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A METHOD FOR THE ANISOTROPIC ETCHING OF METAL FILMS IN THE FABRICATION OF INTERCONNECTS

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to the field of fabricating semiconductor devices, and more particularly to anisotropically etching metal films formed on a semiconductor substrate of an integrated circuit for the fabrication of interconnects.

(2) Prior Art

In the manufacture of integrated circuits, it is often desired to etch certain areas of a metal film deposited on a semiconductor substrate to form metal interconnects between semiconductor devices. It is also desired to form metal interconnects having high aspect ratios for increasing the performance characteristics of the interconnects and for maximizing the device density of the integrated circuit. In the prior art, this has been accomplished through reactive ion etching of aluminum films wherein the ion-assisted etch process produces an anisotropic etch of the aluminum film to obtain the well-defined, high aspect ratios currently required in many of todays applications.

However, due to the increased speed and current density requirements for devices reaching submicron dimensions, the use of aluminum interconnects have become increasingly marginal. This is because the relatively high resistivity of aluminum as a metal, as seen in Table I shown below, hinders the performance and reliability of interconnects made from aluminum. This problem is particularly acute in current ultra-large scale integration (ULSI) devices which have relatively high aspect ratios of 2-3:1 or more. In addition, the present method for etching aluminum

interconnects also involves several drawbacks, including the formation of a native oxide on the aluminum film that is difficult to remove, the use of chlorine-based gasses that are either carcinogenic or highly toxic, and the formation of reactive compounds that degrade the pumping fluids used in the etch process.

TABLE I

RESISTIVITY OF METALS DEISIREABLE FOR USE IN INTERCONNECTS

	(in μΩ-cm)
Silver	1.6
Copper	1.7
Gold	2.4
Aluminum	2.65

Due to the marginal performance and reliability of aluminum interconnects, some prior art methods have attempted to use copper instead of aluminum films since copper films provide a substantially lower resistivity and higher electromigration resistance. However, several problems in the formation of copper interconnects have rendered the prior art use of copper ineffective for interconnect applications. One of the problems with copper has been the difficulty in patterning the copper film. Although this problem was somewhat resolved through the use of selective deposition techniques, i.e. selective CVD or electrolysis plating, such techniques cannot be used in production because the presence of small defects or particulate contamination results in the loss of selectivity or the growth of large precipitates. For this reason, integrated circuit manufacturers have

been trying to develop etching techniques for copper films that result in highly anisotropic and very selective etches.

Recently, it has been found that the anisotropic etching of copper using a chlorine-based gas chemistry in a reactive ion etch process can be achieved at submicron dimensions using elevated temperatures, i.e. around 250 to 300 ºC. Although the anisotropic etching of copper is a major break through, the high temperature requirement poses severe difficulties for plasma etch equipment manufacturers as well as process engineers in trying to develop a manufacturable etcher and process. This is because the volatile compound, copper chloride, produced in the high temperature etch process condenses on cold surfaces, thereby creating the problem of copper chloride deposition in the vacuum lines, in the pumps and even on the unheated walls of the etch chamber. In addition, the high temperature requirement further prevents the use of a suitable masking material since most masks cannot withstand temperatures above approximately 120ºC.

Although the prior art methods for etching interconnects have found some success with the anisotropic etching of aluminum and copper, it is widely recognized that a method which permits the anisotropic etching of other highly conductive metals such as silver, gold and molybdenum would also be of great importance and utility.

Accordingly, it is an object of the present invention to provide a method for anisotropically etching a variety of metal films to obtain metal interconnects having very high aspect ratios and minimal undercutting.

It is a further object of the present invention to provide a method for anisotropically etching highly conductive metal films to form ULSI interconnects having a very low resistivity and high electromigration

resistance in order to obtain ULSI interconnects that meet the increased speed and current density requirements.

It is another object of the invention to provide a method for anisotropically etching silver, copper, gold, aluminum and molybdenum films at low temperatures for interconnect applications.

SUMMARY OF THE INVENTION

The present invention discloses a method for anisotropically etching metal interconnects, especially ULSI interconnects, having high aspect ratios. A metal film is first deposited on the appropriate layer of a semiconductor substrate by techniques well-known in the art. A mask layer is deposited over the metal film with openings defined in the mask layer for patterning of the metal film.

