as illustrated in FIG. 4D, the diffusion-barrier film 17 and the copper film 18 are removed by CMP until the second insulating film 12b appears. Thus, there is obtained ⁴⁵ a copper wiring structure having high reliability.

The reason of enhancement in barrier characteristic of preventing copper diffusion is to introduce nitrogen into the metal film 16. In addition, the metal film 16 containing ⁵⁰ nitrogen ensures high adhesion with copper. The amorphous metal nitride film 15 also has a characteristic of preventing copper diffusion, and further enhances adhesion with the second insulating film 12b. Thus, it is possible to ensure high adhesion between the copper film 18 and the diffusion-barrier film 17, and to prevent copper from being diffused from the copper film 18 into the second insulating film 12b.

Hereinbelow are explained detailed examples of the above-mentioned embodiment.

FIRST EXAMPLE

In the first example, hereinbelow is explained sputtering for fabricating a multi-layered structure comprised of a crystalline metal film containing nitrogen therein and an amorphous metal nitride film.

The sputtering in the first example is carried out in a RF magnetron sputtering apparatus illustrated in FIG. 5.

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In the illustrated RF magnetron sputtering apparatus, a chamber 21 is kept to be in vacuum, specifically, to have an internal pressure of about 1×10^{-7} Pa to about 1×10^{-6} Pa by means of a pump 33 such as a dry pump, a cryosorption pump or a turbo pump. In the chamber 21 is placed a heater 34 which can heat a semiconductor substrate 22 introduced into the chamber 21, up to about 20 to 300 degrees centigrade. A metal target 28 or the semiconductor substrate 22 is designed to be able to raise or lower, and hence, a distance between the metal target 28 and the semiconductor substrate 22 can be varied in the range of 102 mm to 134 mm.

Argon and nitrogen gases are adjusted with respect to a flow rate by means of mass flow controllers 31, and then, introduced into the chamber 21. When the argon and nitrogen gases are introduced into the chamber 21, the chamber 21 has an internal pressure of about 2 Pa to about 17 Pa.

The metal target 28 has a diameter, for instance, in the range of about 300 mm to about 320 mm. The metal target 28 is fixed to the chamber 21 through a target holder 27, a cathode 23 and insulators 29. In the cathodes 23 are rotatably arranged a plurality of permanent magnets 24. By rotating the permanent magnets 24, magnetic field 30 in the chamber 21 is uniformized, and erosion at a surface of the metal target 28 is also uniformized. As a result, it is possible to enhance uniformity of a film to be formed on the semiconductor substrate 22.

A RF electric power source 25 for introducing RF power into the chamber 21 is in electrical connection with the cathode 23 through a matching box 32 carrying out impedance matching. The RF electric power source 25 applies radio frequency (RF) having a frequency of 13.56 MHz to the metal target 28 having a diameter of 300 mm, at 0 to 10 kW.

Turning the RF electric power source 25 on to thereby introduce RF into the chamber 21, there is generated argon plasma containing nitrogen therein. The target metal 28 is sputtered by argon ions generated in the argon plasma 26. As a result, metal particles of the target metal 28 fly into the semiconductor substrate 22, and thus, the crystalline metal film 16 containing nitrogen therein or the amorphous metal nitride film 15 is formed.

The inventor actually formed a tantalum film covering therewith the hole 14 (see FIG. 4A) formed through the second insulating film 12b by means of the above-mentioned RF magnetron sputtering apparatus. The coverage characteristic of the tantalum film is shown in FIG. 6.

The hole 14 had a diameter in the range of 0.3 μ m to 1.5 μ m. The second insulating film 12b had a thickness of about 1.5 μ m where the hole 14 was formed.

As is obvious in view of FIG. 6, as a sputtering pressure is increased from 2 Pa to 17 Pa, bottom coverage is enhanced. Herein, bottom coverage is defined as a ratio of a thickness of the tantalum film at a bottom of the hole 14 to a thickness of the tantalum film at a surface of the second insulating film 12b. Specifically, when a sputtering pressure is over 5 Pa, sufficient coverage can be obtained to a hole having a great aspect ratio.

A thickness of the tantalum film at an inner sidewall of the hole 14 is equal to about a half of a thickness of the tantalum film at a bottom of the hole 14. As a sputtering pressure is increased, the tantalum film covers an inner sidewall of the hole 14 therewith to a greater degree.

The reason of this phenomenon is considered as follows. The first reason is an increase in the number of Ta ions in plasma gas, as illustrated in FIG. 7.

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As a sputtering pressure is increased, tantalum atomics increasingly make collision with excited argon atomics, resulting in that argon atomics are facilitated to be ionized. The resultant tantalum ions are attracted to negative self-bias generated at the semiconductor substrate 22. As a result, an incident angle at which tantalum ion flux 35 is radiated to the semiconductor substrate 22 becomes nearly 90 degrees. Thus, overhanging which occurs in the vicinity of an edge of recess or hole in conventional sputtering is suppressed, ensuring tantalum atomics to reach a bottom of the hole 14 or recess 13. As a result, a tantalum film 36 entirely covers an inner sidewall of the hole 14.

The second reason is that the deposited tantalum film 36 is re-sputtered by argon ions 39, as illustrated in FIG. 8.

The argon ions 39 which are primary constituents of ¹⁵ plasma gas are accelerated by electric field and reach not only a target but also the semiconductor substrate 22 which is in a condition of negative self-bias. This means that the tantalum film 36 having been deposited onto the semiconductor substrate 22 is re-sputtered. Since the tantalum film ₂₀ deposited in the vicinity of an edge of the hole 14 or recess 13 and causing overhanging is re-sputtered by the argon ions 39, as indicated with an arrow 37, tantalum atomics 38 directing to a bottom of the hole 14 or recess 13 are not interfered at the edge of the hole 14 or recess 13. Accordingly, it is ensured that a tantalum film is deposited on a bottom and an inner sidewall of the hole 14 or recess 13.

In addition, since the tantalum film 36 deposited on a bottom of the hole 14 or recess 13 is re-sputtered by the $_{30}$ argon ions 39, tantalum atomics generated by re-sputtering are deposited again on an inner sidewall 40 of the hole 14 or recess 13, ensuring enhancement in coverage at the sidewall 40 of the hole 14 or recess 13.

It is not possible to determine which is a main reason for 35 enhancement in coverage among the above-mentioned first and second reasons. However, since mean free path of plasma ion is just a few millimeters under a pressure over 5 Pa, it is considered that almost 90 degrees of an incident angle of the tantalum ion flux **35** does not contribute to 40 enhancement in coverage so much. The main reason why the coverage is enhanced is considered that argon ions are generated in a sufficient density by virtue of a high pressure, and a tantalum film having been deposited are re-sputtered by the argon ions. 45

In accordance with the experiments the inventor had conducted, it was confirmed that coverage was enhanced in sputtering of a tantalum nitride film, carried out under a high pressure over 5 Pa.

As mentioned so far, it is preferable that a sputtering ⁵⁰ pressure is set equal to or greater than 5 Pa in RF magnetron sputtering.

SECOND EXAMPLE

FIG. 9 shows a relation between a flow rate ratio and 55 resistivity of a film formed by high-pressure RF magnetron sputtering having been explained in the first example, for various RF powers. Herein, the flow rate ratio is defined as a ratio of a volume of argon gas to be introduced into the chamber 21 to a volume of nitrogen gas to be introduced into $_{60}$ the chamber 21 (N₂/(Ar+N₂)).

The relation shown in FIG. 9 was observed when the chamber 21 had a pressure of 13 Pa, the semiconductor substrate 22 was heated at 200 degrees centigrade, the permanent magnets 24 were rotated at 10 r.p.m., and the 65 distance between the metal target 28 and the semiconductor substrate 22 was 134 mm.

As a ratio of N₂ gas in the flow rate ratio N₂/(Ar+N₂) is increased, the resistivity is once reduced, and thereafter, increased again, regardless the RF power. However, an increase rate of the N₂ gas ratio is dependent on the RF power. The resistivity increases at a lower rate at the greater RF power.

FIGS. 10 to 13 show how X-ray diffraction (XRD) patterns vary as the N_2 gas ratio is varied when RF power of 6 kW (8.5 W/cm²) is applied to the tantalum target having a diameter of 300 mm.

Specifically, FIGS. 10 to 13 shows XRD patterns when the N_2 gas ratio is equal to 0%, 1%, 5%, and 7% respectively. Hereinbelow are explained FIGS. 10 to 13 in comparison with FIG. 9.

When the N_2 gas ratio is equal to 0%, there is obtained a β -Ta(002)-oriented crystalline tantalum film which has resistivity in the range of about 160 to 200 $\mu\Omega$ -cm, as illustrated in FIG. 10.

When the N₂ gas ratio is equal to 1%, there is obtained a crystalline metal film (herein, a tantalum film) containing nitrogen therein, which includes β -Ta and TaN_{0.1} in mixture and which has resistivity in the range of about 100 $\mu\Omega$ -cm, as illustrated in FIG. 11.

When the N₂ gas ratio is equal to 5%, it is understood in view of FIG. 12 that XRD pattern strength is reduced, and hence, there is formed an amorphous metal nitride film, which has resistivity in the range of about 200 to 250 $\mu\Omega$ -cm.

When the N_2 gas ratio is equal to 7%, a crystalline metal nitride film (Ta_3N_5) is formed, and resistivity is further increased, as illustrated in FIG. 13.

As mentioned above, when the tantalum target is selected, a crystalline structure, composition and resistivity of a film to be formed by sputtering vary in dependence on both a concentration of nitrogen gas in sputtering gas and RF power. Conversely speaking, this means that it is possible to control characteristics of a film to be formed by sputtering, by controlling both a concentration of nitrogen gas in sputtering gas and RF power. The present invention is based on this discovery.

However, it is difficult to vary a flow rate of sputtering gas (that is, a pressure of sputtering gas) and N_2 composition ratio in sputtering. Accordingly, it is necessary in practical use to keep both a flow rate of sputtering gas (that is, a pressure of sputtering gas) and N_2 composition ratio constant, and to vary only RF power, to thereby control a crystalline structure, composition and resistivity of a film to be formed by sputtering.

FIG. 14 shows how resistivity varies when only RF power is varied while a N_2 gas ratio is kept fixed at 2%. As is obvious in view of FIG. 14, it is understood that it is possible to control film quality and resistivity of a film to be formed by sputtering, even when only RF power is varied. In FIG. 14, resistivity is varied when a gas pressure is equal to 10 Pa, the permanent magnets are rotated at 10 r.p.m., and the substrate was heated at 200 degrees centigrade.

FIGS. 15 to 18 show XRD characteristics relative to RF power. FIGS. 15 to 18 show XRD characteristics observed when RF power is equal to 2 kW, 3 kW, 6 kW and 8 kW, respectively.

Specifically, when RF power is equal to 2 kW, there is obtained amorphous Ta₂N, as illustrated in FIG. 15. By increasing RF power, there is obtained crystalline TaN_{0.1}. When RF power is equal to 8 kW, there is obtained a crystalline metal film containing nitrogen therein, which includes a β -Ta film and TaN_{0.1} in mixture.

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FIGS. 19 and 20 are SEM (Scanning Electron Microscopy) photographs of films obtained when RF power is set equal to 2 kW and 8 kW, respectively.

When RF power is set equal to 2 kW, as is obvious in view of XRD illustrated in FIG. 15, there is not observed grain boundary, because a deposited film has an amorphous structure. In contrast, when RF power is set equal to 8 kW, as is obvious in view of XRD illustrated in FIG. 18, there is obtained a crystalline film including a β -Ta film and TaN_{0.1} in mixture, and having a pillar-like structure.

That is, if Ta_2N , which is an amorphous metal nitride film, is deposited at 2 kW of RF power, and RF power is increased up to 8 kW immediately when the film has acquired a desired thickness, the film is turned into a crystalline metal film containing nitrogen therein. As a result, as illustrated in FIG. 21, a diffusion-barrier film 17 is formed on a semiconductor substrate 11 where the diffusion-barrier film 17 has a multi-layered structure comprised of an amorphous metal nitride film 15 and a crystalline metal film 16 containing nitrogen therein. Specifically, the amorphous metal nitride film 15 is an amorphous Ta_2N film, and the crystalline metal film 16 is composed of crystalline β -Ta and crystalline TaN_{0.1} in mixture.

FIG. 22 is a SEM photograph of a cross section of the diffusion-barrier film 17 which is formed by changing sputtering power from 2 kW to 8 kW while a TaN film is being deposited, to thereby successively deposit the crystalline metal film 16 and the amorphous metal nitride film 15 each by a thickness of about 500 angstroms. It is confirmed in FIG. 22 that the amorphous Ta₂N film 15 and the crystalline metal film 16 containing nitrogen therein form a multi-layered structure.

The reason of this phenomenon is considered as follows.

When sputtering power is set equal to 2 kW, since a $_{35}$ sputtering rate caused by argon ions is relatively low, there is sufficient time for a tantalum target to be nitrided by N₂ at a surface thereof. Hence, the tantalum target is nitrided at a surface thereof, and turned into Ta₂N. Since the thus produced Ta₂N is sputtered by argon ions, a Ta₂N film is $_{40}$ deposited. However, when sputtering power is set equal to 8 kW, the tantalum target is sufficiently nitrided. As a result, there is obtained a tantalum film slightly containing nitrogen.

By utilizing the above-mentioned phenomenon, it is possible to form the diffusion-barrier film 17 having a multilayered structure and covering therewith the recess 13 or the hole 14 formed at the second insulating film 12b formed on the semiconductor substrate 11, as illustrated in FIG. 23.

The lower film or amorphous metal nitride (Ta_2N) film 15 is required to have such a thickness that barrier characteristic of preventing copper diffusion is ensured and adhesion with the underlying insulating film 12*b* is also ensured. A desired thickness of the amorphous metal nitride (Ta_2N) film 15 is 55 in the range of about 80 angstroms to about 150 angstroms.

On the other hand, the crystalline nitrogen-containing metal film 16 composed of crystalline β -Ta and crystalline TaN_{0,1} in mixture is required to have such a thickness that barrier characteristic of preventing copper diffusion is ensured and adhesion with copper is also ensured. A desired thickness of the crystalline metal film 16 is in the range of about 60 angstroms to about 300 angstroms.

THIRD EXAMPLE

The RF magnetron sputtering having been explained in the first example makes it possible to enhance coverage

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characteristic of a deposited film for covering a recess or hole therewith, by introducing a gas having a higher pressure than usual, specifically, a pressure equal to or greater than 5 Pa, into a chamber. That is, it is possible to form the multi-layered barrier film 17 under desired coverage characteristic by switching RF power with a sputtering pressure being kept equal to or greater than 5 Pa, even when there is carried out dual-damassin process in which the recess 13 and the hole 14 formed at a surface of the second insulating film 12b formed on the semiconductor substrate 11 are concurrently filled with the diffusion-barrier film 17.

FOURTH EXAMPLE

In the above-mentioned first and second examples, the process in which a multi-layered barrier film is successively formed by switching RF power while the film is being formed is applied to RF magnetron sputtering. This process may be applied to DC magnetron sputtering, as illustrated in FIG. 24, though a N_2 gas ratio and RF power are different from those in the first and second examples.

FIG. 24 illustrates a DC magnetron sputtering apparatus. The apparatus is comprised of a chamber 21, a heater 34 fixed on a bottom of the chamber 21 for heating a semiconductor substrate 22, a target metal 28 fixed to a top of the chamber 21 by means of insulators 29 and a cathode 23, a pump 33 for exhausting air from the chamber 21 such that a pressure in the chamber 21 is in the range of about 1×10^{-7} Pa to about 1×10^{-6} Pa, a magnet 42 positioned above the target metal 28, mass flow controllers 31 for adjusting flow rates of argon gas and nitrogen gas, and allowing the gases to enter the chamber 21, and a DC electric power source 41 for applying a DC voltage to both the cathode 23 and the heater 34.

Turning the DC electric power source 41 on, argon plasma containing nitrogen therein is generated in the chamber 21.

FIFTH EXAMPLE

In the first and second examples, there is formed only one via-hole and wiring. However, it should be noted that the present invention may be applied to a copper wiring structure including two or more via-holes and wirings.

In the fifth example, as illustrated in FIG. 25, a first insulating film 12a is formed on a semiconductor substrate 11. The first insulating film 12a is formed with via-holes which is filled with a copper wiring layer 44 with a diffusion-barrier film 17 being sandwiched between an inner surface of each of the via-holes and the copper wiring layer 44. A second insulating film 12b is formed on the first insulating film 12a. The second insulating film 12b is also formed with recesses and via-holes which is filled with a copper wiring (not illustrated) with a diffusion-barrier film 17 being sandwiched between inner surfaces of the recesses and the via-holes, and the copper wiring.

Thus, recesses and/or holes formed throughout each of multi-layered insulating films are covered with the diffusion-barrier film 17, and then, the recesses and/or holes may be filled with a copper wiring layer.

An example of the multi-layered structure is illustrated in FIG. 26. The illustrated multi-layered structure is comprised of three insulating layers. Each of the insulating layers is formed with recesses and via-holes, which are covered at their surfaces with a diffusion-barrier layer 17, and filled with copper wiring layers 44a and 44b.

Hereinbelow is explained a method of fabricating the multi-layered structure illustrated in FIG. 26.

A semiconductor substrate 11 is formed at a surface thereof with oxide layers 11a. A semiconductor device 11b is formed on the semiconductor substrate 11 between the oxide layers 11a.

A first insulating film 12a is formed on the semiconductor ⁵ substrate 11. The first insulating film 12a is comprised of, for instance, a silicon dioxide film. The first insulating film 12a is formed with recess and holes reaching the semiconductor device 11b. The recesses and holes are covered at their inner surfaces with the diffusion-barrier film 17. The diffusion-¹⁰ barrier film 17 has a multi-layered structure comprised of a crystalline nitrogen-containing metal film and an amorphous metal nitride film, and has sufficient coverage to cover recesses and holes therewith. The diffusion-barrier film 17 may be formed by such high-pressure RF magnetron sput-¹⁵ tering as mentioned in the first example.

Then, the recesses and holes are filled with copper in vacuum. Then, the copper film and the diffusion-barrier film 17 are removed by CMP until the first insulating film 12a appears. Thus, there is fabricated the copper wiring layer ²⁰ 44a.

Since copper does not form passive state at a surface, the copper wiring layer 44a may be oxidized. In order to prevent oxidation of the copper wiring layer 44a, a silicon nitride film 12a is formed over the first insulating film 12a.

Then, a second insulating film 12b is formed on the first insulating film 12a. The second insulating film 12b is formed with recesses and holes reaching the copper wiring layer 44a formed in the first insulating film 12a. Then, the 30 recesses and holes formed in the second insulating film 12b are covered with the diffusion-barrier film 17, and the recesses and holes are filled with the copper wiring layer 44b. By repeating the above-mentioned steps by the desired number, there can be fabricated a semiconductor device 35 having such a multi-layered copper wiring structure as illustrated in FIG. 26.

SIXTH EXAMPLE

The sixth example relates to an apparatus and a method of 40 successively forming both a diffusion-barrier film having a multi-layered structure and copper wiring layer.

FIG. 27 is a top plan view of an apparatus of forming a copper wiring layer, in accordance with the sixth example.

The apparatus includes a cluster chamber 51 including a separation chamber 51 at a center. The separation chamber 51 is equipped therein with a robot 52 for transferring a semiconductor substrate.

The cluster chamber **51** is comprised further of two lord lock chambers **45**, a chamber **46** used for heating a semiconductor substrate, an etching chamber **47** used for cleaning recesses and holes, a sputter chamber **48** used for fabricating a diffusion-barrier film, and a chamber **49** used for forming a copper wiring layer, arranged around the separation chamber **51**.

It is possible to form a copper wiring layer without exposure of a semiconductor substrate to atmosphere through the use of the cluster chamber **50**.

Hereinbelow are explained steps of fabricating a copper ₆₀ wiring layer.

First, a semiconductor substrate is introduced into one of the lord lock chambers 45. An insulating film is formed in advance on the semiconductor substrate, and the insulating film is formed in advance with a recess and/or hole.

Then, the lord lock chamber 45 is evacuated of air by means of a dry pump and a turbo pump for about five

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minutes. As a result, the lord lock chamber 45 has a vacuum degree of 7×10^{-3} Pa to 8×10^{-3} Pa.

Then, a gate valve between the lord lock chamber 45 and the separation chamber 51 is made open. The separation chamber 51 is in advance kept in a vacuum degree of about 5×10^{-5} Pa to 1×10^{-5} Pa by means of a dry pump and a turbo pump. Hence, the semiconductor substrate is transferred into the separation chamber 52 by the robot 52 without being exposed to atmosphere.

Then, the semiconductor substrate is transferred into the chamber 46 which is in advance kept in a vacuum degree of about 6×10^{315} Pa by means of a dry pump and a turbo pump. The semiconductor substrate is heated at about 50 to about 200 degrees centigrade in the chamber 46 to thereby remove moisture existing at a surface of the semiconductor substrate and clean a surface of the semiconductor substrate.

Then, the semiconductor substrate is transferred into the etching chamber 47 from the chamber 46 through the separation chamber 51. The etching chamber 47 is kept in a vacuum degree of about 5×10^{-6} Pa by means of a cryosorption pump, dry pump and a turbo pump.

After introducing the semiconductor substrate into the etching chamber 47, the semiconductor substrate is plasmaetched in argon gas or argon gas diluted with hydrogen gas $(H_2/Ar=3\%)$. By carrying out plasma-etching, a surface of the semiconductor substrate and inner surfaces of a recess and a hole are reduced and cleaned.

The plasma-etching has an advantage that edges of a recess and a hole are ground by the plasma-etching, and accordingly, an opening area of the recess and hole is broadened, ensuring enhancement in coverage characteristic.

Then, the semiconductor substrate is transferred into the sputter chamber 48 from the etching chamber 47 by means of the robot 52. The sputter chamber 48 is kept in a vacuum degree of about 4×10^{-6} Pa by means of a cryosorption pump, dry pump and a turbo pump. The high-pressure RF magnetron sputtering as having been explained in the first example is carried out in the sputter chamber 48.

In the sputter chamber 48, a crystalline nitrogencontaining metal film (a film composed of crystalline β -Ta and crystalline TaN_{0.1} in mixture) and an amorphous metal nitride film (a Ta₂N film) are deposited on the semiconductor substrate by the method having been explained in the first and second examples, wherein RF power is instantaneously switched. In this example, a gas pressure is kept at 10 Pa, a substrate temperature is kept at 200 degrees centigrade, a N₂ gas ratio is kept at 2%, and RF power is switched from 2 kW to 8 kW. As a result, there is obtained a diffusion-barrier film having a multi-layered structure and also having enhanced coverage characteristic under the characteristics illustrated in FIG. 6.

Then, the semiconductor substrate is transferred in vacuum to the chamber 49 from the sputter chamber 48. The chamber 49 is kept in a vacuum degree of about 4×10^{-4} Pa by means of a dry pump and a turbo pump. Since the semiconductor substrate is transferred in vacuum, the crystalline nitrogen-containing metal film in the diffusion-barrier film is kept clean at a surface thereof. A copper film is deposited on the crystalline nitrogen-containing metal film by chemical vapor deposition (CVD) such that the recess and hole is filled with copper, as follows.

The semiconductor substrate is kept at about 170 to about 200 degrees centigrade. A source including Cu (hfac) tmvs (trimethylvinylsilyl hexafluoroacetylacetonate copper (I)) as a main constituent is introduced into a carburetor at 1 to 2

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grams per minute through a liquid transfer system. The source gasified in the carburetor is introduced into the chamber 49 together with nitrogen carrier gas, resulting in that the chamber 49 is kept at about 1 kPa.

The gas introduced into the chamber 49 makes chemical ⁵ reaction on the semiconductor substrate, and is turned into copper, and then, deposited on the semiconductor substrate. Herein, copper is deposited by such a thickness that a recess and/or hole is sufficiently filled with copper, for instance, a thickness in the range of about 8000 angstroms to about ¹⁰ 15000 angstroms.

In particular, when a copper film is formed by CVD, segregation of fluorine at a surface of the diffusion-barrier film, diffusion of fluorine into the diffusion-barrier film, and diffusion of copper into the diffusion-barrier film exert a ¹⁵ great influence on the adhesion, which fluorine is contained in Cu (hfac) tmvs which is a source for carrying out CVD.

FIGS. 28 and 29 illustrate diffusion profiles of fluorine and copper into the diffusion-barrier film, respectively, 20 which profiles were measured by SIMS (secondary ion mass spectroscopy).

In a β -Ta film obtained by sputtering carried out in argon atmosphere, since fluorine segregates at an interface between copper and tantalum, the β -Ta film would have poor adhesion. With respect to a Ta₂N film, though fluorine is diffused into the Ta₂N film, copper is scarcely diffused in the Ta₂N film. As a result, atomics are coupled with each other with a poor force, and hence, the Ta₂N film would have poor adhesion. In contrast, with respect to a TaN_{0.1} film, since copper and fluorine are allowed to be diffused into the TaN_{0.1} film, atomics are coupled with each other with a strong force, and as a result, the TaN_{0.1} film would high adhesion.

Thus, it is understood that if copper is deposited by CVD, 35 the diffusion-barrier film having a multi-layered structure comprised of a crystalline $TaN_{0.1}$ film and an amorphous Ta_2N film would have enhanced adhesion and barrier characteristic of preventing copper diffusion.

In accordance with the sixth example, a copper wiring ⁴⁰ layer can be formed on a semiconductor substrate without the semiconductor substrate being exposed to atmosphere. Accordingly, the diffusion-barrier film is kept clean at a surface, and hence, film quality of a copper film formed by CVD is likely to be reflected to a crystalline structure of a ⁴⁵ tantalum film of the diffusion-barrier film. Thus, it is possible to enhance crystal orientation of copper and adhesion between copper and a diffusion-barrier film.

SEVENTH EXAMPLE

The seventh example relates to the cluster chamber 50 illustrated in FIG. 27. In the seventh example, the sputter chamber 48 is positioned in a region where a copper wiring layer is to be formed, which region corresponds to the chamber 49 in which a copper wiring layer is formed. Since the diffusion-barrier film includes a $TaN_{0.1}$ film containing crystalline β -Ta therein, at a surface, adhesion between the diffusion-barrier film and a copper film formed by sputtering is kept the same as adhesion between the diffusion-barrier $_{60}$ film and a copper film formed by CVD.

EIGHTH EXAMPLE

In the eighth example, the semiconductor substrate is taken out of the cluster chamber 50 illustrated in FIG. 27. 65 The semiconductor substrate has such a copper wiring structure as illustrated in FIG. 30. Specifically, recesses and

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holes formed in the second insulating film 12b are covered with the diffusion-barrier film 17, and a copper film 53 is formed covering the diffusion-barrier film 17 therewith.

A second copper film 54 is deposited over the copper film 53 by plating such that the recesses and holes are filled with the second copper film 54. As a result, as illustrated in FIG. 31, if is possible to fabricate a structure comprised of the multi-layered barrier layer 17, the copper film 53 formed by CVD or sputtering, and the second copper film 54 formed by plating. Thereafter, as illustrated in FIG. 4D, for instance, the second copper film 54, the copper film 53 and the diffusion-barrier film 17 are removed by CMP. Thus, there is obtained a copper wiring structure.

While the present invention has been described in connection with the preferred embodiments, the present invention provides the following advantages.

The first advantage is that it is possible to have a diffusion-barrier film having sufficient barrier characteristic of preventing copper diffusion and high adhesion with a copper film. This is because the diffusion-barrier film is designed to have a multi-layered structure comprised of an amorphous metal nitride film having a high barrier characteristic of preventing copper diffusion and a crystalline nitrogen-containing metal film having high adhesion with copper.

The second advantage is that it is possible to successively fabricate the diffusion-barrier film in a common chamber. This ensures reduction in apparatus cost and reduction in time for fabricating the diffusion-barrier film.

This is because that it is possible to successively form an amorphous metal nitride film and a crystalline nitrogencontaining metal film by instantaneously changing only RF power with a volume ratio of a nitrogen gas to a process gas introduced into a chamber, being kept constant. In accordance with this method, an upper metal film in the diffusionbarrier film inevitably contains nitrogen therein.

The third advantage is that a copper film can be formed with a surface of the diffusion-barrier film being kept clean, through the use of an apparatus of transferring a semiconductor substrate in vacuum. As a result, reliability in a copper wiring layer can be enhanced.

While the present invention has been described in connection with certain preferred embodiments, it is to be ⁴⁵ understood that the subject matter encompassed by way of the present invention is not to be limited to those specific embodiments. On the contrary, it is intended for the subject matter of the invention to include all alternatives, modifications and equivalents as can be included within the spirit ⁵⁰ and scope of the following claims.

The entire disclosure of Japanese Patent Application No. 11-214110 filed on Jun. 24, 1999 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

What is claimed is:

1. A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films,

said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride.

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film in direct contact with said second film, said first film containing nitrogen in a smaller content than that of said second film.

2. The barrier film as set forth in claim 1, wherein said second film has a thickness in the range of 80 angstroms to ⁵ 150 angstroms both inclusive.

3. The barrier film as set forth in claim 1, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

4. The barrier film as set forth in claim 1, wherein said first ¹⁰ film is composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

5. A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

said barrier film having a multi-layered structure of first and second films,

- said first film being composed of crystalline metal containing nitrogen therein,
- said second film being composed of amorphous metal nitride,
- said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film in direct contact with said second film,

said first film containing nitrogen in a smaller content than that of said second film.

6. The multi-layered wiring structure as set forth in claim 5, wherein said second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

7. The multi-layered wiring structure as set forth in claim 5, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

8. The multi-layered wiring structure as set forth in claim
5; wherein said barrier film covers a recess and a hole
15 formed throughout an insulating film formed on an underlying wiring layer.

9. The multi-layered wiring structure as set forth in claim 5, further comprising a copper film formed on said first film.

10. The multi-layered wiring structure as set forth in claim 5, wherein said first film is composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

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MULTI-LAYERED WIRING LAYER

AND

METHOD OF FABRICATING THE SAME

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The invention relates to a semiconductor integrated circuit including a copper wiring layer, and more particularly to a barrier film which prevents copper diffusion from such a copper wiring layer.

DESCRIPTION OF THE RELATED ART

As a semiconductor device has been designed to be smaller and smaller in size, wiring delay exerts greater influence on a silicon ULSI device. As a result, though a wiring layer has been composed of aluminum, it is necessary to compose a wiring layer of copper in place of aluminum.

Resistivity of copper is equal to about 70% of resistivity of aluminum. However, since copper does not form passive state composed of an oxide film, at a surface thereof, unlike aluminum, copper is more corrosive than aluminum.

In addition, since copper has a high diffusion rate in both silicon (Si) 20 and silicon dioxide (SiO₂), if copper enters MOSFET formed on a silicon substrate, copper would induce reduction in carrier lifetime.

Hence, it is absolutely necessary for a semiconductor device having a copper wiring layer to have a diffusion-barrier film for preventing diffusion of copper into an interlayer insulating film formed between copper wiring layers. In addition, since such a diffusion-barrier film has to have high adhesion characteristic to both an interlayer insulating film and a copper wiring layer in order to keep reliability in wiring.

Thus, there have been made many suggestions about a structure of a barrier metal layer and a method of fabricating the same, in order to prevent

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copper diffusion form a copper wiring layer.

For instance, a structure of a barrier metal layer is suggested in the following articles:

(a) Semiconductor World, Nobuyoshi Awaya, February 1998, pp. 91-96 (hereinafter, referred to as Prior Art 1);

(b) Advanced Metallization and Interconnect Systems for ULSI Applications in 1997, Kee-Won Kwon et al., 1998, pp. 711-716 (hereinafter, referred to Prior Art 2);

(c) Journal Electrochemical Society, M. T. Wang et al., July 1998, pp. 25382545 (hereinafter, referred to as Prior Art 3); and

(d) 1998 Symposium on VLSI Technology Digest of Technical Papers, D. Denning et al., 1998, pp. 22-23.

In addition, a structure of a barrier metal layer and a method of fabricating the same both for preventing copper diffusion is suggested also in Japanese Unexamined Patent Publications 8-139092, 8-274098, 9-64044 and 10-256256, and Japanese Patent Application No. 10-330938. Herein, Japanese Patent Application No. 10-330938 is not published yet, and hence does not constitute prior art to the present invention. However, it is explained in the specification only for better understanding of the present invention. The applicant does not admit that Japanese Patent Application No. 10-330938 constitutes prior art to the present invention.

It is quite difficult to dry-etch copper, and hence, a copper wiring layer is formed generally by chemical mechanical polishing (CMP).

Specifically, a copper wiring layer is formed as follows.

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An insulating film is formed on an underlying copper wiring layer. Then, the insulating film is formed with a recess and a through-hole reaching the underlying copper wiring layer. Then, a thin diffusion-barrier film is formed on surfaces of the recess and the through-hole therewith such that the recess and the through-hole is completely covered at surfaces thereof with the diffusion-barrier film in order to prevent copper diffusion from uncovered region.

Thereafter, a copper film is deposited filling the recess and the through-hole therewith by CVD or sputtering. Then, the copper film and the diffusion-barrier film are removed in selected regions by CMP. Thus, a copper wiring layer is completed.

As will be obvious to those skilled in the art, the diffusion-barrier film is required to have high coverage as well as capability of preventing copper diffusion and adhesion to copper.

The diffusion-barrier film is composed, for instance, of refractive metal such as tungsten (W), tantalum (Ta) or titanium (Ti), or nitride of such refractive metal such as tungsten nitride (WN), titanium nitride (TiN) or tantalum nitride (TaN).

As explained in Prior Art 2, for instance, a tantalum (Ta) barrier film has high adhesion with a copper film formed on the tantalum barrier film by sputtering, ensuring improvement in crystallinity of the copper film. However, since copper is diffused into the tantalum film, it would be necessary for the tantalum barrier film formed below the copper film, to have a thickness of 50 nm or greater.

Prior Art 4 reports that if a copper film is formed on a tantalum film by CVD, fluorine (F) segregates at an interface between the copper film and TaN, resulting in degradation in adhesion therebetween.

Prior Art 3 reports that a crystalline TaN barrier film oriented in directions of (200) and (111) can prevent copper diffusion more highly than a crystalline Ta barrier film.

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As an solution to enhance a characteristic of preventing copper diffusion and adhesion to copper, a multi-layered structure of a metal film and a metal nitride film has been suggested.

For instance, the above-mentioned Japanese Patent Application No. 10-330938 has suggested a method of fabricating a multi-layered barrier film

including a titanium film and formed by sputtering.

As illustrated in Fig. 1, in accordance with the suggested method, only an argon gas is introduced into a sputter chamber to thereby form a titanium film 1. Then, a nitrogen gas is introduced into the sputter chamber, and a thin titanium nitride film 2 is formed on the titanium film 1 auxiliarily making use of reaction between titanium and nitrogen. Thus, there is formed a multi-layered barrier structure 3 comprised of the titanium film 1 and the thin titanium nitride film 2.

In the method, a metal oxide film formed on an underlying wiring film 10 is removed by argon plasma prior to carrying out sputtering.

However, the conventional barrier film for preventing copper diffusion is accompanied with the following problems.

The first problem is that it is quite difficult to make a diffusion-barrier film have both a characteristic of preventing copper diffusion and a sufficient adhesive force with copper.

As illustrated in Fig. 2, it is now assumed to form a metal film 5 having a crystallized pillar structure, on a semiconductor substrate 4. In the metal film 5, a lot of grains each comprised of individual crystals, and grain boundaries 7 each defining an interface between the grains 6 exist throughout the metal film 5, that is, from an upper surface to a bottom of the metal film 5. The grain boundaries 7 define paths 8 through which copper is diffused. As a result, the metal film 5 has low barrier characteristic of preventing copper diffusion.

As illustrated in Fig. 3, it is now assumed to form a metal film 5a on a semiconductor substrate 4. If the metal film 5a is composed of metals having small resistivity, such as tungsten (W), titanium (Ti) or tantalum (Ta), the metal film 5 would have a polycrystal structure. As a result, the metal film 5a would have a pillar-like structure similarly to the metal film 5 illustrated in Fig. 2, and accordingly, the metal film 5a would have small barrier characteristic of preventing copper diffusion.

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However, it should be noted that if a copper film is formed on a crystalline metal film, such as a β -Ta (002) film as obtained in sputtering of a tantalum film, by sputtering, the copper film would have high adhesion and rich crystal orientation, though a barrier characteristic of preventing copper diffusion would be deteriorated. As a result, the copper film would enhance reliability in copper wiring.

In contrast, the metal film 5a illustrated in Fig. 3, which is composed of particles 9 such as amorphous TaN and formed on the semiconductor substrate 4, has small resistivity, specifically in the range of about 200 to 250 $\mu \Omega$ cm, and does not have the paths through which copper is diffused unlike the crystalline metal film 5 illustrated in Fig. 2. As a result, the metal film 5a would have high barrier characteristic of preventing copper diffusion.

However, since a surface of the metal film 5a is amorphous and hence crystal lattice is not uniformly arranged, if a copper film s formed on the amorphous metal film 5a by CVD or sputtering, copper crystallinity and adhesion to copper are degraded.

As mentioned so far, it is quite difficult to form a diffusion-barrier film having a single-layered structure comprised only of a crystalline metal film or an amorphous metal nitride film, and further having high barrier characteristic of preventing copper diffusion and high adhesion to copper.

The second problem is caused when a diffusion-barrier film is designed to have a multi-layered structure in order to avoid the above-mentioned problem of the single-layered diffusion-barrier film.

For instance, if a diffusion-barrier film is designed to have a multilayered structure comprised of a crystalline metal film having high adhesion to copper and an amorphous metal nitride film having high barrier characteristic, such as TaN, there would be obtained a diffusion-barrier film having high barrier characteristic of preventing copper diffusion and high adhesion to copper.

However, since it was not possible in a conventional method to

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successively form a crystalline metal film and an amorphous metal nitride film by sputtering, the crystalline metal film and the amorphous metal nitride film had to be separately formed in the same sputtering chamber or be formed in separate sputtering chambers.

For instance, the above-mentioned Japanese Patent Application No. 10-330938 has suggested a method including the steps of introducing an argon gas into a sputtering chamber to thereby form a titanium film, and introducing a nitrogen gas into the sputtering chamber to thereby form a titanium nitride film on the titanium film.

However, in accordance with this method, the titanium nitride film cannot be formed until partial pressures of argon and nitrogen become stable by varying a mixture ratio of argon and nitrogen. Hence, it is impossible to enhance a fabrication yield of fabricating a diffusion-barrier film having a multi-layered structure.

The third problem relates to coverage of a film formed by sputtering.

In general, when a metal film or a metal nitride film is formed by sputtering, a metal target is sputtered by argon plasma generated by virtue of rotational magnetic field and application of DC bias, and resultingly, a metal film or a metal nitride film is deposited on a substrate located in facing relation to the metal target.

In sputtering, a pressure at which a metal target is sputtered is low, specifically, equal to 1 Pa or smaller. Since metal particles sputtered by argon plasma are radiated randomly to a surface of a substrate, for instance, if the substrate is formed at a surface thereof with a deep recess or hole, it would almost impossible to deposit a metal film such that such a recess or hole is completely covered with the metal film.

In addition, since a sputtering pressure is low, argon plasma could have a low plasma density, and hence, there cannot be expected re-sputtering effect in which a metal film deposited onto a surface of a substrate is sputtered by argon

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In order to enhance coverage of a metal film, there has been suggested collimate sputtering in which a metal plate formed with a lot of through-holes is located between a sputtering target and a substrate, and metal particles are caused to pass through the through-holes to thereby uniform direction of metal particles. In accordance with the collimate sputtering, it is possible to deposit a metal film on a bottom of a recess formed at a surface of a substrate, but it is not possible to deposit a metal film onto an inner sidewall of the recess.

The fourth problem is that a crystalline metal film having high adhesion with a copper film tends to react with atmosphere to thereby a reaction layer at a surface thereof.

Such a reaction layer would much deteriorate adhesion of a metal film with a copper film.

The fifth problem is a copper oxide film is adhered again to a recess or hole.

An oxide film formed on a surface of an underlying wiring metal film is removed by argon plasma prior to deposition of a diffusion-barrier film by sputtering. When an underlying wiring layer is composed of copper, a copper oxide film is scattered by argon sputtering, and as a result, the thus scattered copper oxide is adhered again to a recess or hole formed at a surface of an insulating film.

The sixth problem is that when a copper film is formed on a tantalum film and an amorphous TaN film by CVD, adhesion between the copper film and a diffusion-barrier film is deteriorated.

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SUMMARY OF THE INVENTION

In view of the above-mentioned problems in a conventional diffusionbarrier film, it is an object of the present invention to provide a diffusion-barrier film having both a diffusion-barrier characteristic of preventing copper from being diffused into a semiconductor device and high adhesion between a copper film and an interlayer insulating film.

It is also an object of the present invention to provide a multi-layered wiring structure including the above-mentioned diffusion-barrier film.

Another object of the present invention is to provide a method of fabricating such the above-mentioned diffusion-barrier film.

A further object of the present invention is to provide a method of fabricating a multi-layered copper wiring layer in which copper is buried above the above-mentioned diffusion-barrier film.

In one aspect of the present invention, there is provided a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, including a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of common metal atomic species.

It is preferable that the first film is formed on the second film.

It is preferable that the second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

It is preferable that the first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

In another aspect of the present invention, there is provided a multilayered wiring structure including a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate, the barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of common metal atomic species.

It is preferable that the barrier film covers a recess and a hole formed throughout an insulating film formed on an underlying wiring layer.

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It is preferable that the multi-layered wiring structure further includes a copper film formed on the first film.

In still another aspect of the present invention, there is provided a method of forming a diffusion-barrier film by sputtering, including the steps of (a) preparing gas containing nitrogen therein, and (b) varying only power of an electric power source for generating plasma to thereby successively form a diffusion-barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of metal atomic species of sputter target.

It is preferable that the gas containing nitrogen therein has a pressure equal to or greater than 5 Pa.

It is preferable that the gas contains nitrogen at 10 volume % or smaller.

It is preferable that the metal atomic species of sputter target is one of tantalum, tungsten, titanium, molybdenum and niobium alone or in combination.

It is preferable that the second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

It is preferable that the first film has a thickness in the range of 60 20 angstroms to 300 angstroms both inclusive.

There is further provided a method of forming a diffusion-barrier film by RF magnetron sputtering making use of rotational magnetic field and RF power, including the steps of (a) preparing gas containing nitrogen therein, and (b) varying the RF power to thereby successively form a diffusion-barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, the barrier film being constituted of metal atomic species of sputter target.

There is still further provided a method of forming a diffusion-barrier

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film by RF magnetron sputtering, including the steps of (a) setting an electric power source for generation plasma to generate power having a first value, to thereby a first film, with a concentration of nitrogen in plasma gas being kept at a constant, and (b) setting the electric power source to generate power having a 'second value greater than the first value at the moment when the first film is formed by a predetermined thickness, to thereby form a second film on the first film.

It is preferable that the first film is composed of amorphous metal nitride, and the second film is composed of crystalline metal containing nitrogen therein.

There is yet further provided a method of forming a copper wiring film, including the steps of (a) radiating plasma of argon containing hydrogen therein, to a recess or hole formed at an insulating film formed on a semiconductor substrate, (b) forming a diffusion-barrier film to cover the recess or hole therewith without exposing to atmosphere, the diffusion-barrier film having a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride, and (c) forming a copper film on the diffusion-barrier film without exposing to atmosphere.

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It is preferable that the diffusion-barrier film is formed by sputtering. It is preferable that the copper film is formed in vacuum.

It is preferable that the copper film is formed by thermal chemical vapor deposition in which thermal dismutation in a complex of organic metal is utilized.

It is preferable that the copper film is formed by sputtering in which copper target is used.

The advantages obtained by the aforementioned present invention will be described hereinbelow.

In the diffusion-barrier film in accordance with the present invention, a

copper film makes direct contact with a crystalline metal film containing nitrogen therein, ensuring high adhesion therebetween and high crystallinity of a copper film.

In addition, since the metal film contains nitrogen therein, copper diffusion into a semiconductor device can be prevented more effectively than a metal film having pure crystals.

In the diffusion-barrier film in accordance with the present invention, an amorphous metal film containing nitrogen therein lies under a crystalline metal film containing nitrogen therein. Hence, it is possible to effectively prevent copper diffusion, and to ensure high adhesion with an underlying insulating film such as a silicon dioxide film. That is, by forming a copper wiring layer on the diffusion-barrier film in accordance with the present invention, it is possible to not only ensure high crystallinity and high adhesion of a copper wiring layer, but also to prevent copper diffusion.

The method in accordance with the present invention makes it possible to successively form a diffusion-barrier film having a multi-layered structure of first and second films, by varying only power of an electric power source for generating plasma in sputtering in which gas containing nitrogen therein is employed. Herein, the first film is composed of crystalline metal containing nitrogen therein, and the second film is composed of amorphous metal nitride. The barrier film is constituted of metal atomic species of sputter target.

Specifically, an electric power source for generating plasma is first set to generate relatively low power with a concentration of nitrogen in plasma gas being kept constant. A film is formed in such a condition. Target metal makes sufficient reaction with nitrogen, and resultingly, an amorphous metal nitride film is formed. Immediately after the formation of the amorphous metal nitride film, the electric power source is set to generate relatively high power to thereby form a film without allowing sufficient time for reaction between nitrogen and target metal. As a result, there is obtained a crystalline metal film containing nitrogen

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Thus, it is possible to successively form a diffusion-barrier film in the same chamber, wherein the diffusion-barrier film has a multi-layered structure including a crystalline metal film containing nitrogen therein and an amorphous metal nitride film.

The method of fabricating a diffusion-barrier film employs RF magnetron sputtering in which rotational magnetic field and RF power are utilized. Since the method makes it possible to carry out sputtering where a nitrogen-containing gas has a pressure equal to or greater than 5 Pa, plasma density of argon which is a main constituent of sputtering gas can be enhanced, and thus, there can be obtained coverage for entirely covering a recess or hole formed at a surface of a substrate, with the diffusion-barrier film.

The method of fabricating a diffusion-barrier film, in accordance with the present invention, includes the step of radiating plasma of argon containing hydrogen therein, to a recess or hole formed at an insulating film formed on a semiconductor substrate. This step reduces a copper oxide film formed on a surface of an underlying copper wiring layer, to thereby turn copper oxide back to copper, ensuring remarkable reduction in re-sputtering of a copper oxide film to a surface of a recess or hole formed at a surface of an insulating film.

Then, a diffusion-barrier film is formed to cover the recess or hole therewith without exposing to atmosphere, wherein the diffusion-barrier film has a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein, the second film being composed of amorphous metal nitride. Then, a thin copper film is formed on the diffusionbarrier film in vacuum. As a result, there is obtained a multi-layered structure comprised of the diffusion-barrier film and the copper wiring film without a metal oxide layer being sandwiched therebetween.

The above and other objects and advantageous features of the present invention will be made apparent from the following description made with

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reference to the accompanying drawings, in which like reference characters designate the same or similar parts throughout the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a conventional copper wiring structure.

Fig. 2 is a cross-sectional view of another conventional copper wiring structure.

Fig. 3 is a cross-sectional view of still another conventional copper wiring structure.

Fig. 4A is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the first step of a method of fabricating the same.

Fig. 4B is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the second step of a method of fabricating the same.

Fig. 4C is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the third step of a method of fabricating the same.

Fig. 4D is a cross-sectional view of a diffusion-barrier film in accordance with the first embodiment of the present invention, illustrating the fourth step of a method of fabricating the same.

Fig. 5 illustrates a high-pressure RF magnetron sputtering apparatus used in the first embodiment.

Fig. 6 is a graph showing coverage characteristic of a tantalum film in high-pressure RF magnetron sputtering.

Figs. 7 and 8 are cross-sectional views of a recess covered with a tantalum film in high-pressure RF magnetron sputtering.

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Fig. 9 is a graph showing a relation among a ratio of a nitrogen gas in a

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mixture gas introduced into a chamber, RF power, and resistivity of a film formed by sputtering.

Figs. 10 to 18 are graphs each showing film quality and characteristics of TaN and Ta films in high-pressure RF magnetron sputtering.

Figs. 19 and 20 are photographs of a film formed by high-pressure RF magnetron sputtering which photograph is taken by means of a scanning electron microscopy (SEM).

Fig. 21 is a cross-sectional view of a diffusion-barrier film formed by high-pressure RF magnetron sputtering which barrier-diffusion film is comprised of a crystalline Ta film containing nitrogen in solid solution and an amorphous metal TaN film.

Fig. 22 is a photograph of a film formed by high-pressure RF magnetron sputtering which photograph is taken by means of a scanning electron microscopy (SEM).

Fig. 23 is a cross-sectional view of a diffusion-barrier film covering a recess therewith.

Fig. 24 illustrates a DC magnetron sputtering apparatus used in the fourth embodiment.

Fig. 25 is a cross-sectional view of a diffusion-barrier film covering a 20 recess formed at a surface of an insulating film formed above a lower wiring layer.

Fig. 26 is a cross-sectional view of a diffusion-barrier film covering a recess formed at a surface of an insulating film formed above lower wiring layers.

Fig. 27 is a plan view of a cluster apparatus used for forming a copper wiring layer.

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Fig. 28 is a graph showing a diffusion profile of fluorine into a diffusion-barrier film.

Fig. 29 is a graph showing a diffusion profile of copper into a diffusion-barrier film. \langle

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Fig. 30 is a cross-sectional view of a copper wiring structure in

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accordance with the seventh embodiment.

Fig. 31 is a cross-sectional view of a copper wiring structure in accordance with the seventh embodiment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments in accordance with the present invention will be explained hereinbelow with reference to drawings.