Ions are then driven into an exposed region of the metal film to anisotropically form a converted layer of the metal film comprising compounds of the metal. The introduction of the ions into the metal film can be performed by conventional methods, such as through the use of a reactive ion etch system or an ion implantation system, or by any other method which anisotropically forms the converted layer.

If a reactive ion etch system is utilized, the gasses used in the system are chosen in accordance with the metal compounds to be formed rather than a volatile species used for etching. If an ion implanter is utilized, an implant barrier may be formed beneath the metal film in order to prevent the ions from being implanted into the underlying layers, which barrier may also be used as a diffusion barrier. Furthermore, a thermal treatment step may be implemented after ion implantation so as to ensure that the ions have thoroughly diffused into the exposed region and have completely reacted with the metal atoms to form the metal compounds.

The mask layer is then removed by conventional means to leave behind the metal film having a converted layer of metal compounds. Finally, the metal compounds are selectively removed by a suitable removal means

chosen for its properties in removing the metal compounds without causing significant etching or degradation of the metal film itself.

In this manner, metal interconnects can be formed without directly etching the metal film itself with a volatile species of the metal, thereby avoiding isotropic etching which results in undercutting and further avoiding the problematic high temperature requirement of the prior art methods. In addition, a wide variety of metals can now be utilized in the fabrication of interconnects, especially ULSI interconnects, so as to achieve interconnects having higher electromigration resistance and lower resistivity.

BRIEF DESCRIPTION OF THE DRAWINGS

The objects, features and advantages of the present invention will become apparent from the following detailed description of the preferred embodiment in which:

Figures 1A to 1D are cross-sectional views of a semiconductor substrate with a metal interconnect being formed thereon according to the general method of the present invention.

Figures 2A to 2B are cross-sectional views of a semiconductor substrate with a metal interconnect being formed thereon according to the preferred embodiment of the present invention.

Figures 3A to 3D are cross-sectional views of a semiconductor substrate with a metal interconnect being formed thereon according to an alternate embodiment of the present invention.

Figures 4A and 4B are cross-sectional views of a semiconductor substrate showing the formation of multiple-layer interconnects according to an alternate embodiment of the present invention.

Figures 5A and 5B are cross-sectional views of a semiconductor substrate showing the formation of multiple-layer interconnects according to an alternate embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A method for anisotropically etching metal interconnects is described. In the following description, numerous details such as specific materials, structures, gas mixtures and etching parameters are set forth in order to provide a more complete understanding of the present invention. However, it is understood by those skilled in the art that the present invention can be practiced without these specific details. In other instances, well-known elements, devices, solvents and the like are not set forth in detail in order to avoid unnecessarily obscuring the present invention.

In the fabrication of metal interconnects according to the present invention, as shown in Fig. 1, a metal film 3 is deposited on a silicon dioxide layer 14 of a substrate 1 during the fabrication of a semiconductor device by techniques well-known in the art, such as CVD, sputter deposition or electrolysis deposition. Following the deposition of the metal film 3, a mask layer 4 is formed thereon for patterning the metal film 3 before the formation of the metal compounds to be etched. As shown in Fig. 1, openings are defined in the mask layer 4 using well-known photolithographic methods in order to define an exposed region 6 of the metal film 3 to be etched. The mask layer 4 may take the form of either a photoresist or a hard mask, with the hard mask formed from a material selected from the group of dielectric films, metal films, and tightly bonded metal oxide films. The selection of a suitable material for the mask layer 4 will depend upon the specific process utilized for converting the exposed region 6 and the removal means subsequently used to remove the converted layer 7 as will be described below. If a hard mask is selected for the mask layer 4, a photoresist layer 5 may be formed thereon for patterning of the hard mask.

As shown in Figs. 1A to 1C, the exposed region 6 is anisotropically converted into a converted layer 7 of metal compounds 8 of a type that can be removed without affecting the metal film 3 itself. This conversion step is performed by driving ions 9 into the exposed region 6 of the metal film 3 by techniques well-known in the art, including plasma etching and ion implantation, although other processes which anisotropically form the converted layer 7 may be used as well.

According to the preferred embodiment of the present invention, as shown in Figs. 2A to 2C, the first technique used to anisotropically form the converted layer 7 is based on the same principles as plasma etching wherein an ionic plasma 10 in conjunction with an electric potential is used to drive the ions 9 into the exposed region 6 of the metal film 3. However, unlike the typical plasma etch process, the gasses chosen to form the plasma 10 in the present invention are selected in accordance with the metal compounds 8 to be formed rather than a volatile species used for etching. Hence, the same plasma etch system can be used to both form the compounds 8 within the exposed region and then subsequently remove the converted layer 7 from the metal film 3. In the preferred embodiment, an IPC Branson reactive ion etch system is used to form the converted layer 7. However, as will be obvious to one skilled in the art, the conversion process is not limited to this specific type of system. Any plasma etch system utilizing an electric potential for driving the ions 9 into the metal film 3 will achieve approximately the same results as long as the dosage of driven ions 9 is large enough to convert a substantial portion of the exposed region 6.

In an alternate embodiment of the present invention, as shown in Figs. 3A to 3D, a second technique that can be utilized for conversion of the exposed region 6 is that of ion implantation where a beam of ions 12 is

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focused on the substrate 1 to directionally implant the ions 9 into the metal film 3. In the present invention, a high-current Extrion implanter manufactured by Varian Associates-Extrion is used for implanting the ions 9 into the metal film 3, although the particular ion implantation system used need not be limited to an implanter of this type. Similarly, a medium-current or a high-energy implanter can be used in the present invention depending upon the density of the metal film 3, the type of ions 9 to be implanted and the volume of the metal film 3 to be implanted.

An important consideration in the use of an ion implantation system is the possible use of a implant barrier 11 beneath the metal film 3 for protection of the underlying layers 13 from the ion implants 9. This implant barrier 11 may also be used as a diffusion barrier during the actual conversion of the exposed region 6 to prevent diffusion of the metal film 3 into the underlying layers 13. During ion implantation, the profile of the implants 9 exhibits an implant tail that may reach beyond the metal film 3 and into the underlying layers 13. In order to avoid charging and/or conversion of the underlying layers 13 into an unstable material, the implant barrier 11 is placed beneath the metal film 3 for absorption and neutralization of the ion implants 9. This implant barrier 11 should be formed from a material that is electrically and chemically stable with respect to the ion implants 9. For example, if oxygen ions were implanted into the metal film 3, a silicon oxide layer could be used to receive the implant tail so as to prevent any ionic contamination of the underlying layers 13.

As shown in Figs. 3B and 3C, after the exposed region 6 of the metal film 3 is thoroughly saturated with the ions 9, the mask layer 5 can then be removed by dissolution in a solvent or by other techniques well-known in the art. Following the removal of the mask layer 5, the substrate 1

may be thermally treated or annealed to assist in the reaction of the ions 9 with the metal atoms to form the metal compounds 8. Thermal treatment of the converted layer 7 is normally not required unless the ions 9 are driven into the metal film 3 at a relatively low temperature and the compounds 8 to be formed require more energy than that present. In addition, the mask layer 5 need not always be removed before applying thermal treatment (unless of course a photoresist layer is used) since, in some instances, it can be removed simultaneously with the converted layer 7 itself.

With respect to the use of a thermal treatment step in using the reactive ion etch technique shown in Figs. 2A to 2C, the conversion of the exposed region 6 is performed at elevated temperatures in the plasma etch system so that the formation of the compounds 8 occurs almost simultaneously with the introduction of the ions 9 into the metal film 3. Hence, the preferred embodiment may be practiced without a thermal treatment step unless higher temperatures are required to form the specific compounds 8. With regard to the ion implantation process, ion implantation is sometimes performed at lower temperatures than the typical etch processes. Therefore, thermal treatment may also be used during or after implantation of the ions 9 in order to diffuse the implanted ions 9 throughout the exposed region 6 and ensure thorough conversion of the metal film 3. Obviously, the use and duration of the thermal treatment step is dependent upon several parameters, including the type of ions 9 to be implanted, the type of metal receiving the implant and the volume of metal to be converted.

The metal compounds 8 thus formed are then selectively removed through the use of a removal means which includes but is not limited to the application of a wet or dry solvent, evaporation and water solubilization. It is noted that in practice, it may be desireable to follow the

initial removal of the converted layer 7, as described above, with a short dry etch in order to clean out any remaining residue left from the initial removal process.

As previously mentioned, the removal means must be chosen in accordance with the specific metal compounds 8 formed so that no substantial degradation of the metal film 3 or other structures of the substrate 1 results. If a liquid is used for the removal of the converted layer 7, the resulting etch is anisotropic rather than isotropic as would be the case in the prior art processes. This results from the fact that the converted layer 7 is formed by use of an anisotropic conversion process wherein the metal compounds 8 are selectively formed only within the exposed region 6 by directional driving of the ions 9 into the metal film 3.