A method of fabricating a diffusion-barrier film in accordance with the preferred embodiment is explained hereinbelow with reference to Figs. 4A to 4D.

As illustrated in Fig. 4A, a first insulating film 12a is formed on a semiconductor substrate 11, and a second insulating film 12b is formed on the first insulating film 12a. A copper wiring layer 44 is buried in the first insulating film 12a. The second insulating film 12b is formed at a surface thereof with recesses 13 in each of which a wiring is to be formed. Holes 14 reach the first insulating film 12a from a bottom of each of the recesses 13.

First, the semiconductor substrate 11 is exposed to argon plasma containing hydrogen therein, in a first chamber.

Then, the semiconductor substrate 11 is transferred in vacuum to a second chamber, and a film is formed on the semiconductor substrate 11 in a nitrogen-containing gas by sputtering in which a sputtering target is composed of refractive metal.

First, an electric power source for generating plasma is set to generate relatively low power with a concentration of nitrogen in plasma gas being kept constant. As a result, the target metal makes sufficient reaction with nitrogen, and an amorphous metal nitride film 15 is deposited over a surface of the second insulating film 12b, as illustrated in Fig. 4B.

Then, immediately after the formation of the amorphous metal nitride film 15, the electric power source is set to generate relatively high power to thereby form a film without allowing sufficient time for reaction between nitrogen

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and the target metal. As a result, a crystalline metal film 16 containing nitrogen therein is formed on the amorphous metal nitride film 15.

Thus, as illustrated in Fig. 4B, it is possible to successively and effectively fabricate the diffusion-barrier film 17 having a multi-layered structure, on both an inner sidewall and a bottom of the recesses 13 and the holes 14 in the same chamber. By setting a sputtering pressure sufficiently high while deposition of the diffusion-barrier film 17 by sputtering, it would be possible to enhance coverage of the diffusion-barrier film 17.

Thereafter, the semiconductor substrate 11 is transferred into a third chamber in vacuum. Then, a copper film 18 is deposited over the diffusionbarrier film 17 in vacuum in the third chamber to thereby completely fill the recesses 13 and the holes 14 with the copper film 18, as illustrated in Fig. 4C. Since the crystal metal film 16 containing nitrogen therein is exposed outside and the semiconductor substrate 11 is transferred in vacuum, an oxide film is not formed at a surface of the crystal metal film 16.

Then, as illustrated in Fig. 4D, the diffusion-barrier film 17 and the copper film 18 are removed by CMP until the second insulating film 12b appears. Thus, there is obtained a copper wiring structure having high reliability.

The reason of enhancement in barrier characteristic of preventing copper diffusion is to introduce nitrogen into the metal film 16. In addition, the metal film 16 containing nitrogen ensures high adhesion with copper. The amorphous metal nitride film 15 also has a characteristic of preventing copper diffusion, and further enhances adhesion with the second insulating film 12b. Thus, it is possible to ensure high adhesion between the copper film 18 and the diffusion-barrier film 17, and to prevent copper from being diffused from the copper film 18 into the second insulating film 12b.

Hereinbelow are explained detailed examples of the above-mentioned embodiment.

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[First Example]

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In the first example, hereinbelow is explained sputtering for fabricating a multi-layered structure comprised of a crystalline metal film containing nitrogen therein and an amorphous metal nitride film.

The sputtering in the first example is carried out in a RF magnetron 5 sputtering apparatus illustrated in Fig. 5.

In the illustrated RF magnetron sputtering apparatus, a chamber 21 is kept to be in vacuum, specifically, to have an internal pressure of about 1×10^{-7} Pa to about 1×10^{-6} Pa by means of a pump 33 such as a dry pump, a cryosorption pump or a turbo pump. In the chamber 21 is placed a heater 34 which can heat a semiconductor substrate 22 introduced into the chamber 21, up to about 20 to 300 degrees centigrade. A metal target 28 or the semiconductor substrate 22 is designed to be able to raise or lower, and hence, a distance between the metal target 28 and the semiconductor substrate 22 can be varied in the range of 102 mm to 134 mm.

Argon and nitrogen gases are adjusted with respect to a flow rate by means of mass flow controllers 31, and then, introduced into the chamber 21. When the argon and nitrogen gases are introduced into the chamber 21, the chamber 21 has an internal pressure of about 2 Pa to about 17 Pa.

The metal target 28 has a diameter, for instance, in the range of about 300 mm to about 320 mm. The metal target 28 is fixed to the chamber 21 through a target holder 27, a cathode 23 and insulators 29. In the cathodes 23 are rotatably arranged a plurality of permanent magnets 24. By rotating the permanent magnets 24, magnetic field 30 in the chamber 21 is uniformized, and erosion at a surface of the metal target 28 is also uniformized. As a result, it is possible to enhance uniformity of a film to be formed on the semiconductor substrate 22.

A RF electric power source 25 for introducing RF power into the chamber 21 is in electrical connection with the cathode 23 through a matching box 32 carrying out impedance matching. The RF electric power source 25 applies

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radio frequency (RF) having a frequency of 13.56 MHz to the metal target 28 having a diameter of 300 mm, at 0 to 10 kW.

Turning the RF electric power source 25 on to thereby introduce RF into the chamber 21, there is generated argon plasma containing nitrogen therein. The target metal 28 is sputtered by argon ions generated in the argon plasma 26. As a result, metal particles of the target metal 28 fly into the semiconductor substrate 22, and thus, the crystalline metal film 16 containing nitrogen therein or the amorphous metal nitride film 15 is formed.

The inventor actually formed a tantalum film covering therewith the hole 14 (see Fig. 4A) formed through the second insulating film 12b by means of the above-mentioned RF magnetron sputtering apparatus. The coverage characteristic of the tantalum film is shown in Fig. 6.

The hole 14 had a diameter in the range of $0.3 \,\mu$ m to $1.5 \,\mu$ m. The second insulating film 12b had a thickness of about $1.5 \,\mu$ m where the hole 14 was formed.

As is obvious in view of Fig. 6, as a sputtering pressure is increased from 2 Pa to 17 Pa, bottom coverage is enhanced. Herein, bottom coverage is defined as a ratio of a thickness of the tantalum film at a bottom of the hole 14 to a thickness of the tantalum film at a surface of the second insulating film 12b. Specifically, when a sputtering pressure is over 5 Pa, sufficient coverage can be obtained to a hole having a great aspect ratio.

A thickness of the tantalum film at an inner sidewall of the hole 14 is equal to about a half of a thickness of the tantalum film at a bottom of the hole 14. As a sputtering pressure is increased, the tantalum film covers an inner sidewall of the hole 14 therewith to a greater degree.

The reason of this phenomenon is considered as follows.

The first reason is an increase in the number of Ta ions in plasma gas, as illustrated in Fig. 7.

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As a sputtering pressure is increased, tantalum atomics increasingly

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make collision with excited argon atomics, resulting in that argon atomics are facilitated to be ionized. The resultant tantalum ions are attracted to negative self-bias generated at the semiconductor substrate 22. As a result, an incident angle at which tantalum ion flux 35 is radiated to the semiconductor substrate 22 becomes nearly 90 degrees. Thus, overhanging which occurs in the vicinity of an edge of recess or hole in conventional sputtering is suppressed, ensuring tantalum atomics to reach a bottom of the hole 14 or recess 13. As a result, a tantalum film 36 entirely covers an inner sidewall of the hole 14.

The second reason is that the deposited tantalum film 36 is re-10 sputtered by argon ions 39, as illustrated in Fig. 8.

The argon ions 39 which are primary constituents of plasma gas are accelerated by electric field and reach not only a target but also the semiconductor substrate 22 which is in a condition of negative self-bias. This means that the tantalum film 36 having been deposited onto the semiconductor substrate 22 is re-sputtered. Since the tantalum film deposited in the vicinity of an edge of the hole 14 or recess 13 and causing overhanging is re-sputtered by the argon ions 39, as indicated with an arrow 37, tantalum atomics 38 directing to a bottom of the hole 14 or recess 13 are not interfered at the edge of the hole 14 or recess 13. Accordingly, it is ensured that a tantalum film is deposited on a bottom and an inner sidewall of the hole 14 or recess 13.

In addition, since the tantalum film 36 deposited on a bottom of the hole 14 or recess 13 is re-sputtered by the argon ions 39, tantalum atomics generated by re-sputtering are deposited again on an inner sidewall 40 of the hole 14 or recess 13, ensuring enhancement in coverage at the sidewall 40 of the hole 14 or recess 13.

It is not possible to determine which is a main reason for enhancement in coverage among the above-mentioned first and second reasons. However, since mean free path of plasma ion is just a few millimeters under a pressure over 5 Pa, it is considered that almost 90 degrees of an incident angle of the tantalum

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ion flux 35 does not contribute to enhancement in coverage so much. The main reason why the coverage is enhanced is considered that argon ions are generated in a sufficient density by virtue of a high pressure, and a tantalum film having been deposited are re-sputtered by the argon ions.

In accordance with the experiments the inventor had conducted, it was confirmed that coverage was enhanced in sputtering of a tantalum nitride film, carried out under a high pressure over 5 Pa.

As mentioned so far, it is preferable that a sputtering pressure is set equal to or greater than 5 Pa in RF magnetron sputtering.

10 [Second Example]

Fig. 9 shows a relation between a flow rate ratio and resistivity of a film formed by high-pressure RF magnetron sputtering having been explained in the first example, for various RF powers. Herein, the flow rate ratio is defined as a ratio of a volume of argon gas to be introduced into the chamber 21 to a volume of nitrogen gas to be introduced into the chamber 21 $(N_2 / (Ar + N_2))$.

The relation shown in Fig. 9 was observed when the chamber 21 had a pressure of 13 Pa, the semiconductor substrate 22 was heated at 200 degrees centigrade, the permanent magnets 24 were rotated at 10 r.p.m., and the distance between the metal target 28 and the semiconductor substrate 22 was 134 mm.

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As a ratio of N_2 gas in the flow rate ratio $N_2 \swarrow (Ar + N_2)$ is increased, the resistivity is once reduced, and thereafter, increased again, regardless the RF power. However, an increase rate of the N_2 gas ratio is dependent on the RF power. The resistivity increases at a lower rate at the greater RF power.

Figs. 10 to 13 show how X-ray diffraction (XRD) patterns vary as the N_2 gas ratio is varied when RF power of 6 kW (8.5 W/cm²) is applied to the tantalum target having a diameter of 300 mm.

Specifically, Figs. 10 to 13 shows XRD patterns when the N_2 gas ratio is equal to 0%, 1%, 5%, and 7% respectively. Hereinbelow are explained Figs. 10 to 13 in comparison with Fig. 9.

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When the N₂ gas ratio is equal to 0%, there is obtained a β – Ta (002)oriented crystalline tantalum film which has resistivity in the range of about 160 to 200 μ Ω -cm, as illustrated in Fig. 10.

When the N₂ gas ratio is equal to 1%, there is obtained a crystalline metal film (herein, a tantalum film) containing nitrogen therein, which includes β - Ta and TaN_{0.1} in mixture and which has resistivity in the range of about 100 μ Ω -cm, as illustrated in Fig. 11.

When the N₂ gas ratio is equal to 5%, it is understood in view of Fig. 12 that XRD pattern strength is reduced, and hence, there is formed an amorphous metal nitride film, which has resistivity in the range of about 200 to 250 μ Ω -cm.

When the N_2 gas ratio is equal to 7%, a crystalline metal nitride film (Ta_3N_5) is formed, and resistivity is further increased, as illustrated in Fig. 13.

As mentioned above, when the tantalum target is selected, a crystalline structure, composition and resistivity of a film to be formed by sputtering vary in dependence on both a concentration of nitrogen gas in sputtering gas and RF power. Conversely speaking, this means that it is possible to control characteristics of a film to be formed by sputtering, by controlling both a concentration of nitrogen gas in sputtering gas and RF power. The present invention is based on this discovery.

However, it is difficult to vary a flow rate of sputtering gas (that is, a pressure of sputtering gas) and N_2 composition ratio in sputtering. Accordingly, it is necessary in practical use to keep both a flow rate of sputtering gas (that is, a pressure of sputtering gas) and N_2 composition ratio constant, and to vary only RF power, to thereby control a crystalline structure, composition and resistivity of a film to be formed by sputtering.

Fig. 14 shows how resistivity varies when only RF power is varied while a N_2 gas ratio is kept fixed at 2%. As is obvious in view of Fig. 14, it is understood that it is possible to control film quality and resistivity of a film to be formed by sputtering, even when only RF power is varied. In Fig. 14, resistivity is varied

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when a gas pressure is equal to 10 Pa, the permanent magnets are rotated at 10 r.p.m., and the substrate was heated at 200 degrees centigrade.

Figs. 15 to 18 show XRD characteristics relative to RF power. Figs. 15 to 18 show XRD characteristics observed when RF power is equal to 2 kW, 3 kW, 6 kW and 8 kW, respectively.

Specifically, when RF power is equal to 2 kW, there is obtained amorphous Ta_2N , as illustrated in Fig. 15. By increasing RF power, there is obtained crystalline $TaN_{0.1}$. When RF power is equal to 8 kW, there is obtained a crystalline metal film containing nitrogen therein, which includes a β -Ta film and $TaN_{0.1}$ in mixture.

Figs. 19 and 20 are SEM (Scanning Electron Microscopy) photographs of films obtained when RF power is set equal to 2 kW and 8 kW, respectively.

When RF power is set equal to 2 kW, as is obvious in view of XRD illustrated in Fig. 15, there is not observed grain boundary, because a deposited film has an amorphous structure. In contrast, when RF power is set equal to 8 kW, as is obvious in view of XRD illustrated in Fig. 18, there is obtained a crystalline film including a β -Ta film and TaN_{0.1} in mixture, and having a pillar-like structure.

That is, if Ta₂N, which is an amorphous metal nitride film, is deposited at 2 kW of RF power, and RF power is increased up to 8 kW immediately when the film has acquired a desired thickness, the film is turned into a crystalline metal film containing nitrogen therein. As a result, as illustrated in Fig. 21, a diffusion-barrier film 17 is formed on a semiconductor substrate 11 where the diffusion-barrier film 17 has a multi-layered structure comprised of an amorphous metal nitride film 15 and a crystalline metal film 16 containing nitrogen therein. Specifically, the amorphous metal nitride film 15 is an amorphous Ta₂N film, and the crystalline metal film 16 is composed of crystalline β -Ta and crystalline TaN_{0.1} in mixture.

Fig. 22 is a SEM photograph of a cross-section of the diffusion-barrier

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film 17 which is formed by changing sputtering power from 2 kW to 8 kW while a TaN film is being deposited, to thereby successively deposit the crystalline metal film 16 and the amorphous metal nitride film 15 each by a thickness of about 500 angstroms. It is confirmed in Fig. 22 that the amorphous Ta₂N film 15 and the crystalline metal film 16 containing nitrogen therein form a multi-layered structure.

The reason of this phenomenon is considered as follows.

When sputtering power is set equal to 2 kW, since a sputtering rate caused by argon ions is relatively low, there is sufficient time for a tantalum target to be nitrided by N_2 at a surface thereof. Hence, the tantalum target is nitrided at a surface thereof, and turned into Ta_2N . Since the thus produced Ta_2N is sputtered by argon ions, a Ta_2N film is deposited. However, when sputtering power is set equal to 8 kW, the tantalum target is sputtered by argon ions before a surface of the tantalum target is sufficiently nitrided. As a result, there is obtained a tantalum film slightly containing nitrogen.

By utilizing the above-mentioned phenomenon, it is possible to form the diffusion-barrier film 17 having a multi-layered structure and covering therewith the recess 13 or the hole 14 formed at the second insulating film 12b formed on the semiconductor substrate 11, as illustrated in Fig. 23.

The lower film or amorphous metal nitride (Ta_2N) film 15 is required to have such a thickness that barrier characteristic of preventing copper diffusion is ensured and adhesion with the underlying insulating film 12b is also ensured. A desired thickness of the amorphous metal nitride (Ta_2N) film 15 is in the range of about 80 angstroms to about 150 angstroms.

On the other hand, the crystalline nitrogen-containing metal film 16 composed of crystalline β -Ta and crystalline TaN_{0.1} in mixture is required to have such a thickness that barrier characteristic of preventing copper diffusion is ensured and adhesion with copper is also ensured. A desired thickness of the crystalline metal film 16 is in the range of about 60 angstroms to about 300

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[Third Example]

The RF magnetron sputtering having been explained in the first example makes it possible to enhance coverage characteristic of a deposited film for covering a recess or hole therewith, by introducing a gas having a higher pressure than usual, specifically, a pressure equal to or greater than 5 Pa, into a chamber. That is, it is possible to form the multi-layered barrier film 17 under desired coverage characteristic by switching RF power with a sputtering pressure being kept equal to or greater than 5 Pa, even when there is carried out dualdamassin process in which the recess 13 and the hole 14 formed at a surface of the second insulating film 12b formed on the semiconductor substrate 11 are concurrently filled with the diffusion-barrier film 17.

[Fourth Example]

In the above-mentioned first and second examples, the process in which a multi-layered barrier film is successively formed by switching RF power while the film is being formed is applied to RF magnetron sputtering. This process may be applied to DC magnetron sputtering, as illustrated in Fig. 24, though a N_2 gas ratio and RF power are different from those in the first and second examples.

Fig. 24 illustrates a DC magnetron sputtering apparatus. The apparatus is comprised of a chamber 21, a heater 34 fixed on a bottom of the chamber 21 for heating a semiconductor substrate 22, a target metal 28 fixed to a top of the chamber 21 by means of insulators 29 and a cathode 23, a pump 33 for exhausting air from the chamber 21 such that a pressure in the chamber 21 is in the range of about 1×10^{-7} Pa to about 1×10^{-6} Pa, a magnet 42 positioned above the target metal 28, mass flow controllers 31 for adjusting flow rates of argon gas and nitrogen gas, and allowing the gases to enter the chamber 21, and a DC electric power source 41 for applying a DC voltage to both the cathode 23 and the heater 34.

Turning the DC electric power source 41 on, argon plasma containing

nitrogen therein is generated in the chamber 21. [Fifth Example]

In the first and second examples, there is formed only one via-hole and wiring. However, it should be noted that the present invention may be applied to a copper wiring structure including two or more via-holes and wirings.

In the fifth example, as illustrated in Fig. 25, a first insulating film 12a is formed on a semiconductor substrate 11. The first insulating film 12a is formed with via-holes which is filled with a copper wiring layer 44 with a diffusion-barrier film 17 being sandwiched between an inner surface of each of the via-holes and the copper wiring layer 44. A second insulating film 12b is formed on the first insulating film 12a. The second insulating film 12b is also formed with recesses and via-holes which is filled with a copper wiring (not illustrated) with a diffusion-barrier film 17 being sandwiched between inner surfaces of the recesses and the via-holes, and the copper wiring.

Thus, recesses and/or holes formed throughout each of multi-layered insulating films are covered with the diffusion-barrier film 17, and then, the recesses and/or holes may be filled with a copper wiring layer.

An example of the multi-layered structure is illustrated in Fig. 26. The illustrated multi-layered structure is comprised of three insulating layers. Each of the insulating layers is formed with recesses and via-holes, which are covered at their surfaces with a diffusion-barrier layer 17, and filled with copper wiring layers 44a and 44b.

Hereinbelow is explained a method of fabricating the multi-layered structure illustrated in Fig. 26.

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A semiconductor substrate 11 is formed at a surface thereof with oxide layers 11a. A semiconductor device 11b is formed on the semiconductor substrate 11 between the oxide layers 11a.

A first insulating film 12a is formed on the semiconductor substrate 11. The first insulating film 12a is comprised of, for instance, a silicon dioxide film. The first insulating film 12a is formed with recess and holes reaching the semiconductor device 11b. The recesses and holes are covered at their inner surfaces with the diffusion-barrier film 17. The diffusion-barrier film 17 has a multi-layered structure comprised of a crystalline nitrogen-containing metal film and an amorphous metal nitride film, and has sufficient coverage to cover recesses and holes therewith. The diffusion-barrier film 17 may be formed by such highpressure RF magnetron sputtering as mentioned in the first example.

Then, the recesses and holes are filled with copper in vacuum. Then, the copper film and the diffusion-barrier film 17 are removed by CMP until the first insulating film 12a appears. Thus, there is fabricated the copper wiring layer 44a.

Since copper does not form passive state at a surface, the copper wiring layer 44a may be oxidized. In order to prevent oxidation of the copper wiring layer 44a, a silicon nitride film 12d is formed over the first insulating film 12a.

Then, a second insulating film 12b is formed on the first insulating film 12a. The second insulating film 12b is formed with recesses and holes reaching the copper wiring layer 44a formed in the first insulating film 12a. Then, the recesses and holes formed in the second insulating film 12b are covered with the diffusion-barrier film 17, and the recesses and holes are filled with the copper wiring layer 44b. By repeating the above-mentioned steps by the desired number, there can be fabricated a semiconductor device having such a multilayered copper wiring structure as illustrated in Fig. 26. [Sixth Example]

The sixth example relates to an apparatus and a method of successively 25forming both a diffusion-barrier film having a multi-layered structure and copper wiring layer.

Fig. 27 is a top plan view of an apparatus of forming a copper wiring layer, in accordance with the sixth example.

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The apparatus includes a cluster chamber 51 including a separation

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chamber 51 at a center. The separation chamber 51 is equipped therein with a robot 52 for transferring a semiconductor substrate.

The cluster chamber 51 is comprised further of two lord lock chambers 45, a chamber 46 used for heating a semiconductor substrate, an etching chamber 47 used for cleaning recesses and holes, a sputter chamber 48 used for fabricating a diffusion-barrier film, and a chamber 49 used for forming a copper wiring layer, arranged around the separation chamber 51.

It is possible to form a copper wiring layer without exposure of a semiconductor substrate to atmosphere through the use of the cluster chamber 50.

Hereinbelow are explained steps of fabricating a copper wiring layer.

First, a semiconductor substrate is introduced into one of the lord lock chambers 45. An insulating film is formed in advance on the semiconductor substrate, and the insulating film is formed in advance with a recess and/or hole.

Then, the lord lock chamber 45 is evacuated of air by means of a dry pump and a turbo pump for about five minutes. As a result, the lord lock chamber 45 has a vacuum degree of 7×10^{-3} Pa to 8×10^{-3} Pa.

Then, a gate value between the lord lock chamber 45 and the separation chamber 51 is made open. The separation chamber 51 is in advance kept in a vacuum degree of about 5×10^{-5} Pa to 1×10^{-5} Pa by means of a dry pump and a turbo pump. Hence, the semiconductor substrate is transferred into the separation chamber 52 by the robot 52 without being exposed to atmosphere.

Then, the semiconductor substrate is transferred into the chamber 46 which is in advance kept in a vacuum degree of about 6×10^{-5} Pa by means of a dry pump and a turbo pump. The semiconductor substrate is heated at about 50 to about 200 degrees centigrade in the chamber 46 to thereby remove moisture existing at a surface of the semiconductor substrate and clean a surface of the semiconductor substrate.

Then, the semiconductor substrate is transferred into the etching chamber 47 from the chamber 46 through the separation chamber 51. The

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etching chamber 47 is kept in a vacuum degree of about 5×10^{-6} Pa by means of a cryosorption pump, dry pump and a turbo pump.

After introducing the semiconductor substrate into the etching chamber 47, the semiconductor substrate is plasma-etched in argon gas or argon gas diluted with hydrogen gas (H_2 /Ar = 3%). By carrying out plasma-etching, a surface of the semiconductor substrate and inner surfaces of a recess and a hole are reduced and cleaned.

The plasma-etching has an advantage that edges of a recess and a hole are ground by the plasma-etching, and accordingly, an opening area of the recess and hole is broadened, ensuring enhancement in coverage characteristic.

Then, the semiconductor substrate is transferred into the sputter chamber 48 from the etching chamber 47 by means of the robot 52. The sputter chamber 48 is kept in a vacuum degree of about 4×10^{-6} Pa by means of a cryosorption pump, dry pump and a turbo pump. The high-pressure RF magnetron sputtering as having been explained in the first example is carried out in the sputter chamber 48.

In the sputter chamber 48, a crystalline nitrogen-containing metal film (a film composed of crystalline β – Ta and crystalline TaN_{0.1} in mixture) and an amorphous metal nitride film (a Ta₂N film) are deposited on the semiconductor substrate by the method having been explained in the first and second examples, wherein RF power is instantaneously switched. In this example, a gas pressure is kept at 10 Pa, a substrate temperature is kept at 200 degrees centigrade, a N₂ gas ratio is kept at 2%, and RF power is switched from 2 kW to 8 kW. As a result, there is obtained a diffusion-barrier film having a multi-layered structure and also having enhanced coverage characteristic under the characteristics illustrated in Fig. 6.

Then, the semiconductor substrate is transferred in vacuum to the chamber 49 from the sputter chamber 48. The chamber 49 is kept in a vacuum degree of about 4×10^{-4} Pa by means of a dry pump and a turbo pump. Since the

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semiconductor substrate is transferred in vacuum, the crystalline nitrogencontaining metal film in the diffusion-barrier film is kept clean at a surface thereof. A copper film is deposited on the crystalline nitrogen-containing metal film by chemical vapor deposition (CVD) such that the recess and hole is filled with copper, as follows.

The semiconductor substrate is kept at about 170 to about 200 degrees centigrade. A source including Cu (hfac) tmvs (trimethylvinylsilyl hexafluoroacetylacetonate copper (I)) as a main constituent is introduced into a carburetor at 1 to 2 grams per minute through a liquid transfer system. The source gasified in the carburetor is introduced into the chamber 49 together with nitrogen carrier gas, resulting in that the chamber 49 is kept at about 1 kPa.

The gas introduced into the chamber 49 makes chemical reaction on the semiconductor substrate, and is turned into copper, and then, deposited on the semiconductor substrate. Herein, copper is deposited by such a thickness that a recess and/or hole is sufficiently filled with copper, for instance, a thickness in the range of about 8000 angstroms to about 15000 angstroms.

In particular, when a copper film is formed by CVD, segregation of fluorine at a surface of the diffusion-barrier film, diffusion of fluorine into the diffusion-barrier film, and diffusion of copper into the diffusion-barrier film exert a great influence on the adhesion, which fluorine is contained in Cu (hfac) tmvs which is a source for carrying out CVD.

Figs. 28 and 29 illustrate diffusion profiles of fluorine and copper into the diffusion-barrier film, respectively, which profiles were measured by SIMS (secondary ion mass spectroscopy).

In a β – Ta film obtained by sputtering carried out in argon atmosphere, since fluorine segregates at an interface between copper and tantalum, the β – Ta film would have poor adhesion. With respect to a Ta₂N film, though fluorine is diffused into the Ta₂N film, copper is scarcely diffused in the Ta₂N film. As a result, atomics are coupled with each other with a poor force,

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and hence, the Ta_2N film would have poor adhesion. In contrast, with respect to a $TaN_{0.1}$ film, since copper and fluorine are allowed to be diffused into the $TaN_{0.1}$ film, atomics are coupled with each other with a strong force, and as a result, the $TaN_{0.1}$ film would high adhesion.

Thus, it is understood that if copper is deposited by CVD, the diffusionbarrier film having a multi-layered structure comprised of a crystalline $TaN_{0.1}$ film and an amorphous Ta_2N film would have enhanced adhesion and barrier characteristic of preventing copper diffusion.

In accordance with the sixth example, a copper wiring layer can be formed on a semiconductor substrate without the semiconductor substrate being exposed to atmosphere. Accordingly, the diffusion-barrier film is kept clean at a surface, and hence, film quality of a copper film formed by CVD is likely to be reflected to a crystalline structure of a tantalum film of the diffusion-barrier film. Thus, it is possible to enhance crystal orientation of copper and adhesion between copper and a diffusion-barrier film.

[Seventh Example]

The seventh example relates to the cluster chamber 50 illustrated in Fig. 27. In the seventh example, the sputter chamber 48 is positioned in a region where a copper wiring layer is to be formed, which region corresponds to the chamber 49 in which a copper wiring layer is formed. Since the diffusion-barrier film includes a $TaN_{0.1}$ film containing crystalline β – Ta therein, at a surface, adhesion between the diffusion-barrier film and a copper film formed by sputtering is kept the same as adhesion between the diffusion-barrier film and a copper film formed by CVD.

25 [Eighth Example]

In the eighth example, the semiconductor substrate is taken out of the cluster chamber 50 illustrated in Fig. 27. The semiconductor substrate has such a copper wiring structure as illustrated in Fig. 30. Specifically, recesses and holes formed in the second insulating film 12b are covered with the diffusion-

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barrier film 17, and a copper film 53 is formed covering the diffusion-barrier film 17 therewith.

A second copper film 54 is deposited over the copper film 53 by plating such that the recesses and holes are filled with the second copper film 54. As a result, as illustrated in Fig. 31, it is possible to fabricate a structure comprised of the multi-layered barrier layer 17, the copper film 53 formed by CVD or sputtering, and the second copper film 54 formed by plating. Thereafter, as illustrated in Fig. 4D, for instance, the second copper film 54, the copper film 53 and the diffusion-barrier film 17 are removed by CMP. Thus, there is obtained a copper wiring structure.

While the present invention has been described in connection with the preferred embodiments, the present invention provides the following advantages.

The first advantage is that it is possible to have a diffusion-barrier film having sufficient barrier characteristic of preventing copper diffusion and high adhesion with a copper film. This is because the diffusion-barrier film is designed to have a multi-layered structure comprised of an amorphous metal nitride film having a high barrier characteristic of preventing copper diffusion and a crystalline nitrogen-containing metal film having high adhesion with copper.

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The second advantage is that it is possible to successively fabricate the diffusion-barrier film in a common chamber. This ensures reduction in apparatus cost and reduction in time for fabricating the diffusion-barrier film.

This is because that it is possible to successively form an amorphous metal nitride film and a crystalline nitrogen-containing metal film by instantaneously changing only RF power with a volume ratio of a nitrogen gas to a process gas introduced into a chamber, being kept constant. In accordance with this method, an upper metal film in the diffusion-barrier film inevitably contains nitrogen therein.

The third advantage is that a copper film can be formed with a surface

of the diffusion-barrier film being kept clean, through the use of an apparatus of transferring a semiconductor substrate in vacuum. As a result, reliability in a copper wiring layer can be enhanced.

While the present invention has been described in connection with certain preferred embodiments, it is to be understood that the subject matter encompassed by way of the present invention is not to be limited to those specific embodiments. On the contrary, it is intended for the subject matter of the invention to include all alternatives, modifications and equivalents as can be included within the spirit and scope of the following claims.

The entire disclosure of Japanese Patent Application No. 11-214110 filed on June 24, 1999 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

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WHAT IS CLAIMED IS:

A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first
 and second films,

said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride,

said barrier film being constituted of common metal atomic species.

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2. The barkier film as set forth in claim 1, wherein said first film is formed on said second film.

2 X. The barrier film as set forth in claim 1, wherein said second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

 \checkmark . The barrier film as set forth in claim 1, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

5. A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

said barrier film having a multi-layered structure of first and second films, said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride, said barrier film being constituted of common metal atomic species.

6. The multi-layered wiring structure as set forth in claim 5, wherein said

first film is formed on said second film.

The multi-layered wiring structure as set forth in claim 5, wherein said second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

7 .8. The multi-layered wiring structure as set forth in claim 5, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

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 \mathscr{S} . The multi-layered wiring structure as set forth in claim 5, wherein said barrier film covers a recess and a hole formed throughout an insulating film formed on an underlying wiring layer.

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10. The multi-layered wiring structure as set forth in claim 5, further comprising a copper film formed on said first film.

11. A method of forming a diffusion-barrier film by sputtering, comprising the steps of:

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(a) preparing gas containing nitrogen therein; and

(b) varying only power of an electric power source for generating plasma to thereby successively form a diffusion-barrier film having a multi-layered structure of first and second films, said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride, said barrier film being constituted of metal atomic species of sputter target.

12. The method as set forth in claim 11, wherein said gas containing nitrogen therein has a pressure equal to or greater than 5 Pa.

13. The method as set forth in claim 11, wherein said gas contains nitrogen at 10 volume % or smaller.

14. The method as set forth in claim 11, wherein said metal atomic species of sputter target is one of tantalum, tungsten, titanium, molybdenum and niobium alone or in combination.

15. The method as set forth in claim 11/wherein said second film has a thickness in the range of 80 angstroms to 150/angstroms both inclusive.

16. The method as set forth in claim 11, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

17. A method of forming a diffusion-barrier film by RF magnetron sputtering making use of rotational magnetic field and RF power, comprising the steps of:

(a) preparing gas containing nitrogen therein; and

(b) varying said RF power to thereby successively form a diffusion-barrier film having a multi-layered structure of first and second films, said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride, said barrier film being constituted of metal atomic species of sputter target.

18. The method as set forth in claim 17, wherein said gas containing nitrogentherein has a pressure equal to or greater than 5 Pa.

19. The method as set forth in claim 17, wherein said gas contains nitrogen at 10 volume % or smaller.

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20. The method as set forth in claim 17, wherein said metal atomic species of sputter target is one of tantalum, tungsten, titanium, molybdenum and niobium alone or in combination.

21. The method as set forth in claim 17, wherein said second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

22. The method as set forth in claim 17, wherein said first film has a thickness in the range of 60 angstroms to 300 angstroms both inclusive.

23. A method of forming a diffusion-barrier film by RF magnetron sputtering, comprising the steps of:

(a) setting an electric power source for generation plasma to generate power having a first value, to thereby a first film, with a concentration of nitrogen in plasma gas being kept at a constant; and

(b) setting said electric power source to generate power having a second value greater than said first value at the moment when said first film is formed by a predetermined thickness to thereby form a second film on said first film.

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24. The method as set forth in claim 23, wherein said first film is composed of amorphous metal nitride, and said second film is composed of crystalline metal containing nitrogen therein.

25. The method as set forth in claim 23, wherein said plasma gas contains nitrogen gas at a pressure equal to or greater than 5 Pa.

26. The method as set forth in claim 23, wherein said plasma gas contains nitrogen gas at 10 volume % or smaller.

27. The method as set forth in claim 23, wherein metal atomic species of sputter target is one of tantalum, tungsten, titanium, molybdenum and niobium alone or in combination.

28. The method as set forth in claim 23, wherein said first film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

29. The method as set forth in claim 23/wherein said second film has a thickness in the range of 60 angstroms to 300/angstroms both inclusive.

30. A method of forming a copper wiring film, comprising the steps of:

(a) radiating plasma of argon containing hydrogen therein, to a recess or hole formed at an insulating film formed on a semiconductor substrate;

(b) forming a diffusion-barrier/film to cover said recess or hole therewith without exposing to atmosphere, said diffusion-barrier film having a multilayered structure of first and second films, said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride; and

(c) forming a copper film on said diffusion-barrier film without exposing to20 atmosphere.

31. The method as set forth in claim 30, wherein said diffusion-barrier film is formed by sputtering.

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32. The method as set forth in claim 30, wherein said copper film is formed in vacuum.

33. The method as set forth in claim 32, wherein said copper film is formed by thermal chemical vapor deposition in which thermal dismutation in a complex

of organic metal is utilized.

34. The method as set forth in claim 32, wherein said copper film is formed by sputtering in which copper target is used.

35. The method as set forth in claim 30, wherein said first film has a thickness in the range of 60 agestroms to 300 angstroms both inclusive.

36. The method as set forth in claim 30, wherein said second film has a thickness in the range of 80 angstroms to 150 angstroms both inclusive.

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ABSTRACT OF THE DISCLOSURE

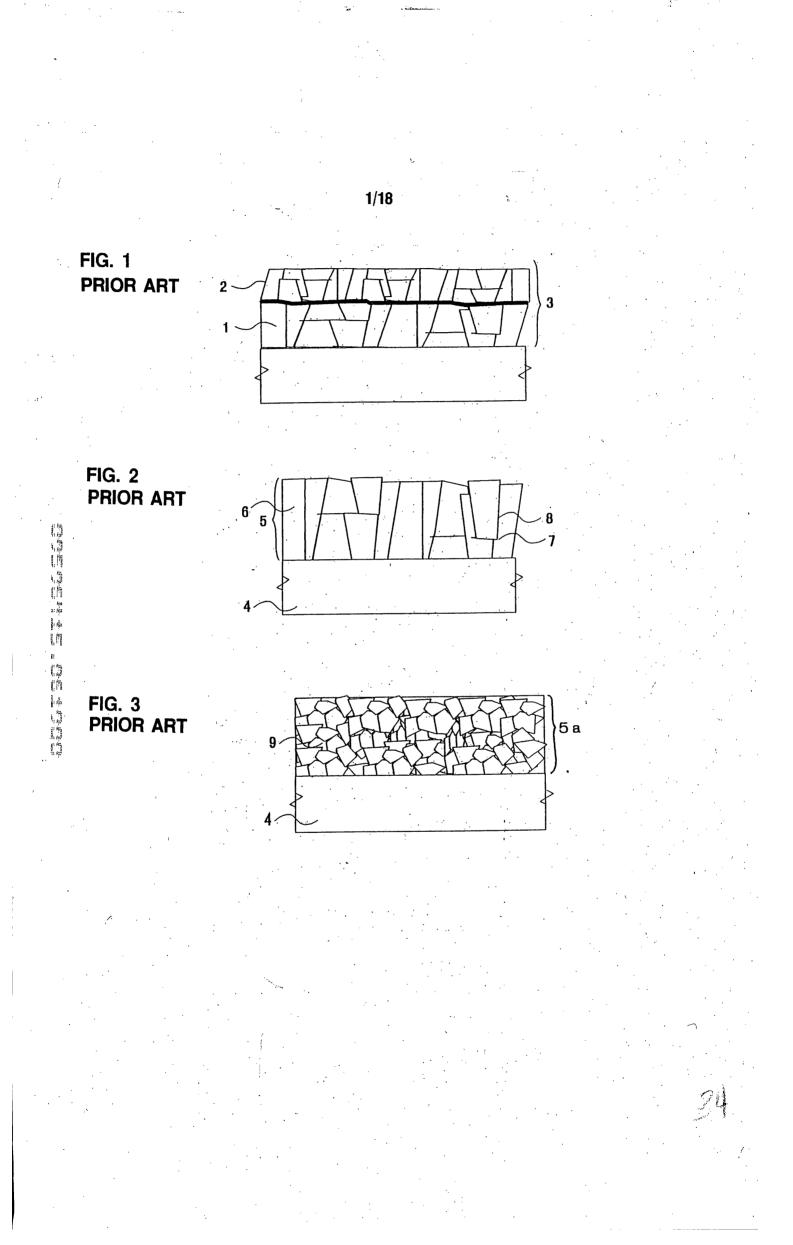
There is provided a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate. The barrier film has a multi-layered structure of first and second films wherein the first film is composed of crystalline metal containing nitrogen therein, and the second film is composed of amorphous metal nitride. The barrier film is constituted of common metal atomic species. The barrier film prevents copper diffusion from a copper wiring layer into a semiconductor device, and has sufficient adhesion characteristic to both a copper film and an interlayer insulating film.

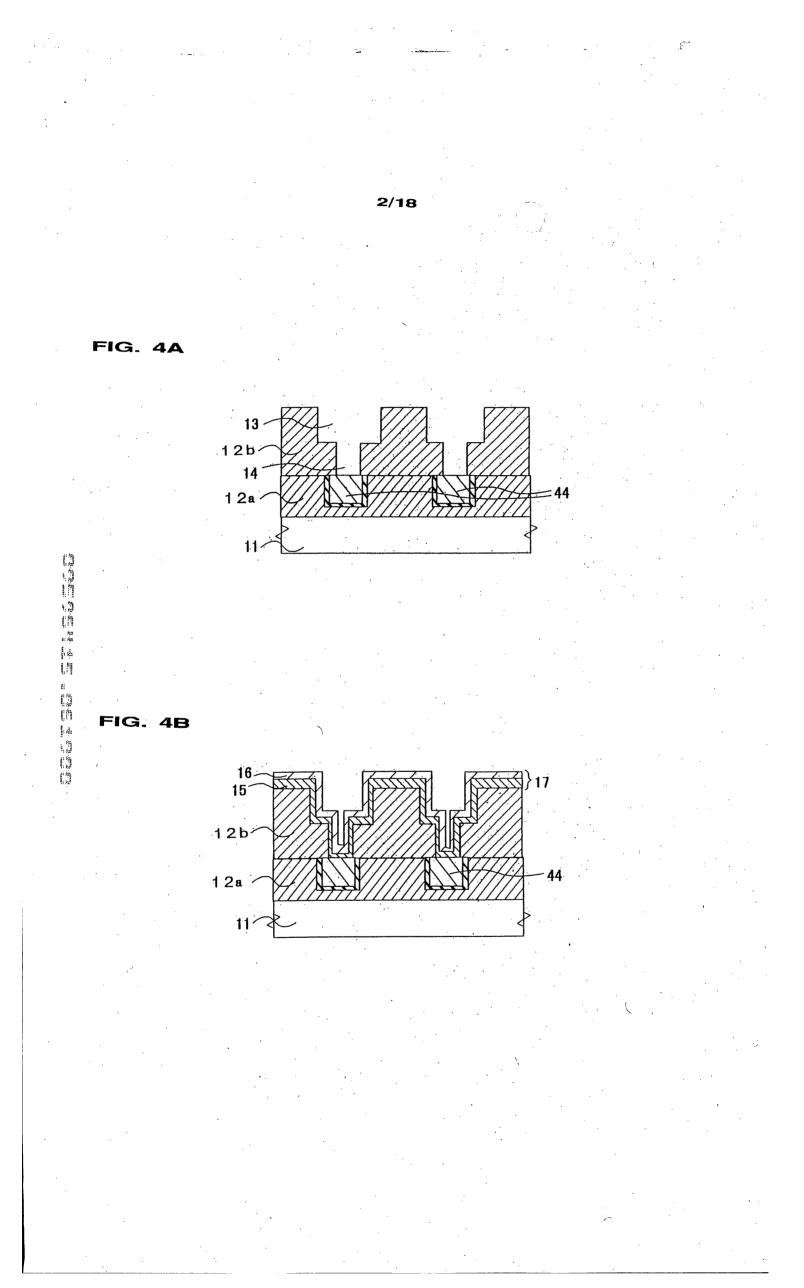
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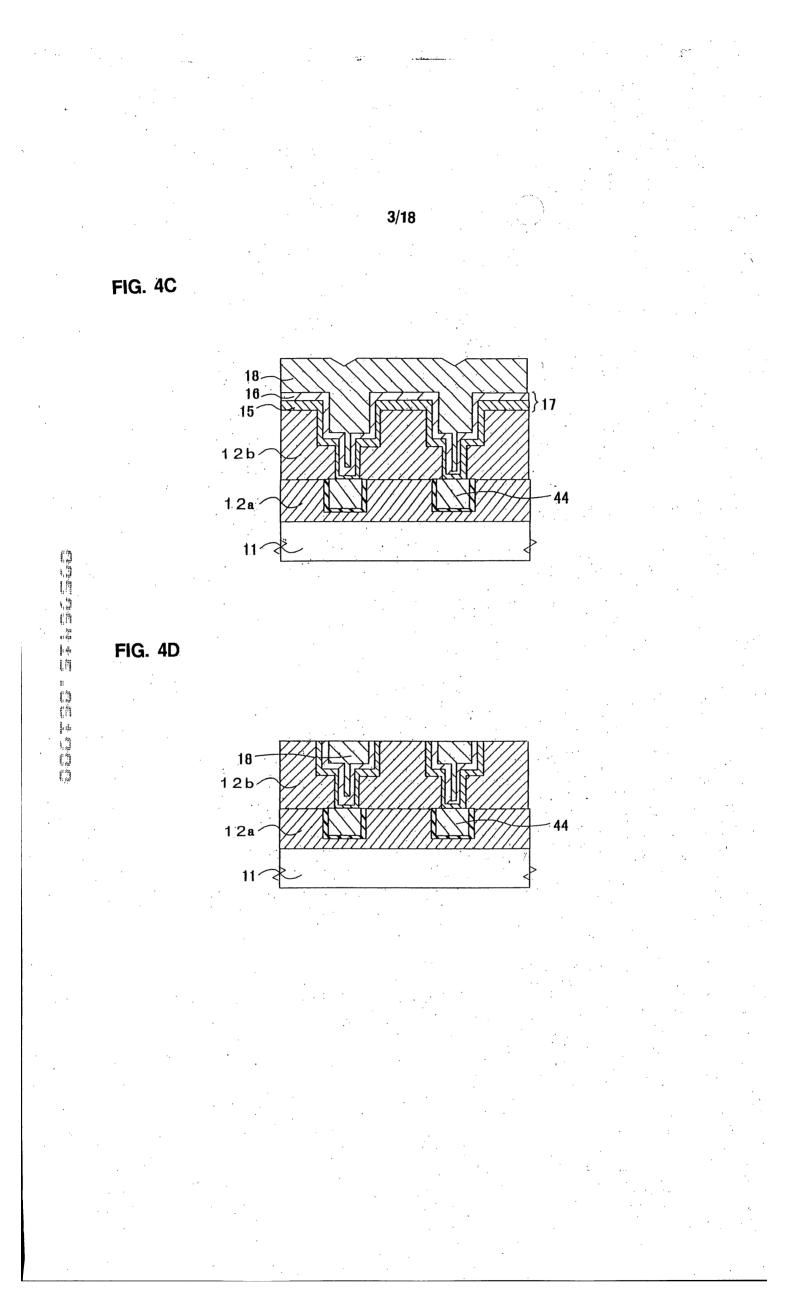
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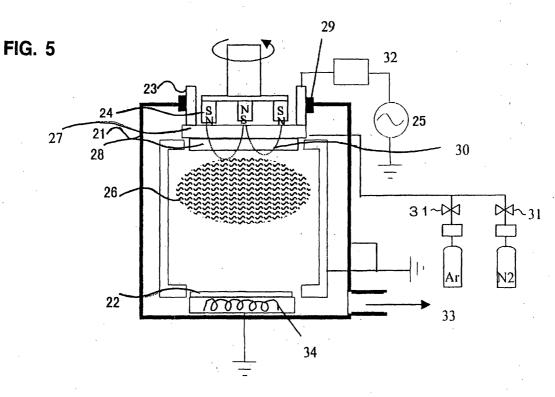
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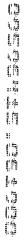


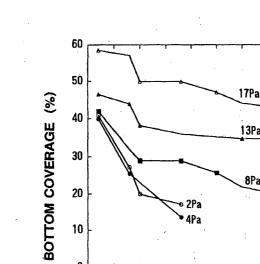




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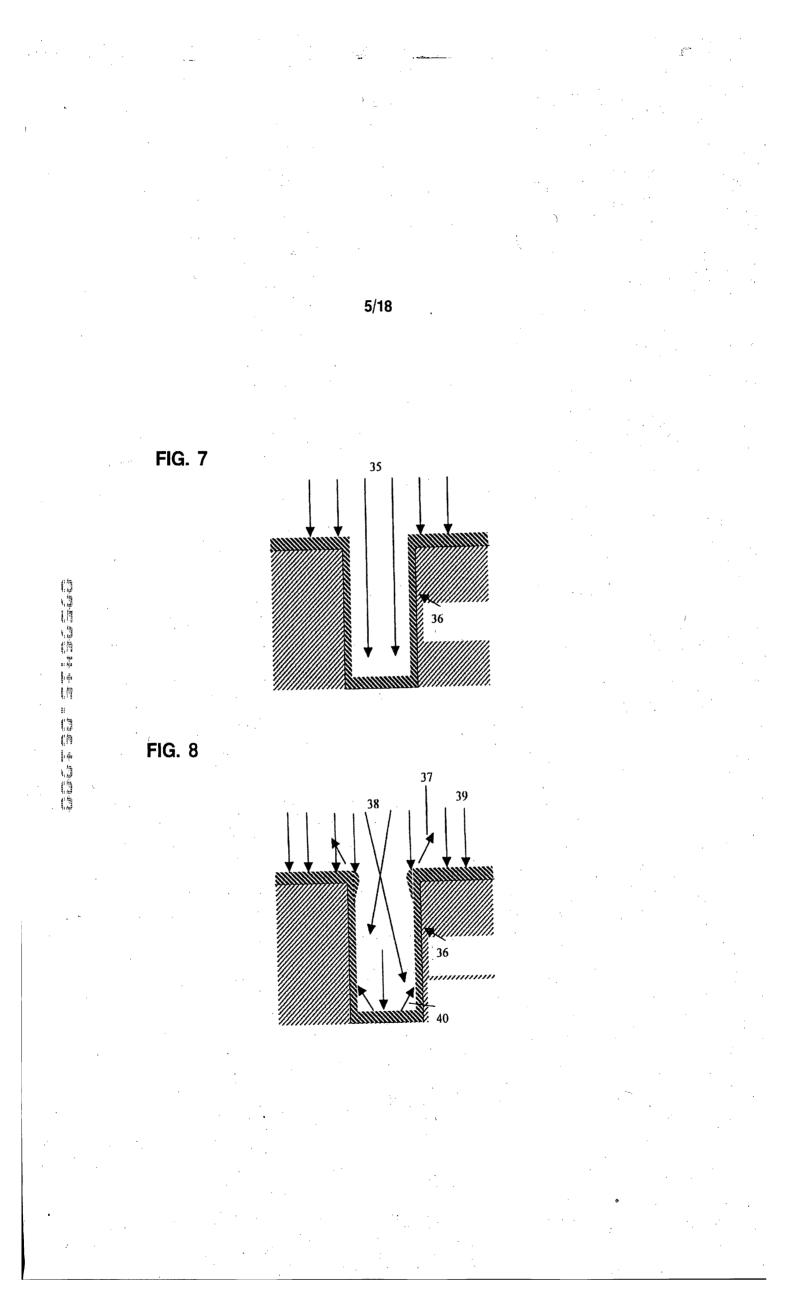
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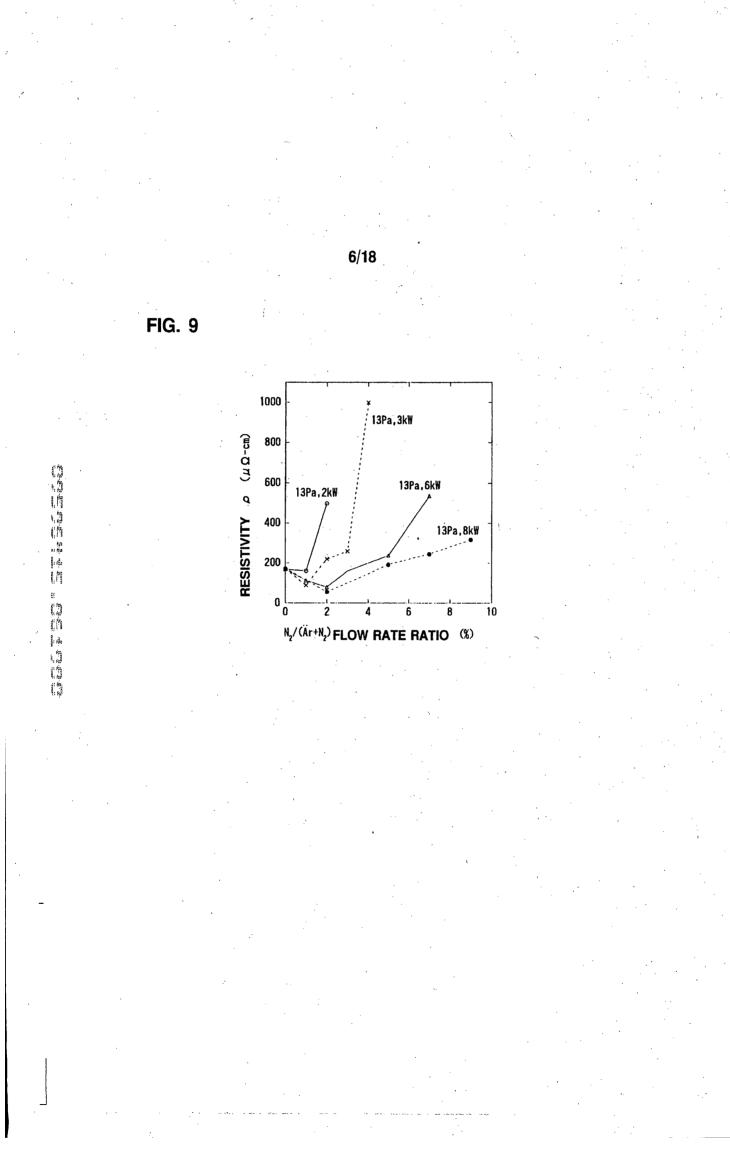
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FIG. 6