In selecting the appropriate ions 9 and removal means to use in anisotropically etching a particular metal film 3, the general approach is to select ions 9 which form compounds 8 of the metal that can be removed from the metal film 3 without substantial etching or degradation of the metal film 3 itself. Hence, the first step is to determine what removal means cause significant etching or degradation of the metal film 3 (so that these can later be avoided). The next step is to define a group compounds of the metal that can be readily formed through either of the above-described conversion processes. The last step then involves selecting those compounds out of the group that can be readily removed by removal means other than those that significantly etch or degrade the metal.

For example, with reference to Table II shown below, if copper is chosen as the metal film 3, the solvents which must be avoided are HNO_3 and H_2SO_4 since they are known to significantly etch copper. With the use of a chemistry handbook, the copper compounds 8 that are readily etchable with

etchants other than those noted above have been listed in column 2. The corresponding etchants for those compounds 8 are then listed in column 4. Therefore, with the copper compounds 8 having been selected, the type of ions 9 to be implanted to obtain those compounds then become apparent, as shown in column 1.

In addition to using the above-described processes to form single layer metal interconnects, the same processes may be used to form multi-layer interconnects having layers formed from different metal films 15 and 16 as shown in Figs. 4 and 5. With reference to Figs. 4A and 4B, the lower and upper layers 15 and 16 of such an interconnect may be converted in one step (Fig. 4A) and thereafter etched simultaneously with an appropriate removal means to form the simple bi-planar structure shown in Fig. 4B. Alternatively, the conversion (Fig. 5A) and/or removal of the converted layer 7 of each metal film 15 and 16 can be performed separately to form multi-layer interconnects having a plurality of shapes and dimensions as shown in Fig. 5B.

For purposes of explanation, an example of the present invention according to each of the above-described conversion processes will be described below.

EXAMPLE I

In the first case, shown in Fig. 2, a reactive ion etch system is utilized to drive oxygen ions 9 into a copper film 3 to form copper oxide compounds 8. Because copper does not readily adhere to silicon dioxide, an adhesion layer 2 is first deposited on the silicon dioxide layer 14 of the substrate 1. The adhesion layer 2 may include but is not limited to Ta, Mo or TiN formed by sputtering deposition. The copper film 3 is then deposited on

the adhesion layer 2 through sputtering deposition techniques well-known in the art. A hard mask layer 4 comprised of silicon nitride is next deposited on top of the copper film 3 followed by a photoresist layer 5 for patterning of the hard mask layer 4. The exposed portion of the hard mask 4 is then etched to reveal the exposed region of the metal film. In the example given, the use of the hard mask layer in combination with the photoresist layer is necessitated due to the fact that the photoresist 5 will etch away during the conversion step when exposed to the oxygen plasma created in the reactor chamber. Hence, the hard mask layer 4 is needed to prevent driving the oxygen ions 9 into unwanted areas of the copper film 3 as the photoresist layer 5 is etched.

Next, the conversion step is performed in an IPC Branson reactive ion system, wherein an oxygen gas is introduced into a pressure controlled system. Formation of the plasma 10, shown in Fig. 2B, takes place at an RF power of approximately 1000 watts and a pressure of 1.5 Torr. Once the plasma 10 is created, anisotropic formation of copper oxide occurs as a result of the electric field lines between the plasma 10 and the copper film 3 which drive the oxygen ions 9 into the copper perpendicular to the surface of the film 3.

After conversion of the exposed region 6 into the copper oxide compounds 8, the compounds 8 are removed from the metal film 3 using a wet clean of $(NH_4)Cl$. As mentioned above, this solvent is chosen for its ability to remove the copper oxide compounds 8 without any deleterious effect of the copper film 3 itself. Finally, the hard mask 4 is removed by techniques well-known in the art, such as by reactive ion etching with a chlorine-oxygen (CHF_3 / O_2) chemistry in order to obtain the final result shown in Fig. 2C.

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An advantage of this new method over the prior art method of etching copper is that the ULSI interconnect is anisotropically formed in a conventional reactive ion etch system without the usual high temperature requirement. Therefore, the present invention avoids the formation of the undesired copper chloride compounds which eliminates the problem of copper chloride condensation and particle formation.

EXAMPLE II

In the second case, shown in Fig. 3, an ion implantation system is utilized to implant chlorine ions 9 into a copper film 3 to form copper chloride compounds 8. To prevent contamination of the layers 13 underlying the copper film 3 resulting from the implantation of chlorine ions 9 beyond the film 3, an implant barrier layer 11 of Molybdenum is first deposited on the substrate 1. After the copper film 3 is deposited as described above, a mask layer 5, comprising a photoresist in this case, is formed thereon and lithographically developed for patterning of the copper film 3. The conversion step is then performed using a high-current Extrion implanter with an accelleration potential of approximately 50-250 Kev to implant a large dose ($10^{18}/cm^2$) of the chlorine ions 9 into the copper film 3 at an angle of approximately 90° to the surface of the copper film 3.

If the implant is performed at a lower temperature than that required to react the chlorine ions 9 with the copper atoms, the substrate 1 is then heated to assist in the reaction. Once copper chloride compounds 8 are formed throughout the exposed region 6 of the metal film 3, the converted layer 7 can be removed by either evaporating the compounds 8 in a ligand ambient at a temperature of 100°C or by using a wet clean comprised of $(NH_4)Cl$.

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In addition to the foregoing examples, the the following tables are provided to illustrate more clearly the various combinations of metals, ions, metal compounds and removal means that can be selected to form the metal interconnects as described above. However, it is noted that the combinations which may properly be used in the method of the present invention are not limited to the particular metals, ions, metal compounds and removal means listed below.

TABLE II

SILVER COMBINATIONS

IONS	SILVER-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon	Silver acetylide	Ag_2C_2	acid, alcohol
Arsenic/oxygen	Silver orthoarsenate	Ag_3AsO_4	NH_4OH, acetic acid
Arsenic/oxygen	Silver orthoarsenite	Ag_3AsO_3	acetic acid, NH_4OH
Nitrogen	Silver azide	AgN_3	NH_4OH
Carbon/hydrogen/ oxygen	Silver benzoate	$AgC_7H_5O_2$	0.017 alcohol
Boron/oxygen	Silver tetraborate	$Ag_2B_4O_7.2H_2O$	H_2O; acid
Bromine/oxygen	Silver bromate	$AgBrO_3$	NH_4OH
Bromine	Silver bromide	Bromyrite; AgBr	NaCl sol; NH_4OH
Carbon/oxygen	Silver carbonate	Ag_2CO_3	NH_4OH, $Na_2S_2O_3$
Chlorine/oxygen	Silver chlorate	$AgClO_3$	alcohol
Chlorine/oxygen	Silver perchlorate	$AgClO_4$	H_2O; alcohol; 101 toluene; 5.3 benzene
Chlorine	Silver chloride	Nat. cerargyrite. AgCl	NH_4OH, $Na_2S_2O_3$
Chromium/oxygen	Silver chromate	Ag_2CrO_4	NH_4OH

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Chromium/oxygen	Silver dichromate	$Ag_2Cr_2O_7$	H_2O; acid, NH_4OH
Carbon/hydrogen/ oxygen	Silver citrate	$Ag_3C_6H_5O_7$	H_2O; NH_4OH, $Na_2S_2O_3$
Oxygen/carbon/ nitrogen	Silver cyanate	AgOCN	H_2O; NH_4OH
Carbon/nitrogen	Silver cyanide	AgCN	NH_4OH, $Na_2S_2O_3$
Iron/carbon/nitrogen	Silver ferricyanide	$Ag_3Fe(CN)_6$	NH4OH, $(NH_4)_2CO_3$
Gallium/fluorine	Silver fluogallate	$Ag_3[GaF_6].10H_2O$	H_2O
Fluorine	Silver Fluoride	AgF	NH_4OH
Fluorine	Silver difluoride	AgF_2	H_2O
Fluorine	Silver (di-)fluoride	Ag_2F	H_2O
Silicon/fluorine	Silver fluosilicate	$Ag_2SiF_6.4H_2O$	H_2O
Carbon/nitrogen/oxygen	Silver fulminate	$Ag_2C_2N_2O_2$	H_2O; NH_4OH
Iodine/oxygen	Silver iodate	$AgIO_3$	NH_4OH, KI
Iodine/oxygen	Silver periodate	$AgIO_4$	H_2O
Iodine	Silver iodide (α)	Nat. iodyrite. AgI	Na2S2O3, KI; NH4OH
Iodine/mercury	Silver iodomercurate (α)	Ag2HgI4	KI
Iodine/mercury	Silver iodomercurate (β)	Ag_2HgI_4	KI
Carbon/hydrogen/ oxygen	Silver laurate	$AgC_{12}H_{23}O_2$	0.007^{25} alcohol; 0.008^{15} ether
Carbon/hydrogen/ oxygen	Silver levunilate	$AgC_5H_7O_3$	H_2O
Manganese/oxygen	Silver permanganate	$AgMnO_4$	alcohol
Carbon/hydrogen/ oxygen	Silver myristate	$AgC_{14}H_{27}O_2$	0.006^{25} alcohol; 0.007^{15} ether
Nitrogen/oxygen	Silver nitrate	$AgNO_3$	ether, glycerin
Nitrogen/oxygen	Silver nitrite	$AgNO_2$	acetic acid, NH_4OH
Platinum/nitrogen/ oxygen	Silver nitroplatinite	$Ag_2[Pt(NO_2)_4]$	H_2O
Iron/nitrogen/oxygen/ carbon	Silver nitroprusside	$Ag_2[FeNO(CN)_5]$	NH_4OH
Carbon/oxygen	Silver oxalate	$Ag_2C_2O_4$	NH_4OH, acid