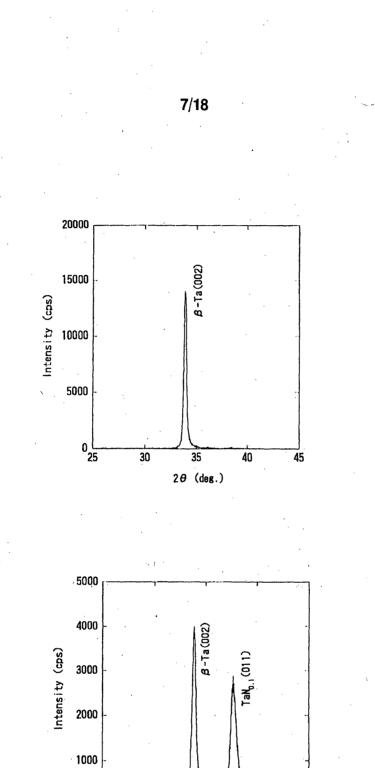
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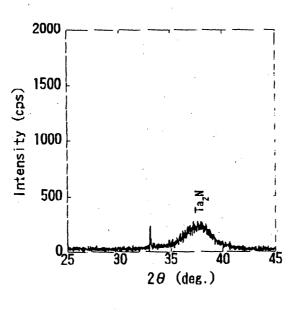
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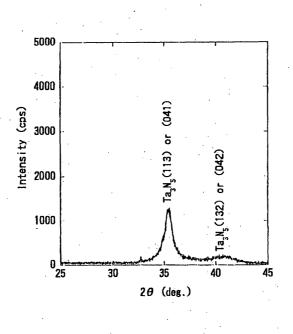
FIG. 11



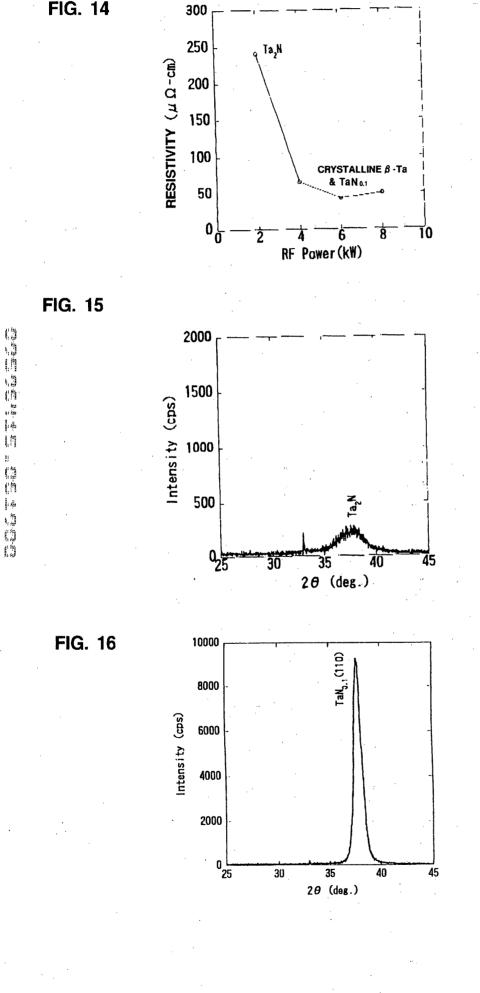




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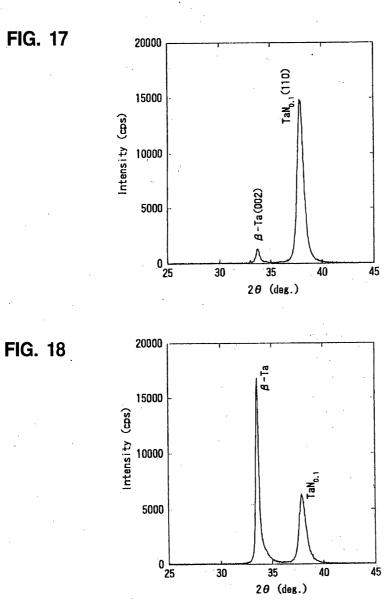
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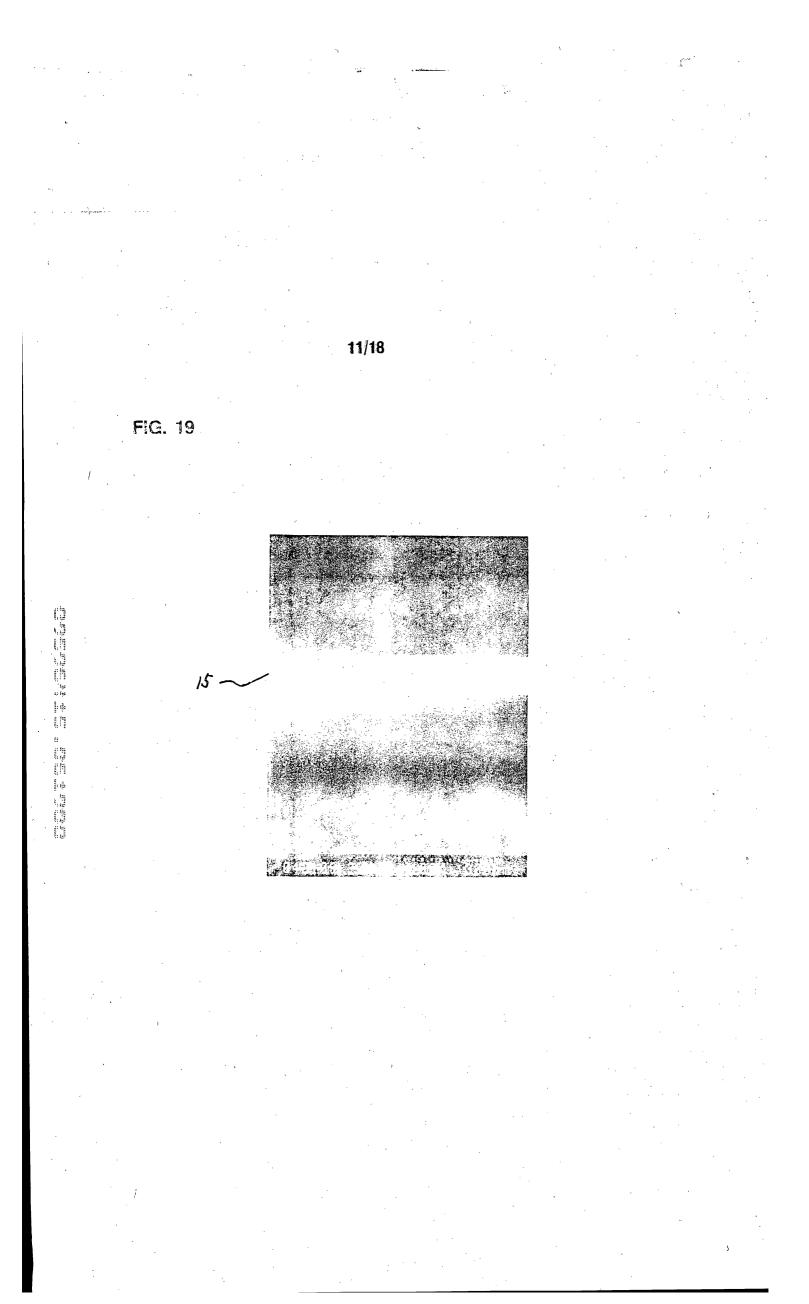
FIG. 14

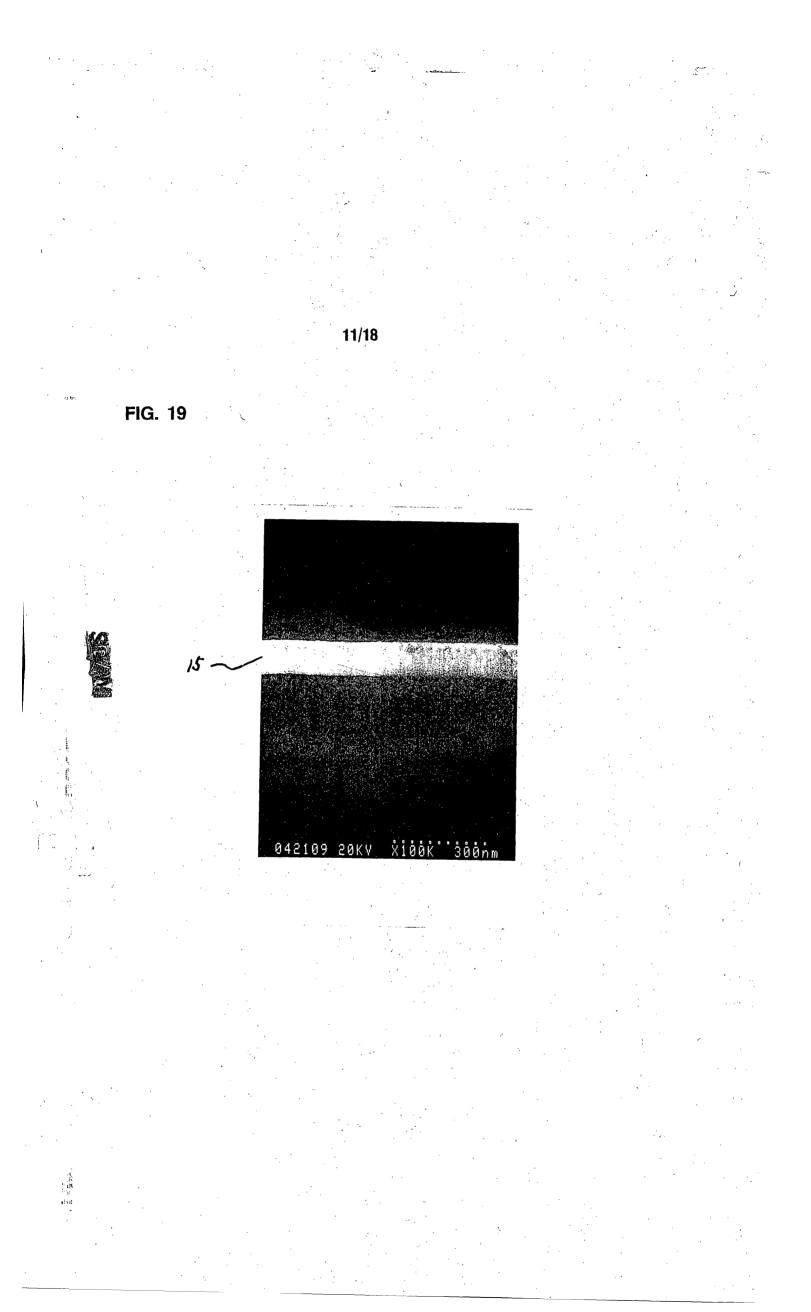
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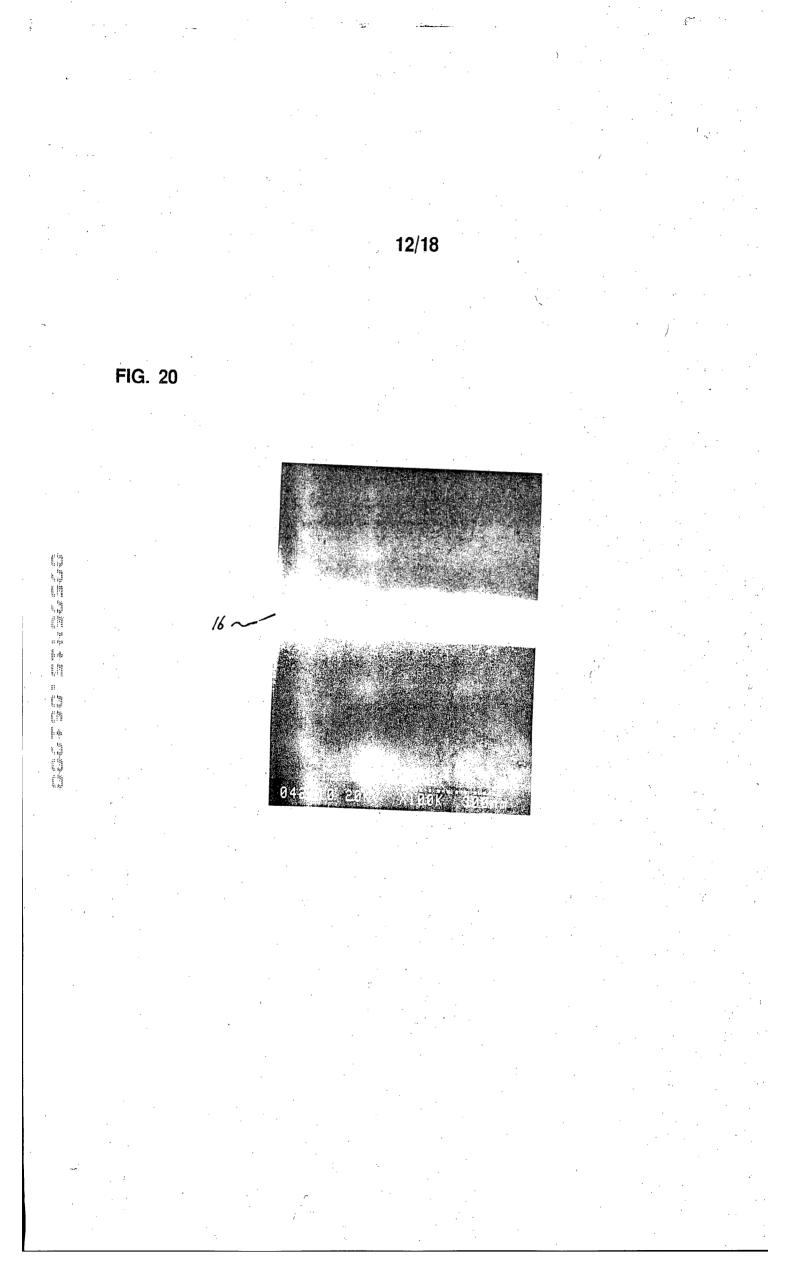


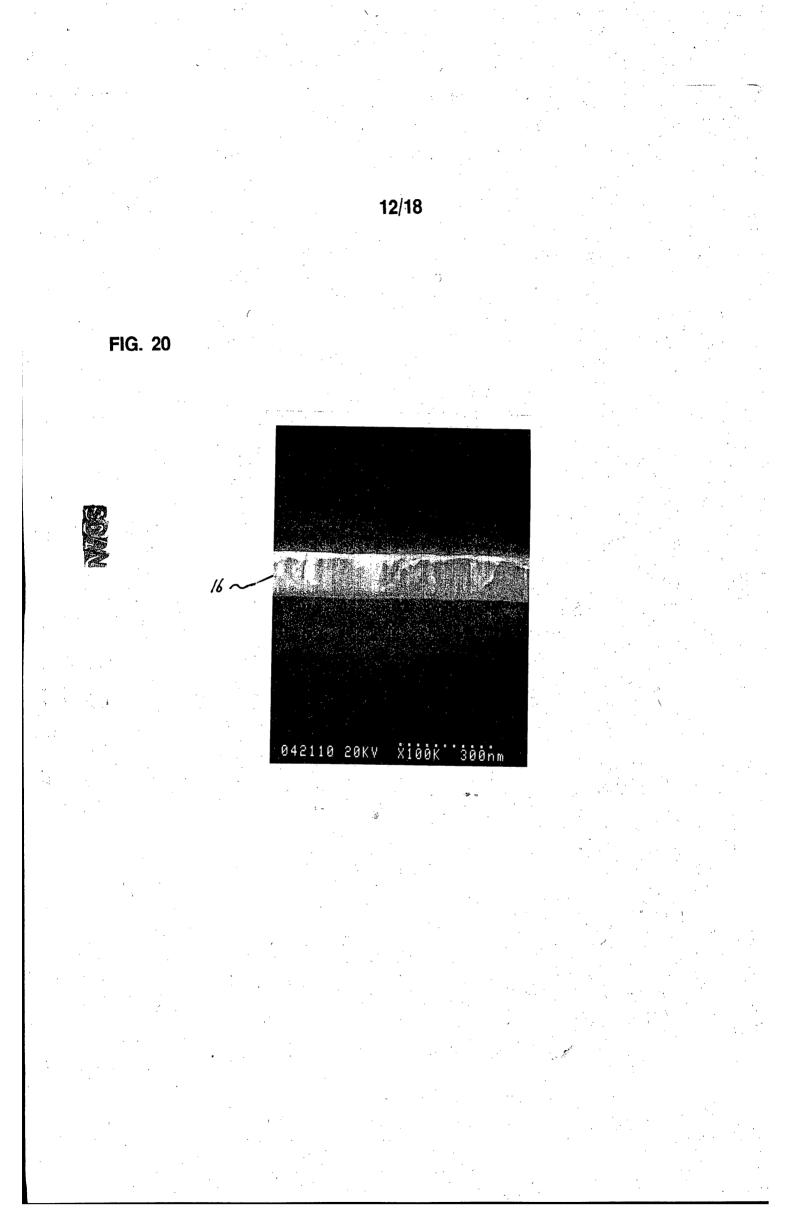
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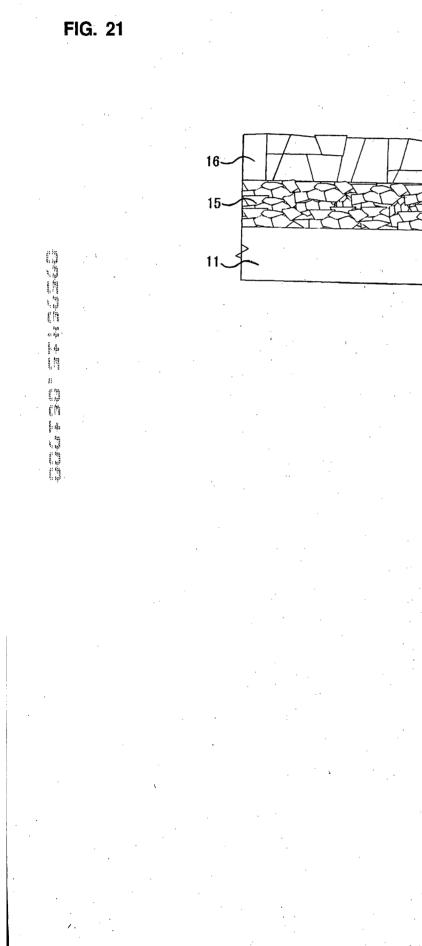
FIG. 17











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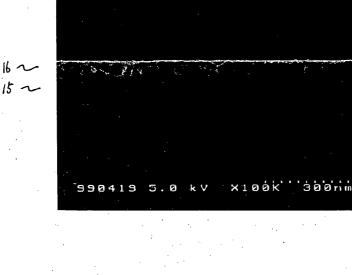


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FIG. 23

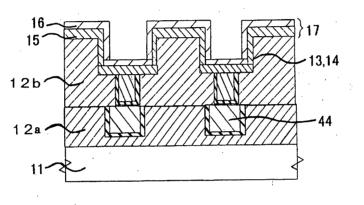
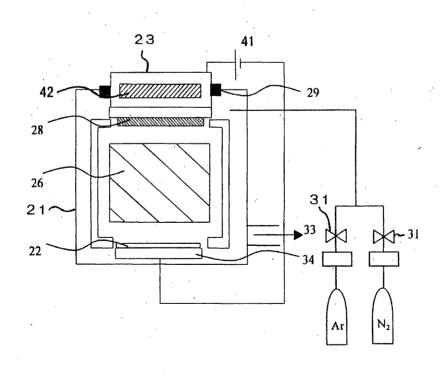
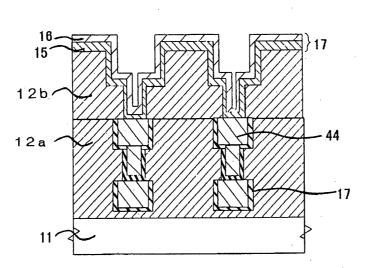
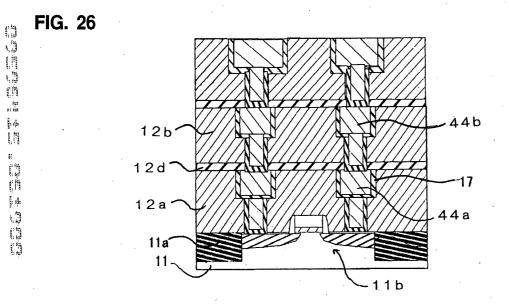


FIG. 24





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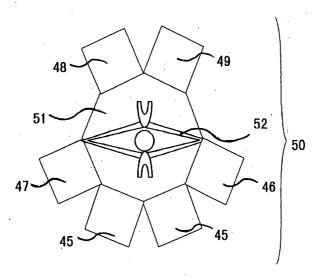
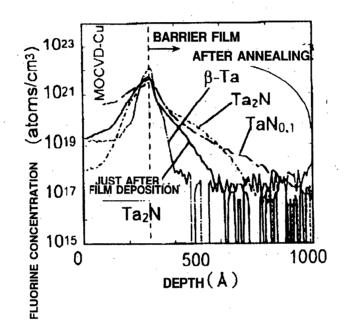


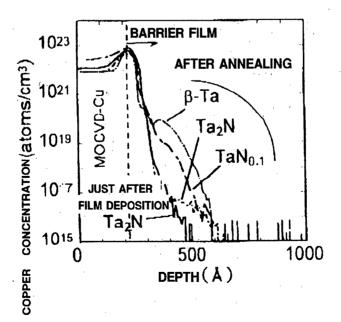
FIG. 25

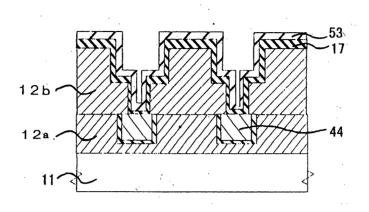




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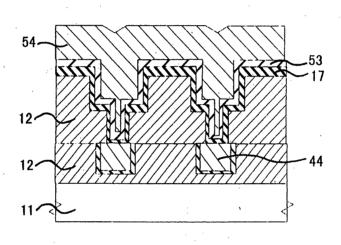


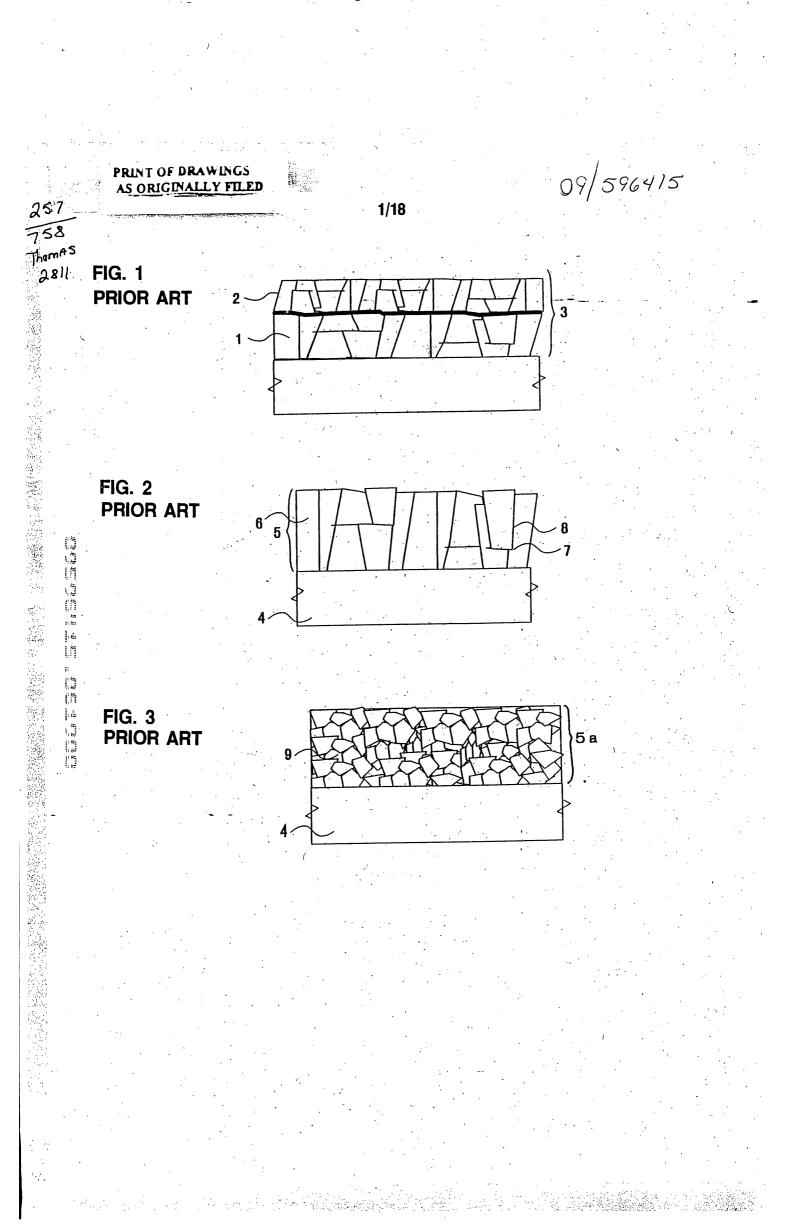


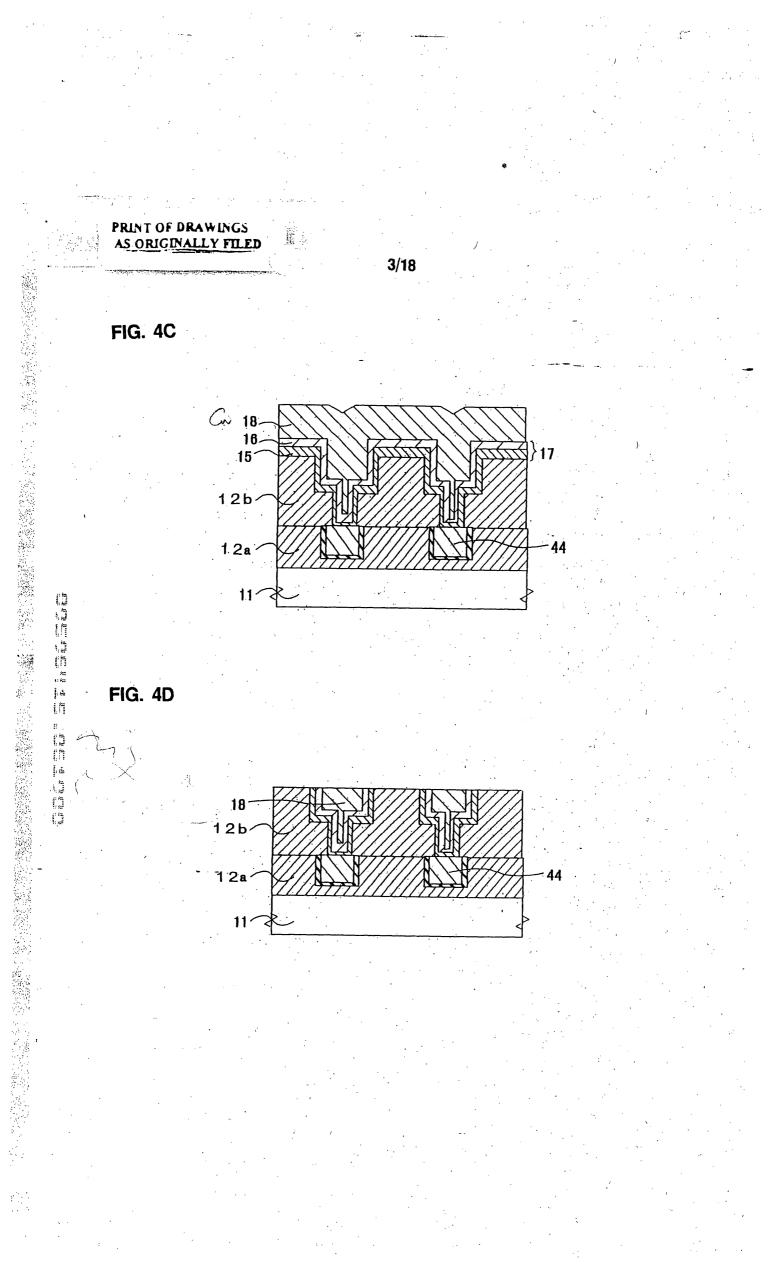
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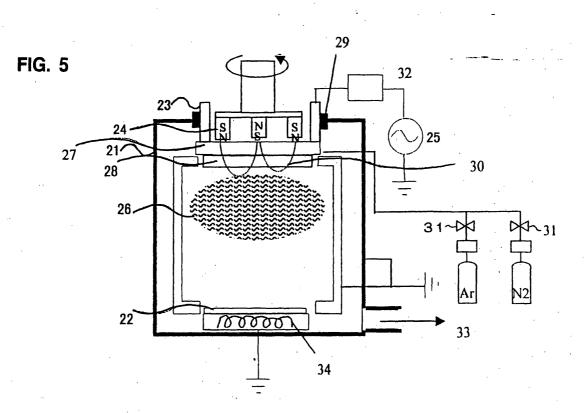
FIG. 30





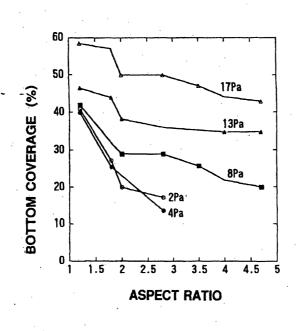


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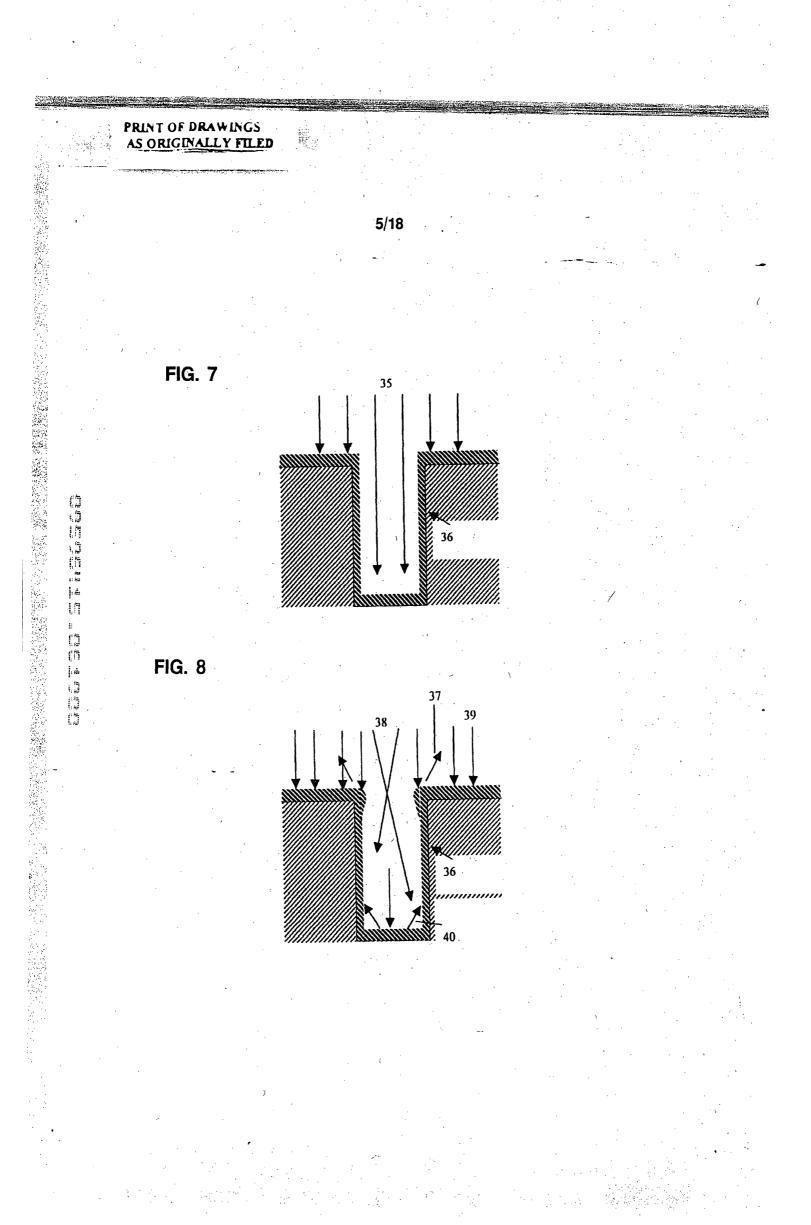
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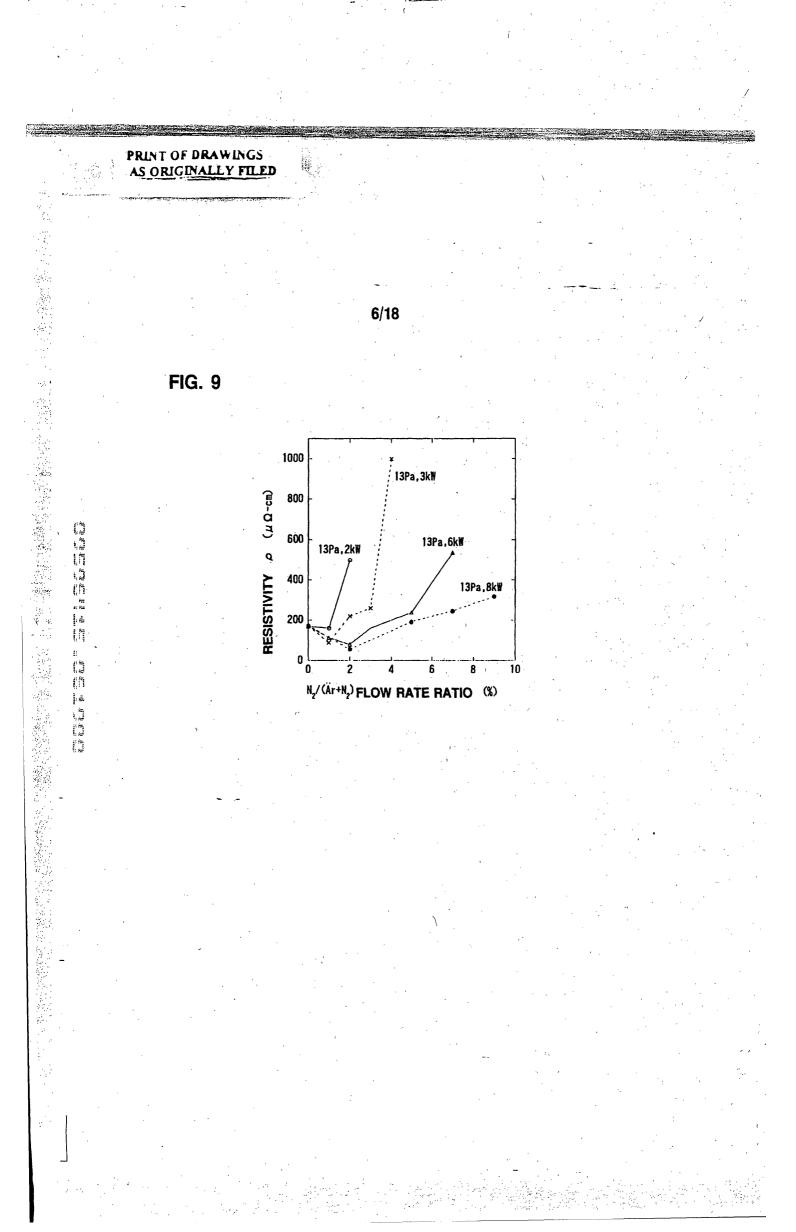


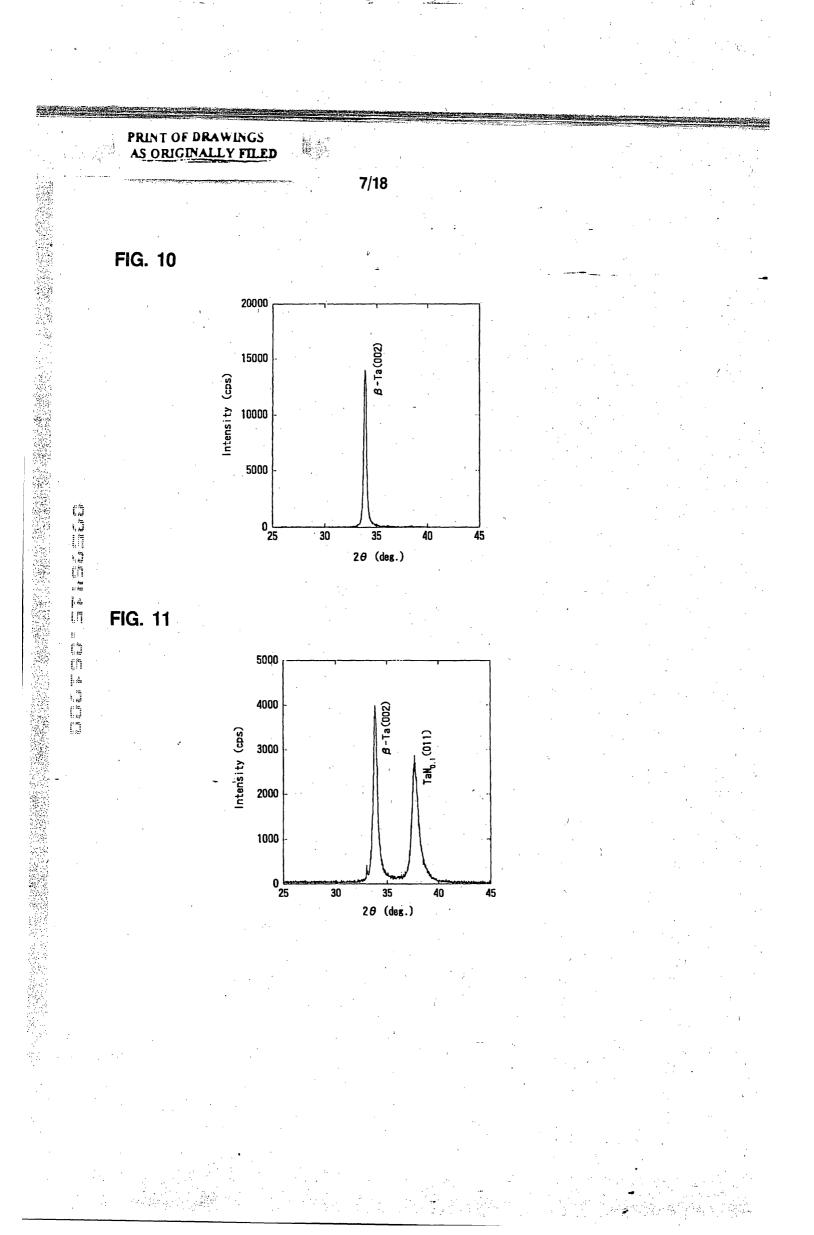


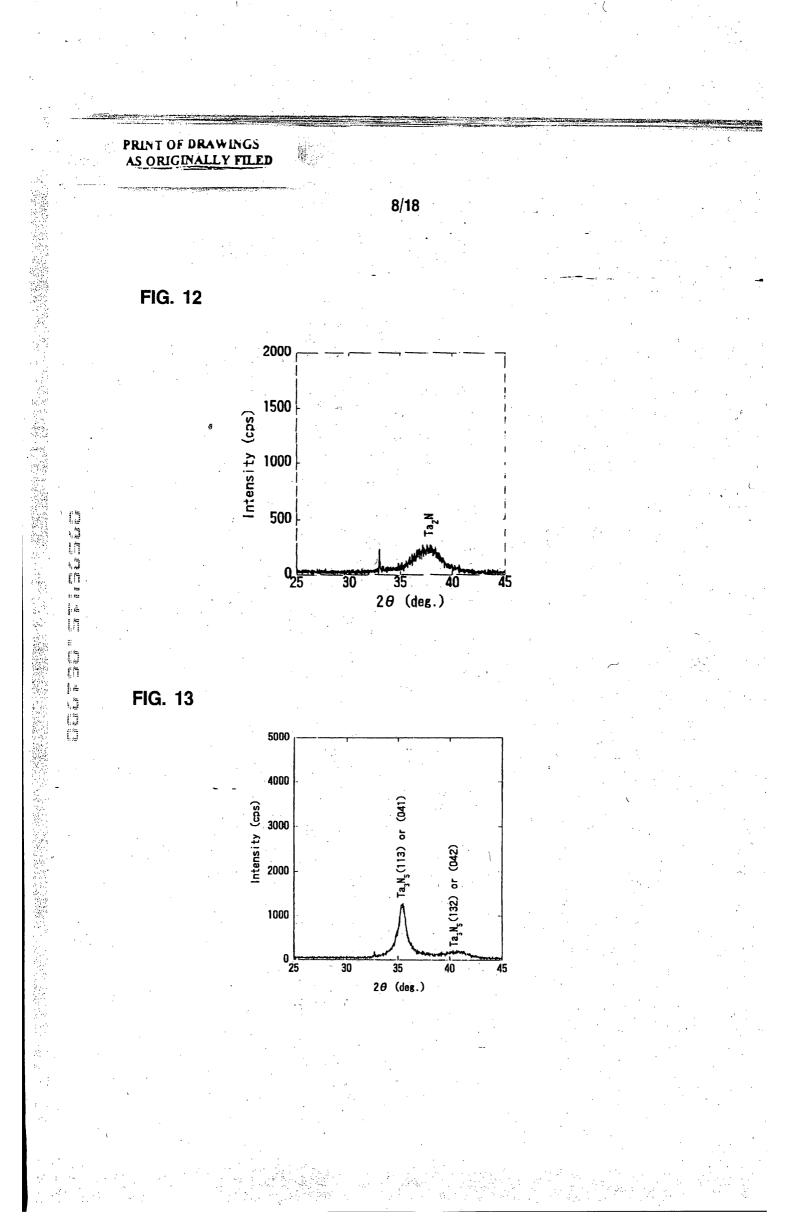
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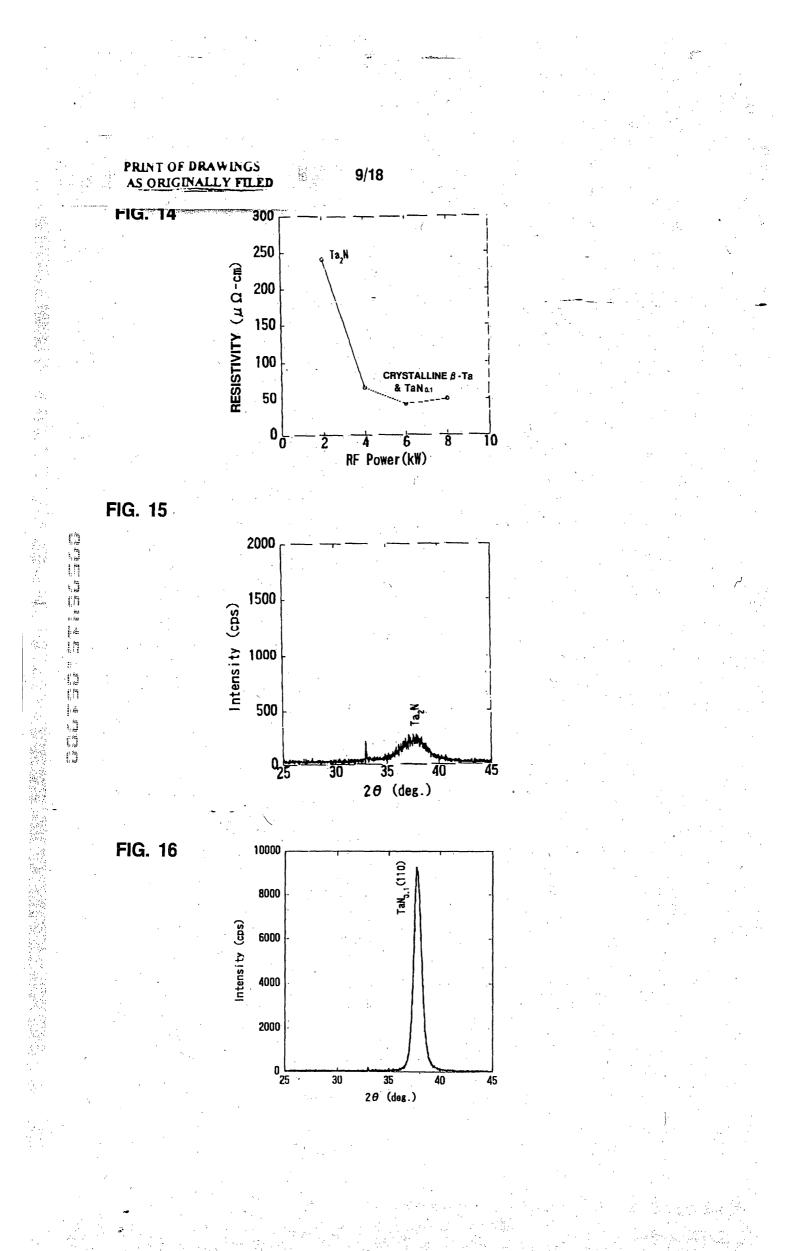


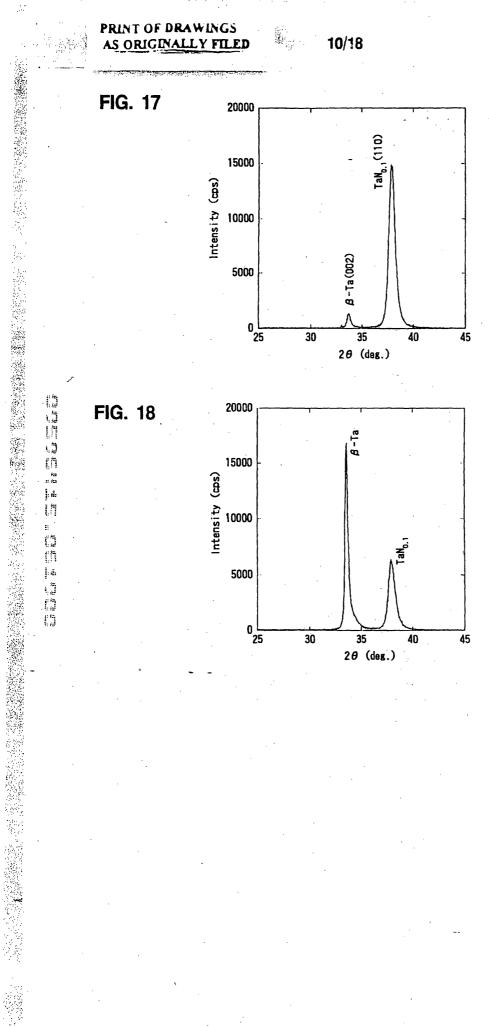


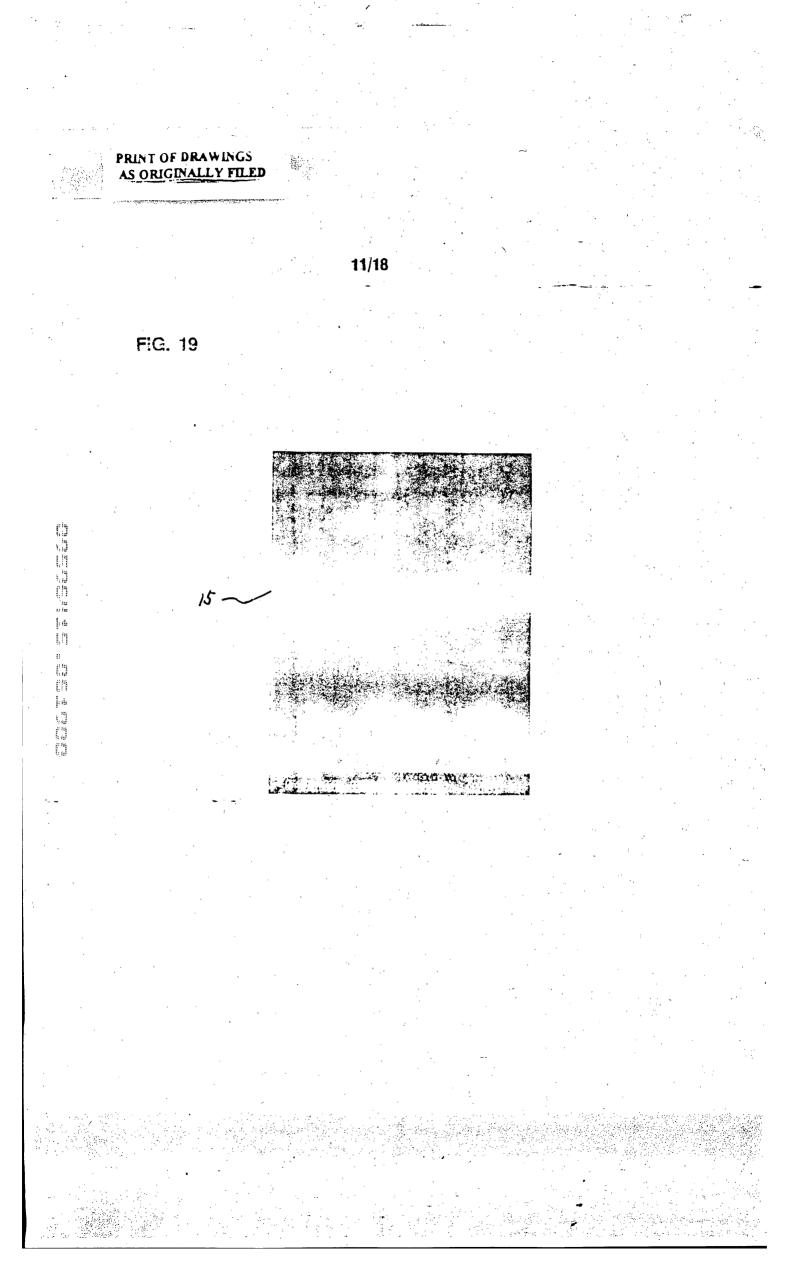


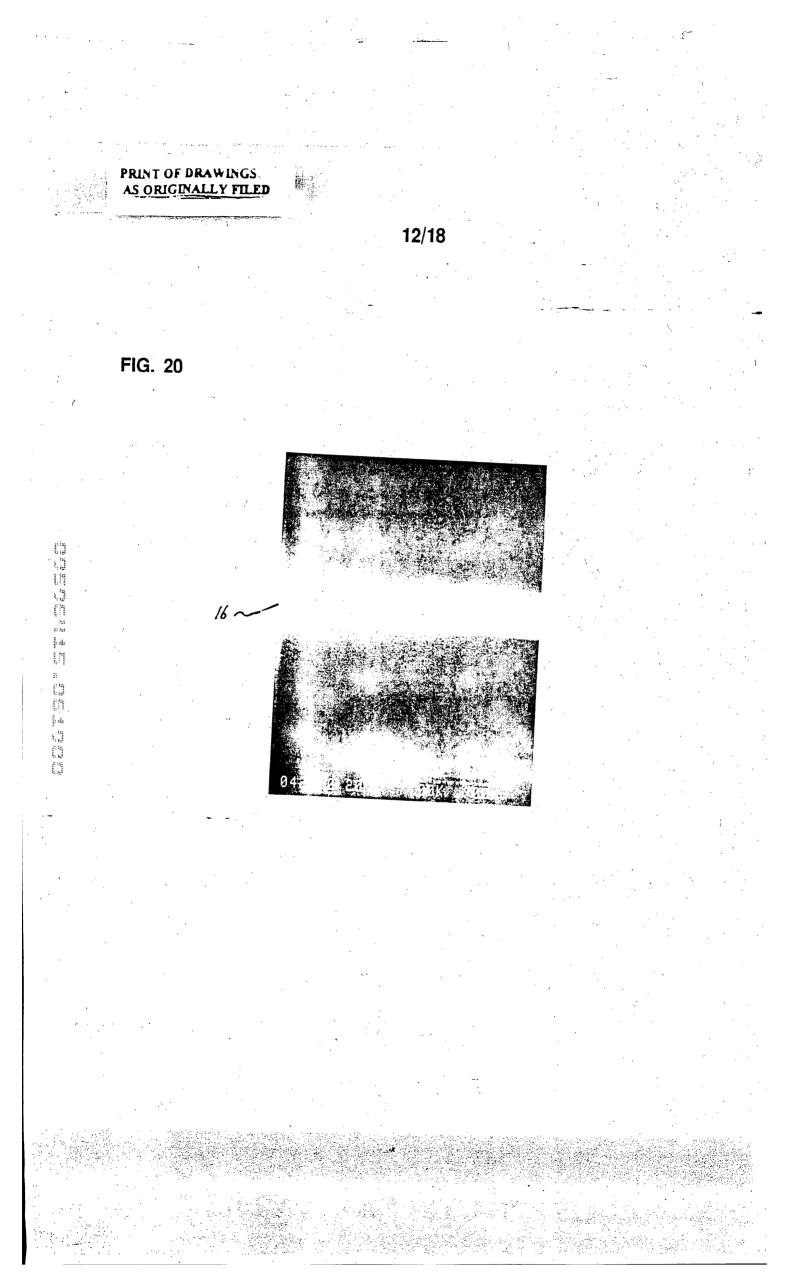


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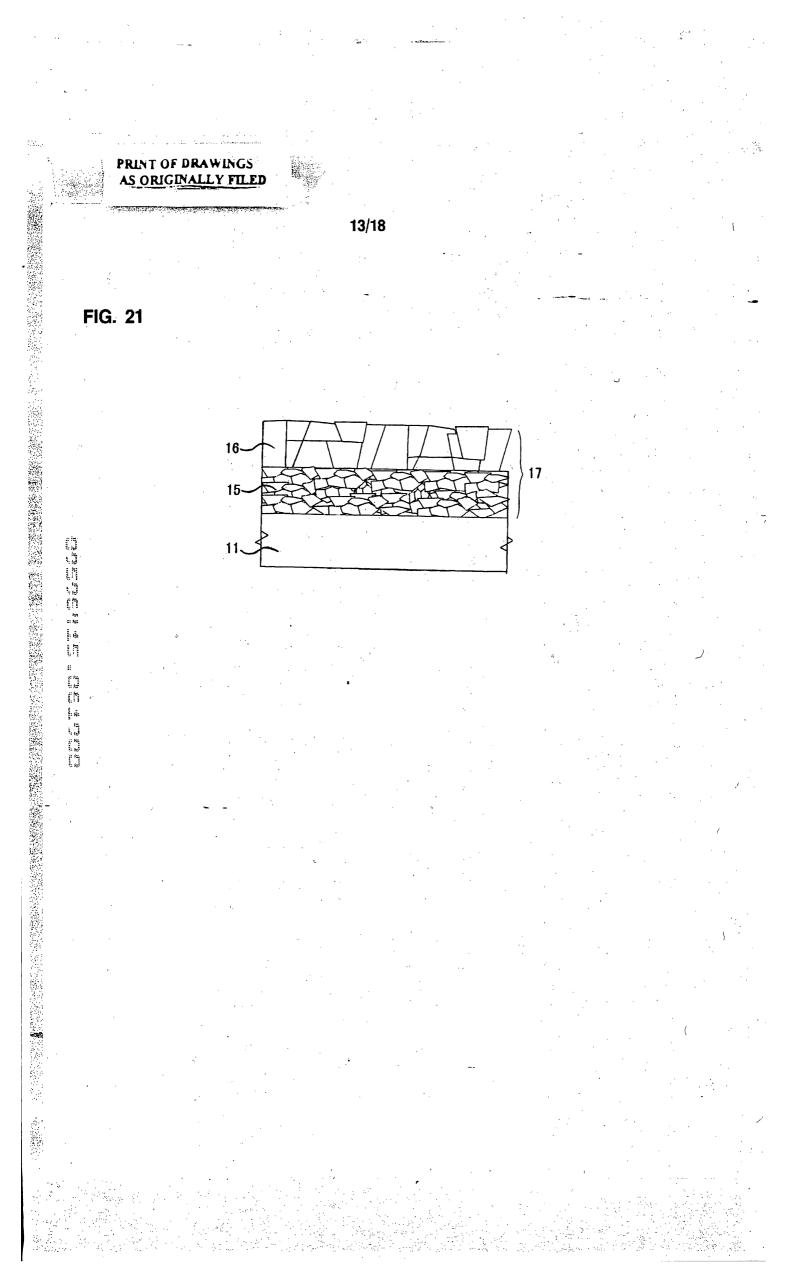


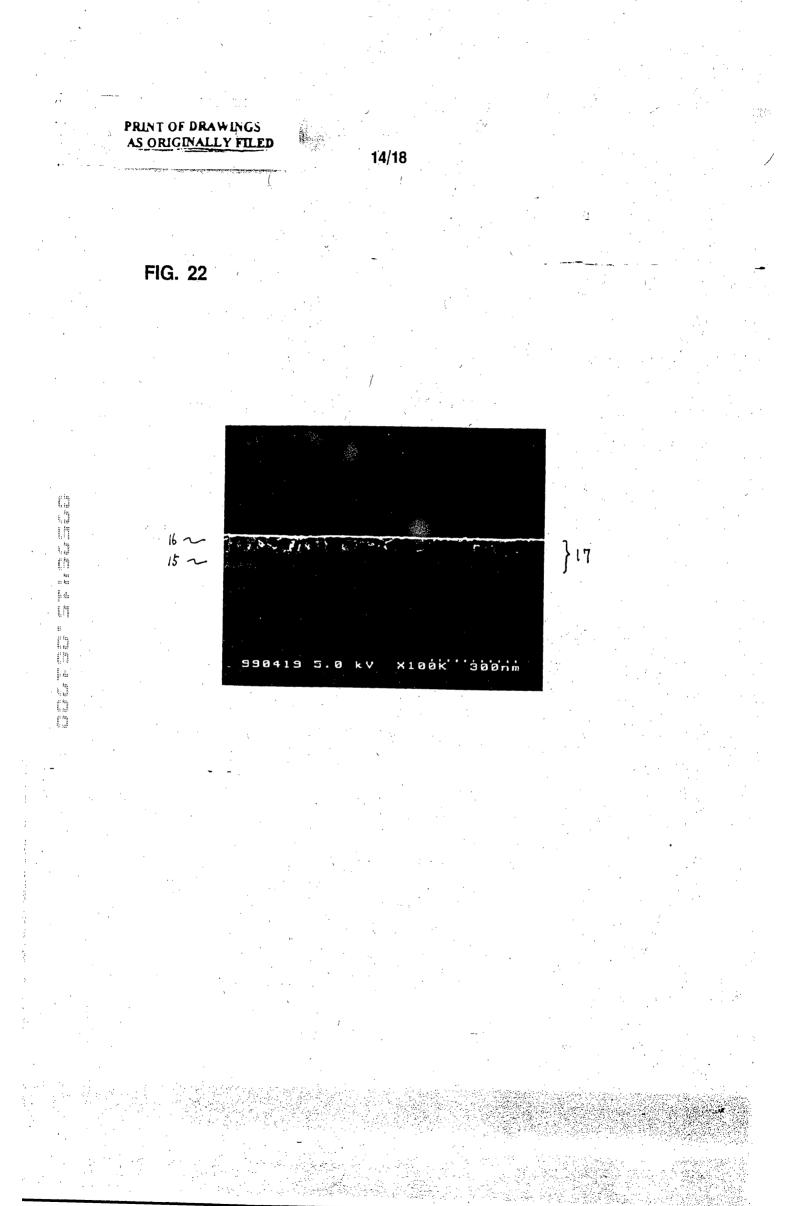


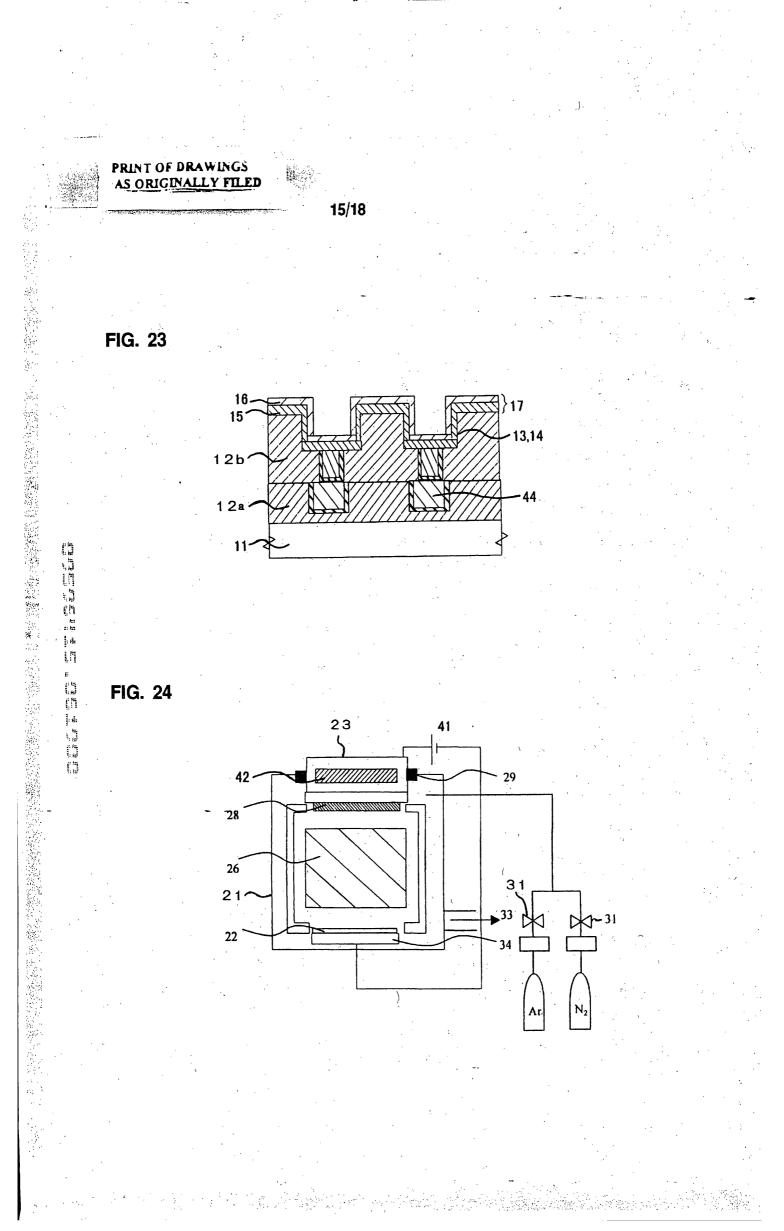




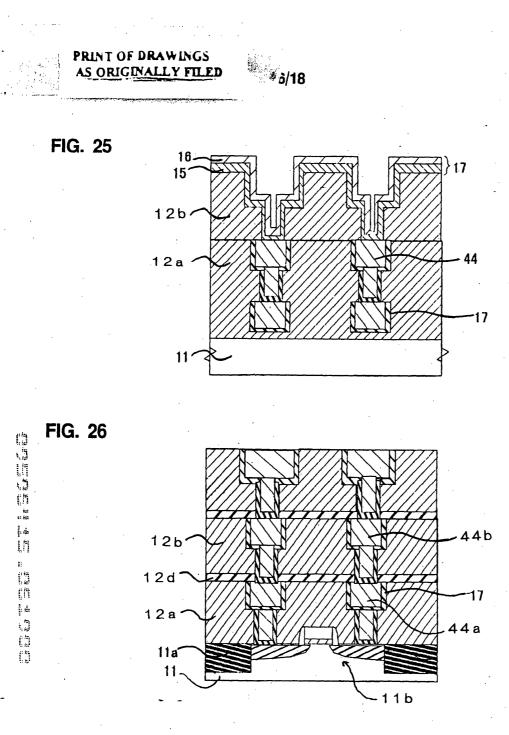
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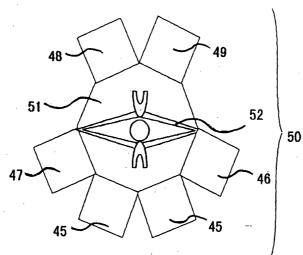
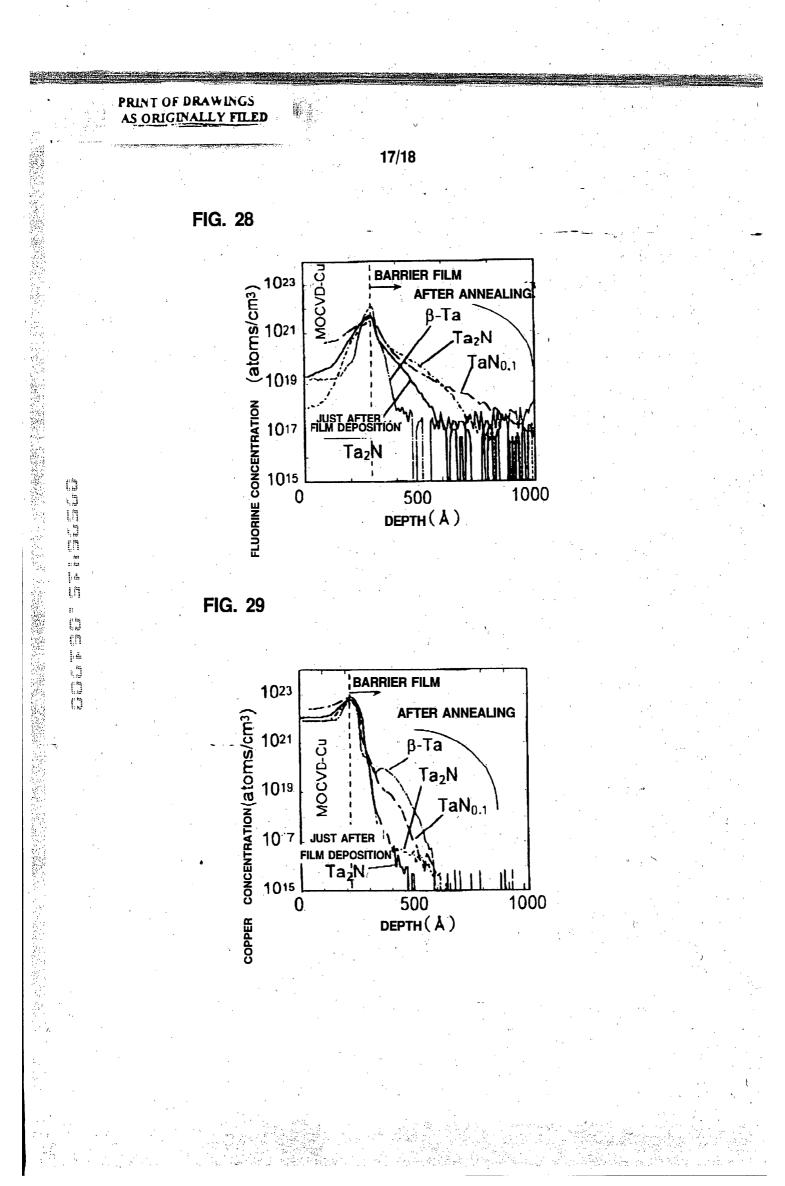
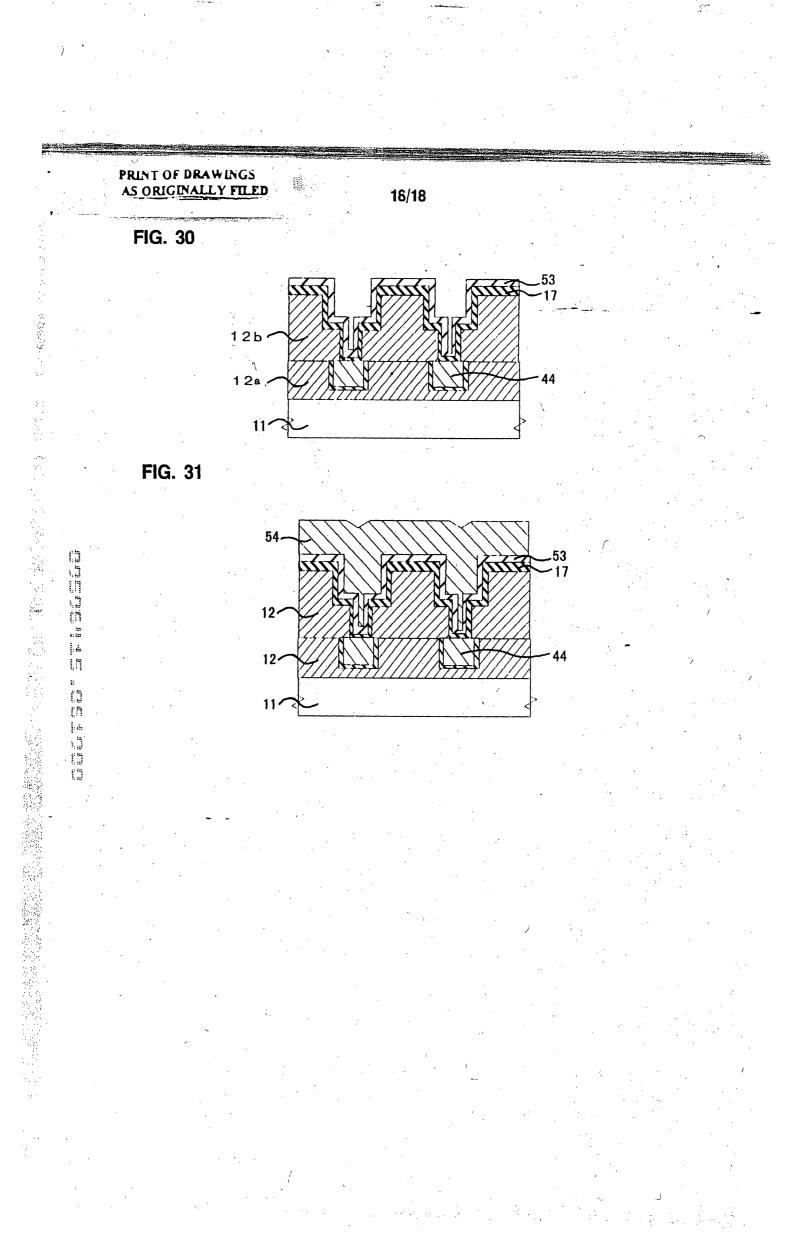


FIG. 27



Page 129 of 333



Page 130 of 333

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13715

Patent and Trademark Office-U.S. DEPARTMENT OF COMMERCE

Docket No.

Page 1 of

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

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

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

the specification of which

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🖾 is attached hereto.

u was filed on ______as United States Application No. or PCT International

Application Number

and was amended on

(if applicable)

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

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)		• • •		Priority Not Claimed
11_214110 (Number)	Japan (Country)	_	24/6/1999 (Day/Month/Year Filed)	
(Number)	(Country)	-	(Day/Month/Year Filed)	
(Number)	(Country)	-	(Day/Month/Year Filed)	

Form PTO-SB-01 (9-95) (Modified)

- 214110 E野 A224

Page 2 of

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

592 21 592

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(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

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

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Full name of se	cond Inventor, if any YOSHIHIRO HAYA	ASHI					
Second invento	or's signature	1. 1.	1/0.00	6) 14		Date	
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Page 133 of 333

Application Assignment Record

According to the application transmittal letter, an assignment recording ownership was filed with this application; however, a copy of this record was not located in the original file history record obtained from the United States Patent and Trademark Office. Upon your request, we will attempt to obtain the assignment documents from the Assignment Recordation Branch of of the United States Patent and Trademark Office or from a related application case (if applicable). Please note that additional charges will apply for this service.

This page is not part of the official USPTO record. It has been determined that content identified on this document is missing from the original file history record.

9-13-00 R. States

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

For: MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

Assistant Commissioner for Patents Washington, D.C. 20231

INFORMATION DISCLOSURE STATEMENT

Sir:

In accordance with 37 C.F.R. §§ 1.97 and 1.98, it is requested that the following references, which are also listed on the attached Form PTO-1449, be made of record in the aboveidentified case.

- Semiconductor World, Nobuyoshi Awaya, February 1998, pp. 91-96;
- 2. Kee-Won Kwon et al., "Characteristics of Ta As An Underlayer for Cu Interconnects", Advanced Metallization and Interconnect Systems for ULSI Applications in 1997, 1998, pp.711-716;
- 3. M.T. Wang, et al., "Barrier Properties of Very Thin Ta and TaN Layers Against Copper Diffusion", Journal Electrochemical Society, July 1998, pp.2538-2545;

CERTIFICATE OF MAILING BY "EXPRESS MAIL"

"Express Mail" Mailing Label Number: EE692181515US Date of Deposit: June 19, 2000

I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. §1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Mishelle Spina

Dated: June 19, 2000

D. Denning, et al., "An Inlaid CVD Cu Based Integration for Sub 0.25µm Technology, 1998 Symposium on VLSI Technology Digest of Technical Papers, 1998, pp. 22-23;

 Japanese Unexamined Patent Publication No. 8-139092, dated May 31, 1996;

 Japanese Unexamined Patent Publication No. 8-274098, dated October 18, 1996;

 Japanese Unexamined Patent Publication No. 9-64044, dated March 7, 1997;

8. Japanese Unexamined Patent Publication No. 10-256256, dated September 25, 1998.

Applicants are submitting copies of the above-cited references. The relevance of the references has been described in the specification. Therefore, translations are not required.

Inasmuch as this Information Disclosure Statement is being submitted in accordance with the schedule set out in 37 C.F.R. § 1.97(b), no petition, certification or fee is required.

-2-

Respectfully submitted,

Paul J. Esatto, Jr. Registration No. 30,749

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Scully, Scott, Murphy & Presser 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343

PJE/am

4.

ATTY DOCKET NO. SERIAL NO. 09 596,415 13715 To be gned INFORMATION DISCLOSURE CITATION APPLICANT(S Masayoshi Tagami, et al. (Use several sheets if necessary) FILING DATE E 06/19/00 Herewith GROUP 2811 Unassigned **U.S. PATENT DOCUMENTS** FILING DATE *EXAMINER SUBCLASS DOCUMENT NUMBER DATE NAME CLASS INITIAL IF APPROPRIATE FOREIGN PATENT DOCUMENTS TRANSLATION CLASS SUBCLASS DOCUMENT NUMBER DATE COUNTRY YES NÖ 8-139092 5/31/96 Japan V Vu 8-274098 V. 10/18/96 Japan 9-64044 3/7/97 Japan N 9/25/98 10-256256 Japan V OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.) Semiconductor World Nobuyoshi Awaya, February 1998, pp.91-96 ٧L Kee-Won Kwon et al., "Characteristics of Ta As An Underlayer for Cu Interconnects", Advanced Metallization and Interconnect Systems for ULSIApplications in 1997, 1998, pp.711-716 Ľ۵ DATE CONSIDERED EXAMINER K. VU HUNG Oalilou *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. P09C/REV03 Patent and Trademark Office * U.S. DEPARTMENT OF COMMERCE Form PTO-A820 (also form PTO-1449) OF 2 PAGE 1

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Docket No. CERTIFICATE OF MAILING br "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): Masayoshi Tagami, et al. 13715 Group Art Unit Filing Date Examiner Serial No. Herewith Unassigned Unassigned To be assigned Invention: MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME I hereby certify that this New Patent Application (Identify type of correspondence) is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 15 1,5 June 19, 2000 on 1,fi (Date) の時間 Mishelle Spinz 14-57 ų. I []] []] EE692181515US ("Express Mail" Mailing Label N Note: Each paper must have its own certificate of mailing. P06A/REV02 Copyright 1995 Legalsoft

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PRIORITO #2 PAPER TENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Masayoshi Tagami, et al.Docket: 13715Serial No.:To be assignedDated:June 19, 2000

Filed: Herewith

For: MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME

Assistant Commissioner for Patents Washington, DC 20231

CLAIM OF PRIORITY

Sir:

Applicants in the above-identified application hereby claim the right of priority in connection with Title 35 U.S.C. § 119 and in support thereof, herewith submit a certified copy of Japanese Patent Application 11-214110 filed on June 24, 1999.

Respectfully submitted,

Paul J. Esatto, Jr.

Registration No. 30,749

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Scully, Scott, Murphy & Presser 400 Garden City Plaza Garden City, NY 11530 (516) 742-4343

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厅 B E 特 許 本 PATENT OFFICE JAPANESE GOVERNMENT 別紙添付の書類に記載されている事項は下記の出願書類に記載されて る事項と同一であることを証明する。 This is to certify that the annexed is a true copy of the following application as filed h this Office. 出願年月日 ate of Application: 1999年 6月24日 願番号 plication Number: 平成11年特許願第214110号 願 人 日本電気株式会社 licant (s): 2000年 2月18日 特許庁長官 近藤隆 Commissioner, Patent Office 出証番号 出証特2000-3008346 Triff - datum - dat \$3. Said Suid

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【書類名】 明細書

【発明の名称】 多層配線の構造及びその製造方法

【特許請求の範囲】

【請求項1】 半導体基板上に形成された銅配線からの銅拡散を防止する拡 散バリア膜において、

前記拡散バリア膜は、結晶質の窒素含有金属膜と非晶質の金属窒化膜とからなる積層構造を有し、

前記拡散バリア膜を構成する金属原子種は同一であることを特徴とする拡散バリア膜。

【請求項2】 前記非晶質金属窒化膜の膜厚は80乃至150オングストロ ームであることを特徴とする請求項1に記載の拡散バリア膜。

【請求項3】 前記結晶質窒素含有金属膜の膜厚は60乃至300オングス トロームであることを特徴とする請求項1又は2に記載の拡散バリア膜。

【請求項4】 半導体基板上に形成された銅配線からの銅拡散を防止する拡 散バリア膜を有する多層配線の構造において、

前記拡散バリア膜は、結晶質の窒素含有金属膜と非晶質の金属窒化膜とからな る積層構造を有し、

前記拡散バリア膜を構成する金属原子種は同一であることを特徴とする多層配 線の構造。

【請求項5】 前記拡散バリア膜は、下地配線層上の絶縁膜に形成された配線溝及び孔の表面を覆うように形成されていることを特徴とする請求項4に記載の多層配線の構造。

【請求項6】 前記窒素含有金属膜上に銅膜が形成されていることを特徴と する請求項4又は5に記載の多層配線の構造。

【請求項7】 前記非晶質金属窒化膜の膜厚は80乃至150オングストロ ームであることを特徴とする請求項4乃至6の何れか一項に記載の拡散バリア膜

【請求項8】 前記結晶質窒素含有金属膜の膜厚は60乃至300オングス トロームであることを特徴とする請求項4乃至7の何れか一項に記載の拡散バリ

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ア膜。

【請求項9】 スパッタ法による拡散バリア膜の製造方法において、

窒素含有ガスを用い、プラズマを発生させる電源のパワーのみを変化させ、ス パッタターゲットの金属原子種を成分とする結晶質の窒素含有金属膜と非晶質の 金属窒化膜とからなる積層構造の拡散バリア膜を連続的に形成することを特徴と する拡散バリア膜の製造方法。

【請求項10】 回転磁場とRFパワーとを利用するRFマグネトロンスパ ッタ方式による拡散バリア膜の製造方法であって、

窒素含有ガスを用い、前記RFパワーを変化させ、スパッタターゲットの金属 原子種を成分とする結晶質の窒素含有金属膜と非晶質の金属窒化膜とからなる積 層構造の拡散バリア膜を連続的に形成することを特徴とする拡散バリア膜の製造 方法。

【請求項11】 前記窒素含有ガスの圧力は5Pa以上であることを特徴と する請求項9又は10に記載の拡散バリア膜の製造方法。

【請求項12】 前記窒素含有ガスの窒素ガス濃度が10%以下であること を特徴とする請求項9乃至11の何れか一項に記載の拡散バリア膜の製造方法。

【請求項13】 前記スパッタターゲットの金属原子種がタンタル、タング ステン、チタン、モリブデン、ニオブあるいはこれらの混合物であることを特徴 とする請求項9乃至12の何れか一項に記載の拡散バリア膜の製造方法。

【請求項14】 RFマグネトロンスパッタ方式による拡散バリア膜の製造 方法であって、

プラズマガス中の窒素濃度を一定値に維持した状態において、プラズマ発生電 源を第一の値のパワーに設定し、第一の膜を成膜する過程と、

所望の膜厚が得られた瞬間に前記プラズマ発生電源を前記第一の値よりも大き い第二の値のパワーに設定し、前記第一の膜上に第二の膜を成膜する過程と、

を備えることを特徴とする拡散バリア膜の製造方法。

【請求項15】 前記第一の膜は非晶質の金属窒化膜であり、前記第二の膜 は結晶質の窒素含有金属膜であることを特徴とする請求項14に記載の拡散バリ ア膜の製造方法。

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【請求項16】 前記プラズマガス中の窒素ガスの圧力は5Pa以上である ことを特徴とする請求項14に記載の拡散バリア膜の製造方法。

【請求項17】 前記窒素ガスの濃度が10%以下であることを特徴とする 請求項14乃至16の何れか一項に記載の拡散バリア膜の製造方法。

【請求項18】 スパッタターゲットの金属原子種がタンタル、タングステン、チタン、モリブデン、ニオブあるいはこれらの混合物であることを特徴とする請求項14乃至17の何れか一項に記載の拡散バリア膜の製造方法。

【請求項19】 前記非晶質金属窒化膜の膜厚は80乃至150オングスト ロームであることを特徴とする請求項9乃至18の何れか一項に記載の拡散バリ ア膜の製造方法。

【請求項20】 前記結晶質窒素含有金属膜の膜厚は60乃至300オング ストロームであることを特徴とする請求項9乃至19の何れか一項に記載の拡散 バリア膜の製造方法。

【請求項21】 半導体基板上の絶縁膜に形成された配線溝あるいは孔に対して水素含有アルゴンのプラズマを照射処理する工程と、

大気に曝すことなく、前記配線溝あるいは孔の表面層を覆うように、結晶質の 窒素含有金属膜と非晶質の金属窒化膜からなる積層構造の拡散バリア膜を形成す る工程と、

大気に曝すことなく、前記拡散バリア膜上に銅薄膜を成長する工程と、

を備える銅配線膜の製造方法。

【請求項22】 前記拡散バリア膜はスパッタ法により形成されるものであることを特徴とする請求項21に記載の銅配線膜の製造方法。

【請求項23】 前記銅薄膜は真空成膜法により形成されるものであること を特徴とする請求項21に記載の銅配線膜の製造方法。

【請求項24】 前記真空成膜法は有機金属錯体の熱不均化反応を用いる熱 化学気相堆積法(熱CVD法)であることを特徴とする請求項23に記載の銅配 線膜の製造方法。

【請求項25】 前記真空成膜法は銅ターゲットを用いたスパッタ法である ことを特徴とする請求項23に記載の銅配線膜の製造方法。

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【請求項26】 前記非晶質金属窒化膜の膜厚は80乃至150オングスト ロームであることを特徴とする請求項21乃至25の何れか一項に記載の銅配線 膜の製造方法。

【請求項27】 前記結晶質窒素含有金属膜の膜厚は60乃至300オング ストロームであることを特徴とする請求項21乃至26の何れか一項に記載の銅 配線膜の製造方法。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】

本発明は、配線材料として銅(Cu)を用いた半導体集積回路の構造及びその 製造方法に関するものであり、特に、銅配線膜からの銅の拡散を防止する拡散バ リア膜に関する。

[0002]

【従来の技術】

半導体装置の微細化の進展に伴い、配線遅延がシリコンULSIデバイスの性 能に及ぼす影響が増大し、従来のアルミニウム配線材を銅に置きかえることが必 要となってきている。銅の比抵抗はアルミニウムの比抵抗の70%程度であるが 、銅は、アルミニウムと異なり、その表面層に酸化膜不動態を形成しないため、 腐食しやすい。

[0003]

また、銅は珪素(シリコン:Si)及び二酸化珪素(二酸化シリコン:SiO 2)中を非常に大きい速度で拡散するため、シリコン基板に形成されるMOSF ET中に浸入すると、キャリヤーライフタイムの劣化を引き起こす。

[0004]

このため、銅配線を用いた半導体装置においては、銅の配線層間絶縁膜への銅 拡散を防止するための拡散防止膜(拡散バリア膜)を設けることが必要となる。 さらに、拡散バリア膜は、配線信頼性を保持するために、層間絶縁膜及び銅との 密着性が高くなくてはならない。

[0005]

このため、これまでに、半導体集積回路における銅配線膜からの銅の拡散を防 止するためのバリアメタル層の構造及びその製造方法について、多くの提案がな されている。

[0006]

例えば、「Semiconductor World」(1998年2月発行、筆者粟屋信義)の91-94頁(以下、「従来例1」と呼ぶ)、「Advanced Met allization and Interconnect Systems for ULSI Applications in 1997」(1998年発行、筆者 キーーウォン・クウォン(Kee-Won Kwon))の712頁17行-713頁10行及び図3-5(以下、「従来例2」と呼ぶ)、「Journal Electrochemical Society」(1998年7月発行、筆者 エム・ティー・ワン(M. T. Wang))の2538-2545頁(以下、「従来例3」と呼ぶ)、「1998 Symposium on VLSI Technology Digest of Technical Papers」(1998年発行、筆者 ディー・デニング(D. Denning)他)の22-23頁(以下、「従来例4」と呼ぶ)にバリアメタル層についての考察がなされている。

【0007】

また、特開平8-139092号公報、特開平8-274098号公報、特開 平9-64044号公報、特開平10-256256号公報及び特願平10-3 30938号には、銅拡散を防止するためのバリアメタル層の構造及びその製造 方法が提案されている。

[0008]

一般に、銅はドライエッチングを行うことが困難であることから、化学機械研 摩法(CMP:Chemical Mechanical Polishing)を利用して銅配線を形成する。

[0009]

具体的には、下地銅配線上に絶縁膜を形成し、この絶縁膜に配線溝と、下地配 線層に至る孔とを形成する。次に、配線溝と孔の表面層に薄い拡散バリア膜を形

成する。この際、配線溝と孔の表面層が完全に拡散バリア膜で覆われているよう にする。未覆領域からの銅の拡散を防止するためである。その後、電解メッキ法 、CVD法あるいはスパッタ法によって、拡散バリア膜で覆われた配線溝と孔と を埋め込みながら銅膜を成長し、CMP法によって、絶縁膜表面に形成された銅 膜と拡散バリア膜とを選択的に除去する。

[0010]

このように、拡散バリア膜には、先に述べた銅の拡散防止性と銅に対する密着 性に加えて、高い被覆性が要求される。

【0011】

このような銅配線に対する拡散バリア膜の材質としては、従来例1に記載され ているように、高融点金属(タングステン(W)、タンタル(Ta)など)やそ の窒化物(窒化タングステン(WN)、チタン(Ti)、窒化チタン(TiN) 、窒化タンタル(TaN)など)が検討されている。

[0012]

例えば、従来例2に記載されているように、Taバリア膜はその上にスパッタ 法により形成される銅膜との密着性が良く、銅膜の結晶性を改善することができ る。しかしながら、銅はTa膜中へも拡散するため、銅膜の下に形成されるTa バリア膜は50nm以上の膜厚を有することが必要となる。

[0013]

しかしながら、従来例4には、Ta膜上にCVD法により銅膜を成膜した場合、銅とTaNとの界面にフッ素(F)が偏析し、密着性が劣化することが報告されている。

[0014]

また、従来例3に記載されているように、(200)及び(111)方向に配向した結晶質TaNバリア膜は、結晶質Taバリア膜と比較して、銅拡散阻止の機能に富むことが報告されている。

[0015]

また、銅の拡散防止機能と銅に対する密着性を改善する方策として、金属膜と 金属窒化膜とを積層する試みもなされている。

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[0016]

例えば、上記の特願平10-330938号には、チタンを金属膜として用い た、スパッタ法による積層バリア膜の製造方法が記載されている。図32に示す ように、この製造方法においては、まず、Arガスのみをスパッタチャンバー内 に導入し、チタン膜1を成膜する。その後、窒素ガスを導入することにより、チ タンと窒素の反応を補助的に利用しながら、チタン膜1上に窒化チタン薄膜2を 形成する。このようにして、チタン膜1と窒化チタン薄膜2とからなる積層バリ ア構造3が形成される。この製造方法においては、スパッタ前処理として下地配 線膜表面の金属酸化膜を除去するために、アルゴンプラズマ処理が行われる。

[0017]

【発明が解決しようとする課題】

以上のような従来の銅の拡散バリア膜は、以下に述べるような技術的課題を有 するものであった。

[0018]

第1の技術的課題は、銅に対する拡散防止性能と銅との密着性を兼ね備えた拡 散バリア膜を作ることが難しいことである。

[0019]

図33に示すように、半導体基板4上に結晶化した柱状構造の金属膜5を成膜 した場合を想定する。この金属膜5においては、一個の結晶の集まりであるグレ イン6と、グレイン6の界面となる粒界7とが金属膜5の表面から底部に至るま で存在するため、この粒界7が銅の拡散する経路8となる。このため、金属膜5 の銅拡散のバリア性は低いものとなる。

[0020]

また、図34に示すように、タングステン(W)、チタン(Ti)、タンタル (Ta)などの比抵抗が小さい金属を用いて、半導体基板4上に金属膜5aを形 成すると、金属膜5aは多結晶構造となる。このため、この金属膜5aは、図3 3に示した金属膜5と同様の柱状構造となってしまい、銅拡散に対するバリア性 が低いものとなる。

[0021]

ただし、通常のTa膜のスパッタにおいて得られるようなβ-Ta(002) 膜などの結晶化した金属膜上にスパッタ法により銅を成膜した場合には、銅の拡 散防止性は劣るものの密着性に優れ、結晶配向性に富んだ銅膜を形成することが できることから、銅配線の信頼性は向上する。

[0022]

一方、図34に示すような半導体基板4上に成膜された非晶質(アモルファス)のTaNのような微粒子9からなる金属膜5aにおいては、比抵抗も約200 -250μΩ-cmと低く、図33に示したような結晶化した金属膜5と異なり 、銅の拡散経路8も存在しないため、銅拡散に対するバリア性は非常に高いもの となる。

[0023]

しかしながら、金属膜5 a の表面はアモルファス状で結晶格子が均等に配列さ れていないため、この非晶質(アモルファス)状膜上にCVD法又はスパッタ法 により銅を成膜すると、銅の結晶性と銅に対する密着性が劣化する。

[0024]

このように、結晶質の金属膜あるいは非晶質の金属窒化膜のみからなる単層構 造膜においては、銅の拡散防止性と密着性に富んだ拡散バリア膜を得ることは困 難である。

第2の技術的課題は、単層構造の拡散バリア膜の欠点を回避することを目的と して、拡散バリア膜を多層構造膜とする際に発生するものである。

[0025]

例えば、銅との密着性が高い結晶質の金属膜とTaNのような拡散バリア性の 高い非晶質の金属窒化膜との積層構造として拡散バリア膜を形成すると、銅の拡 散防止性と密着性に富んだ拡散バリア膜を得ることができる。

[0026]

しかしながら、従来は、結晶質の金属膜と非晶質の金属窒化膜とを連続的にス パッタ成膜することが不可能あったため、結晶質の金属膜と非晶質の金属窒化膜 とをそれぞれ別個に、すなわち、2回に分けて成膜を行うか、あるいは、異なる 2つ以上のスパッタ成膜チャンバーを用いる必要があった。

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[0027]

例えば、上記の特願平10-330938号においては、スパッタ成膜チャン バーにArガスを導入してチタン膜を成膜した後、窒素ガスを導入して窒化チタ ンを成膜している。しかしながら、この方法によれば、チタン膜を成膜してから 窒化チタンの成膜を行うまでの間においては、導入ガスの混合比を変化させるこ とによりチャンバー内のArと窒素の分圧が安定するまで、窒化チタンの成膜を 行うことはできないため、生産性が時間的に非効率なものとならざるを得ない。

[0028]

第3の技術的課題は、スパッタ膜の被覆性に関するものである。

[0029]

一般に、金属膜及びその金属窒化膜をスパッタ成膜する場合、回転磁場と直流 バイアス印加によって発生するArプラズマで金属ターゲットを叩き、対極に設 置されている基板に金属膜あるいはその窒化膜を成長させる。

[0030]

この場合、スパッタ圧力は1 P a 以下の低圧力である。A r プラズマで叩かれ た金属粒子は基板表面に対してランダムに照射されるため、例えば、基板表面に 深い配線溝や孔が存在した場合、これらの開口部を完全に覆うように金属膜を成 長することは困難であった。また、スパッタ圧力が低いため、A r プラズマ密度 が低く、基板表面に被着した金属膜をA r プラズマ粒子で叩くという再スパッタ 効果を期待することはできない。

[0031]

被覆性を向上させるためにスパッタターゲットと基板との間に多数の孔を形成 した金属板を設置して、この孔を通過させることにより、スパッタ金属粒子の方 向性を揃えるコリメートスパッタ法が提案されている。このコリメートスパッタ 法によれば、基板表面に形成された開口部の底面に金属膜を成長することは可能 であるが、開口部の側面に金属膜を付着させることは困難であった。

[0032]

第4の技術的課題は、銅膜との間で良好な密着性を有する結晶性の金属膜は大 気中と容易に反応して表面反応層を形成する点である。

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このような表面反応層は銅膜との密着性を著しく劣化させてしまう。

[0033]

第5の技術的課題は、銅酸化膜の再付着の問題である。

拡散バリア膜のスパッタ成長前に下地配線金属膜表面の酸化膜を除去するため 、Arプラズマ処理が行われる。下地配線が銅の場合、銅酸化膜がArスパッタ により飛散し、絶縁膜に形成された孔の表面に銅酸化膜が再付着してしまうとい う問題があった。

[0034]

第6の技術的課題は、CVD法により、Ta膜及び非晶質のTaN膜上に銅膜 を成膜した場合、銅と拡散バリア層との間の密着性が悪くなる点である。

[0035]

本発明は、以上のような従来技術における間題点に鑑みてなされたものであり 、銅配線を用いた半導体装置において、銅の半導体装置中への拡散を防止する拡 散バリア性能と、銅及び配線層間膜の間の密着性能とを兼ね備えた拡散バリア膜 、そのような拡散バリア膜を有する多層配線構造、及び、そのような拡散バリア 膜の製造方法を提供することを目的とする。

[0036]

さらには、本発明は、上記のような拡散バリア膜上に銅を埋め込んだ銅多層配 線の製造方法を提供することを目的とする。

[0037]

【課題を解決するための手段】

この目的を達成するため、本発明の請求項1は、半導体基板上に形成された銅 配線からの銅拡散を防止する拡散バリア膜において、 拡散バリア膜は、結晶質 の窒素含有金属膜と非晶質の金属窒化膜とからなる積層構造を有し、 拡散バリ ア膜を構成する金属原子種は同一であることを特徴とする拡散バリア膜を提供す る。

[0038]

また、請求項4は、半導体基板上に形成された銅配線からの銅拡散を防止する 拡散バリア膜を有する多層配線の構造において、拡散バリア膜は、結晶質の窒素

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含有金属膜と非晶質の金属窒化膜とからなる積層構造を有し、拡散バリア膜を構 成する金属原子種は同一であることを特徴とする多層配線の構造を提供する。

[0039]

この多層配線の構造においては、請求項5に記載されているように、拡散バリ ア膜は、下地配線層上の絶縁膜に形成された配線溝及び孔の表面を覆うように形 成されていることが好ましい。

[0040]

また、請求項6に記載されているように、窒素含有金属膜上には銅膜を形成す ることができる。

[0041]

請求項9は、スパッタ法による拡散バリア膜の製造方法において、窒素含有ガ スを用い、プラズマを発生させる電源のパワーのみを変化させ、スパッタターゲ ットの金属原子種を成分とする結晶質の窒素含有金属膜と非晶質の金属窒化膜と からなる積層構造の拡散バリア膜を連続的に形成することを特徴とする拡散バリ ア膜の製造方法を提供する。

[0042]

また、請求項10は、回転磁場とRFパワーとを利用するRFマグネトロンス パッタ方式による拡散バリア膜の製造方法であって、窒素含有ガスを用い、RF パワーを変化させ、スパッタターゲットの金属原子種を成分とする結晶質の窒素 含有金属膜と非晶質の金属窒化膜とからなる積層構造の拡散バリア膜を連続的に 形成することを特徴とする拡散バリア膜の製造方法を提供する。

[0043]

請求項11に記載されているように、窒素含有ガスの圧力は5Pa以上である ことが好ましい。

[0044]

また、請求項12に記載されているように、窒素含有ガスの窒素ガス濃度は1 0%以下であることが好ましい。

[0045]

請求項13に記載されているように、スパッタターゲットの金属原子種として

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は、タンタル、タングステン、チタン、モリブデン、ニオブあるいはこれらの混 合物から選択することができる。

[0046]

請求項14は、RFマグネトロンスパッタ方式による拡散バリア膜の製造方法 であって、プラズマガス中の窒素濃度を一定値に維持した状態において、プラズ マ発生電源を第一の値のパワーに設定し、第一の膜を成膜する過程と、所望の膜 厚が得られた瞬間にプラズマ発生電源を第一の値よりも大きい第二の値のパワー に設定し、第一の膜上に第二の膜を成膜する過程と、を備えることを特徴とする 拡散バリア膜の製造方法を提供する。

[0047]

この拡散バリア膜の製造方法においては、請求項15に記載されているように 、第一の膜としては、例えば、非晶質の金属窒化膜を、第二の膜としては、例え ば、結晶質の窒素含有金属膜を選択することができる。

[0048]

請求項21は、半導体基板上の絶縁膜に形成された配線溝あるいは孔に対して 水素含有アルゴンのプラズマを照射処理する工程と、大気に曝すことなく、配線 溝あるいは孔の表面層を覆うように、結晶質の窒素含有金属膜と非晶質の金属窒 化膜からなる積層構造の拡散バリア膜を形成する工程と、大気に曝すことなく、 拡散バリア膜上に銅薄膜を成長する工程と、を備える銅配線膜の製造方法を提供 する。

[0049]

拡散バリア膜は、請求項22に記載されているように、例えば、スパッタ法に より形成することができる。

[0050]

また、銅薄膜は、請求項23に記載されているように、例えば、真空成膜法に より形成することができる。

[0051]

真空成膜法としては、請求項24に記載されているように、例えば、有機金属 錯体の熱不均化反応を用いる熱化学気相堆積法(熱CVD法)を用いることがで

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きる。あるいは、請求項25に記載されているように、銅ターゲットを用いたス パッタ法を用いることができる。

[0052]

請求項2、7、19、26に記載されているように、非晶質金属窒化膜の膜厚 は80乃至150オングストロームであることが好ましい。

[0053]

請求項3、8、20、27に記載されているように、結晶質窒素含有金属膜の 膜厚は60乃至300オングストロームであることが好ましい。

[0054]

【作用】

本発明に係る拡散バリア膜によれば、銅膜と直接的に接する膜は結晶質の窒素 含有金属膜であるため、密着性と銅膜の高い結晶性を確保することができる。

[0055]

また、金属結晶中に窒素を含有させたことにより、純粋な金属結晶膜と比較し て、銅の拡散を抑制させることができる。

[0056]

さらには、本発明に係る拡散バリア膜によれば、結晶質の窒素含有金属膜の下 に非晶質の金属窒化膜が存在するため、銅の拡散を防止することができるととも に、下地絶縁膜(ここでは、シリコン酸化膜)との密着性をも確保することがで きる。すなわち、本発明に係る拡散バリア膜上に銅配線膜を形成することにより 、銅配線膜の高結晶性と密着性とを確保することができると同時に、銅拡散を防 止することができるという効果を発揮する。

[0057]

また、本発明に係る拡散バリア膜の製造方法によれば、窒素含有ガスを用いる スパッタ法におけるプラズマ発生電源パワーのみを変化させることによって、ス パッタターゲットの金属原子種を成分とする結晶質の窒素含有金属膜と非晶質の 金属窒化膜とからなる積層構造を連続的に形成することが可能になる。

[0058]

具体的には、プラズマガス中の窒素濃度を一定に保った状態で、先ず、プラズ

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マ発生電源を低パワーとして成膜を行うと、ターゲット金属と窒素との十分な反応により、非晶質の金属窒化膜が成長する。その直後に、プラズマ発生電源を高パワーに変化させ、窒素とターゲット金属との間の十分な反応時間を与えることなく膜成長させることにより、結晶質の窒素含有金属膜が得られる。その結果、 同一チャンバー内において、結晶質の窒素含有金属膜と非晶質の金属窒化膜とからなる積層構造の拡散バリア膜を連続的に効率良く成膜することができるといった効果を発揮する。

[0059]

また、本発明に係る拡散バリア膜の製造方法によれば、回転磁場とRFパワー とを導入したRFマグネトロンスパッタ方式を採用し、窒素含有ガスの圧力が5 Pa以上であるようなスパッタを実現することを可能にしているため、スパッタ ガスの主成分であるArプラズマ密度を向上させて基板開口部の全面に渡る被覆 性を確保できるという効果を得ることができる。

[0060]

また、本発明による拡散バリア膜の製造方法は、半導体基板上の絶縁膜に形成 された配線溝あるいは孔に対して水素含有アルゴンのプラズマを照射処理する工 程を含む。この工程により、下地銅配線層の表面に形成されていた銅酸化膜を還 元して金属銅に戻すことができ、ひいては、絶縁膜に形成された孔の表面への銅 酸化膜の再スパッタ被着を大幅に減らすことができる。

【0061】

さらに、その後、大気に曝すことなく、配線溝あるいは孔の表面層を覆うよう に結晶質の窒素含有金属膜と非晶質の金属窒化膜とからなる積層構造の拡散バリ ア膜を形成する工程と真空成膜法により銅薄膜を成長する工程とにより、金属酸 化膜層を界面に介在させずに、拡散バリア膜/銅配線膜からなる構造を得ること ができるという効果を発揮する。

[0062]

【発明の実施の形態】

次に、図1乃至図4を参照して、本発明の第一の実施の形態に係る拡散バリア 膜の製造方法を説明する。

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[0063]

図1に示すように、半導体基板11上には、第一の絶縁膜12aが形成され、 この第1の絶縁膜12aには銅配線44が形成されている。第一の絶縁膜12a 上には、第二の絶縁膜12bが形成されており、この第二の絶縁膜12bの表面 には配線溝13が形成され、配線溝13の底面には、第一の絶縁膜12aに達す る孔14が配線溝13と連続して形成されている。

[0064]

先ず、第1のチャンバーにおいて、半導体基板11を水素含有アルゴンプラズ マに曝し、下地銅配線44の表面に形成された銅酸化膜を還元除去する。次いで 、かかる半導体基板11を真空搬送し、第2のチャンバーにおいて、窒素含有ガ スを用いて、高融点金属ターゲットからのスパッタ成膜を行う。

[0065]

この際、プラズマガス中の窒素濃度を一定に保った状態で、まず、プラズマ発 生電源を低パワーにして成膜を行うと、ターゲット金属と窒素との十分な反応に より、図2に示すように、非晶質の金属窒化膜15が成長する。その後、プラズ マ発生電源を瞬時に高パワーに変化させ、窒素とターゲット金属との十分な反応 時間を与えることなく、膜成長を行うことにより、非晶質の金属窒化膜15上に 結晶質の窒素含有金属膜16を得る。

[0066]

その結果、図2に示すように、積層構造を有する拡散バリア膜17を配線溝1 3及び孔14の側壁部及び底部において同一チャンバー内で連続的に効率良く成 膜することができる。この拡散バリア膜17のスパッタ成長の際、スパッタ圧力 を十分に高くすることにより、拡散バリア膜17の被覆性を向上させることがで きる。

[0067]

その後、半導体基板11を真空搬送し、第3のチャンバーにおいて、図3に示 すように、拡散バリア膜17上に銅膜18を真空成膜し、配線溝13及び孔14 を銅膜18で埋め込む。この際、拡散バリア膜17の表面は結晶質の窒素含有金 属膜16であり、かつ、半導体基板11の真空搬送により、窒素含有金属膜16

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の表面には酸化膜が形成されていない。

[0068]

最後に、図4に示すように、CMP法で第二の絶縁膜12bの表面に形成され ている拡散バリア膜17と銅膜18とを選択的に除去することにより、信頼性の 高い銅配線を得ることができる。

[0069]

銅の拡散バリア性の向上の原因は金属膜16に窒素を含有させたことである。 また、この窒素含有金属膜16は銅との密着性を確保することに大きな効果を有 する。非晶質金属窒化膜15も銅拡散防止に効力を発揮する他、下地層間絶縁膜 12bとの密着性の向上に大きく寄与する。その結果、銅膜18と拡散バリア膜 17との間の密着性を確保することができ、また、銅膜18から第二の絶縁膜1 2bへの銅の拡散も防止することができる。

[0070]

【実施例】

以下、上記の第一の実施形態の各実施例について説明する。

[0071]

【第一の実施例】

第一の実施例においては、結晶性の窒素含有金属と非晶質の金属窒化膜とから なる積層構造を形成するスパッタ法について説明する。

[0072]

第一の実施例におけるスパッタ法は、図5に示すRFマグネトロンスパッタ装置において実行される。

[0073]

図5に示すRFマグネトロンスパッタ装置においては、ドライポンプ、クライ オポンプ及びターボポンプなどの排気ポンプ33により、チャンバー21は、そ の内部圧力が約1×10⁻⁷Pa乃至約1×10⁻⁶Paの真空状態になるよう に、排気されている。チャンバー21には基板加熱ヒーター34が設置されてお り、チャンバー21内に導入された半導体基板22を約20乃至300℃に加熱 することができるようになっている。また、金属ターゲット28と半導体基板2

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2との間の距離は102mm乃至134mmの範囲内において変化させることが 可能である。

[0074]

また、アルゴン(Ar)ガスと窒素(N₂)ガスとがそれぞれマスフローコン トローラ31を介して流量が調整された状態でチャンバー21内に導入されるよ うになっている。これらのガスをチャンバー21に導入したときのチャンバー2 1内の圧力は2Pa乃至17Paである。

[0075]

金属ターゲット28の直径は、例えば、300乃至320mm程度であり、金 属ターゲット28は金属製のターゲットホルダ27とカソード23と絶縁体29 とを介してスパッタチャンバー21に取り付けられている。カソード23の内部 には永久磁石24が回転可能に配置されており、永久磁石24を回転させること により、チャンバー21内部の磁場30を均一にして、金属ターゲット28の表 面の削れ(エロージョン)が一定になるようにしている。これにより、半導体基 板22上に成膜される膜の均一性を高めることができる。

[0076]

また、チャンバー21内にRFを導入するためのRF電源25は、インピーダ ンスマッチングを行うための整合器(マッチングボックス)32を介して、カソ ード23に接続されており、300mmøの金属ターゲット28に対して13. 56MHzの高周波を0乃至10kWのパワーで印加することが可能である。

[0077]

RF電源25をONにしてRFをチャンバー21内に導入すると、窒素を含む Arプラズマ26が発生する。このArプラズマ26で発生するArイオンにより、ターゲット金属28がスパッタされ、半導体基板22に到達し、結晶質の窒 素含有金属16あるいは非晶質の金属窒化膜15が堆積される。

[0078]

上述のようなRFマグネトロンスパッタ方式を用いて、半導体基板22上の絶 縁膜12b(図1参照)内に形成された孔14(図1参照)に対してTa成膜を 行った。その埋め込み特性の結果を図6に示す。

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[0079]

孔14の直径は0.3 μ m乃至1.5 μ mであり、孔14が開口されている箇 所における絶縁膜12bの厚さは約1.5 μ mであった。図6から明らかである ように、スパッタ圧力を増加させていくにつれて (2→4→8→13→17Pa)、ボトムカバレッジ (孔14の底における堆積膜厚/絶縁膜12bの表面での 堆積膜厚の比)が向上していくことが分かる。具体的には、スパッタ圧力が5P aを超えると、アスペクト比の大きな孔に対しても十分な被覆性を示しているこ とがわかる。

[0080]

なお、孔14の側面におけるTa堆積膜厚は孔14の底部における堆積膜厚の 半分程度であり、スパッタ圧力の増加に伴い、孔14の内壁面全体を被覆するT a膜が形成された。

[0081]

この現象の原因としては次のような2つの点が考えられる。

まず、第1の原因として考えられることは、図7に示すように、プラズマガス 中のTaイオン数の増加である。

[0082]

スパッタ圧力が増加することにより、Ta原子と励起Ar原子との衝突が増加 し、Ta原子のイオン化が促進される。その結果として生じたTaイオンが、半 導体基板22に発生する負のセルフバイアスに引っ張られる結果、半導体基板面 に対するTaイオン流束35の入射角の垂直性が向上する。このため、通常のス パッタで起こるような開口部付近におけるオーバーハングが抑制され、孔14や 配線溝13の底部までTaが到達しやすくなる。その結果、孔14の内壁面全体 を被覆するTa膜36が形成される。

[0083]

第2の原因としては、図8に示すようなArイオン39による堆積Ta膜36 の再スパッタが考えられる。

【0084】

スパッタプラズマガスの主成分であるAェイオン39はターゲットに対しての

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みでなく、負のセルフバイアス状態にある半導体基板22に対しても、電界により加速された状態で到達する。すなわち、半導体基板22上に堆積したTa膜も 再びスパッタされることになる。このArイオン39により、孔14や配線溝1 3の開口部付近に堆積してオーバーハングを起こす原因となるTa膜が矢印37 で示されるように再スパッタされるため、孔14や配線溝13の底部に向かうT a原子38が開口部付近で妨げられにくくなる。このため、孔14の底部や側面 におけるTaの堆積が行われやすくなる。

[0085]

さらに、孔14や配線溝13の底部におけるTa膜36もArイオン39によ り再スパッタされるため、再スパッタされた底部のTa原子が孔14や配線溝1 3の側面40に再堆積し、孔14の側面40におけるカバレッジが向上するもの と考えられる。

[0086]

現時点においては、上記のどちらの効果が主因となって埋め込み被覆性が向上 するのか断定はできない。ただし、5Paを超える高圧力の下におけるプラズマ イオンの平均自由行程は数mmであることから、Taイオン流束35の入射角の 垂直性の向上による効果はそれほど大きくはないものと考えられる。高圧力によ り十分な密度のArイオンが発生し、このArイオンによるTa堆積膜の再スパ ッタが主因となって、被覆性が向上するものと推定される。

[0087]

なお、タンタル窒化膜のスパッタ成膜についても、同様に、5 P a を超える高 圧力スパッタにおいて良好な被覆性が認められた。

[0088]

以上述べたように、RFマグネトロンスパッタ方式においては、スパッタ圧力 を5Pa以上の高圧力とすることが望ましい。

[0089]

【第二の実施例】

図9に、第一の実施例で挙げた高圧RFマグネトロンスパッタ方式を用いて、 チャンバー21内に導入するアルゴンガス(Ar)の量に対する窒素ガス(N₂

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)の量の比(N₂/(Ar+N₂))を変化させた場合のRFパワーとスパッタ 成長膜の比抵抗の変化との間の関係を示す。

[0090]

この時のチャンパー21内の圧力は13Pa、半導体基板22の加熱温度は2 00℃、マグネット24の回転速度は10rpm、金属ターゲット28と半導体 基板22との間の距離は134mmである。

[0091]

RFパワーに関わらず、N₂/(Ar+N₂)におけるN₂割合の増加に伴って、一旦、比抵抗が減少し、その後、再び増加して行く傾向が見られる。ただし、その増加率はRFパワーに依存し、RFパワーが大きいほど比抵抗の増加率は低減する。

[0092]

図10から図13に、300mm ϕ のTaターゲットに対してRFパワー=6 kW(8.5W/cm²)を投入した時のN₂比の変化によるX線回折パターン (XRD)の変化を示す。

[0093]

具体的には、図10はN₂比=0%、図11はN₂比=1%、図12はN₂比
 =5%、図13にN₂比=7%の場合のXRDパターンを示す。以下、図10乃
 至図13と比抵抗を示す図9とを対応させながら説明する。

[0094]

N₂比=0%の場合には、図10に示すように、 β -Ta(002)配向した 結晶質のTa金属膜が得られ、その比抵抗は160乃至200 μ Ω-cmである

[0095]

N₂比=1%の場合には、図11に示すように、 β -TaとTaN_{0.1}とが 混在した結晶性の窒素含有金属膜(ここでは、Ta膜)が得られ、その比抵抗の 値は約100 μ Ω-cm程度に減少する。

[0096]

N₂比=5%の場合には、図12に示すように、XRDパターン強度が低下し

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ており、非晶質の金属窒化膜が形成されていることがわかる。その比抵抗は約2 00乃至250μΩ-cm程度であった。

[0097]

更にN₂比を増加させていくと、図13に示すように、N₂比=7%の場合に は、Ta₃N₅の結晶性の金属窒化膜が成長し、比抵抗は更に上昇する。

[0098]

このように、Taターゲットを用いた場合、スパッタガス中のN₂濃度とRF パワー値とに依存して、成長する膜の結晶構造、組成及び比抵抗が変化する。こ のことは、逆に見れば、スパッタガス中のN₂濃度とRFパワー値を制御するこ とによって、成長膜の特性を制御することができることを意味している。本発明 はこのような見地に基づくものである。

[0099]

しかしながら、スパッタ法の場合、スパッタガスの流量(ガス圧力)やN₂組 成比を変化させることは容易ではない。従って、実用的には、スパッタガスの流 量(ガス圧力)やN₂組成比を一定値に維持し、RFパワーのみを変化させるこ とにより、スパッタ成長した膜の結晶構造、組成及び比抵抗を制御することが必 要となる。

[0100]

そこで、N₂比を2%に固定してRFパワーのみを変化させた場合の比抵抗の 変化を図14に示す。図14から明らかであるように、RFパワーのみを変化さ せた場合においても、スパッタ膜質及び比抵抗を制御できることがわかる。図1 4に示す比抵抗の変化におけるガス圧力は10Pa、マグネット回転速度は10 rpm、基板温度は200℃である。

[0101]

また、各RFパワーに対するXRDの特性を図15乃至図18に示す。図15
 はRFパワー=2kW、図16はRFパワー=3kW、図17はRFパワー=6
 kW、図18はRFパワー=8kWの場合のXRDの特性である。

[0102]

具体的には、RFパワー=2kWの場合には、図15に示すように、非晶質の

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T a $_2$ Nが得られ、RFパワーを増加させるにつれて結晶質のT a N $_{0.1}$ が得られ、さらに、RFパワー=8kWの場合においては、図18に示すように、 β - T a 膜とT a N $_{0.1}$ とが混合した結晶質の窒素含有金属膜へと変化している

[0103]

図19と図20に、それぞれRFパワー=2kWとRFパワー=8kWの場合 に得られた膜の断面走査型電子顕微鏡(Scanning Electron Microscopy:SEM)写真を示す。

[0104]

RFパワー=2kWの場合には、図15に示すXRDからも明らかであるよう
 に、成長膜は非晶質構造を持つため、結晶粒界は認められない。一方、RFパワ
 ー=8kWの場合には、図18に示すXRDからも分かるように、β-Ta膜と
 TaN_{0.1}とが混合したような結晶膜が得られており、膜も柱状構造を有して
 いることが分かる。

[0105]

すなわち、非晶質の金属窒化膜であるTa₂Nを2kWのRFパワーで成膜し、 所望の膜厚が得られた瞬間にスパッタパワーを8kWに変化させることにより 、結晶性の窒素含有金属膜に膜質を変化させると、図21に示すように、半導体 基板11上に、非晶質の金属窒化膜15(非晶質のTa₂N)と、結晶質の窒素 含有金属膜16(結晶質の β -Taと結晶質のTaN_{0.1}とからなる混合膜) とからなる積層構造の拡散パリア膜17が成膜される。

[0106]

実際に、TaN成膜中にスパッタパワーを2kWから8kWに変化させ、結晶 質の窒素含有金属膜16と非晶質の金属窒化膜15とをそれぞれ約500Aずつ 連続的に成長した膜の断面のSEM写真を図22に示す。非晶質のTa2N膜1 5と柱状結晶質の窒素含有金属膜(Ta2N膜)16とが連続的に積層構造を構 成して成膜されていることが確認できる。

[0107]

この現象の原理は以下のように考えられる。スパッタパワーが2 k Wの場合に

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出

は、Arイオンによるスパッタ率が低いために、Taターゲットの表面がN₂に より十分に窒化される時間が存在する。このため、Taターゲットの表面が窒化 され、Ta₂Nに変化する。このように窒化されたTa₂NがArイオンにより スパッタされるためにTa₂Nが堆積される。しかしながら、スパッタパワーが 8kWになると、Taターゲットの表面が十分に窒化される時間が与えられる前 にArイオンによりスパッタされるため、スパッタされるTa膜に窒素が微量の み含まれるような窒素含有の金属膜が得られやすくなるものと推定される。

[0108]

この現象を利用することにより、図23に示すように、半導体基板11上に成 膜された絶縁膜12b内に形成された配線溝13またはビア孔14を覆うように して、積層構造の拡散バリア膜17を成膜することが可能となる。下層に位置す る非晶質の金属窒化膜(Ta₂N)15は、銅の拡散バリア性を確保することが でき、かつ、下地絶縁膜12bとの密着性を保持できる程度の膜厚を有するごと が必要である。そのような膜厚としては、約80A乃至150Aが好ましい。一 方、結晶質の窒素含有金属膜(結晶質の β – Taと結晶質のTaN_{0.1}とから なる混合膜)16は銅の拡散バリア性を保持でき、かつ、銅との密着性を確保す ることができれば良く、窒素含有金属膜16の膜厚としては、60A乃至300 A程度が最適である。

[0109]

【第三の実施例】

第一実施例において述べたRFマグネトロンスパッタ方式においては、チャン バー内に導入する圧力を通常のスパッタよりも高圧にすることにより、すなわち 、5Pa以上とすることにより、配線溝又は孔への埋め込み性能を向上させるこ とが可能になる。すなわち、この領域の圧力の下で成膜中にパワーを切り替える ことにより、図1に示したように、半導体基板11上に成膜された絶縁膜12b 中に形成された配線溝13と孔14とを同時に埋め込むようなデュアルダマシン プロセスを用いる際にも、良好な埋め込み特性の下で積層バリア膜17を得るこ とが可能になる。

[0110]

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【第四の実施例】

上述の第一及び第二の実施例においては、スパッタパワーを切り替えることに より連続的に積層バリア膜を作製するプロセスをRFマグネトロンスパッタ形式 に適用した場合について述べた。このプロセスは、N₂比や成膜パワーは異なる 条件になるが、図24に示すようなDCマグネトロンスパッタ方式にも適用する ことができる。

[0111]

図24に示すDCマグネトロンスパッタ装置は、チャンバー21と、チャンバ -21の底面に設置され、半導体基板22を加熱する基板加熱ヒーター34と、 絶縁体29とカソード23とを介してチャンバー21の内部の上方に配置された ターゲット金属28と、チャンバー21の内部圧力が約1×10⁻⁷Pa乃至約 1×10⁻⁶Paの真空状態になるように排気を行う排気ポンプ33と、ターゲ ット金属28の上方に配置されたマグネット42と、絶縁体29を介してチャン バー21と、アルゴンガスと窒素ガスの流量を調整してチャンバー21内に送り 込むマスフローコントローラ31と、カソード23と基板加熱ヒーター34に直 流電圧を印加するDC電源41と、からなっている。

[0112]

DC電源41をオンにすることにより、窒素を含むアルゴンプラズマ26がチャンバー21内に発生する。

[0113]

【第五の実施例】

第一及び第二の実施例においては、一つのビア及び配線が形成されている例を 挙げたが、本発明を適用することができる構造は、一つのビア及び配線が形成さ れている構造には限定されない。

[0114]

図25に示すように、半導体基板11上に第一の絶縁膜12aが形成され、こ の第一の絶縁膜12aにはビア孔の内部に拡散バリア膜17を介して銅配線44 が形成され、さらに、第一の絶縁膜12a上には第二の絶縁膜12b形成されて いる。第二の絶縁膜12b内に形成された配線溝及びビア孔の表面にも拡散バリ

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ア膜17が形成されており、配線溝及ビア孔は拡散バリア膜17を介して銅配線 (図示せず)で埋め込まれる。

[0115]

このように、積層された複数の絶縁膜のそれぞれに形成された配線溝及びビア 孔の表面を拡散バリア膜17で覆い、次いで、銅配線層で配線溝及びビア孔を埋 め込むことが可能である。

[0116]

その一例を図26に示す。図26に示す積層構造は、3層の絶縁膜からなり、 各絶縁膜には配線溝及びビア孔が形成され、それらの配線溝及びビア孔の表面は 拡散バリア層17で覆われ、さらに、銅配線44が埋め込まれている。

[0117]

以下、図26に示す積層構造の製造方法を説明する。

半導体基板11には、素子分離層11aにより分離された半導体素子11bが 形成されている。その半導体基板11上に成膜されたシリコン酸化膜等の第一の 絶縁膜12aには、半導体素子11bとコンタクトを取るための配線溝及び孔が 形成されており、これらの配線溝及び孔の表面には、第一の実施例において述べ たような高圧RFマグネトロンスパッタ法により、良好な埋め込み性の下に結晶 質の窒素含有金属膜と非晶質の金属窒化膜とからなる積層構造を有する拡散バリ ア膜17が形成されている。

[0118]

その後、真空成膜法により銅膜を配線溝及び孔に埋め込んで形成し、化学的機 械的研磨法(CMP法)により、第一の絶縁膜12a上の余剰の銅膜及び拡散パ リア膜17を選択的に研磨し、銅配線44aを形成する。

[0119]

銅は表面に不動体を作らないため、銅膜44a中への酸化が進行する恐れがある。このため、銅配線44aの酸化を防止するためのシリコン窒化膜12dを第 一の絶縁膜12a上に形成する。

[0120]

さらに、第一の絶縁膜12a上に第二の絶縁膜12bを形成し、下層の銅配線

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44 aと接触するような配線溝及び孔を第二の絶縁膜12b中に形成する。次い で、その配線溝及び孔に拡散バリア膜17を形成し、さらに、銅膜44bで配線 溝及び孔を埋め込むような製造過程を所望の回数だけ繰り返すことにより、図2 6に示すような銅多層配線構造を有する半導体装置を製作することができる。

[0121]

【第六の実施例】

第六の実施例においては、積層構造の拡散バリア膜と銅配線膜とを連続して形 成するための装置及びその製造工程について述べる。

[0122]

図27は、本実施例に係る銅配線膜形成装置を上方から見たときの平面図であ る。

[0123]

銅配線膜形成装置は中心部にセパレーションチャンバー51を備えており、こ のセパレーションチャンバー51の内部には、搬送用ロボット52が保持されて いる。セパレーションチャンバー51の周囲には、さらに、2個のロードロック チャンバー45、基板加熱ガス出しチャンバー46、配線溝及び孔クリーニング 用エッチングチャンバー47、積層構造の拡散バリア膜形成用のスパッタチャン バー48、銅配線成膜チャンバー49が付設されている。このような構成のクラ スタチャンバー50を用いることにより、半導体基板を大気に曝すことなく、銅 配線金属を成膜することが可能である。

[0124]

銅配線金属膜の具体的な製造工程を以下に述べる。

まず、半導体基板をロードロックチャンバー45に導入する。半導体基板上に は絶縁膜が形成され、この絶縁膜には配線溝又は孔が形成されているものとする 。次いで、ドライポンプ及びターボポンプを用いて、ロードロックチャンバー4 5を排気する。排気時間は約5分程度であり、排気後の真空度は7×10⁻³ 乃 至8×10⁻³ Paである。

[0125]

その後、ロードロックチャンバー45とセパレーションチャンバー51との間

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のゲートバルブを開ける。この時、セパレーションチャンバー51は、クライオ ポンプ及びドライポンプ及びターボポンプによって、5×10⁻⁵乃至1×10⁻⁵ Pa程度の真空度に保たれており、半導体基板は、真空を破ることなく、搬 送用ロボット52によってセパレーションチャンバー51の内部に搬送される。

[0126]

その後、先ず、半導体基板表面上の水分を飛ばし、アライニングを行うために 、半導体基板を基板加熱ガス出しチャンバー46に搬送する。この時、基板加熱 ガス出しチャンバー46は、ドライポンプ及びターボポンプによって、6×10 ⁻⁵ Pa程度の真空度に保たれている。基板加熱ガス出しチャンバー46の内部 において、半導体基板を150℃乃至200℃程度に加熱し、半導体基板表面の 水分を飛ばし、半導体基板の表面を清浄化する。

[0127]

次に、半導体基板を基板加熱ガス出しチャンバー46からセパレーションチャンバー51を経由してクリーニング用エッチングチャンバー47に搬送する。クリーニング用エッチングチャンバー47は、クライオポンプ、ターボポンプ及び ドライポンプによって、5×10⁻⁶Pa程度の真空度に保たれている。

[0128]

半導体基板をクリーニング用エッチングチャンバー47の内部に搬入した後、 アルゴン(Ar)ガスまたは水素希釈Arガス(H₂/Ar=3%)を用いて、 半導体基板のプラズマエッチングを行うことにより、半導体基板の表面、配線溝 の内部及び孔の内部を還元清浄化する。

[0129]

また、このプラズマエッチングには、孔及び配線溝の形状の角を削って、開口 部を擬似的に広げ、埋め込み特性を向上させる効果もある。

[0130]

次に、搬送用ロボット52によって、半導体基板をクリーニング用エッチング チャンバー47からスパッタチャンバー48に搬送する。スパッタチャンバー4 8においては、第一の実施例で挙げた高圧RFマグネトロンスパッタ法によるス パッタが実施される。スパッタチャンバー48の内部は、ドライポンプ、クライ

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オポンプ及びターボポンプによって、 4×10^{-6} P a 程度の真空度に保たれている。

[0131]

スパッタチャンバー48に導入された半導体基板は、第一及び第二の実施例に おいて説明したようなRFパワーを瞬間的に切り替える方法によって、結晶性の 窒素含有金属膜(結晶質のβ-Taと結晶質のTaN_{0.1}とからなる混合膜) と非晶質の金属窒化膜(Ta₂N)とを堆積させる。ここでは、ガス圧力10P a、基板温度200℃、N₂分圧比=2%とし、パワーを2kWから8kWに切 り替えることにより、図6に示したような特性の下で、良好な埋め込み性の下に 積層構造の拡散バリア膜を得ることができる。

[0132]

最後に、半導体基板をスパッタチャンバー48から銅配線成膜チャンバー49 に真空搬送する。真空搬送を行うため、拡散バリア膜の上層に位置する結晶性の 窒素含有金属膜の表面は清浄に保たれる。この結晶性の窒素含有金属膜上に、化 学気相堆積法(CVD法)により、配線溝及び孔を埋め込みながら銅を成膜する 。銅配線成膜チャンバー49内はドライポンプ及びターボポンプにより4×10 ⁻⁴ Pa程度の真空度に排気されている。

[0133]

先ず、半導体基板の温度を170乃至200℃程度に維持し、Cu (hfac)) tmvs (トリメチルビニルシリルヘキサフルオロアセチルアセトネートカッ パ:trimethylvinylsilyl hexafluoroacet ylacetonate copper (I))を主とする原料1乃至2g/分 を液体輸送方式により気化器に導入する。気化器で気化された原料は窒素キャリ アガスにより銅配線成膜チャンバー49内に導入され、その結果、銅配線成膜チャンバー49内の圧力は約1kPa程度に保たれる。

[0134]

導入された原料ガスは半導体基板上で化学反応を起こし、銅膜となって半導体 基板上に堆積される。ここでは、配線溝及び孔を十分に埋設するような膜厚、例 えば、8000乃至15000Å程度の膜厚になるように堆積する。

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【0135】

特に、CVD法を用いて銅の成膜を行う場合、CVD原料であるトリメチルビ ニルシリルヘキサフルオロアセチルアセトネートカッパ(trimethylv inylsilyl hexafluoroacetylacetonate copper(Cu(hfac)tmvs))の中に含まれているフッ素(F) の拡散バリア膜の表面への偏析及び膜中への拡散並びに銅の拡散が密着性に大き な影響を及ぼす。

【0136】

図28及び図29にSIMS法(Secondary Ion Mass S pectroscopy)により測定した拡散バリア膜中へのフッ素及び銅の拡 散プロファイルをそれぞれ示す。

[0137]

Ar雰囲気のスパッタにより得られる β -Taでは、フッ素が銅とTaとの界面に偏析するため、密着性は悪くなる。一方、Ta₂Nでは、フッ素が膜中に拡散するものの、銅をほとんど膜中に拡散させないため、原子間の結びつきが悪く、密着性は悪くなる。TaN_{0.1}では、銅及びフッ素を膜中に拡散させるため、原子間の結びつきが向上し、密着性が良好となる。

[0138]

すなわち、CVD法によって銅を堆積する場合には、結晶質TaN_{0.1}/非 晶質Ta₂Nの積層バリア構造が密着性及び拡散バリア性を極めて向上させるも のであることがわかる。

[0139]

以上のような過程を経ることにより、銅配線形成時に、半導体基板を大気に曝 すことなく、銅配線膜を成膜できることから、拡散バリア膜の表面を清浄な状態 に保つことが可能となり、CVD法で作製される銅の膜質が拡散バリア膜の表面 のTa膜の結晶構造に反映しやすくなるため、銅の結晶配向性及び拡散バリア膜 との密着性を向上させることが可能である。

[0140]

【第七の実施例】

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本実施例においては、図27に示したクラスタチャンバー50の銅配線成膜部 (銅配線成膜チャンバー49に対応する領域)にスパッタチャンバー48が取り 付けられている。拡散バリア膜の表面には、結晶性のβ-Taを含んだTaN₀ .1が存在するため、スパッタ法により成膜された銅膜との密着性は、CVD法 により成膜された銅膜との密着性と同様に、保持される。

[0141]

【第八の実施例】

本実施例においては、先ず、図27に示したクラスタチャンバー50から半導体基板を取り出す。この半導体基板は図30に示すような構造を有している。すなわち、第二の絶縁膜12bに形成されている配線溝及び孔の表面には拡散バリア膜17が形成され、拡散バリア膜17上には銅下地膜53が形成されている。

【0142】

この半導体基板に対して、メッキ法により、銅膜54を配線溝及び孔が埋め込 まれるように成膜する。この結果、図31に示すように、積層バリア構造17、 CVD法またはスパッタ法により形成された銅下地膜53、メッキ法により形成 された埋め込み銅構造54を作製することが可能となる。この後、例えば、図4 に示したように、銅膜54、銅下地膜53、拡散バリア膜17をCMP法により 選択的に除去することにより、銅配線構造を得ることができる。

[0143]

【発明の効果】

本発明により、以下のような効果を得ることができる。

第1の効果は、銅に対する拡散バリア性及び密着性を兼ね備えた拡散バリア膜 を得ることが可能になることである。これは、拡散バリア膜を、銅の拡散バリア 性能の高い非晶質の金属窒化膜と密着性の高い結晶化した窒素含有金属膜とから なる積層構造として構成するためである。

[0144]

第2の効果は、拡散バリア膜を同一チャンバーで連続的に成膜することが可能 であることである。このため、装置コスト及び時間的コストを低減することが可 能となる。

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[0145]

この理由は、スパッタ時にチャンバー内に導入するガスの窒素比を固定した状態で、スパッタパワーのみを瞬間的に変化させることにより、連続的に非晶質の 金属窒化膜と結晶質の窒素含有金属膜とを成膜することが可能であるためである 。この方法の場合、上層の金属膜には必然的に窒素が含有されることとなる。

[0146]

第3の効果は、例えば、半導体基板を真空搬送する装置を用いることにより、 拡散バリア膜の表面を清浄に保った状態で銅膜を成長させることが可能になり、 銅配線の信頼性を向上させることができる。

【図面の簡単な説明】

【図1】

本発明の第一の実施の形態に係る拡散バリア膜の製造方法における第一の工程 を示す断面図である。

【図2】

本発明の第一の実施の形態に係る拡散バリア膜の製造方法における第二の工程を示す断面図である。

【図3】

本発明の第一の実施の形態に係る拡散バリア膜の製造方法における第三の工程を示す断面図である。

【図4】

本発明の第一の実施の形態に係る拡散バリア膜の製造方法における第四の工程 を示す断面図である。

【図5】

第一の実施例における高圧RFマグネトロンスパッタ装置の構成を示す概略図である。

【図6】

高圧 R F マグネトロンスパッタ方式における T a 膜の埋め込み特性を示すグラ フである。

【図7】

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高圧RFマグネトロンスパッタ方式においてTa膜の埋め込み特性が向上する 理由を説明するための断面図である。

【図8】

高圧RFマグネトロンスパッタ方式においてTa膜の埋め込み特性が向上する 理由を説明するための断面図である。

【図9】

高圧RFマグネトロンスパッタ方式において、チャンバーに導入する窒素ガスの比率を変化させた場合のRFパワーとスパッタ成長膜の比抵抗の変化との間の 関係を示すグラフである。

【図10】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図11】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図12】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図13】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図14】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図15】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図16】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性

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を示すグラフである。

【図17】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図18】

高圧RFマグネトロンスパッタ方式におけるTaN及びTa膜の成膜膜質特性 を示すグラフである。

【図19】

高圧RFマグネトロンスパッタ方式における成長膜の断面走査型電子顕微鏡写 真である。

【図20】

高圧RFマグネトロンスパッタ方式における成長膜の断面走査型電子顕微鏡写 真である。

【図21】

高圧RFマグネトロンスパッタ方式により形成された結晶性窒素固溶Ta膜及 びアモルファス金属TaN膜とからなる拡散バリア膜の断面図である。

【図22】

高圧RFマグネトロンスパッタ方式により形成された拡散バリア膜の断面走査 型電子顕微鏡写真である。

【図23】

配線溝または孔に埋め込まれた拡散バリア膜の断面図である。

【図24】

第四の実施例におけるDCマグネトロンスパッタ装置の概略図である。

【図25】

下層配線及びビア孔を有する構造上に形成された配線溝及び孔を示した断面図である。

【図26】

複数の下層配線及びビア孔を有する構造上に形成された配線溝及び孔を示した 断面図である。

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【図27】

銅配線形成用クラスタ装置の平面図である。

【図28】

拡散バリア膜中へのフッ素の拡散プロファイルを示すグラフである。

【図29】

拡散バリア膜中への銅の拡散プロファイルを示すグラフである。

【図30】

第七の実施例における銅配線構造の断面図である。

【図31】

第七の実施例における銅配線構造の断面図である。

【図32】

従来の銅配線構造の断面図である。

【図33】

従来の銅配線構造の断面図である。

【図34】

従来の銅配線構造の断面図である。

【符号の説明】

- 11 半導体基板
- 12a 第一の絶縁膜
- 12b 第二の絶縁膜
- 13 配線溝
- 14 孔

15 非晶質の金属窒化膜

16 結晶質の窒素含有金属膜

17 拡散バリア膜

18 銅膜

21 チャンバー

22 半導体基板

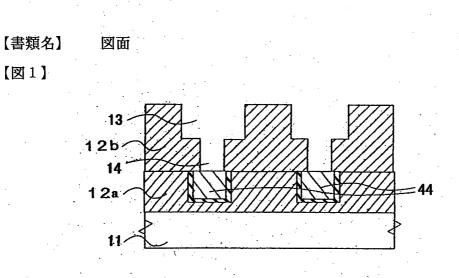
23 カソード

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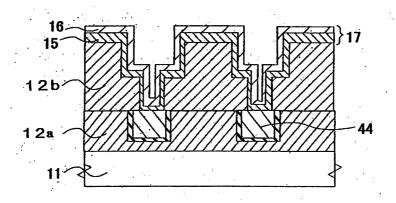
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24	マグネット
25	RF電源
26	Arプラズマ
27	ターゲットホルダ
28	ターゲット金属
29	絶縁体
30	磁場
31	マスフローコントローラ
32	整合器
3 3	排気ポンプ
34	基板加熱ヒータ
41	DC電源
42	マグネット
44	銅配線
45	ロードロックチャンバー
46	基板加熱ガス出しチャンバー
47	クリーニング用エッチングチ
48	スパッタチャンバー
49	銅配線成膜チャンバー
5 0	クラスタチャンバー
51	セパレーションチャンバー
52	搬送用ロボット

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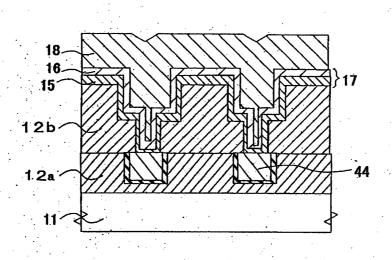
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【図2】

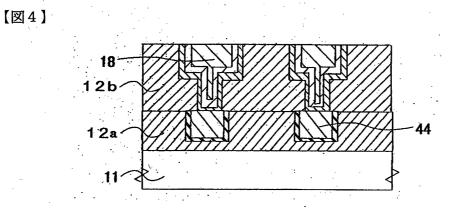


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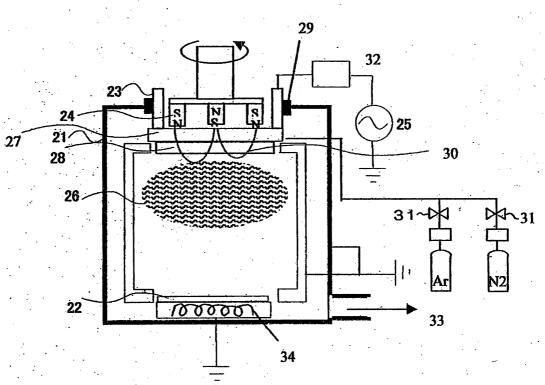


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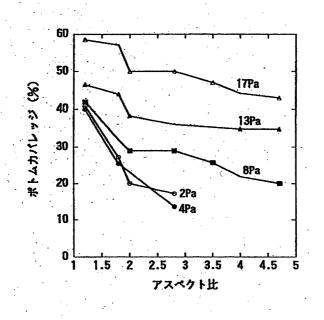


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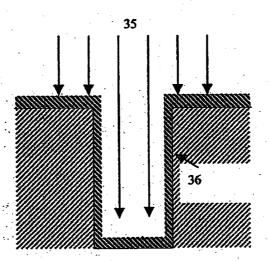


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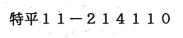
【図6】



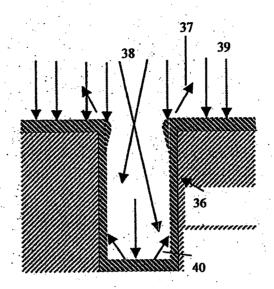




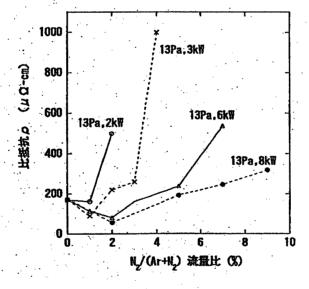
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【図8】

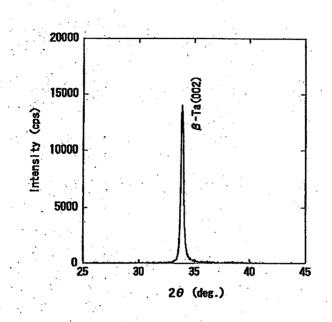




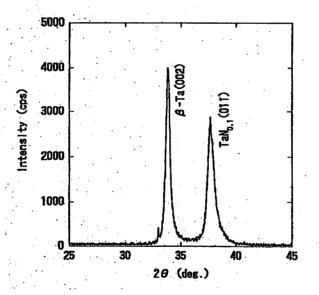


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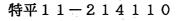


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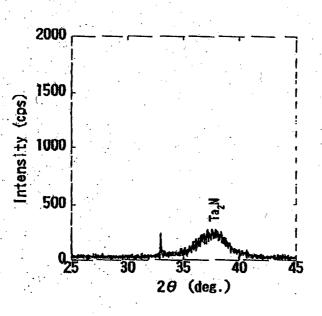


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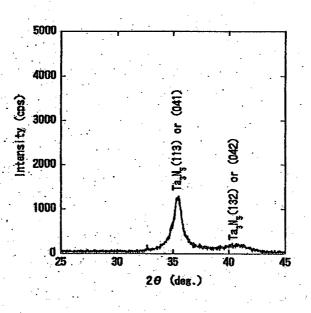
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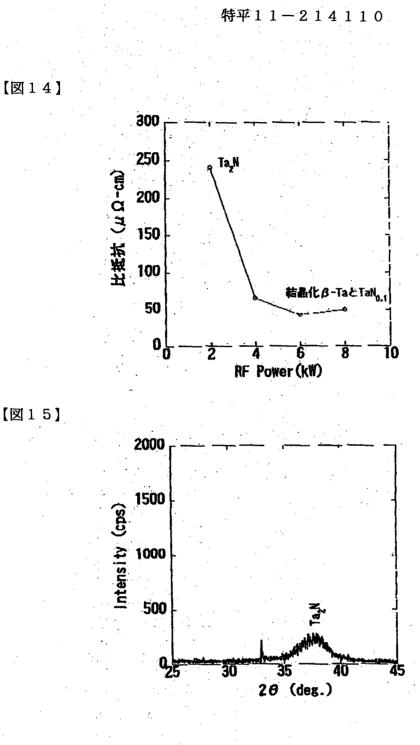


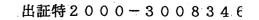


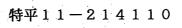




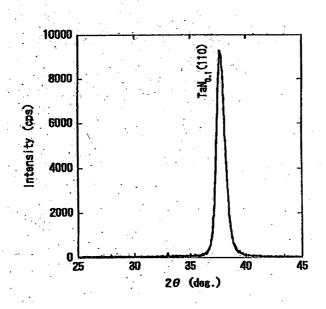




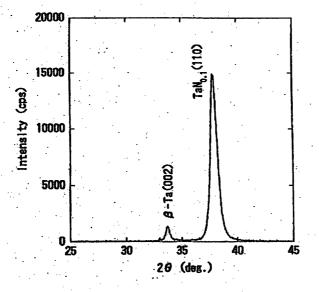


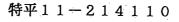




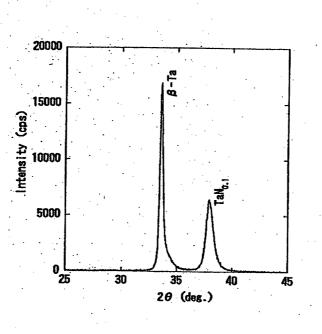




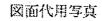


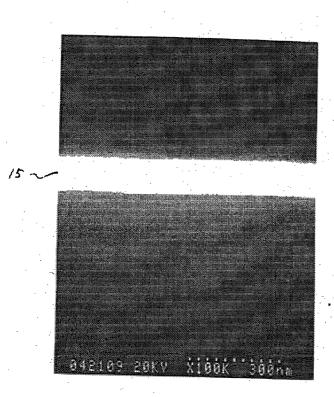




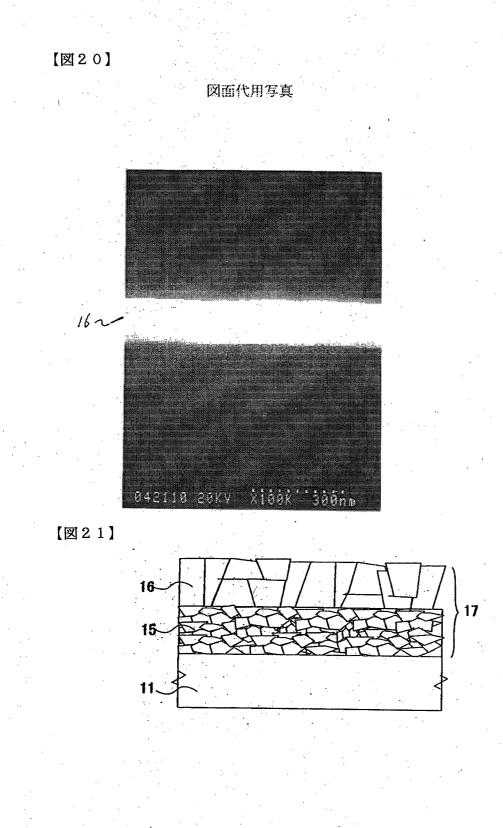






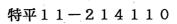


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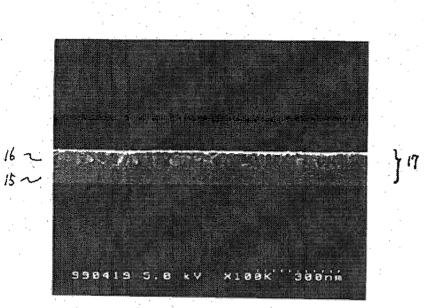


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Page 191 of 333

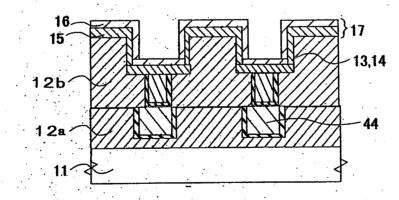


【図22】

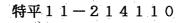


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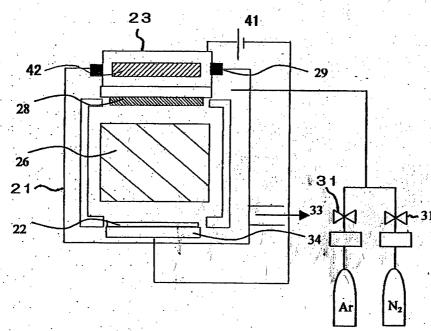




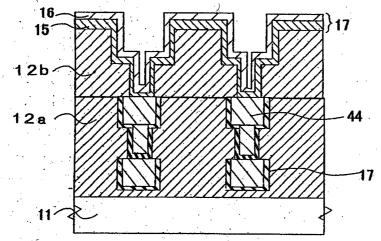
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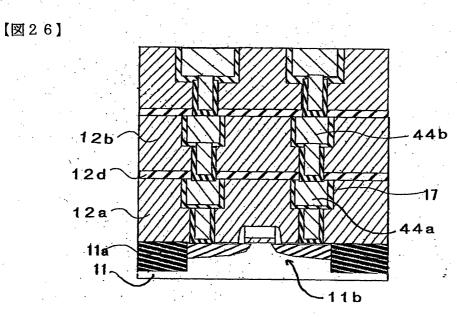




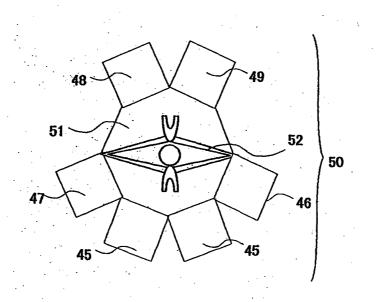






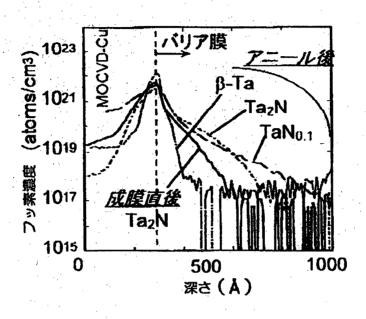


【図27】

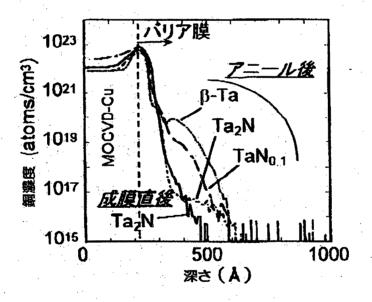


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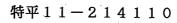
【図28】

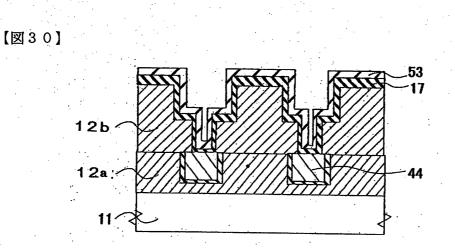


【図29】

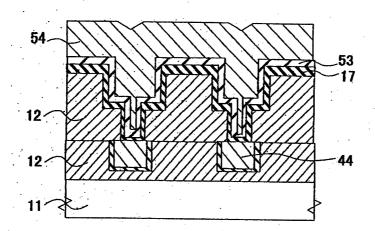


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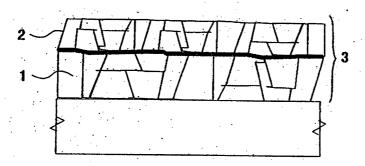




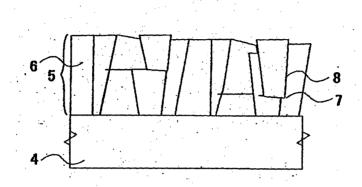




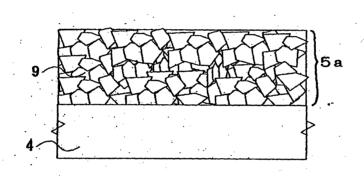
【図32】







【図34】



16

特平11-214110

【書類名】 要約書

【要約】

【課題】銅の拡散を防止するためのバリア膜は、バリア性と共に銅との密着性も 要求されるが、これまでの金属及び金属窒化膜バリア膜ではバリア性と密着性を 両立したものを得ることは難しかった。

【解決手段】バリア性に優れた非晶質金属窒化膜15と密着性に優れた結晶性金 属膜16とを積層構造とすることにより、密着性とバリア性を両立した積層バリ ア膜17が得られる。例えば、半導体基板11上の絶縁膜12bに形成された配 線溝または孔に埋め込み積層バリア膜17を成膜し、拡散バリア膜17上に銅膜 18を形成することにより、良好な密着性と拡散がない銅配線を得ることが可能 となる。

1

【選択図】 図3

出願人履歴情報

1

識別番号

[000004237]

1.	変更年月日	1990年 8月29日
	[変更理由]	新規登録
	住所	東京都港区芝五丁目7番1号
	氏名	日本電気株式会社

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UNITED STATES DEPARTMENT OF COMMERCE United States Patent and Trademark Office Address: COMMISSIONER OF PATENTS AND TRADEMARKS

,	Washington, D.C. 20231		-,,
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APPLICATION NO.	FILING DATE	FIRST NAME	ED INVENTOR	ATTORN	NEY DOCKET NO.
09/596	6,415 06/	19/00 TAGAMI		M	13715
		MM 🕾	1/0605	EXAMIN	IER
PAUL J	I ESATTO JR		170608	VU.H	·
SCULLY	SCOTT MUR	PHY & PRESSER		ART UNIT	PAPER NUMBER
	ARDEN CITY A CITY NY 1	PLAZA 1530		2811	
	· ·	· · · · ·		DATE MAILED:	06/05/01
			· ·		· · · ·

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

Commissioner of Patents and Trademarks

1- File Cop

*****	Application No.	Applicant(s)	<u> </u>
	09/596,415	TAGAMI ET AL.	
Office Action Summary	Examiner	Art Unit	
	Hung K. Vu	2811	· .
The MAILING DATE of this communication a eriod for Reply	appears on the cover sheet wit	th the correspondence addres	;s
A SHORTENED STATUTORY PERIOD FOR RE THE MAILING DATE OF THIS COMMUNICATION - Extensions of time may be available under the provisions of 37 CF after SIX (6) MONTHS from the mailing date of this communication - If the period for reply specified above is less than thirty (30) days, a - If NO period for reply specified above, the maximum statutory pe - Failure to reply within the set or extended period for reply will, by s - Any reply received by the Office later than three months after the n earned patent term adjustment. See 37 CFR 1.704(b).	DN. R 1.136 (a). In no event, however, may a a reply within the statutory minimum of thin riod will apply and will expire SIX (6) MOD tatute, cause the application to become A	reply be timely filed ty (30) days will be considered timely. ITHS from the mailing date of this comm BANDONED (35 U.S.C. § 133).	runication.
1) Responsive to communication(s) filed on	19 June 2000 .		ť I
2a) This action is FINAL . 2b) \boxtimes	This action is non-final.		•
3) Since this application is in condition for al closed in accordance with the practice un			nerits is
sposition of Claims	Х.		
4) Claim(s) <u>1-36</u> is/are pending in the application	ation.	· · · ·	•
4a) Of the above claim(s) is/are with	drawn from consideration.		
5) Claim(s) is/are allowed.	· · · ·	, ,	· · · ·
6) Claim(s) is/are rejected.			• .
7) Claim(s) is/are objected to.	· · · · · · · · · · · · · · · · · · ·		·
8) Claims $1-36$ are subject to restriction and	/or election requirement.		
plication Papers			•
9) The specification is objected to by the Exa	miner.		•
10) The drawing(s) filed on is/are objec	ted to by the Examiner.		
11) The proposed drawing correction filed on _	is: a) approved b)] disapproved.	
12) The oath or declaration is objected to by the	ne Examiner.		
iority under 35 U.S.C. ઠ્ર 119	, ,		
13) Acknowledgment is made of a claim for for	reign priority under 35 U.S.C.	δ 119(a)-(d) or (f).	* .
a) All b) Some * c) None of:			
1. Certified copies of the priority docum	nents have been received.		· · ·
2. Certified copies of the priority docum	nents have been received in <i>i</i>	Application No	· · · ·
3. Copies of the certified copies of the application from the Internationa * See the attached detailed Office action for a	Il Bureau (PCT Rule 17.2(a)).	· · · · · ·	age
14) Acknowledgement is made of a claim for c	Iomestic priority under 35 U.S	S.C. § 119(e).	
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achment(s)			·
)	18) 19) 🗌 Notice (w Summary (PTO-413) Paper No(s of Informal Patent Application (PTO	
Patent and Trademark Office	·	·	1

Page 2

DETAILED ACTION

Election/Restrictions

Restriction to one of the following inventions is required under 35 U.S.C. 121:

- Claims 1-10, drawn to a semiconductor device, classified in class 257, subclass, 758.
- II. Claims 11-36, drawn to a method of making a semiconductor device, classified in class 438, subclass 22+.

The inventions are distinct, each from the other because of the following reasons:

Inventions II and I are related as process of making and product made. The inventions are distinct if either or both of the following can be shown. (1) that the process as claimed can be used to make other and materially different product or (2) that the product as claimed can be made by another and materially different process (MPEP § 806.05(f)). In the instant case unpatentability of the Group I invention would not necessarily imply unpatentability of the Group II invention, since the device of the Group I invention could be made by processes materially different from those of the Group II invention, for example, forming a diffusion barrier film by CVD method or PVD method instead of sputtering method.

Because these inventions are distinct for the reasons given above and have acquired a separate status in the art as shown by their different classification, restriction for examination purposes as indicated is proper.

Applicant is advised that the reply to this requirement to be complete must include an election of the invention to be examined even though the requirement be traversed (37 CFR 1.143).

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

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Hung K. Vu whose telephone number is (703) 308-4079. The examiner can normally be reached on Mon-Thurs 7:00-5:30, Eastern Time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Tom Thomas can be reached on (703) 308-2772. The fax phone numbers for the organization where this application or proceeding is assigned are (703) 308-7722 for regular communications and (703) 308-7722 for After Final communications.

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

Vu

May 26, 2001

Steven Loke Primary Examiner

Page 3

OIPE	· · · · · · · · · · · · · · · · · · ·		GP 281
JUL 0 9 2007 2	TRANSMITTAL LETTER (General - Patent Pending)	×	Docket No. 13715
In Re Application Of:	Masayoshi Tagami, et al.		
Serial No. 09/596,415	Filing Date June 19, 2000	Examiner Hung K. Vu	Group Art Unit 2811
Title: MULTI-LAY	ERED WIRING LAYER AND METI	HOD OF FABRICATING THE	SAME
<u> </u>	TO THE ASSISTANT COM	MISSIONER FOR PATENTS:	
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Transmitted herewith RESPONSE TO RE	IS: QUIREMENT FOR RESTRICTION	[
• •			
in the above identifie	d application		
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Charge	e the amount of any overpayment.		
	e any additional fee required.		RECEIVED
r11		Dated: July 5, 2001	RECEIVED JUL 11 2001 2800 MAIL ROOM
Paul J. Esatto, Jr., Re Scully, Scott, Murphy	& Presser		MOC
400 Garden City Plaza Garden City, New You (516) 742-4343		7/5/01 class mail under 37	ument and fee is being deposited on with the U.S. Postal Service as first C.F.R. 1.8 and is addressed to the ner for Patents, Washington, D.C
		Janet L Signature of I	NOSOMOM Person Mailing Correspondence
CC:			anet Grossman me of Person Mailing Correspondence
Copyright 1995 Legalsoft			P16A/REV01

JUL 0 9 2001	TRANSMITTAL LETTER (General - Patent Pending)		Docket No. 13715
Application Of:	Masayoshi Tagami, et al.		
Serial No. 09/596,415	Filing Date June 19, 2000	Examiner Hung K. Vu	Group Art Unit 2811
itle: MULTI-LAYE	RED WIRING LAYER AND MET	HOD OF FABRICATING T	'HE SAME
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	TO THE ASSISTANT COM	MISSIONER FOR PATEN	<u>TS:</u>
ansmitted herewith is	· · · · · · · · · · · · · · · · · · ·		
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PATENT

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Masayoshi Tagami, et al.

Serial No.: 09/596,415

Filed: June 19, 2000

Examiner: Hung K. Vu Group Art Unit: 2811 Docket: 13715

For: MULTI-LAYERED WIRING LAYER Dated: July 5, 2001 AND METHOD OF FABRICATING THE SAME

Assistant Commissioner for Patents Washington, DC 20231

RESPONSE TO REQUIREMENT FOR RESTRICTION

Sir:

Pursuant to the Restriction Requirement imposed in the Official Action dated June 5,

2001, Applicant provisionally elects the claims of Group I, i.e., Claims 1-10 for continued

prosecution herein.

Claims 1-36 are present in the above-captioned application and have been subjected to

restriction under 35 U.S.C. §121. Specifically, the Official Action avers that the following inventions

are present in the claims:

CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, DC 20231 on July 5, 2001.

Dated: July 5, 2001

Janet Grossman

G:\NEC\1210\13715\amend\13715.am1

Group I, Claims 1-10 drawn to a semiconductor device, classified in class 257, subclass 758, and

Group II, Claims 11-36, drawn to a method of making a semiconductor device, classified in class 438, subclass 22+.

It is the Examiner's position that the inventions listed as Groups I and II are distinct from each other.

In response to the Examiner's requirement for restriction, Applicant provisionally elects to prosecute the subject matter of Group I, Claims 1-10. However, Applicant reserves the right under 35 U.S.C. § 121 to file one or more divisional applications directed to the non-elected claims in this application.

In view of the foregoing, an examination on the merits of the elected claims, at an early date, is earnestly solicited.

-2-

Respectfully submitted,

Paul J./Esatto, Jr. Registration No. 30,749

G:\NEC\1210\13715\amend\13715.am1

SCULLY, SCOTT, MURPHY & PRESSER 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343

PJE:ae



UNITED STATES _PARTMENT OF COMMERCE Patent and Trademark Office Address: COMMISSIONER OF PATENTS AND TRADEMARKS Washington, D.C. 20231

APPLICATION NO. FILING DATE	FIRST NAMED INVENTOR	M 13715
09/596,415 06/19/00	TAGAMI	M 13/15 AA
· · · · · · · · · · · · · · · · · · ·		
	MMC2/0925	EXAMINER
PAUL J ESATTO JR		
SCULLY SCOTT MURPHY &	PRESSER	
400 GARDEN CITY PLAZA		ART UNIT PAPER NUMBER
GARDEN CITY NY 11530	:	<u> </u>
		A. A
		09/25/01
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Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

1- File Copy

······································	Application No.	Applicant(s)	
	09/596,415	TAGAMI ET AL.	ŕ · ,
Office Action Summary	Examiner	Art Unit	· · ·
	Hung K. Vu	2811	1
The MAILING DATE of this communication a	-		dress
 A SHORTENED STATUTORY PERIOD FOR REPTHE MAILING DATE OF THIS COMMUNICATION Extensions of time may be available under the provisions of 37 CFR 1 after SIX (6) MONTHS from the mailing date of this communication. If the period for reply specified above, is less than thirty (30) days, a reinformation of the period for reply specified above, the maximum statutory period Failure to reply within the set or extended period for reply will, by statu - Any reply received by the Office later than three months after the mailing date of this communication (s) filed on 09 (2a) This action is FINAL. 2b) T 3) Since this application is in condition for allow closed in accordance with the practice under the practice under the practice under the application of Claims 4) Claim(s) 1-36 is/are pending in the application (s) of the above claim(s) 11-36 is/are withdra 	. 136(a). In no event, however, may a reply b ply within the statutory minimum of thirty (30) d will apply and will expire SIX (6) MONTHS f ite, cause the application to become ABANDC ing date of this communication, even if timely 0. July 2001 his action is non-final. wance except for formal matters or <i>Ex parte Quayle</i> , 1935 C.D. 1 Dn.	e timely filed days will be considered time rom the mailing date of this o DNED (35 U.S.C. § 133). filed, may reduce any , prosecution as to ti	ommunication.
5) Claim(s) is/are allowed.			· ··
6)⊠ Claim(s) <u>1-10</u> is/are rejected. —			<i></i>
7) Claim(s) is/are objected to.			
8) Claim(s) are subject to restriction and/	or election requirement.	, .	$\sim 10^{-1}$ s $\sim 10^{-1}$
pplication Papers		· ·	· .
9) The specification is objected to by the Examin	ier.		•
10) The drawing(s) filed on is/are: a) acc	epted or b) objected to by the E	xaminer.	
Applicant may not request that any objection to t			
11) The proposed drawing correction filed on			her
If approved, corrected drawings are required in r			
12) The oath or declaration is objected to by the E			,
		. ·	
Priority under 35 U.S.C. §§ 119 and 120		· .	
13) \boxtimes Acknowledgment is made of a claim for foreign	gn priority under 35 U.S.C. § 11	9(a)-(d) or (f).	
a)⊠ All b)□ Some * c)□ None of:			
1. 🛛 Certified copies of the priority docume	nts have been received.		
2. Certified copies of the priority docume		cation No	. •
3. Copies of the certified copies of the pri			Stane
application from the International E * See the attached detailed Office action for a lis	Bureau (PCT Rule 17.2(a)).	· · · ·	
14) Acknowledgment is made of a claim for domes	stic priority under 35 U.S.C. § 11	19(e) (to a provisiona	al application)
a) The translation of the foreign language p 15) Acknowledgment is made of a claim for dome	rovisional application has been	received.	
ttachment(s)	; · · · ·		ar an
) ⊠ Notice of References Cited (PTO-892)) □ Notice of Draftsperson's Patent Drawing Review (PTO-948)) ⊠ Information Disclosure Statement(s) (PTO-1449) Paper No(s)	5) 🔲 Notice of Inform	mary (PTO-413) Paper No nal Patent Application (P	

DETAILED ACTION

Election/Restrictions

1. Applicant's election of Invention of Group I, Claims 1-10, in Paper No. 5 is acknowledged. Because applicant did not distinctly and specifically point out the supposed errors in the restriction requirement, the election has been treated as an election without traverse (MPEP § 818.03(a)).

Applicant's election without traverse of Invention of Group I, Claims 1-10, in Paper No. 5 is acknowledged.

Claims 11-36 are withdrawn from further consideration pursuant to 37 CFR 1.142(b) as being drawn to a nonelected Invention, there being no allowable generic or linking claim. Election was made **without** traverse in Paper No. 5.

Claim Rejections - 35 USC § 102

2. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless -

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1-3, 5-7, and 10 are rejected under 35 U.S.C. 102(b) as being anticipated by

Vitkavage et al. (PN 5,858,873).

Vitkavage et al. discloses a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate (2), comprising a multi-layered structure of first and second films,

Page 2

A first film (14) being composed of crystalline metal containing nitrogen therein,

Page 3

The second film (12) being composed of amorphous metal nitride,

The barrier film being constituted of common metal atomic species. Note Figures 1-4 of Vitkavage et al.

With regard to claims 2 and 6, Vitkavage et al. discloses wherein the first film is formed on the second film.

With regard to claims 3 and 7, Vitkavage et al. discloses wherein the second film has a thickness

in the range of 60 angstroms to 300 angstroms both inclusive.

With regard to claim 10, Vitkavage et al. discloses a copper film (18) formed on the first film.

Claim Rejections - 35 USC § 103

3. 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 4, 8, and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over

Vitkavage et al. (PN 5,858,873).

With regard to claims 4 and 8, Vitkavage et al. discloses all of the claimed limitations except the

thickness of the first film. However, it would have been obvious to one of ordinary skill in the

art to form Vitkavage et al.'s first film having a thickness as claimed range because the thickness of the first film is variable of importance subject to routine experimentation and optimization. Also, the thickness differences are considered obvious design choices and are not patentable unless unobvious or unexpected results are obtained from these chances. It appears that these changes produce no functional differences and therefore would have been obvious. See In re Woodruff, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With regard to claim 9, Vitkavage et al. discloses wherein the barrier film covers a recess and a hole (10) formed throughout an insulating film (8) formed on an underlying region (4). Vitkavage et al. discloses the underlying region is a diffusion region. Vitkavage et al. does not disclose the underlying region is a wiring layer. However, it would have been obvious to one of ordinary skill in the art at the time the invention was made to form the underlying region of Vitkavage et al. as the wiring layer in order to connect to other parts of the circuit to perform additional functions.

Conclusion

4. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Hung K. Vu whose telephone number is (703) 308-4079. The examiner can normally be reached on Mon-Thurs 7:00-5:30, Eastern Time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Tom Thomas can be reached on (703) 308-2772. The fax phone numbers for the

Page 4

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

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

Steven Loke Primary Examiner

Page 5

September 19, 2001

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AMENDMENT TRANSMITTAL LETTER (Large Entity) Applicant(s): Masayoshi Tagami, et al.					Docket No. 13715		
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PATENTS N THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Masayoshi Tagami, et al.	Έ
Serial No:	09/596,415	A
Filed:	June 19, 2000	D
For:	MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME	D

Examiner: H. Vu Art Unit: 2811 Docket: 13715 Dated: December 20, 20

Assistant Commissioner for Patents United States Patent and Trademark Office Washington, D.C. 20231

RESPONSE UNDER 37 C.F.R. § 1.111

Sir:

In response to the official Office Action dated September 25, 2001, the

applicant respectfully presents the following Amendment and Remarks as set forth herein

below.

IN THE CLAIMS:

Please cancel claims 2 and 6.

Please amend claim 1 to read as follows:

1. (Amended) A barrier tim preventing diffusion of copper from a copper

wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films,

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on December 20, 2001.

Dated: December 20, 2001

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Mishelle Mustafa

09/596,415

said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride, said barrier film being constituted of common metal atomic species. said first film being formed on said second film,

said first film containing nitrogen in a smaller content than that of said second

film.

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Please amend claim 5 to read as follows:

5. (Amended) A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

> said barrier film having a multi-layered structure of first and second films, said first film being composed of crystalline, metal containing nitrogen therein, said second film being composed of amorphous metal nitride, said barrier film being constituted of common metal atomic species, said first film being formed on said second film,

> said first film containing nitrogen in a smaller content than that of said second

film.

Please add the following new claims 37 and 38.

4. (New) The barrier film as set forth in claim 1, wherein said first film is

composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

38. (New) The multi-layered wiring structure as set forth in claim 5, wherein

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said first film is composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

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REMARKS

Reconsideration of this application based on the foregoing Amendment and the following Remarks is respectfully requested.

The Examiner has acknowledged the applicant's election of Group I, claims 1-10, in the applicant's Response to a Requirement for Restriction of July 5, 2001. Claims 11-36 are withdrawn from consideration pursuant to 37 C.F.R. § 1.142(b) as being drawn to a nonelected invention, there being no allowable generic or linking claim. The Examiner has treated the election as an election without traverse, in that the election was made without traverse in the applicant's July 5, 2001 response.

Claims 1-3, 5-7 and 10 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Vitkavage et al. (U.S. 5,858,873) and claims 4, 8 and 9 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Vitkavage et al.

In response, the applicants have amended claims 1 and 5 to recite that the first film is formed on the second film, the first film containing nitrogen in a smaller content than that of the second film. The applicants have added new claims 37 and 38 which recite that the first film is composed of β –Ta and TaN_{0.1} and the second film is composed of Ta₂N. Support for the amendment to claims 1 and 5 and the addition of new claims 37 and 38 is provided in the specification on page 23, line 20, to page 30, line 1, of the application. No new matter has been added.

Vitkavage et al. discloses in column 4, lines 1-12, that the first layer 14 is comprised of a refractory material such as refractory nitride, carbide or boronide. For instance, the first layer 14 is comprised of TiN, TiC or TiB. The adhesion or second layer 12 is comprised of a metal such as Ti, Ta, Zr, Hf or W. The first layer 14 is formed on the

-3-

second layer 12. In a typical case in the cited reference, the first layer 14 is composed of TiN is formed on the second layer 12 composed of Ti. <u>Herein, the first layer 14 contains nitrogen</u> in a *higher* content than that of the second layer 12.

In contrast, in the present invention, claims 1 and 5, as amended, and the corresponding new dependent claims 37 and 38, recite that the first film 16 in the present invention is comprised of a crystalline metal film containing nitrogen therein. For instance, the first film 16 is composed of TaN_{0.1} which is called nitrogen-containing α -Ta, or a combination of TaN_{0.1} and β -Ta. The second film 15 in the present invention is comprised of a amorphous metal nitride film. For instance, the second film 15 is composed of Ta₂N. That is, the first film 16 is composed of crystalline metal containing nitrogen at 10% or smaller, and the second film 15 is composed of amorphous metal nitride containing nitrogen at about 30%. The first layer 16 contains nitrogen in a *smaller content* than that of the second film 15, which is structurally different from the cited reference.

In addition, in the present invention of amended claims 1 and 5, the copper film 18 makes contact with the first film 16 beneath which the second film 16 is formed. As illustrated in Fig. 9, the first film 16 composed of nitrogen-containing crystalline metal has a smaller resistivity that that of a Ta film containing no nitrogen. <u>Hence, the first film is formed</u> <u>of not a pure-metal film, but a nitrogen-containing crystalline metal film.</u>

Therefore, the applicants respectfully maintain that the present invention of amended claims 1 and 5, and new claims 37 and 38 patentably distinguish over Vitkavage et al and that the claims are not anticipated by Vitkavage et al. under 35 U.S.C. § 102(b). Claim 3 stands together with claim 1 and claims 7 and 10 stand together with claim 5.

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With regard to the rejections of claims 4, 8 and 9 under 35 U.S.C. § 103(a), the applicants respectfully maintain that claim 4 stands together with claim 1, as amended, and claims 8 and 9 stand together with claim 5, as amended.

The foregoing Amendment and Remarks establish the patentable nature of all of the claims under consideration in the application, i.e., claims 1, 3-5, and 7-10. Claims 2 and 6 have been cancelled. No new matter has been added, wherefore, early and favorable reconsideration of the present application and issuance of a Notice of Allowability are respectfully requested.

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Respectfully submitted

Anthony N./Fresco Registration No.: 45,784

Scully, Scott, Murphy & Presser 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343

ANF:cm Encl. (Version with Markings to Show Changes Made)

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Claims:

Claims 2 and 6 have been cancelled.

Claim 1 has been amended as follows:

1. (Amended) A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films,

> said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride,

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film containing nitrogen in a smaller content than that of said second

<u>film</u>.

Claim 5 has been amended as follows:

5. (Amended) A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

> said barrier film having a multi-layered structure of first and second films, said first film being composed of crystalline metal containing nitrogen therein, said second film being composed of amorphous metal nitride,

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

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said first film containing nitrogen in a smaller content than that of said second film.

New claims 37 and 38 have been added as follows:

37. (New) The barrier film as set forth in claim 1, wherein said first film is composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

38. (New) The multi-layered wiring structure as set forth in claim 5, wherein

said first film is composed of β -Ta and TaN_{0.1}, and said second film is composed of Ta₂N.

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

PTO-90C (Rev. 07-01)

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1) 🛛 Responsive to communi	ication(s) filed or	n <u>20 December 2001</u> .		
2a) This action is FINAL .	2b)] This action is non-final.		
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4) Claim(s) <u>1,3-5 and 7-38</u>	is/are pending in	n the application.	•	
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8) Claim(s) are subje	74,	and/or election requirement.		
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Priority under 35 U.S.C. §§ 119 a	and 120			· · ·
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DETAILED ACTION

Claim Rejections - 35 USC § 102

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless -

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1, 3-5, 7-10 are rejected under 35 U.S.C. 102(b) as being anticipated by Hong et al. (PN 5,668,411). Note Figures 7-10 and Table 1 of Hong et al..

Hong et al. discloses a barrier film preventing diffusion of copper from a copper wiring layer

formed on a semiconductor substrate (22), comprising a multi-layered structure of first and

second films,

A first film (48) being composed of crystalline metal containing nitrogen therein,

The second film (44) being composed of amorphous metal nitride,

The barrier film being constituted of common metal atomic species (Ti,Ta,W),

The first film being formed on the second film,

The first film containing nitrogen (TiWN, TiAlN, TiSiN, TaSiN) in a smaller content than

that of the second film (TiN,TaN).

With regard to claims 3 and 7, Hong et al. discloses wherein the second film has a thickness 100-6000 angstroms (within the range of 80 angstroms to 150 angstroms both inclusive).

Page 226 of 333

Page 2

With regard to claims 4 and 8, Hong et al. discloses wherein the first film has a thickness 100-1000 angstroms (within the range of 60 angstroms to 300 angstroms both inclusive).

With regard to claim 9, Hong et al. discloses wherein the barrier film covers a recess and a hole formed throughout an insulating film (30) formed on an underlying wiring layer (22).

With regard to claim 10, Hong et al. discloses a copper film (26) formed on the first film.

Response to Arguments

2. Applicant's arguments with respect to claims 1 and 5 have been considered but are moot in view of the new ground(s) of rejection.

Allowable Subject Matter

3. Claims 37 and 38 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.

4. The following is an examiner's statement of reasons for allowance:

Applicants' claims 37 and 38 are allowable over the references of record because none of these references disclose or can be combined to yield the claimed invention such as the first film is composed of β -Ta and TaN_{0.1}, and the second film is composed of Ta₂N.

Page 3

Conclusion

Page 4

5. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Hung K. Vu whose telephone number is (703) 308-4079. The examiner can normally be reached on Mon-Thurs 7:00-5:30, Eastern Time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Tom Thomas can be reached on (703) 308-2772. The fax phone numbers for the organization where this application or proceeding is assigned are (703) 308-7722 for regular communications and (703) 308-7722 for After Final communications.

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

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March 29, 2002

Steven Loke Prince/y Examiner

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Notice of References Cited

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AMENDM Applicant(s): Masa		TAL LETTER (La	rge Entity)		Docket No. 13715
Serial No. 09/596,415		Date 9, 2000 JUN 1/1 20	Examiner H. Vu		Group Art Unit 2811
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Anthony N. Fresco	M. Fresco Signature	D	ated: June 4, 2002	• • • •	
Registration No. 45 SCULLY, SCOTT, 400 Garden City Pl Garden City, New Y (516) 742-4343 ANF:yp	MURPHY & PRESS	ER	on June 4, 20 first class ma Assistant Co 20231	02 with ill under 37 C.F.R.	0
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RESPONSE UNDER 37 C.F.R. § 1.116 EXPEDITED PROCEDURE EXAMINING GROUP 2811

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s):	Masayoshi Tagami, et al.	Examiner:	H. Vu
Serial No.:	09/596,415	Art Unit:	2811 2
Filed:	June 19, 2000	Docket:	13715
For:	MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME	Dated:	June 4, 2002

Assistant Commissioner for Patents United States Patent and Trademark Office Washington, D.C. 20231

RESPONSE AFTER FINAL REJECTION UNDER 37 C.F.R. § 1.116

Sir:

In response to the Final Office Action dated April 4, 2002, the applicant

respectfully requests consideration of the following Remarks in the above-

identified case:

CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on June 4, 2002.

Dated: June 4, 2002

Mishelle Mustafa

REMARKS

This response is submitted in response to the Final Office Action dated April 4, 2002 and respectfully requests that the Examiner reconsider the rejection of the claims as set forth therein.

The Examiner objects to claims 37 and 38 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.

The Examiner has considered the applicants' arguments with respect to claims 1 and 5 but the Examiner considers the arguments moot in view of new grounds of rejection.

The Examiner has rejected claims 1, 3-5 and 7-10 under 35 U.S.C. 102(b) as being anticipated by Hong et al. (U.S. 5,668,411 – filed July 23, 1996 – issued September 16, 1997).

Hong et al is a new reference cited by the Examiner. In the first Office Action, the Examiner cited Vitkavage et al. (U.S. 5,858,873 – filed March 12, 1997 – issued January 12, 1999). The Examiner now asserts that FIGS. 7-10 and Table 1 of Hong et al disclose the limitations of claim 1 of a barrier film preventing diffusion of copper from a copper wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate.

In response, the applicants respectfully maintain with respect to claims 1 and 5 that Hong et al does not disclose the first film being formed on the second film, as recited by claims 1 and 5. Instead, Hong et al, FIGS. 7 and 10 discloses

that there is a seed layer 46 of the diffusion barrier film positioned between the top layer 48 and the bottom layer 44.

Furthermore, the top layer 48 of Hong et al, which corresponds to the first film of the present invention, contains TiN or TiWN. The bottom layer 44 of Hong et al, which corresponds to the second film of the present invention, contains TiN, TiAlN, or TiSiN. Therefore, contrary to the Examiner's assertion, Hong et al does not disclose that the first film contains nitrogen in a smaller content than that of the second film. Instead, in Hong et al, preferably, both the first and second films can be TiN, or both can be TiWN.

Although tungsten has an atomic weight of 183.84 which is greater than the atomic weight of either aluminum or silicon, and the compound TiWN suggested by Hong et al for the top layer or first film does contain nitrogen in a smaller content than that of the bottom layer or second film, Hong et al does not specify that the first layer must contain nitrogen in a smaller content than that of the second layer, as recited by claims 1 and 5.

Therefore, claims 1 and 5, by reciting that the first film is formed on the second film, patentably distinguish over Hong et al. Furthermore, in the best mode described by Hong et al, the nitrogen content of the first and second films are equivalent, being comprised of TiN. Furthermore, Hong et al does not teach or suggest any particular advantage of the first film being comprised of TiWN while the second film is comprised of TiN or TiAIN.

With regard to claims 3-4 and 7-10, in view of the applicants' arguments in favor of claims 1 and 5 as patentably distinguishing over Hong et al, the applicants

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Page 235 of 333

respectfully maintain that claims 3-4 and 7-10 also patentably distinguish over Hong et al.

The applicant respectfully requests that the Examiner consider the foregoing Remarks. The foregoing Remarks establish the patentable nature of all of the claims currently in the application, i.e. claims 1, 3-5, and 7-10. Claims 2 and 6 were previously cancelled. Claims 37 and 38 are objected to as being dependent upon a rejection base claim but would be allowable if rewritten in independent form to include all of the limitations of the base claims and any intervening claims. No new issues have been raised, wherefore, early and favorable reconsideration and issuance of a Notice of Allowance are respectfully solicited.

> Respectfully submitted, Anthony No Fresco

Anthony N. Fresco Registration No.: 45,784

SCULLY, SCOTT, MURPHY & PRESSER 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343/4366 FAX

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/596,415	06/19/2000	Masayoshi Tagami	13715	3425
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Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 07-01)

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	Application No.	Applicant(s)	
Advisory Action	09/596,415	TAGAMI ET AL	
Advisory Action	Examiner	Art Unit	· · · · · · · · · · · · · · · · · · ·
· · · ·	Hung K. Vu	2811	
The MAILING DATE of this communication	appears on the cover sheet w	ith the correspondence addr	ress
HE REPLY FILED 11 June 2002 FAILS TO PLAC herefore, further action by the applicant is required nal rejection under 37 CFR 1.113 may <u>only</u> be eith ondition for allowance; (2) a timely filed Notice of A examination (RCE) in compliance with 37 CFR 1.11	l to avoid abandonment of th er: (1) a timely filed amendm Appeal (with appeal fee); or (3	is application. A proper repleted which places the applic	bly to a ation in
PERIOD FOI	R REPLY [check either a) or	b)]	, :
 a) The period for reply expires <u>3</u> months from the mailing d b) The period for reply expires on: (1) the mailing date of th event, however, will the statutory period for reply expire li ONLY CHECK THIS BOX WHEN THE FIRST REPLY 706.07(f). Extensions of time may be obtained under 37 CFR 1.136(a). The vent filed is the date for purposes of determining the period of 7 CFR 1.17(a) is calculated from: (1) the expiration date of the short the short the vent of vent of	ils Advisory Action, or (2) the date set ater than SIX MONTHS from the mail WAS FILED WITHIN TWO MONTH The date on which the petition under 3 i extension and the corresponding amo intened statutory period for reply origin	ing date of the final rejection. S OF THE FINAL REJECTION. S 7 CFR 1.136(a) and the appropriate ount of the fee. The appropriate ext ally set in the final Office action; or	ee MPEP e extension fee ension fee under (2) as set forth in
 b) above, if checked. Any reply received by the Office later than the arned patent term adjustment. See 37 CFR 1.704(b). 1. A Notice of Appeal was filed on Appeal 	ree months after the mailing date of th Ilant's Brief must be filed witl	e final rejection, even if timely filed, hin the period set forth in	may reduce any
37 CFR 1.192(a), or any extension thereof (3		smissal of the appeal.	
2. The proposed amendment(s) will not be enter	1	· · · · · · · · · · · · · · · · · · ·	*
(a) \square they raise new issues that would require		search (see NOTE below);	
(b) they raise the issue of new matter (see N		l la sur de la della se de seta en de s	
(c) (c) they are not deemed to place the application issues for appeal; and/or			. • .
(d) 🔲 they present additional claims without c	anceling a corresponding nur	mber of finally rejected claim	ms.
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3. Applicant's reply has overcome the following	rejection(s):	· · · · · · · · · · · · · · · · · · · ·	1 - 2 - 4
4. Newly proposed or amended claim(s) canceling the non-allowable claim(s).	would be allowable if submitt	ed in a separate, timely file	d amendmen
5. ☐ The a) ☐ affidavit, b) ☐ exhibit, or c) ☑ requ application in condition for allowance because	se: <u>See Continuation Sheet</u> .		·
6. The affidavit or exhibit will NOT be considered raised by the Examiner in the final rejection.	· · ·		
7. For purposes of Appeal, the proposed amend explanation of how the new or amended clai	dment(s) a)⊠ will not be ento ims would be rejected is prov	ered or b) will be entered vided below or appended.	and an
The status of the claim(s) is (or will be) as fo	llows:		• • •
Claim(s) allowed:			·
Claim(s) objected to: <u>37 and 38</u> .	1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -		
Claim(s) rejected: <u>1,3-5 and 7-10</u> .	•		
Claim(s) withdrawn from consideration: 11-3			· .
8. The proposed drawing correction filed on	is a) 🗌 approved or b)[disapproved by the Example 1 disapproved by the Example 2 disapproved by t	miner.
9. Note the attached Information Disclosure Sta	atement(s)(PTO-1449) Pape	r No(s)	
10. Other:			• ••• •••
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		TOM THOMAS	
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Continuation Sheet (PTO-303) 09/596,415

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Continuation of 5. does NOT place the application in condition for allowance because: Hong et al. discloses forming a first film (48) containing nitrogen (TiWN, TiAIN, TiSIN or TaSIN) in a smaller content than that of the second film (44) which is TiN or TaN. Further, Hong et al. also discloses forming the first film (48) on the second film (44). Note that the claimed language does not state whether the first film is formed on and in directly contact with the second film. Therefore, Applicant's claims 1 and 5 do not distinguish over the Hong et al. reference.

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Application No.

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Page 239 of 333

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Name (Print / Type)	Paul J. Esatto, Jr.			ion No. (Attorney		9	
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REQUEST	Application Number	09/596,415	
FOR	Filing Date	June 19, 2000	•
	First Named Inventor	Masayoshi Tagami, et al.	
TRANSMITTAL	Art Unit	2811	
Address to: Commissioner for Patents	Examiner Name	H. Vu	
Box RCE Washington, DC 20231	Attorney Docket Num	ber 13715	
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Request for Continued Examination (RCE) practice under 37 CFR 1.114 do	es not apply to any utility o	or plant application filed prior to J	une
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Patents; Box RCE, Washington, DC 20231.

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Sir:



PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s)	: Masayoshi Tagami, et al.	Exar
Serial No.:	09/596,415	Art
Filed:	June 19, 2000	Dock
For:	MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME	Date

Assistant Commissioner for Patents United States Patent and Trademark Office Washington, D.C. 20231

Examiner:	H. Vu
Art Unit:	2811
Docket:	13715
Dated:	August 5, 2002



T C T

ONES

In response to the Final Office Action dated April 4, 2002, and the Advisory Action of July 2, 2002 issued in response to the applicants' Response After Final Rejection Under 37 CFR 1.116 of June 4, 2002 and the telephonic interview with the applicants' representative, Anthony N. Fresco, on July 29, 2002, the applicants' respectfully submit the following Preliminary Amendment in conjunction with the concurrently-filed request for continued examination (RCE):

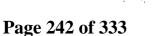
PRELIMINARY AMENDMENT UNDER 37 C.F.R. § 1.115

CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on August 5, 2002.

Dated: August 5, 2002

Mishelle Mustafa



IN THE CLAIMS:

Please amend claim 1 to read as follows:

1. (Twice Amended) A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films,

said first film being composed of crystalline metal containing

nitrogen therein,

said second film being composed of amorphous metal nitride,

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film in direct contact with said second film,

said first film containing nitrogen in a smaller content than that of

said second film.

Please amend claim 5 to read as follows:

5. (Twice Amended) A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

said barrier film having a multi-layered structure of first and second films.

said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride,

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said first film being formed on said second film,

said barrier film being constituted of common metal atomic species,

said first film in direct contact with said second film,

said first film containing nitrogen in a smaller content than that of said second film.

REMARKS

This Preliminary Amendment and the concurrently filed RCE are submitted in response to the Final Office Action dated April 4, 2002 and respectfully requests that the Examiner reconsider the rejection of the claims as set forth therein.

The Examiner objects to claims 37 and 38 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.

The Examiner has considered the applicants' arguments with respect to claims 1 and 5 but the Examiner considers the arguments moot in view of new grounds of rejection.

The Examiner has rejected claims 1, 3-5 and 7-10 under 35 U.S.C. 102(b) as being anticipated by Hong et al. (U.S. 5,668,411 – filed July 23, 1996 – issued September 16, 1997).

Hong et al is a new reference cited by the Examiner. In the first Office Action, the Examiner cited Vitkavage et al. (U.S. 5,858,873 – filed March 12, 1997 – issued January 12, 1999). The Examiner now asserts that FIGS. 7-10 and Table 1

of Hong et al disclose the limitations of claim 1 of a barrier film preventing diffusion of copper from a copper wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate.

In the applicants' June 4, 2002 Response After Final Rejection Under 37 CFR 1.116, the applicants respectfully maintained with respect to claims 1 and 5 that Hong et al does not disclose the first film being formed on the second film, as recited by claims 1 and 5. Instead, Hong et al, FIGS. 7 and 10 discloses that there is a seed layer 46 of the diffusion barrier film positioned between the top layer 48 and the bottom layer 44.

Furthermore, the applicants also argued that the top layer 48 of Hong et al, which corresponds to the first film of the present invention, contains TiN or TiWN. The bottom layer 44 of Hong et al, which corresponds to the second film of the present invention, contains TiN, TiAlN, or TiSiN. Therefore, contrary to the Examiner's assertion, Hong et al does not disclose that the first film contains nitrogen in a smaller content than that of the second film. Instead, in Hong et al, preferably, both the first and second films can be TiN, or both can be TiWN.

Although tungsten has an atomic weight of 183.84 which is greater than the atomic weight of either aluminum or silicon, and the compound TiWN suggested by Hong et al for the top layer or first film does contain nitrogen in a smaller content than that of the bottom layer or second film, Hong et al does not specify that the first layer must contain nitrogen in a smaller content than that of the second layer, as recited by claims 1 and 5.

The applicants argued that, therefore, claims 1 and 5, by reciting that the first film is formed on the second film, patentably distinguish over Hong et al. Furthermore, in the best mode described by Hong et al, the nitrogen content of the first and second films are equivalent, being comprised of TiN. Furthermore, Hong et al does not teach or suggest any particular advantage of the first film being comprised of TiWN while the second film is comprised of TiN or TiAlN.

In the Advisory Action of July 2, 2002, the Examiner rejected the foregoing arguments, asserting that Hong et al discloses forming a first film (48) containing nitrogen (TiWN, TiAlN, TiSiN or TaSiN) in a smaller content than that of the second film (44) which is TiN or TaN. The Examiner's position further is that Hong et al also discloses forming the first film (48) on the second film (44). The Examiner noted however that the claimed language does not state whether the first film is formed on and in direct contact with the second film.

In response, in a facsimile sent on July 25, 2002 to the Examiner, the applicants proposed amendments to claims 1 and 5 to recite "<u>said</u> first film in direct contact with said second film,".

In a telephonic interview with the Examiner on July 29, 2002, based on the proposed amendments to claims 1 and 5 sent by facsimile, the Examiner indicated to the applicants' representative, Anthony N. Fresco, that the proposed amendment to claims 1 and 5 requires further search and consideration, and that a RCE would be required. Therefore, the applicants are herein submitting this Preliminary Amendment Under 37 CFR 1.115 in conjunction with the

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09/577,70,2

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Claims:

Claim 1 has been amended as follows:

1. (Twice Amended) A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films,

said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride,

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film in direct contact with said second film,

said first film containing nitrogen in a smaller content than that of said second film.

Claim 5 has been amended as follows:

films,

5. (Twice Amended) A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

said barrier film having a multi-layered structure of first and second

said first film being composed of crystalline metal containing nitrogen therein,

said second film being composed of amorphous metal nitride,

concurrently filed RCE to enter the amendments to claims 1 and 5 to recite "<u>said</u> <u>first film in direct contact with said second film</u>,". No new matter has been added.

With regard to claims 3-4 and 7-10, in view of the applicants' amendments to claims 1 and 5, which the applicants respectfully maintain establish claims 1 and 5 as patentably distinguishing over Hong et al, the applicants maintain that claims 3-4 and 7-10 also patentably distinguish over Hong et al.

The foregoing Remarks establish the patentable nature of all of the claims currently in the application, i.e. claims 1, 3-5, and 7-10 and 37-38. Claims 2 and 6 were previously cancelled. Claims 37 and 38 are objected to as being dependent upon a rejection base claim but would be allowable if rewritten in independent form to include all of the limitations of the base claims and any intervening claims. No matter has been added and no new issues have been raised, wherefore, early and favorable reconsideration and issuance of a Notice of Allowance are respectfully solicited.

Respectfully submitted Anthony NCFresco

Registration No.: 45,784

SCULLY, SCOTT, MURPHY & PRESSER 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343/4366 FAX

ANF:yd

Enclosure: Version with Markings to Show Changes Made

said barrier film being constituted of common metal atomic species,

said first film being formed on said second film,

said first film in direct contact with said second film,

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said first film containing nitrogen in a smaller content than that of $_{\frown}$

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said second film.

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In Re Application Of: I	Masayoshi Tagami, et al.	AUG 0 9 2002	ATTOR S		
Serial No.	Filing Date	TRADEMAN	Examiner	Group A	Art Unit
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Serial No. 09/596,415	Filing Date June 19, 2000	FILL CHARTER E	xaminer H. Vu	Group Art Unit 2811
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One month	Two months	Three months	Four month	s 🛛 Five months
from:	July 4, 2002	until:	August 4, 2	2002
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Transaction History Date <u>2002-09-10</u> Date Information retrieved from USPTO Patent: Application Information Retrieval (PAIR) system records at www.uspto.gov

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Identifying indicia such as the application number (see 37 CFR 1. of each sheet. The drawings should be filed as a separate paper	84(c)) should be with a transmitta	written on the draw al letter addressed to	rings in the top margin (not the back) o the Official Draftsperson.
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Application/Control Number: 09/596,415 Art Unit: 2811

Examiner's Amendment

1. This application is in condition for allowance except for the presence of claims 11-39 to invention non-elected without traverse. Accordingly, claims 11-36 have been cancelled.

Allowable Subject Matter

2. The following is an examiner's statement of reasons for allowance:

Applicants' claims 1, 3-5,7-10 and 37-38 are allowable over the references of record because none of these references disclose or can be combined to yield the claimed invention such as the barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate comprising, a multi-layered structure of first and second films, the first film being composed of crystalline metal containing nitrogen therein the second film being composed of amorphous metal nitride, the barrier film being constituted of common metal atomic species, the first film being formed on the second film, the first film in direct contact with the second film, the first film containing nitrogen in a smaller content than that of the second film.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance." Application/Control Number: 09/596,415 Art Unit: 2811

Conclusion

3. Papers related to this application may be submitted to Technology Center (TC) 2800 by facsimile transmission. Papers should be faxed to TC 2800 via the TC 2800 Fax center located in Crystal Plaza 4, room 4-C23. The faxing of such papers must conform with the notice published in the Official Gazette, 1096 OG 30 (November 15, 1989). The Group 2811 Fax Center number is (703) 308-7722 and 308-7724. The Group 2811 Fax Center is to be used <u>only</u> for papers related to Group 2811 applications.

Any inquiry concerning this communication or any earlier communication from the Examiner should be directed to *Hung Vu* whose telephone number is (703) 308-4079. The Examiner is in the Office generally between the hours of 7:00 AM to 5:30 PM (Eastern Standard Time) Monday through Thursday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, *Tom Thomas*, can be reached on (703) 308-2772.

Any inquiry of a general nature or relating to the status of this application should be directed to the **Technology Center Receptionists** whose telephone number is (703) 308-0956.

TOM THOMAS SUPERVISORY PATENT EXAMINER TECHNOLOGY CENTER 2800

Vu

September 6, 2002

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Form PTO 948 (Rev. 03/01) U.S. DEPARTMENT OF COMMERCE - Patent and Trademark Office Application NOTICE OF DRAFTSPERSON'S PATENT DRAWING REVIEW 3.97 The dra ing(s) filed (insert date are А. 🖌 approved by the Draftsperson under 37 CFR 1.84 or 1.152. objected to by the Draftscerson under 37 CFR 1.84 or 1.152 for the reasons indicated below. The Examiner will require submission of new, corrected drawings when necessary. Corrected drawing must be sumitted according to the instructions on the back of this notice. 1. DRAWINGS. 37 CFR 1.84(a): Acceptable categories of drawings 8. ARRANGEMENT OF VIEWS. 37 CFR 1.84(i) Black ink. Color. Words do not appear on a horizontal, left-to-right fashion when page is either upright or turned so that the top Color drawings are not acceptable until petiton is granted. Fig(s) becomes the right side, except for graphs. Fig(s) Pencil and non black ink not permitted. Fig(s) 9. SCALE. 37 CER 1.84(k) 2. PHOTOGRAPHS. 37 CFR 1.84(b) Scale not large enough to show mechanism without 1 full-tone set is required. Fig(s) crowding when drawing is reduced in size to two-thirds in Photographs may not be mounted. 37 CFR 1.84(e) reproduction. Poor quality (half-tone). Fig(s) 3. TYPE OF PAPER. 37 CFR 1.84(e) Fig(s) 10. CHARACTER OF LINES, NUMBERS, & LETTERS. Paper not flexible, strong, white, and durable. Fig(s) Lines, numbers & letters not uniformly thick and well defined, clean, turnalle, and shak (poor line quality) Fig(s) Erasures, alterations, overwritings, interlineations folds, copy machine marke not accepted. Fig(s) Mylar, velum paper is not acceptable (too thin). Fig(s) 7 CFR 1.84(m) Ъ ١. Fig(s)______4. SIZE OF PAPER. 37 CFR 1.84(1): Acceptable sizes: Solid black areas pale. Fig(s) Solid black shading not permitted. Fig(s) _____ Shade lines, pale, rough and blurred. Fig(s)._____ 12. NUMBERS, LETTERS, & REFERENCE CHARACTERS. 21.0 cm by 29.7 cm (DIN size A4) 21.6 cm by 27.9 cm (8 1/2 x 11 inches) All drawing sheets not the same size. 37 CFR 1.84(p) Sheet(s) Numbers and reference characters not plain and legible. Drawings sheets not an acceptable size. Fig(s) Fig(s) 5. MARGINS. 37 CFR 1.84(g): Acceptable margins: Figure legends are poor. Fig(s) Numbers and reference characters not oriented in the Top 2.5 cm Left 2.5 cm Right 1.5 cm Bottom 1.0 cm same direction as the view. 37 CFR 1.84(p)(1) SIZE: , A4 Size Fig(s) m Left 2.5 cm Right 1.5 cm Bottom 1.0 cm English alphabet not used. 37 CFR 1.84(p)(2) SIZE: 8 1/2 11 Figs: Numbers, letters and reference characters must be at least .32 cm (1/8 inch) in height. 37 CFR 1.84(p)(3)not acceptable. Fig(s) Top (T) Right (R) Left (L) Fig(s) Bottom (B) LEAD LINES. 37 CFR 1.84(q) VIEWS. 37 CFR 1.84(h) 6. Lead lines cross each other. Fig(s) REMINDER: Specification may require revision to correspond to drawing changes. Partial views. 37 CFR 1.84(h)(2) Sheets not numbered consecutively, and in Arabic numerals Brackets needed to show figure as one entity. beginning with number 1. Sheet(s) 15. NUMBERING OF VIEWS. 37 CFR 1.84(u) Fig(s) Views not labeled separately or properly. Fig(s) Views not numbered consecutively, and in Arabic numerals, beginning with number 1. Fig(s) 16. CORRECTIONS. 37 CFR 1.84(w) Enlarged view not labeled separetely or properly. Fig(s) Corrections not made from prior PTO-948 7. SECTIONAL VIEWS. 37 CFR 1.84 (h)(3) dated 17. DESIGN DRAWINGS. 37 CFR 1.152 Hatching not indicated for sectional portions of an object. Surface shading shown not appropriate. Fig(s) Solid black shading not used for color contrast. Fig(s) Sectional designation should be noted with Arabic or Fig(s) Roman numbers. Fig(s) COMMENTS TELEPHONE NO REVIEWER ATTACHMENT TO PAPER NO.

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Attachment for PTO-948 (Rev. 03/01, or earlier) 6/18/01

The below text replaces the pre-printed text under the heading, "Information on How to Effect Drawing Changes," on the back of the PTO-948 (Rev. 03/01, or earlier) form.

INFORMATION ON HOW TO EFFECT DRAWING CHANGES

1. Correction of Informalities - 37 CFR-1:85

New corrected drawings must be filed with the changes incorporated therein. Identifying indicia, if provided, should include the title of the invention, inventor's name, and application number, or docket number (if any) if an application number has not been assigned to the application. If this information is provided, it must be placed on the front of each sheet and centered within the top margin. If corrected drawings are required in a Notice of Allowability (PTOL-37), the new drawings **MUST** be filed within the **THREE MONTH** shortened statutory period set for reply in the Notice of Allowability. Extensions of time may NOT be obtained under the provisions of 37 CFR 1.136(a) or (b) for filing the corrected drawings after the mailing of a Notice of Allowability. The drawings should be filed as a separate paper with a transmittal letter addressed to the Official Draftsperson.

2. Corrections other than Informalities Noted by Draftsperson on form PTO-948.

All changes to the drawings, other than informalities noted by the Draftsperson, MUST be made in the same manner as above except that, normally, a highlighted (preferably red ink) sketch of the changes to be incorporated into the new drawings MUST be approved by the examiner before the application will be allowed. No changes will be permitted to be made, other than correction of informalities, unless the examiner has approved the proposed changes.

Timing of Corrections

Applicant is required to submit the drawing corrections <u>within the</u> <u>time period set in the attached Office communication</u>. See 37 CFR 1.85(a).

Failure to take corrective action within the set period will result in **ABANDONMENT** of the application.

06/01/01

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PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail Box ISSUE FEE

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Fax (Commissioner for Patents Washington, D.C. 20231 703)746-4000
INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICA appropriate. All further correspondence including the Patent, advance orders and notification o indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new cor maintenance fee notifications.	to maintenance rees will be mained to the current correspondence address as respondence address; and/or (b) indicating a separate "FEE ADDRESS" for
CURRENT CORRESPONDENCE ADDRESS (Note: Legibly mark-up with any corrections or use Block 1) 7590 09/10/2002 Paul J Esatto Jr	Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.
Scully Scott Murphy & Presser 400 Garden City Plaza Garden City, NY 11530	Certificate of Mailing or Transmission I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Box Issue Fee address above, or being facsimile transmitted to the USPTO, on the date indicated below.
	(Depositor's name)
	(Signature)
	(Date)

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/596,415	06/19/2000	Masayoshi Tagami	13715	3425
LITLE OF INVENTION M	ULTI-LAYERED WIRING	LAYER AND METHOD OF FABRICATING THE SAME		

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APPLN. TYPE	SMALL ENTITY	ISSUE FEE	PUBLIC	ATION FEE	TOTAL FEE(S) DUE	DATE DUĘ
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR		ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/596,415	06/19/2000	Masayoshi Tagami		13715	3425
75	90 09/10/2002			EXAMIN	ER
Paul J Esatto Jr Scully Scott Murph	v & Presser			VU, HUI	IG K
400 Garden City Pla				ART UNIT	PAPER NUMBER
Garden City, NY 11	1530			2811	
· · · · ·				DATE MAILED: 09/10/2002	

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The patent term adjustment to date is 0 days. If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the term adjustment will be 0 days.

If a continued prosecution application (CPA) was filed in the above-identified application, the filing date that determines patent term adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) system. (http://pair.uspto.gov)

Page 3 of 4

PTOL-85 (REV. 04-02) Approved for use through 01/31/2004.

		United	ED STATES DEPARTMENT OF COM d States Patent and Trademark Off s: COMMISSIONER OF PATENTS AND T Washington. D.C. 20231 www.uspto.gov	ice
APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO
09/596,415	06/19/2000	Masayoshi Tagami	13715	3425
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Paul J Esatto Jr Scully Scott Murph	N. & Draggar		VU, HUN	GK
400 Garden City P		•.	ART UNIT	PAPER NUMBER
Garden City, NY 1	1530		2811	
UNITED STATES			DATE MAILED: 09/10/2002	

Notice of Possible Fee Increase on October 1, 2002

If a reply to a "Notice of Allowance and Fee(s) Due" is filed in the Office on or after October 1, 2002, then the amount due may be higher than that set forth in the "Notice of Allowance and Fee(s) Due" since there may be an increase in fees effective on October 1, 2002. See Revision of Patent and Trademark Fees for Fiscal Year 2003. Notice of Proposed Rulemaking, 67 Fed. Reg. 30634, 30636 (May 7, 2002). Although a change to the amount of the publication fee is not currently proposed for October 2002, if the issue fee or publication fee is to be paid on or after October 1, 2002, applicant should check the USPTO web site for the current fees before submitting the payment. The USPTO Internet address for the fee schedule is: http://www.uspto.gov/main/howtofees.htm.

If the issue fee paid is the amount shown on the "Notice of Allowance and Fee(s) Due," but not the correct amount in view of any fee increase, a "Notice to Pay Balance of Issue Fee" will be mailed to applicant. In order to avoid processing delays associated with mailing of a "Notice to Pay Balance of Issue Fee," if the response to the Notice of Allowance and Fee(s) due form is to be filed on or after October 1, 2002 (or mailed with a certificate of mailing on or after October 1, 2002), the issue fee paid should be the fee that is required at the time the fee is paid. If the issue fee was previously paid, and the response to the "Notice of Allowance and Fee(s) Due" includes a request to apply a previously-paid issue fee to the issue fee now due, then the difference between the issue fee amount at the time the response is filed and the previously paid issue fee should be paid. See Manual of Patent Examining Procedure, Section 1308.01 (Eighth Edition, August 2001).

Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at (703) 305-8283.

Page 4 of 4

PTOL-85 (REV. 04-02) Approved for use through 01/31/2004.

(Under 37 CFR 1.97(b) or 1.	LOSURE STATEMENT 97(c))	Docket No. 13715
Re Application Of:	Masayoshi Tagami, et al.		
Seriat No.	Filing Date June 19, 2000	Examiner H. Vu	Group Art Unit 2811
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<u></u>		Address to: commissioner for Patents ington, D.C. 20231	EVED
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Re Application Of:	Masayoshi Tagami, et al.				· · ·
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TRANSMITTAL OI	F INFORMATION DISCLO nder 37 CFR 1.97(b) or 1.97	OSURE STATEMENT (c))	Docket No. 13715
In Re Application:	Aasayoshi Tagami, et al.		
Serial No.	Filing Date	Examiner	Group Art Unit
09/596,415	June 19, 2000	H. Vu	2811
MULTI-LAYERE	D WIRING LAYER AND METH	IOD OF FABRICATING THE S	AME
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	Signature	Mishelle	Mailing Correspondence Mustafa
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anthony M		Dated: September 9, 2002	RECEIVED SEP 16 2002 ^{TECHNULUGY CENTER} 2800
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P,10A/REV02



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s):	Masayoshi Tagami, et al	•	Examiner:	H. Vu	
Serial No.:	09/596,415		Art Unit:	2811	· • •
Filed:	June 19, 2000	, , , , , , ,	Docket:	13715	
For:	MULTI-LAYERED WI LAYER AND METHOI FABRICATING THE S	OOF	Dated:	September 9, 2	.002

Assistant Commissioner for Patents United States Patent and Trademark Office Washington, D.C. 20231

STATEMENT PURSUANT TO 37 C.F.R. § 1.97(c)(1) and (e)(1)

Sir:

I hereby state that each item of information contained in this Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of this Information Disclosure Statement.

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

I hereby certify that this correspondence is being deposited with the Untied States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231 on September 9, 2002.

Dated: September 9, 2002

Mishelle Mustafa

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PATENT

Accordingly, it is respectfully requested that the accompanying Information

Disclosure Statement be considered with respect to the above-identified

application.

09/596,415

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Respectfully submitted,

Fresco

Anthony N. Fresco Registration No.: 45,784

SCULLY, SCOTT, MURPHY & PRESSER 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343/4366 Fax

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Applicant(s): Masayoshi Tagami, et al. H. Vu **Examiner:** Serial No.: 09/596,415 Art Unit: 2811 Filed: June 19, 2000 **Docket:** 13715 September 2, 2002 For: MULTI-LAYERED WIRING **Dated:** LAYER AND METHOD OF SEP LUGY CENTER 2800 FABRICATING THE SAME

Assistant Commissioner for Patents United States Patent and Trademark Office Washington, D.C. 20231

INFORMATION DISCLOSURE STATEMENT

Sir:

In accordance with 37 C.F.R. §§ 1.97 and 1.98, it is requested that the

following references, which are also listed on the attached Form PTO-1449, be

made of record in the above-identified case.

1. Japanese Laid-Open Patent Application No. 8-250596 dated September 27, 1996;

10/30/2002 SSURLES 00000006 191013 05586415 2. Japanese Laid-Open Patent Application No. 10-125627 dated May 15, 01 FC:1460 -130.00 - CH 1998;

> 3. Japanese Laid-Open Patent Application No. 11-67686 dated March 9, 1999.

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

I hereby certify that this correspondence is being deposited with the Untied States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D,C. 2023 on September 9, 2002.

Dated: September 9, 2002

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Mishelle Mustafa

justment date: 03/31/200 730/2002 SSURLES 000000 FC:1480 130.00 (

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The references were cited in an Official Action dated July 5, 2002 received from the Japanese Patent Office. Applicants are submitting copies of the abovecited references, together with a translation of the Examiner's comments regarding the references from the Official Action. The relevance of the references is described in the Official Action.

In compliance with the requirements of 37 C.F.R. § 1.98(a)(3), as a concise statement of relevance, as it is presently understood by the individual designated in 37 C.F.R. § 1.56(c) most knowledgeable about the content of the information, the undersigned submits a translation of portions of an official action by a foreign examiner in which the references were cited. The relevance to the pending U.S. patent application is that the references were cited in a foreign patent application on the same subject matter. However, no independent analysis of the references, the accuracy of the statement of the foreign examiner or the claims of the foreign application under the laws of that country or the United States relative to the subject matter claimed in the present application has been made; the present understanding of the contents thereof by the undersigned being based on the translation of the foreign examiner's comments submitted herewith.

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Inasmuch as this Information Disclosure Statement is being submitted in accordance with the schedule set out in 37 C.F.R. § 1.97(b), a statement is

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Respectfully submitted,

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Anthony N. Fresco Registration No.: 45,784

SCULLY, SCOTT, MURPHY & PRESSER 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343/4366 Fax

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a. Serial No.	f. Foreign Priority	k. Print Claim(s)	p. PTO-1449
b. Applicant(s)	g. Disclaimer	I. Print Fig.	g. PTOL-85b
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/596,415	06/19/2000	Masayoshi Tagami	. 13715	3425
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Please find below and/or attached an Office communication concerning this application or proceeding.



Address: ASSISTANT COMMISSIONER FOR PATENTS Washington, D.C. 20231

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FIRST NAMED INVENTOR /

Commissioner of Patents and Trademarks

The IDS filed 09/09/02 had been entered and considered by the examiner.

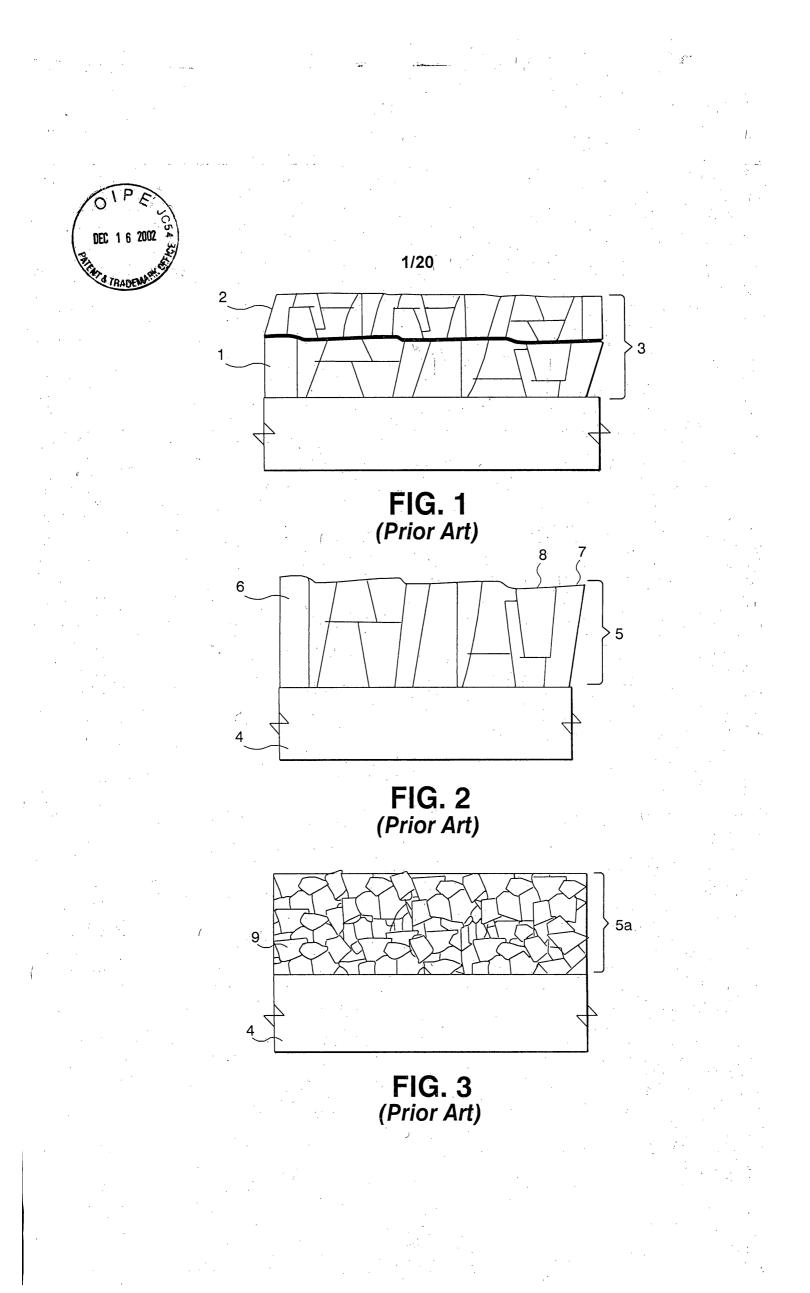
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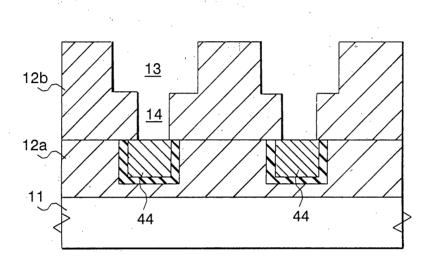
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BEST

P E Docket No. DEC 1 6 2002 **OF FORMAL DRAWINGS** 13715 #17,000 tion Of: Masayoshi Tagami Serial No. Filing Date Batch No. Examiner Art Unit 09/596,415 June 19, 2000 Hung K. VU 2811 Invention: MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME Address to: Assistant Commissioner for Patents Washington, D.C. 20231 Transmitted herewith are: 20 sheets of formal drawing(s) for this application. Each sheet of drawing indicates the identifying indicia suggested in 37 CFR Section 1.84(c). 1. Fresco Dated: December 10, 2002 Anthony N. Fresco **Registration No.: 45,784** SCULLY, SCOTT, MURPHY & PRESSER ertify that this document and attached formal drawings ng deposited on 12/10/2002 with bei 400 Garden City Plaza nder 37 C.F.R./1.8 U.S. Rostal Service as first class mail Garden City, New York 11530 ressed to the Assistant Commissioner for Patents. anda (516) 742-4343/4366 Fax. 2023 on. D. ANF:yd Signature of Person Mailing C responde Mishelle Mustafa Typed or Printed Name of Person Mailing Correspondence 09/02 P23B/REV01

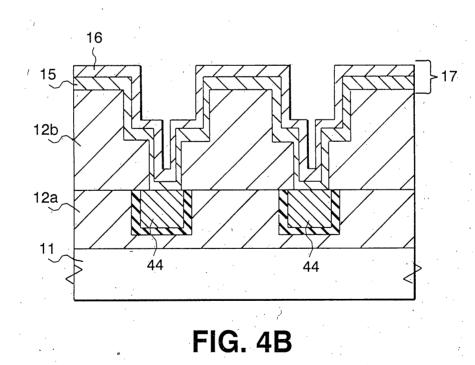




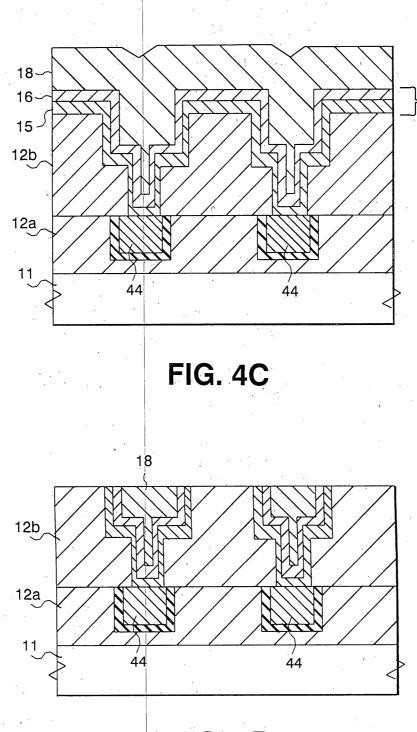


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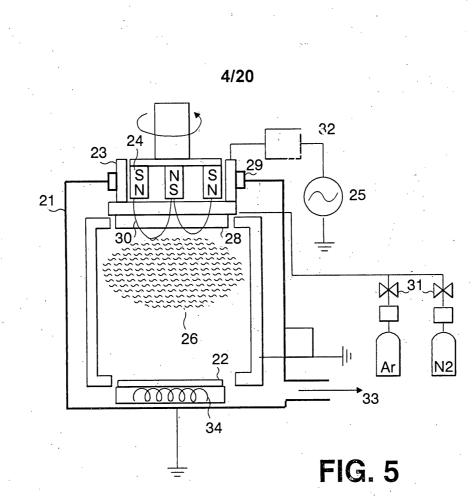






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FIG. 4D



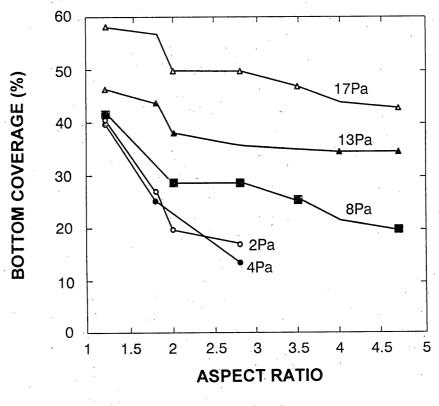


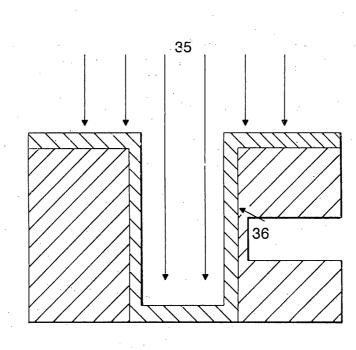
FIG. 6

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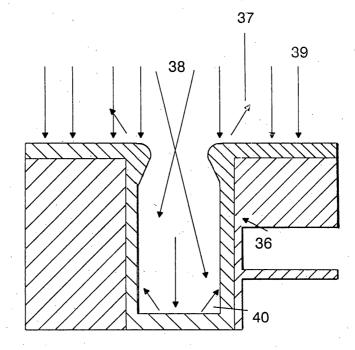
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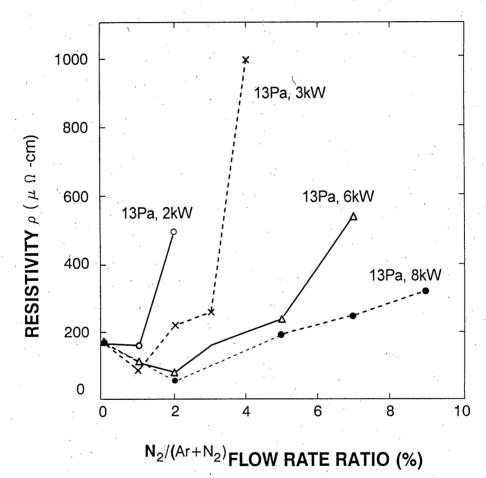
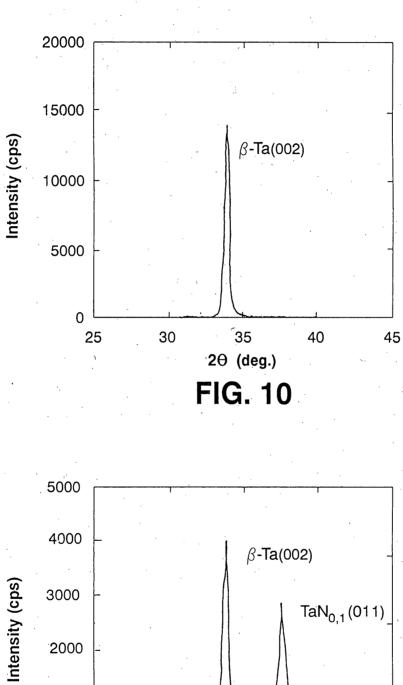
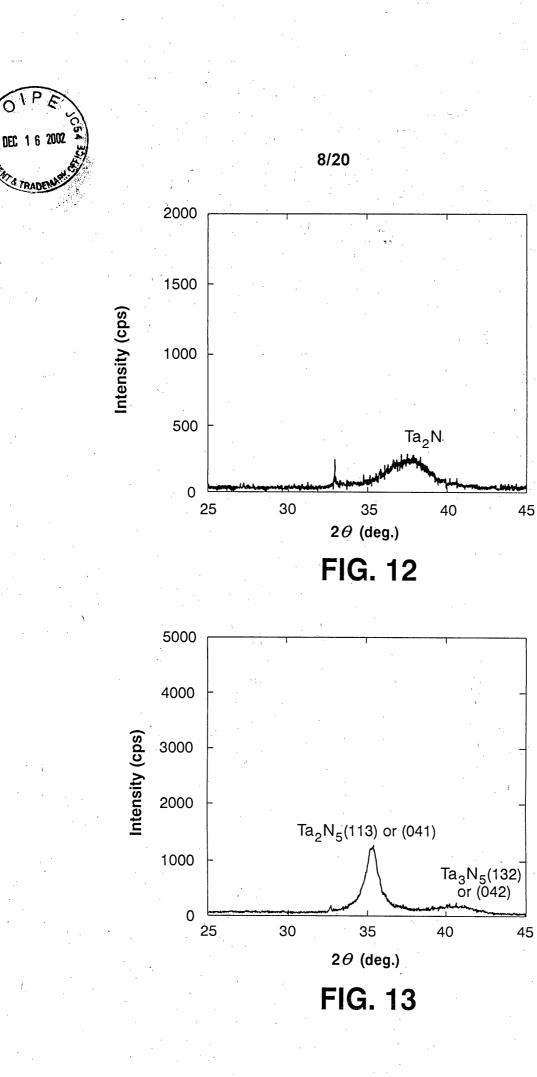


FIG. 9





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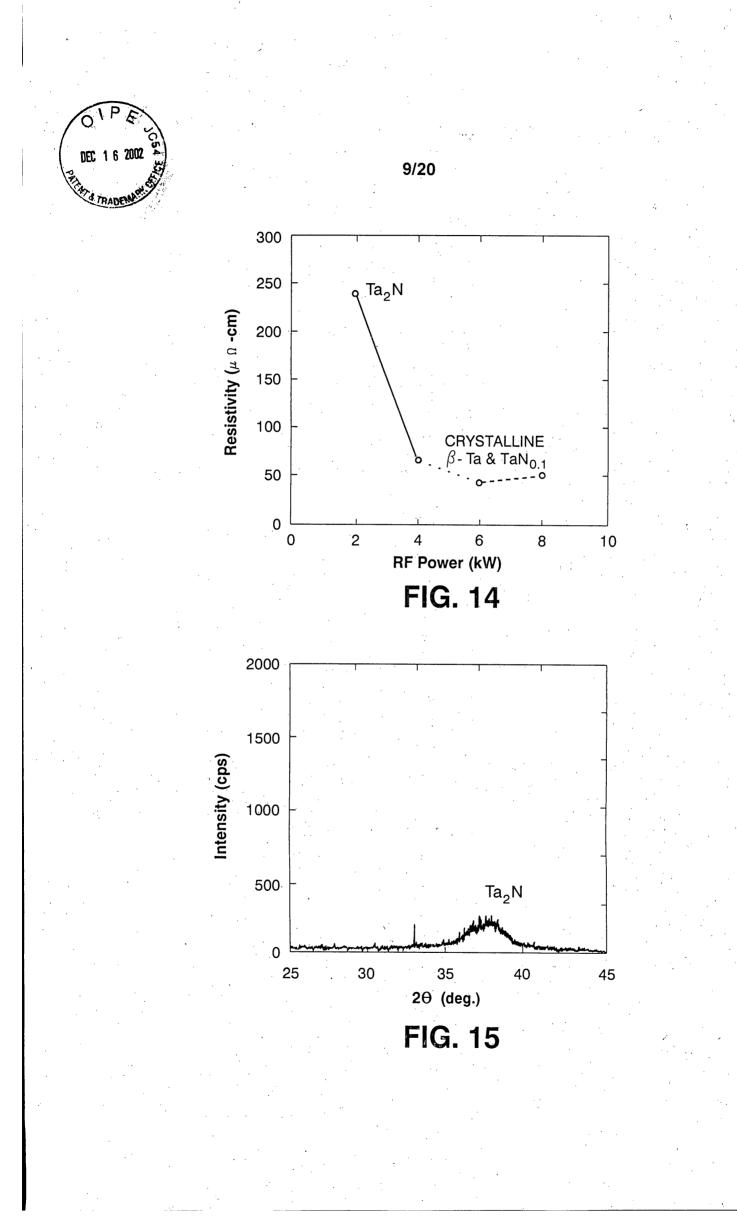


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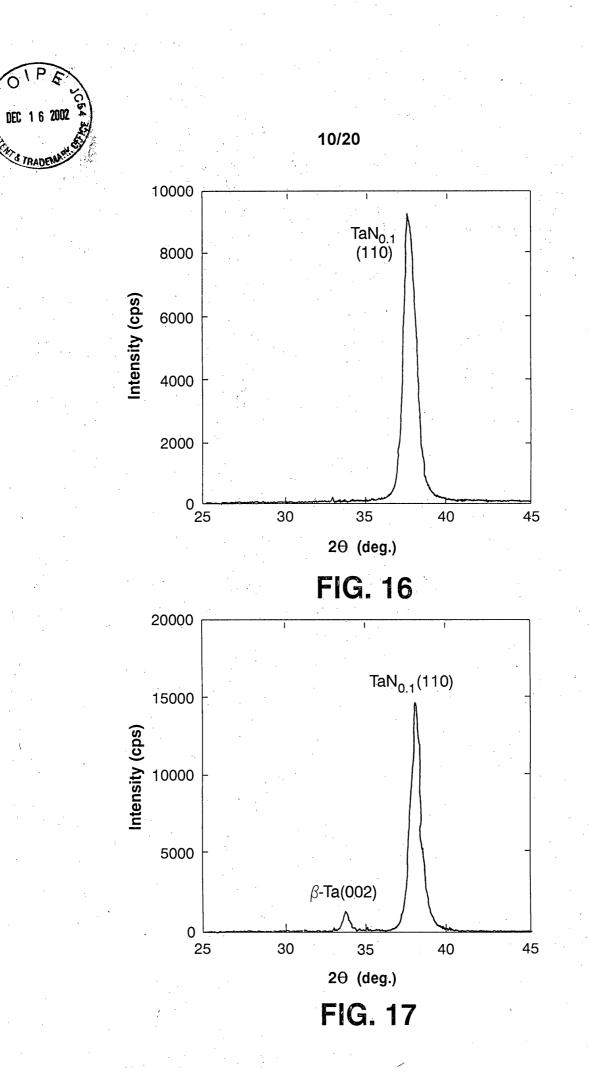
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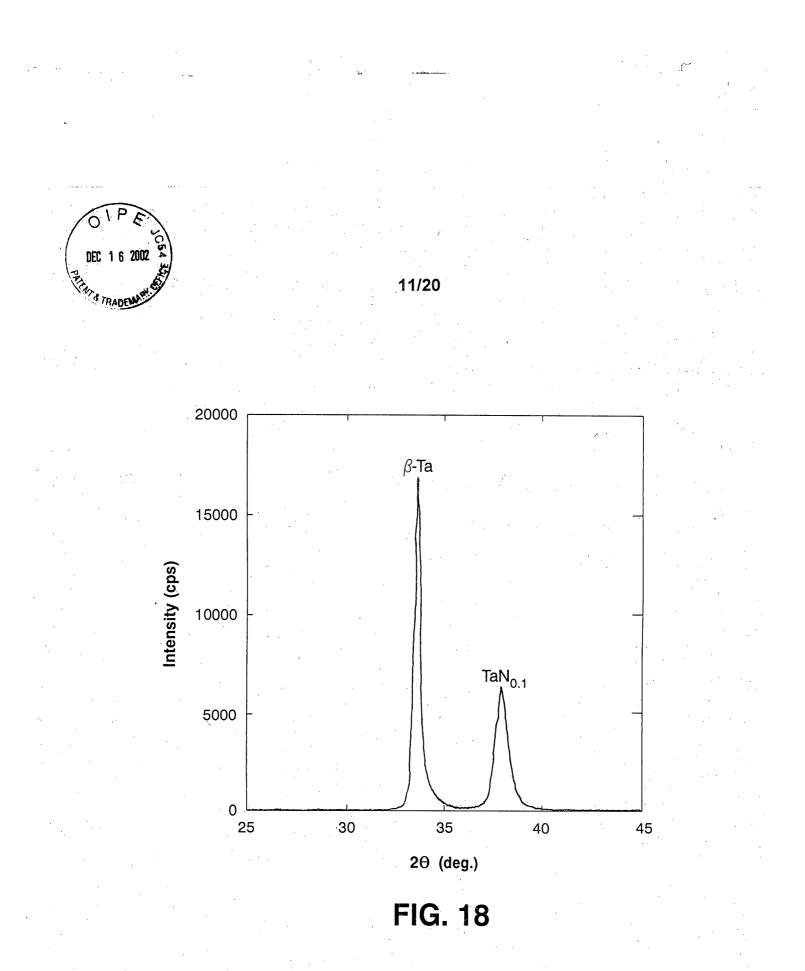
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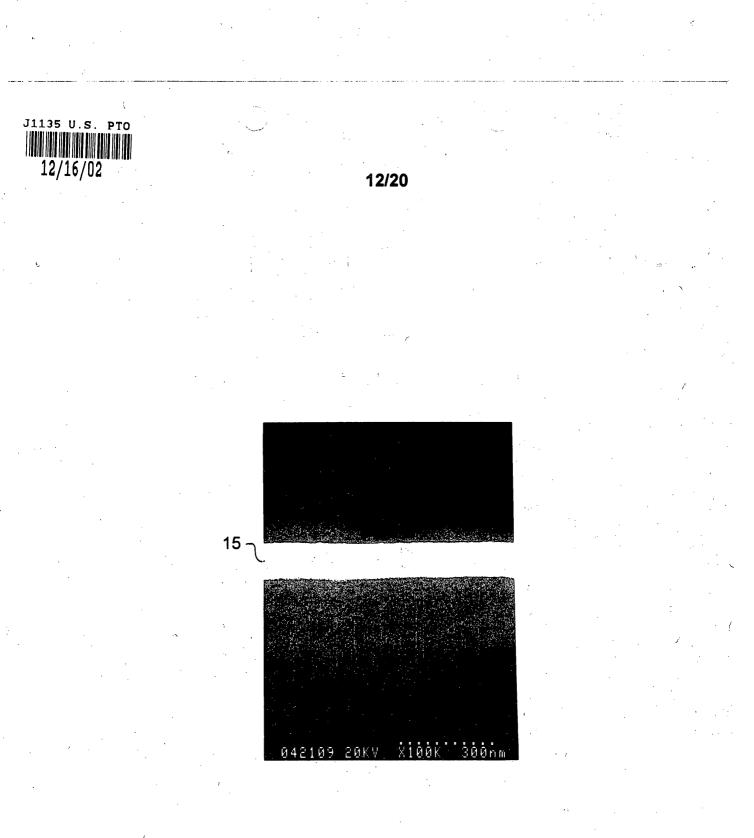
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FIG. 19



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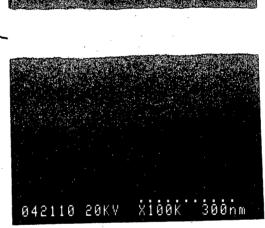
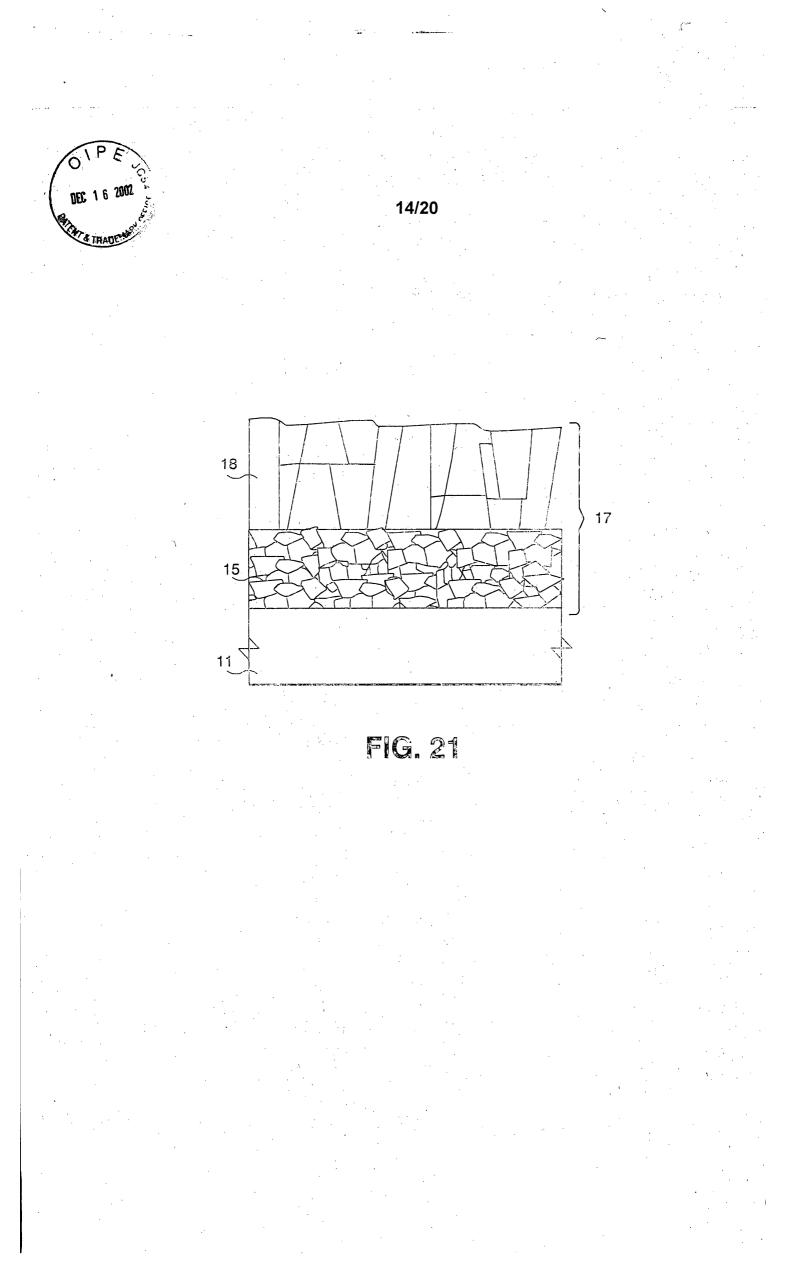
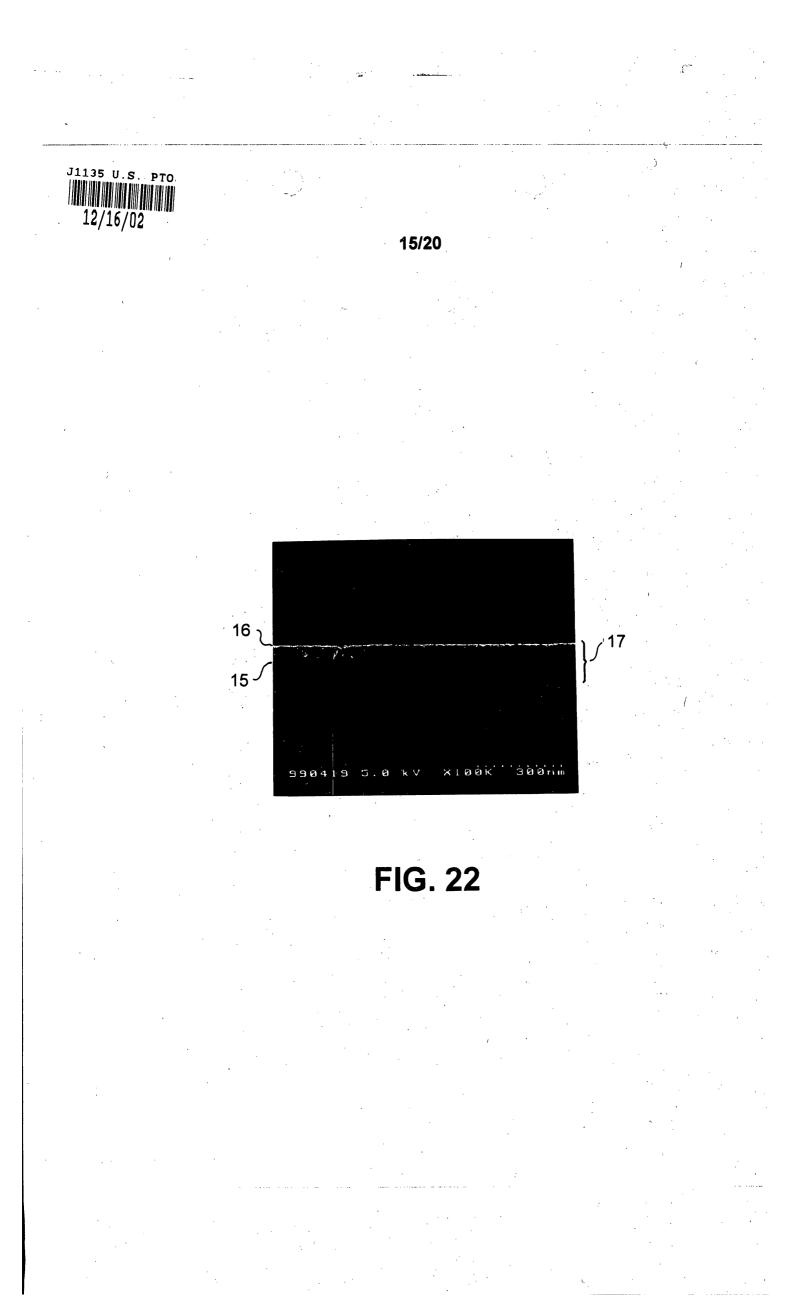
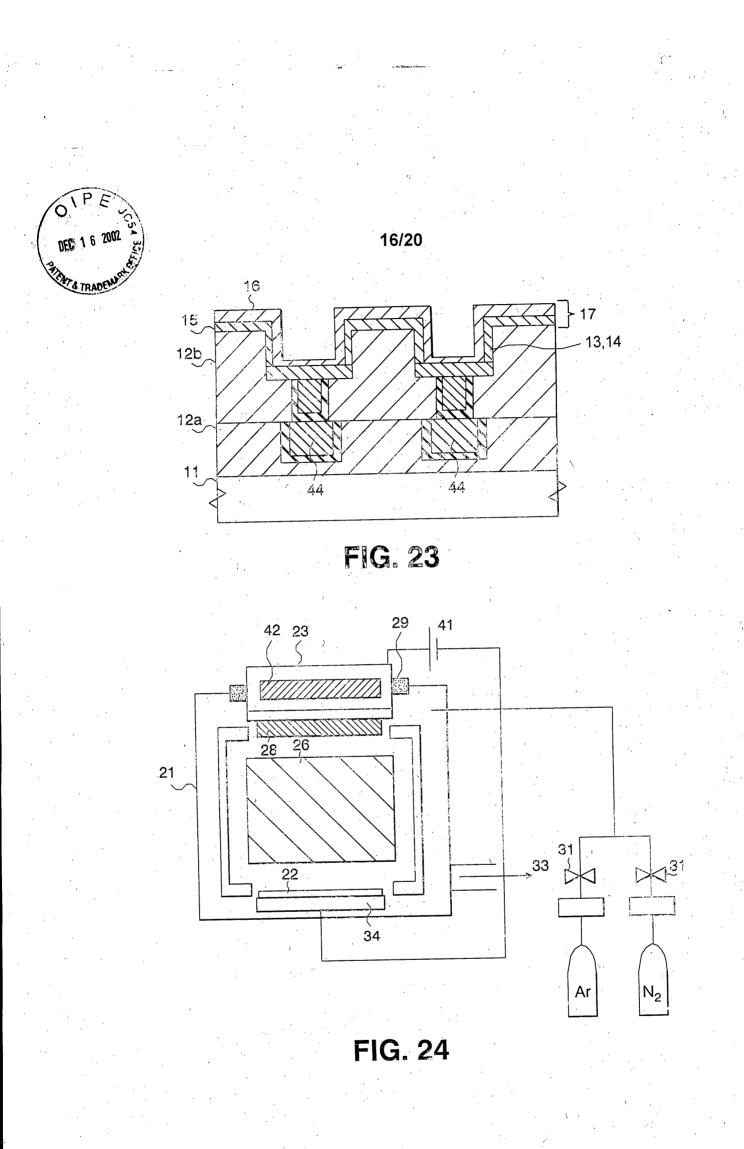


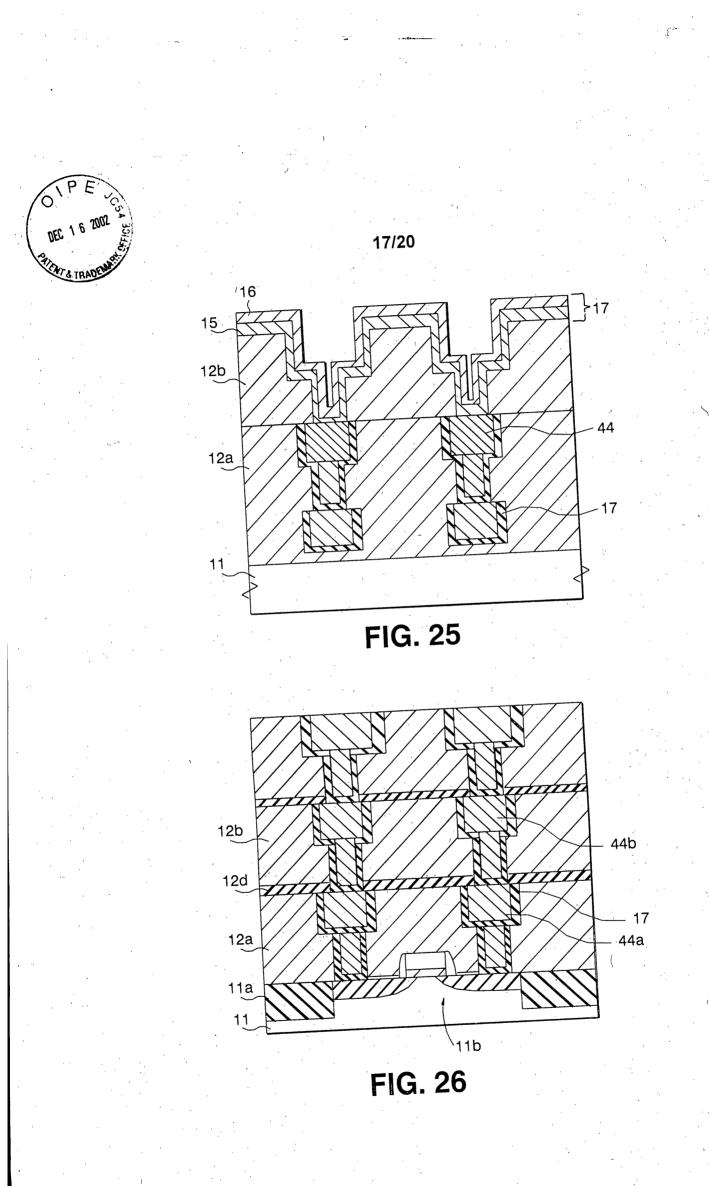
FIG. 20





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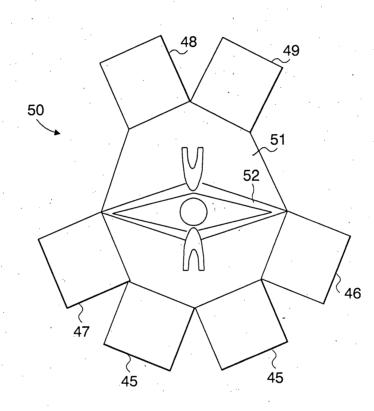
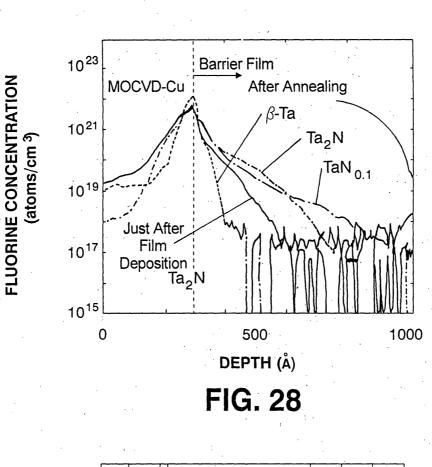


FIG. 27

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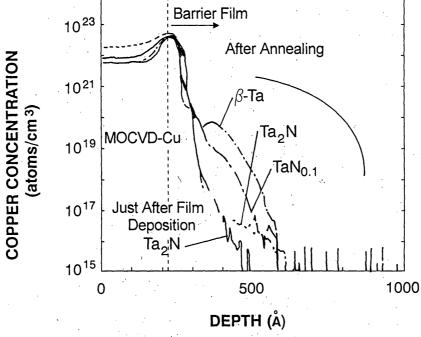


FIG. 29



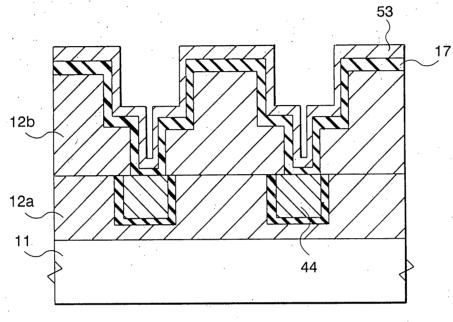


FIG. 30

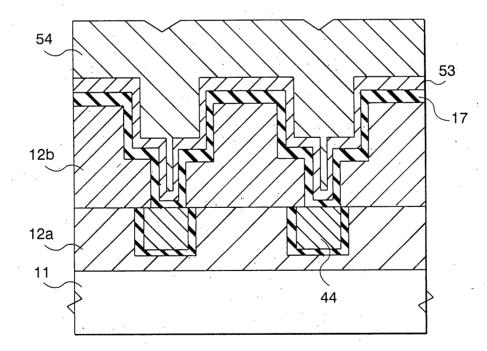


FIG. 31

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To: US Patent & Trademark Office From: Linda Hagemeyer\Office Manager

Refund Section, Accounting Division

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Office of Finance

Fax:	703-308-5077	Pages:	4	
Docket	13715	Date:	January 14, 2003	
Re:	Deposit Account No. 19-	1013 Attn:	Refund Section, O	ffice of Finance
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Attached is another Request for Refund.

Please credit our account in the amount of \$130.00 as soon as possible.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Masayoshi Tagami

Serial No: 09/596,415

June 19, 2000

Filing Date:

Docket No.: 13715

Attention: Refund Section, Accounting Division Office of Finance

REQUEST FOR REFUND

Sir/Madam:

For the reason set forth below, Applicant(s) representatives request that they be refunded \$130.00 by crediting this amount to Deposit Account No. 19-1013. This amount is the official fee for a Petition which was charged to Deposit Account No. 19-1013 on October 30, 2002, Seq. No. 6 (Copy of deposit account attached).

There was no Petition filed in this case, nor was one requested for any reason, therefore, it is respectfully requested that Deposit Account No. 19-1013 be credited in the amount of \$130.00.

Janemeijer Linda Hagemeyer

24366 H 20) Ray : Rugeron 03-31-23

Office Manager

Scully, Scott, Murphy & Presser 400 Garden City Plaza Garden City, New York 11530 (516) 742-4343 Dated: January 14, 2003 osit Account Statement er



PATENT AND **TRADEMARK OFFICE**

Deposit Account Statement

Requested Statement Month: Deposit Account Number: Name: Attention: Address: City: State: Zip:

October 2002 191013 SCULLY, SCOTT, MURPHY & PRESSER DEBORAH SHEEHAN A PROFESSIONAL CORPORATION GARDEN CITY NY 11530-0299

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ANTHONY C. SCOTT (1931-1994) WILLIAM E. MCNULTY (1927-1993)

TELEPHONE: (516) 742-4343 FACSIMILE: (516) 742-4366 E-MAIL: intprop@ssmp.com

January 17, 2003 FEDERAL EXPRESS

US Patent and Trademark Office c/o RTIS 3443 Carlin Spring Road Falls Church, VA 22041

Attention: Toni Hood/Nadine Clark

U.S. Patent Application No.: 09/596,415 Re: Our Docket: 13715

Dear Examiner Clark:

As per our phone conversation of January 16, 2003 you indicated that the twenty (20) sheets of drawings (Figs. 1-31) which we filed on December 16, 2002 with payment of the issue fee were damaged due to irradiation by the US Postal Service.

Therefore, as per your request, we are hereby enclosing a replacement set of drawings via Federal Express to avoid the irradiation process.

Please let us know if there are any further questions.

Sincerely yours Enthony M. Fresco

Anthony N. Fresco

ANF:yd Enclosures

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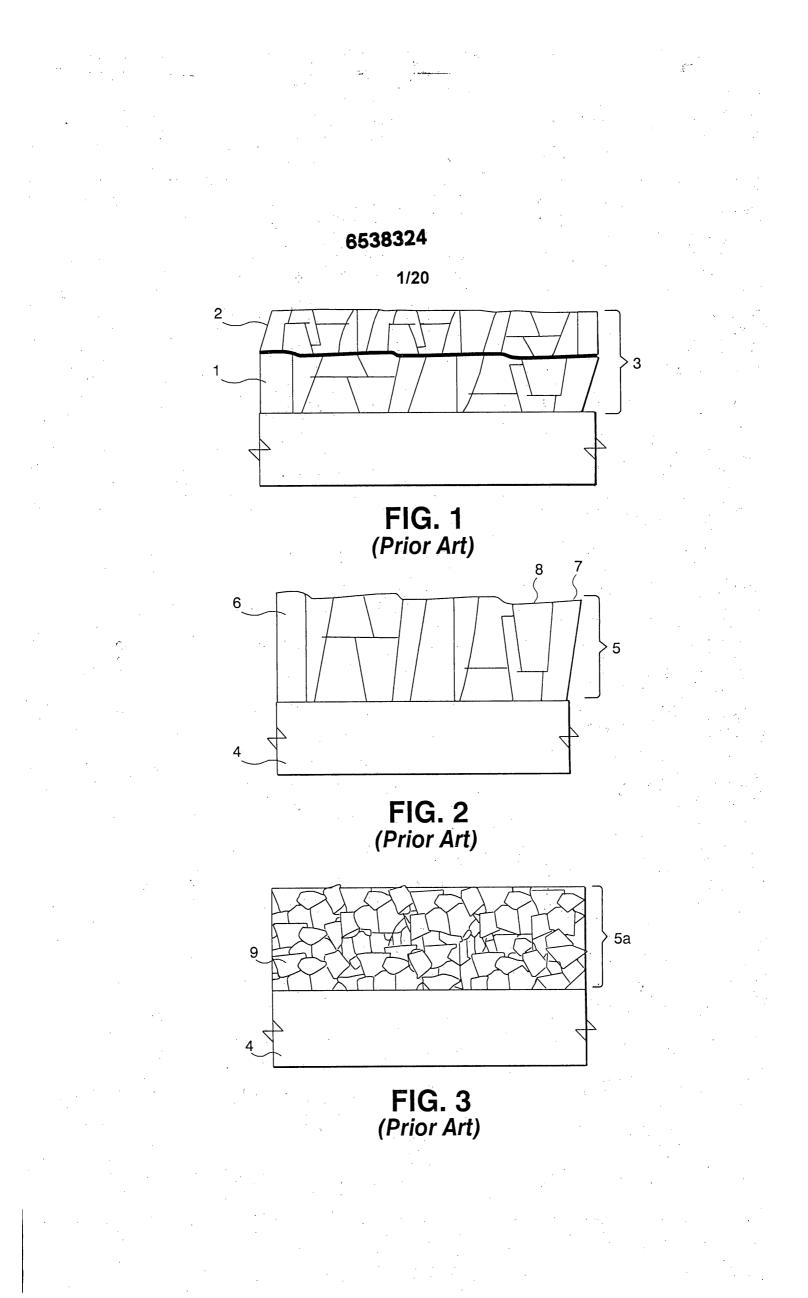
T. DAVID BOMZER PHILIP BRAGINSKY JOHN L. BRECKENRIDGE* MARVIN BRESSLER ERIC P. HALBER® THOMAS SPINELLI ALEXANDER G. VODOVOZOV PATRICIA A. WILCZYNSKI *CO BAR ONLY *D.C. BAR ONLY ANTHONY N. FRESCO LESLIE S. SZIVOS, PH.D. DAVID J. TORRENTE

PATENT AGENTS XIAOCHUN ZHU, PH.D. TECHNICAL CONSULTANT

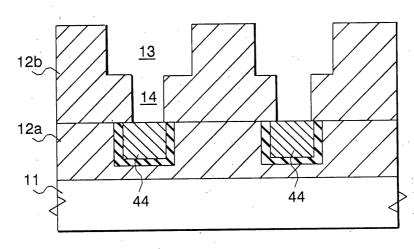
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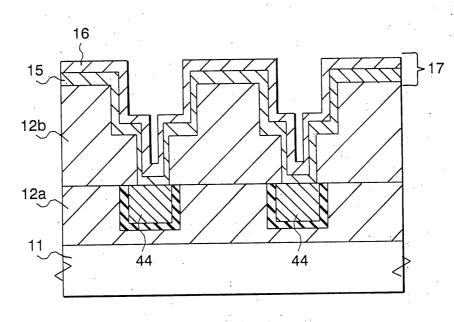


FIG. 4B

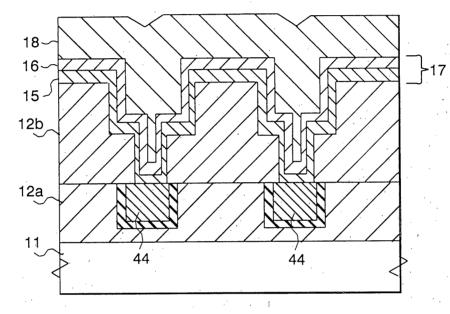


FIG. 4C

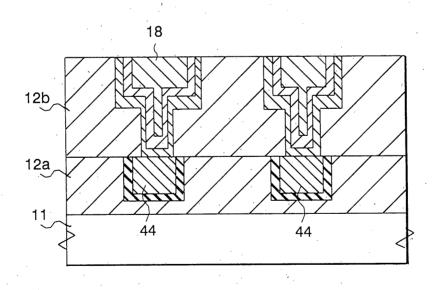
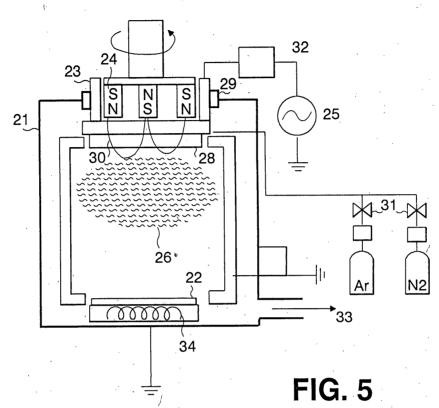
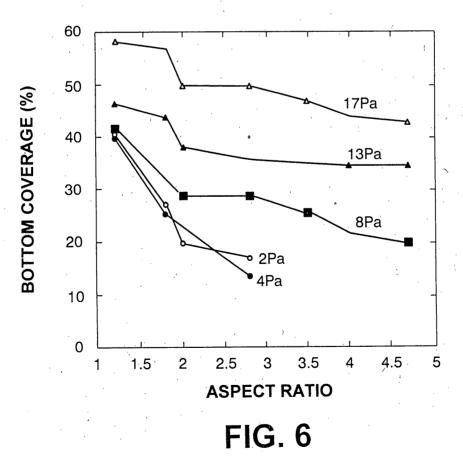
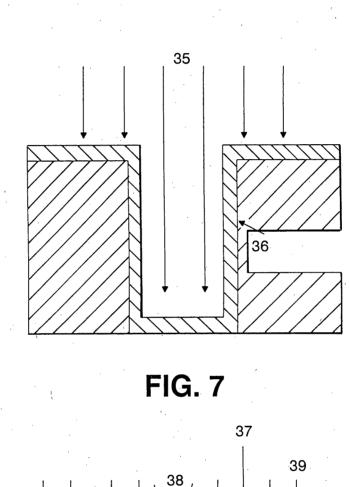


FIG. 4D

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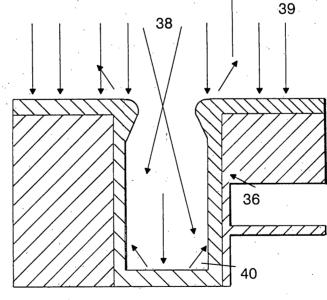
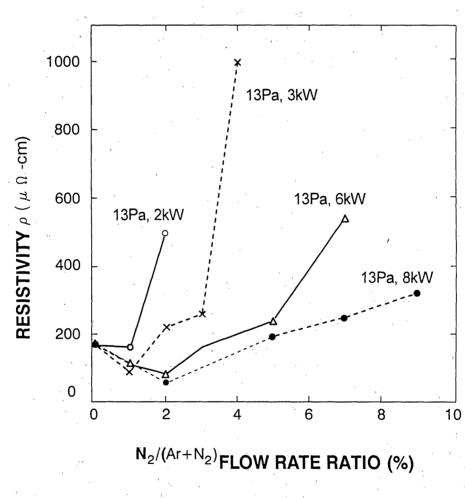
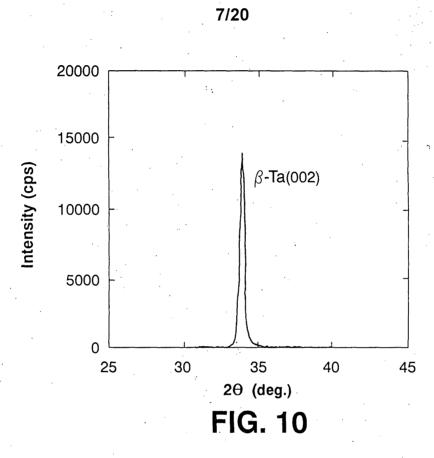
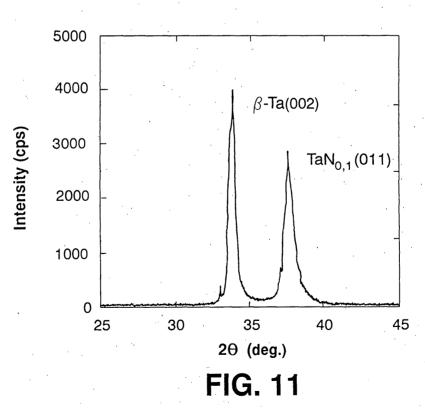


FIG. 8

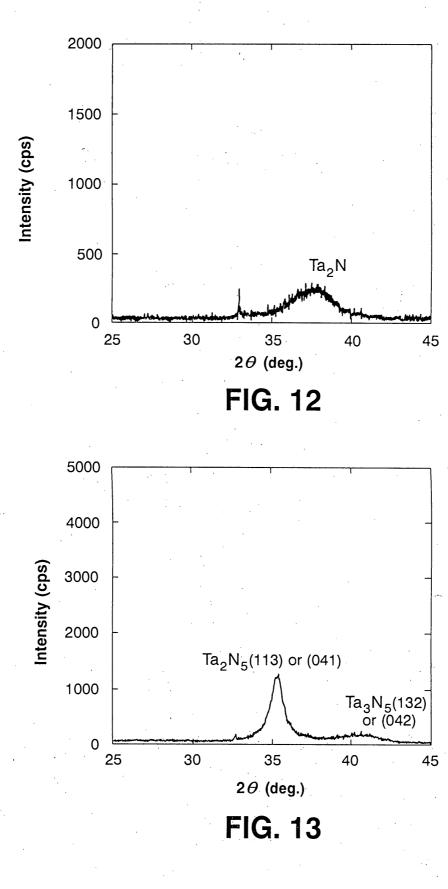




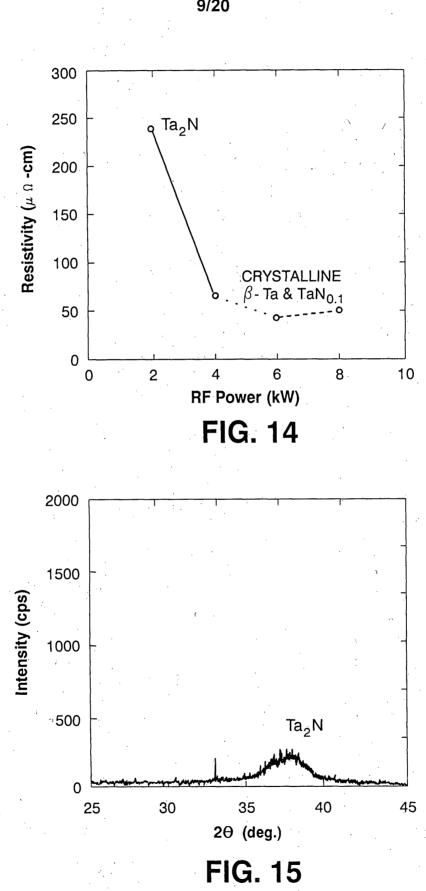


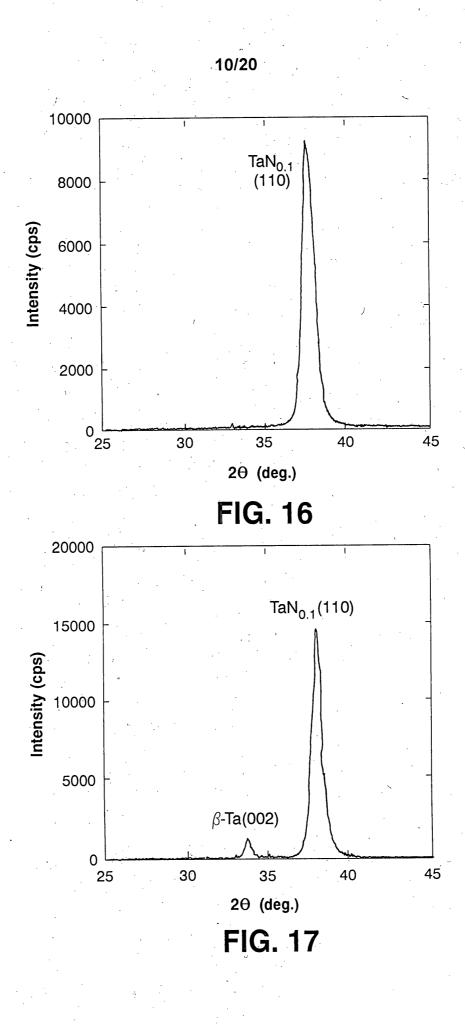


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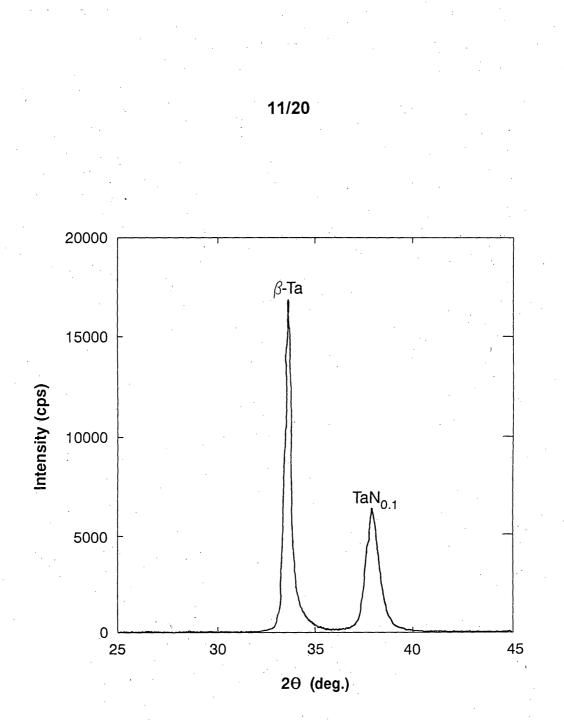


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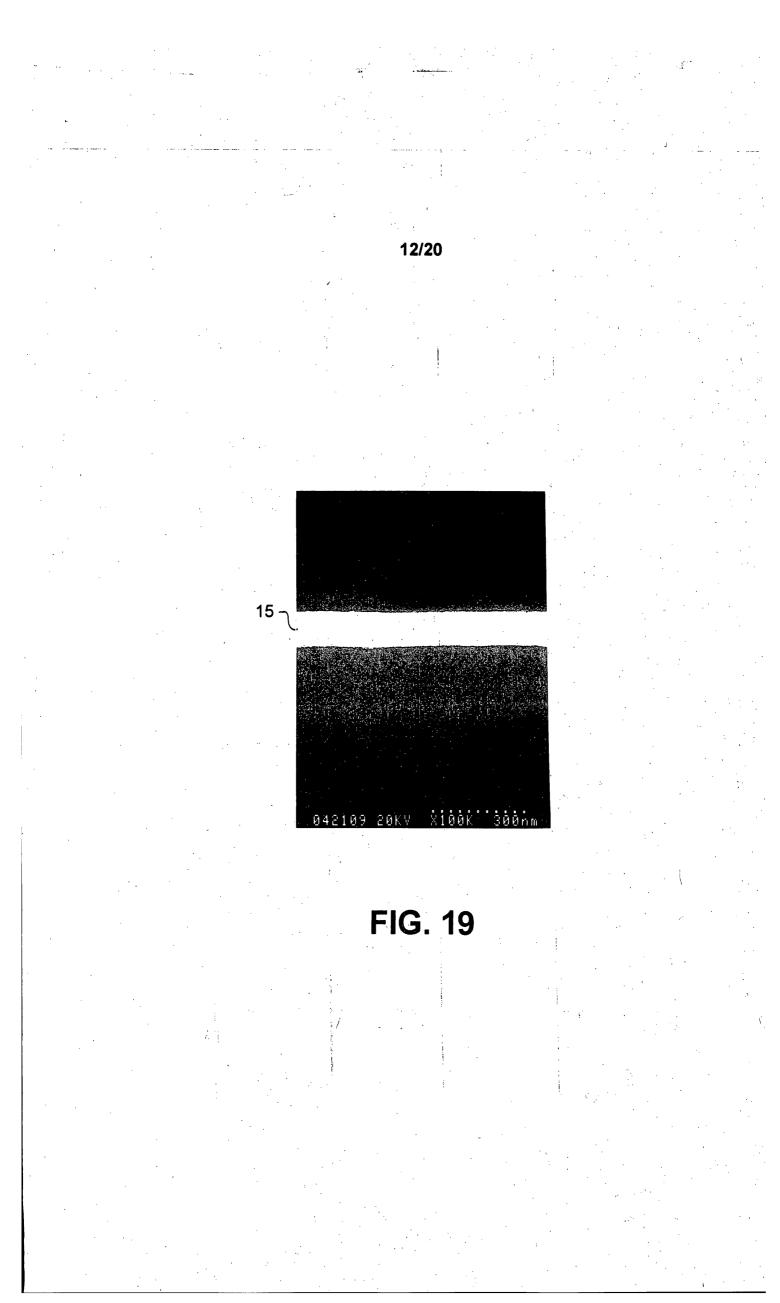


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FIG. 18



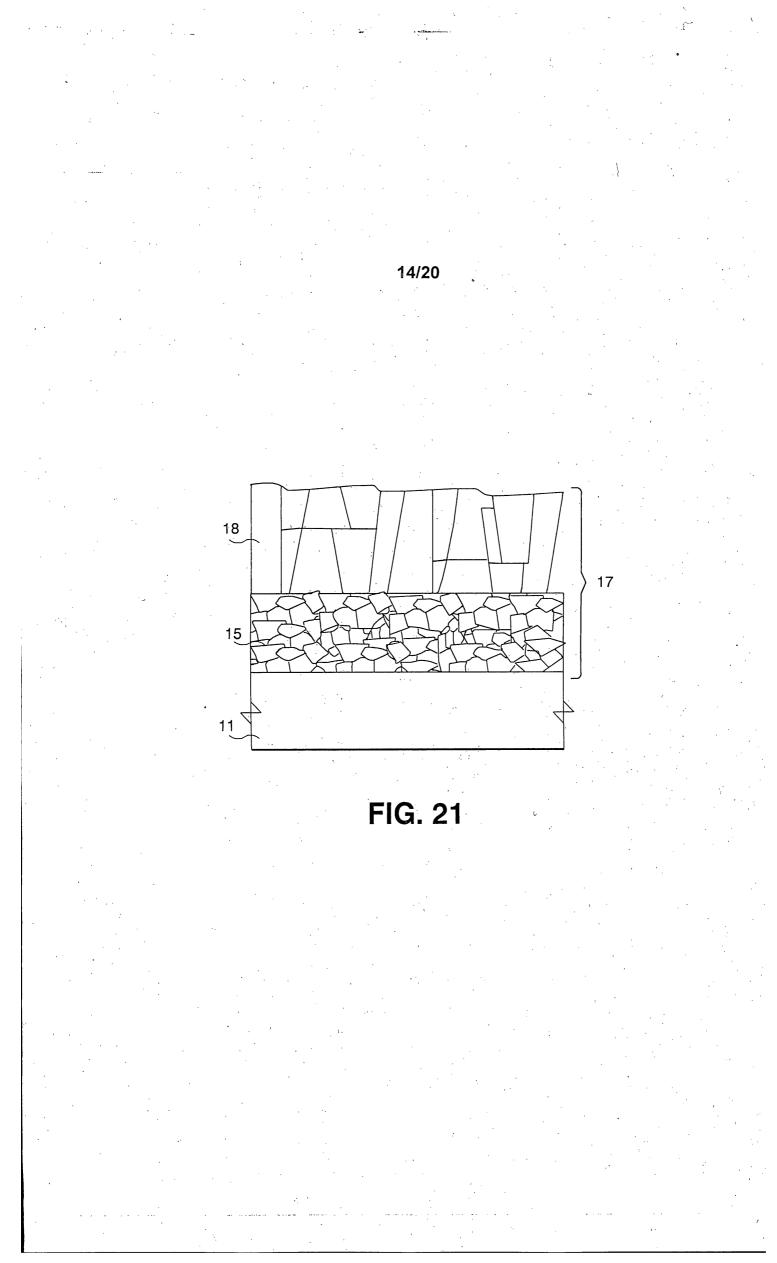
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FIG. 20

Page 314 of 333



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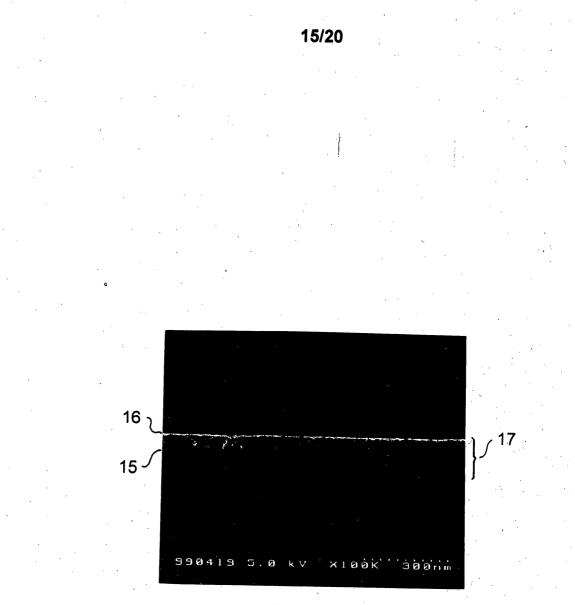


FIG. 22

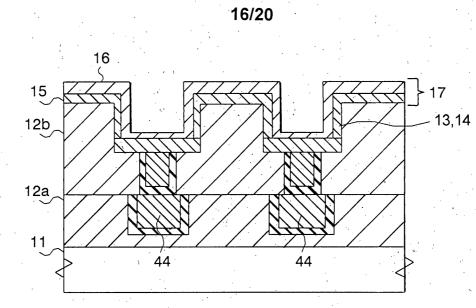
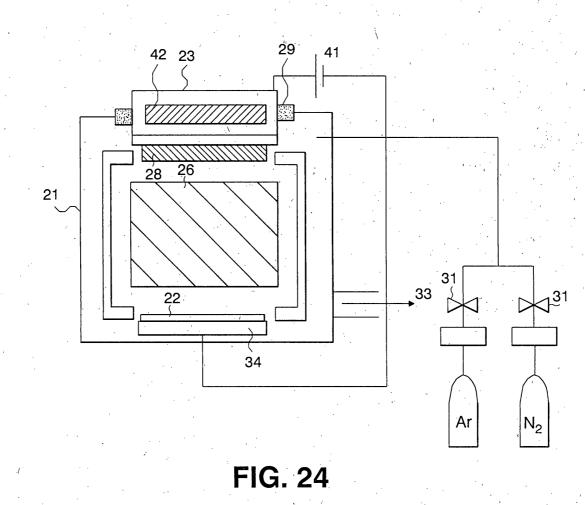
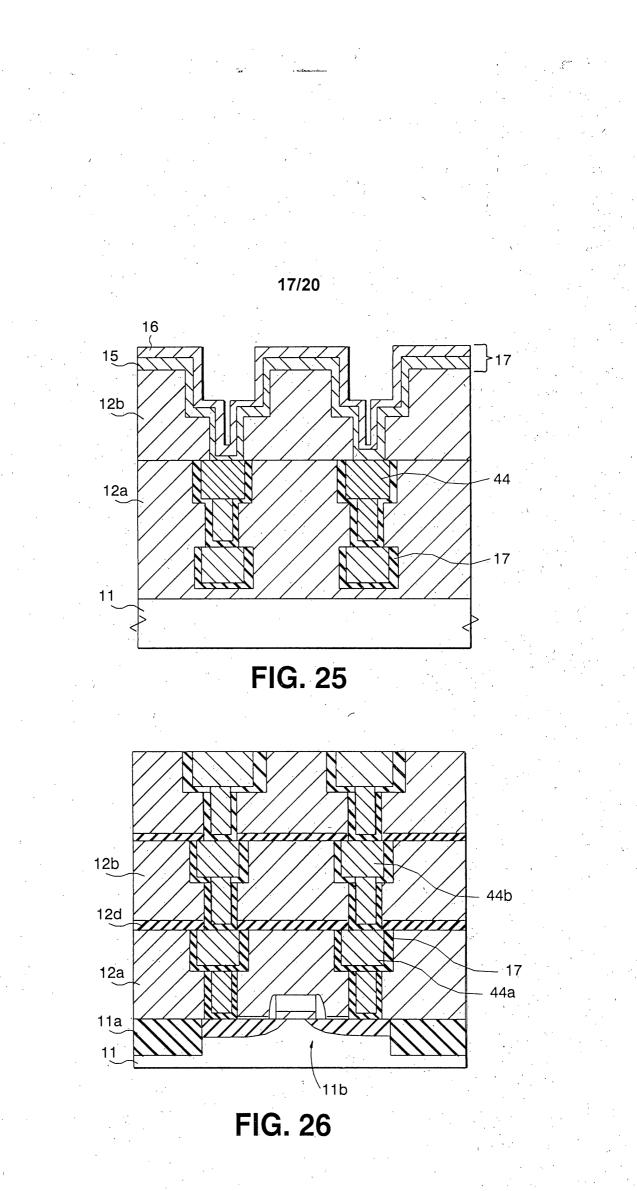


FIG. 23

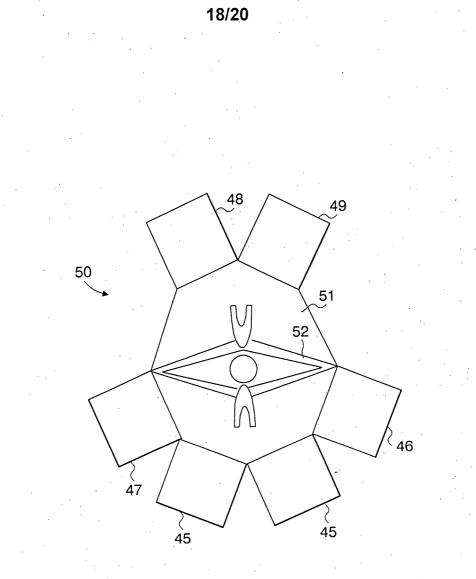


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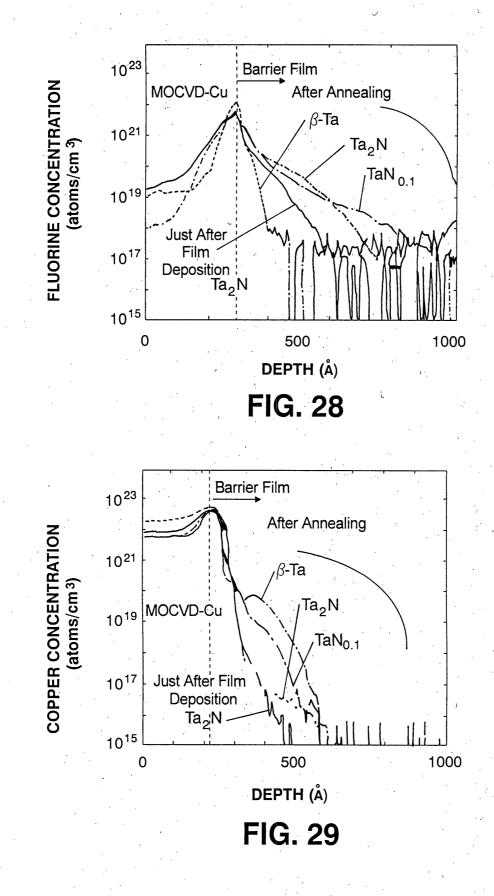
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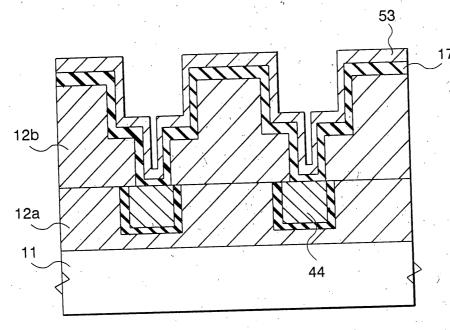


FIG. 30

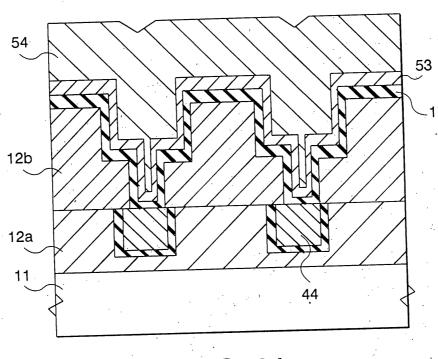


FIG. 31

• .		CLAIMS AS	S FILED - (Columr			mn 2)	SMALL E	NTITY		5964 отнея	THAN
тс	DTAL CLAIMS	· · ·	}	<u></u>			RATE	FEE	OR 1	SMALL RATE	FEE
FC	R		NUMBER	FILED	NUMB	ER EXTRA	BASIC FE	E 370.00	OR	BASIC FEE	
ΓC	TAL CHARGEA	ABLE CLAIMS	mi	nus 20=	*	·	X\$ 9=		OR	X\$18=	
٩C		LAIMS	'n	inus 3 =	*		X42=		OR	X84=	
10	ILTIPLE DEPEN	IDENT CLAIM PI	RESENT				+140=	· · ·	1	+280=	
lf	the difference	in column 1 is	less than z	ero, ente	er "0" in c	olumn 2	TOTAL		OR	TOTAL	
•	С	LAIMS AS A	MENDE) - PAF	RT II	· · ·	TOTAL	L	UR	OTHER	THAN
		(Column 1)		(Colu	imn 2) ⁻	(Column 3)	SMALL	ENTITY	OR	SMALL	4
		CLAIMS REMAINING AFTER AMENDMENT		NUI PREV	HEST MBER IOUSLY DFOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE		RATE	ADD TION FEE
	Total	· 36	Minus	**	36	=	X\$ 9=		OR	X\$18=	• •
	Independent				<u>C</u>		X42=		OR	X84=	
	FINST PRESE	NTATION OF MU		PENDEN			+140=		OR	+280=	
							TOTAL			TOTAL	
		(Column 1)		(Colu	imn 2)	(Column 3)	ADDIT. FEE	L		ADDIT. FEE	
		CLAIMS REMAINING AFTER AMENDMENT		NUN PREV	HEST MBER IOUSLY DFOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE		RATE	ADDI TIONA FEE
	Total	× 34	Minus	**	34	=	X\$ 9=		OR	X\$18=	
	Independent	* 6	Minus	***	6	=	X42=				ì
	FIRST PRESE	NTATION OF MU	JLTIPLE DE	PENDEN	T CLAIM		•		OR		
	•	. <i>1</i> .	· · ·				+140= TOTAL		OR	+280= TOTAL	
							ADDIT. FEE		OR	ADDIT. FEE	
-		(Column 1) CLAIMS			IMN 2) HEST	(Column 3)			·		
		REMAINING AFTER AMENDMENT		PREV	UBER IOUSLY DFOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE	••	RATE	ADD TION/ FEE
	Total	* 10	Minus	** 3	6	=	X\$ 9=		OR	X\$18=	
	Independent FIRST PRESE	NTATION OF MU					X42=		QR	X84=	
							+140=	· · .	OR	+280=	
* **	f the "Highest Nu If the "Highest Nu	mn 1 is less thân th mber Previously Pa mber Previously Pa iber Previously Pai	ud For" IN TH aid For" IN TH	IS SPACE	is less that is less that	n 20, enter "20." n 3, enter "3."	TOTAL ADDIT. FEE	propriate boy	OR	TOTAL ADDIT. FEE	

• .	PATENT AP			TERMINATIO er 29, 1999	ON RECORI	D	596415		ocket Num	ber
	С		FILED -	PART I (Colui	mn 2)	SMALL TYPE		OR	OTHER SMALL I	
FΟ	R	NUMBE	R FILED	NUMBER E	EXTRA	RATE	FEE		RATE	FEE
BAS							345.00	OR		690.00
τo	TAL CLAIMS	36	minus 2	20= *	Ģ	X\$ 9=		OR	X\$18=	288.00
ND	EPENDENT CLAII	vis G	minus	3 = * 🥳	3	X39=	14 .	OR	X78=	23400
NUI	LTIPLE DEPENDE	NT CLAIM PF	RESENT			+130=			+260=	
.lf f	the difference in	column 1 is l	ess than ze	ro, enter "0" in c	olumn 2	TOTAL		OR OR	TOTAL	121900
	CLA	NMS AS A	MENDED	- PART II		TOTAL		JOH.	OTHER	
	-	Column 1)		(Column 2)	(Column 3)	SMALL	ENTITY	OR	SMALL	
ENIA		CLAIMS REMAINING AFTER MENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE		RATE	ADDI TIONA FEE
	Total +		Minus	**	=	X\$ 9=	•	OR	X\$18=	
AMENUMEN	Independent +		Minus	***	=	X39=		OR	X78=	
	FIRST PRESENT	ATION OF MU	JLTIPLE DEF	PENDENT CLAIM	I	+130=		OR	+260=	
				· · ·		TOTAL		OR	TOTAL	
	•	(Column 1)		(Column 2)	(Column 3)	ADDIT. FEE			ADDIT. FEE	l:
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE		RATE	ADDI TIONA FEE
NDMENI	Total +		Minus	**	=	X\$ 9=		OR	X\$18=	
AME	Independent *		Minus	***	=	X39=		OR	X78=	
	FIRST PRESENT	ATION OF MU	JLTIPLE DEF	PENDENT CLAIM		+130=		OR	+260=	
	· . · ·		· · · ·			L		OR	TOTAL	
		(Column 1)		(Column 2)	(Column 3)	ADDIT FEE		1 - · · ·	ADDIT. FEE	
ENT C		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDI- TIONAL FEE		RATE	ADDI TIONA FEE
MON	Total *		Minus	**	=	X\$ 9=	[·	OR	X\$18=	
AMENDMENT	Independent *		Minus	***	=	X39=		OR	X78=	
-	FIRST PRESEN	TATION OF MI	ULTIPLE DEI	PENDENT CLAIM		+130=		1	+260=	
*** ***	If the entry in column If the "Highest Numb If the "Highest Numb The "Highest Numbe	er Previously Pa per Previously P	aid For" IN THI aid For" IN TH	S SPACE is less that IS SPACE is less that	an 20, enter "20." an 3, enter "3."	TOTAL ADDIT. FEE		OR OR ox in co	TOTAL ADDIT. FEE	
	Л РТО-875 12/99)		•		F	Patent and Trad	emark Office, L	J.S. DE	PARTMENT O *U.S. GPO: 200	

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Thomson Innovation Patent Export, 2015-05-22 16:08:45 -0400

Table of Contents

1. US6538324B1 Multi-layered wiring layer and method of fabricating the same

Family 1/1

3 record(s) per family, collapsed by 2 record(s)

Record 1/2 US6538324B1 Multi-layered wiring layer and method of fabricating the same

Publication Number:

US6538324B1 20030325

Title:

Multi-layered wiring layer and method of fabricating the same

Title - DWPI:

Diffusion barrier film for semiconductor integrated circuit, comprises of laminated nitrogencontaining crystalline metal film, amorphous metal nitride film, and same kind of metal atoms

Priority Number:

JP1999214110A

Priority Date:

1999-06-24

Application Number:

US2000596415A

Application Date:

2000-06-19

Publication Date:

2003-03-25

IPC Class Table:

IPC	Section	Class	Subclass	Class Group	Subgroup
H01L002128	н	H01	H01L	H01L0021	H01L002128
H01L0021285	н	H01	H01L	H01L0021	H01L0021285
H01L00213205	н	H01	H01L	H01L0021	H01L00213205
H01L0021768	н	H01	H01L	H01L0021	H01L0021768
H01L002352	н	H01	H01L	H01L0023	H01L002352
H01L0023522	н	H01	H01L	H01L0023	H01L0023522

H01L0023	532 H	H01	H01L	H01L0023	H01L0023532
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IPC Class Table - DWPI:

IPC - DWPI	Section - DWPI	Class - DWPI	Subclass - DWPI	Class Group - DWPI	Subgroup - DWPI
H01L0021768	Н	H01	H01L	H01L0021	H01L0021768
H01L002348	Н	H01	H01L	H01L0023	H01L002348
H01L002128	н	H01	H01L	H01L0021	H01L002128
H01L00213205	Н	H01	H01L	H01L0021	H01L00213205
H01L002352	Н	H01	H01L	H01L0023	H01L002352

Assignee/Applicant:

NEC Corporation, Tokyo, JP

JP F Terms:

JP FI Codes:

Assignee - Original:

NEC Corporation

Any CPC Table:

Туре	Invention	Additional	Version	Office	
Current	H01L 21/76846	H01L 2924/0002	20130101	EP	
Current	H01L 21/2855	H01L 2924/3011	20130101	EP	
Current	H01L 21/76862		20130101	EP	
Current	H01L 21/76865		20130101	EP	
Current	H01L 23/5226		20130101	EP	
Current	H01L 23/53238		20130101	EP	

ECLA:

H01L0021768C3B4 | H01L0021285B4F | H01L0021768C3D4B | H01L0021768C3D6 | H01L0023522E | H01L0023532M1C4 | T01L092430110

Abstract:

There is provided a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate. The barrier film has a multi-layered structure of first and second films wherein the first film is composed of crystalline metal containing nitrogen therein, and the second film is composed of amorphous metal nitride. The barrier film is constituted of common metal atomic species. The barrier film prevents copper diffusion from a copper wiring layer into a semiconductor device, and has sufficient adhesion characteristic to both a copper film and an interlayer insulating film.

Language of Publication:

EN

INPADOC Legal Status Table:

Gazette Date	Code	INPADOC Legal Status Impact
2015-01-28	AS	, 1
	GODO KAISHA IP BRIDGE 1, JAPAN RATION; REEL/FRAME:034834/0806 2	ASSIGNMENT OF ASSIGNORS INTEREST; 014-11-01
2014-08-27	FPAY	+
Description: FEE PAYMEN	π	
2010-08-26	FPAY	+
Description: FEE PAYMEN	Π	
2006-09-01	FPAY	+
Description: FEE PAYMEN	п	
2000-06-19	AS	4.

Post-Issuance (US):

Reassignment (US) Table:

and general	Assignor	Date Signed	Reel/Frame	Date	
GODO KAISHA IP BRIDGE 1,TOKYO,JP	NEC CORPORATION	2014-11-01	034834/0806	2015-01-28	
Conveyance: ASSIGNMENT	OF ASSIGNORS INTEREST	(SEE DOCUMENT FO	OR DETAILS).		
Corresponent: CPA GLOBA	L LIMITED LIBERATION HOUS	SE CASTLE STREET	ST HELIER, JE1 1BL	JERSEY	
NEC	TAGAMI, MASAYOSHI	2000-06-09	010911/0893	2000-06-19	
CORPORATION, TOKYO, JP	HAYASHI, YOSHIHIRO	2000-06-09			

Maintenance Status (US):

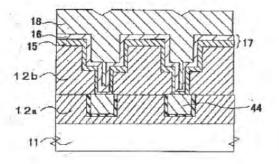
Litigation (US):

Opposition (EP):

License (EP):

EPO Procedural Status:

Front Page Drawing:



Record 2/2 JP03562628B2 A diffusion barrier film|membrane, a multilayer interconnection structure, and a method of producing the same

Publication Number:

JP03562628B2 20040908 JP2001007204A 20010112

Title:

A diffusion barrier film|membrane, a multilayer interconnection structure, and a method of producing the same

Title - DWPI:

Diffusion barrier film for semiconductor integrated circuit, comprises of laminated nitrogencontaining crystalline metal film, amorphous metal nitride film, and same kind of metal atoms **Priority Number**:

JP1999214110A
Priority Date:
1999-06-24
Application Number:
JP1999214110A
Application Date:
1999-06-24
Publication Date:
2004-09-08
IPC Class Table:

IPC	Section	Class	Subclass	Class Group	Subgroup
H01L002128	н	H01	H01L	H01L0021	H01L002128
H01L0021285	Н	H01	H01L	H01L0021	H01L0021285
H01L00213205	Н	H01	H01L	H01L0021	H01L00213205
H01L0021768	н	H01	H01L	H01L0021	H01L0021768
H01L002352	н	H01	H01L	H01L0023	H01L002352
H01L0023522	н	H01	H01L	H01L0023	H01L0023522
H01L0023532	н	H01	H01L	H01L0023	H01L0023532

IPC Class Table - DWPI:

			DWPI	
i i	H01	H01L	H01L0021	H01L0021768
		H01	H01 H01L	

H01L002348	Н	H01	H01L	H01L0023	H01L002348
H01L002128	Н	H01	H01L	H01L0021	H01L002128
H01L00213205	н	H01	H01L	H01L0021	H01L00213205
H01L002352	Н	H01	H01L	H01L0023	H01L002352

Assignee/Applicant:

JP F Terms:

| 4M104BB04 | 4M104BB29 | 4M104BB30 | 4M104BB31 | 4M104BB32 | 4M104BB33 | 4M104BB37 | 4M104CC01 | 4M104DD16 | 4M104DD17 | 4M104DD23 | 4M104DD37 | 4M104DD42 | 4M104DD43 | 4M104DD52 | 4M104DD53 | 4M104FF18 | 4M104FF22 | 4M104HH08 | 4M104HH13 | 4M104HH20 | 5F033HH11 | 5F033HH32 | 5F033HH33 | 5F033HH34 | 5F033JJ11 | 5F033JJ32 | 5F033JJ33 | 5F033JJ34 | 5F033KK11 | 5F033KK32 | 5F033KK33 | 5F033KK34 | 5F033LL06 | 5F033MM01 | 5F033MM02 | 5F033MM12 | 5F033MM13 | 5F033NN06 | 5F033NN07 | 5F033PP06 | 5F033PP15 | 5F033PP16 | 5F033PP27 | 5F033PP28 | 5F033PP33 | 5F033QQ00 | 5F033QQ12 | 5F033QQ48 | 5F033QQ92 | 5F033QQ94 | 5F033QQ98 | 5F033RR04 | 5F033RR06 | 5F033TT02 | 5F033WW02 | 5F033WW04 | 5F033WW05 | 5F033WW07 | 5F033WW10 | 5F033XX02 | 5F033XX13 | 5F033XX20 | 5F033XX28 | JP FI Codes:

| H01L002128-301R | H01L002188-M | H01L002188-R | H01L002190-A Assignee - Original:

Туре	Invention	Additional	Version	Office	
Current	H01L 21/76846	H01L 2924/0002	20130101	EP	
Current	H01L 21/2855	H01L 2924/3011	20130101	EP	
Current	H01L 21/76862		20130101	EP	
Current	H01L 21/76865		20130101	EP	
Current	H01L 23/5226		20130101	EP	
Current	H01L 23/53238		20130101	EP	

Any CPC Table:

ECLA:

H01L0021768C3B4 | H01L0021285B4F | H01L0021768C3D4B | H01L0021768C3D6 | H01L0023522E | H01L0023532M1C4 | T01L092430110 Abstract:

Language of Publication: JA INPADOC Legal Status Table:

Gazette Date	Code	INPADOC Legal Status Impact

2015-01-15		R350	-
Description: W	RITTEN NOTIFICATION C	OF REGISTRATION OF TRANSFER JAPA	ANESE INTERMEDIATE CODE: R350
2015-01-06		S111	-
Description: RE R313113	EQUEST FOR CHANGE C	OF OWNERSHIP OR PART OF OWNERSH	IIP JAPANESE INTERMEDIATE CODE:
2012-06-05		FPAY	+
Description: RE	ENEWAL FEE PAYMENT	(PRS DATE IS RENEWAL DATE OF DATA	BASE) PAYMENT UNTIL: 20130611
2012-05-31		FPAY	+
Description: RE	ENEWAL FEE PAYMENT	(PRS DATE IS RENEWAL DATE OF DATA	BASE) PAYMENT UNTIL: 20120611
2011-10-18		FPAY	+
Description: RE	ENEWAL FEE PAYMENT	(PRS DATE IS RENEWAL DATE OF DATA	BASE) PAYMENT UNTIL: 20120611
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2010-05-27		FPAY	+
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2004-06-11		R150	+
Description: CE		(=GRANT) OR REGISTRATION OF UTILIT	TY MODEL JAPANESE

2004-06-10	A61	
Description: FIRST PAYM A61 2004-05-26	IENT OF ANNUAL FEES (DURING GR/	ANT PROCEDURE) JAPANESE INTERMEDIATE COD
2004-05-14	A01	+
	ECISION TO GRANT A PATENT OR TO TE CODE: A01 2004-05-13	O GRANT A REGISTRATION (UTILITY MODEL)

Post-Issuance (US):

Reassignment (US) Table:

Maintenance Status (US):

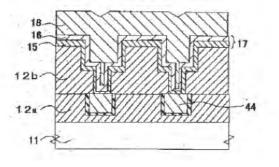
Litigation (US):

Opposition (EP):

License (EP):

EPO Procedural Status:

Front Page Drawing:





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USPTO Maintenance Report

Patent Bibliogr	raphic Data		05/22/2015 04:06 PM		
Patent Number:	6538324		Application Number:	09596415	
Issue Date:	03/25/2003		Filing Date:	06/19/2000	
Title:	MULTI-LAYERED WIRING LAYER AND METHOD OF FABRICATING THE SAME				
Status:	4th, 8th and 12th	n year fees paid		Entity:	LARGE
Window Opens:	N/A	Surcharge Date:	N/A	Expiration:	N/A
Fee Amt Due:	Window not open	Surchg Amt Due:	Window not open	Total Amt Due:	Window not open
Fee Code:					
Surcharge Fee Code:					
Most recent events (up to 7):	08/27/2014 08/26/2010 09/01/2006 09/24/2003 09/24/2003	Payment of Maintenance Fee, 12th Year, Large Entity. Payment of Maintenance Fee, 8th Year, Large Entity. Payment of Maintenance Fee, 4th Year, Large Entity. Payor Number Assigned. Payer Number De-assigned. End of Maintenance History			
Address for fee purposes:	CPA GLOBL LIMITED 2318 Mill Road 12th Floor ALEXANDRIA VA 22314				