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Oxygen	Silver oxide	Ag_2O	acid, NH_4OH, alcohol
Oxygen	Silver peroxide	Ag_2O_2 (or AgO)	NH_4OH
Carbon/hydrogen/ oxygen	Silver palmitate	$AgC_{16}H_{31}O_2$	0.007^{15} ether; 0.006^{25} alcohol
Phosphorous/oxygen	Silver metaphosphate	$AgPO_3$	NH_4OH
Phosphorous/oxygen	Silver orthophosphate	Ag_3PO_4	acid, NH_4OH, NH_3
Phosphorous/oxygen	Silver pyrophosphate	$Ag_4P_2O_7$	acid, NH_4OH, acetic acid
Carbon/hydrogen/ oxygen	Silver salicylate	$AgC_7H_5O_3$	H_2O, alcohol
Selenium	Silver selenide	Ag_2Se	NH_4OH
Carbon/hydrogen/ oxygen	Silver stearate	$AgC_{18}H_{35}O_2$	0.006^{25} alcohol; 0.006^{25} ether
Sulfur/oxygen	Silver sulfate	Ag_2SO_4	acid, NH_4OH
Sulfur	Silver sulfide	Nat. argentite. Ag_2S	acid
Sulfur/oxygen	Silver sulfite	Ag_2SO_3	acid, NH_4OH
Carbon/hydrogen/ oxygen	Silver d-tartrate	$Ag_2C_4H_4O_6$	acid, NH_4OH
Helium/tellurium/ oxygen	Silver orthotellurate, tetra-H	$Ag_2H_4TeO_6$	NH_4OH
Tellurium	Silver telluride	Nat. Hessite, Ag_2Te	NH_4OH
Tellurium/oxygen	Silver tellurite	Ag_2TeO_3	NH_3
Sulfur/carbon/oxygen	Silver thiocyanate	AgSCN	NH_4OH
Sulfur/oxygen	Silver thiosulfate	$Ag_2S_2O_3$	H_2O; $Na_2S_2O_3$, NH_4OH
Tungsten/oxygen	Silver tungstate	Ag_2WO_4	NH_4OH

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TABLE III

COPPER COMBINATIONS

IONS	COPPER-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon	Copper acetylide	CuC_2	H_2O, acid, KCN
Arsenic	Copper arsenide	Cu_5As_2	acid, NH_4OH
Nitrogen	Copper azide	$Cu(N_3)2$	acid
Bromine	Copper bromide	CuBr (or Cu_2Br_2) $CuBr_2$	H_2O, HBr, HCl, NH_4OH, acetone H_2O, alcohol, acetone, NH_3, pyridine
Carbon/Oxygen	Copper carbonate	Cu_2Co_3	acid, NH_4OH
Chlorine/Oxygen	Copper perchlorate	$Cu(ClO_4)_2$	H_2O
Chlorine	Copper chloride	CuCl (or Cu_2Cl_2); $CuCl_2$	HCl, NH_4OH, ether alcohol, MeOH, acetone
Carbon/Nitrogen	Copper cyanide	CuCn; $Cu(CN)_2$	HCl, KCN, NH_4OH acid, alkali, KCN, pyridine
Fluorine	Copper fluoride	CuF (or Cu_2F_2); CuF_2	HCl, HF H_2O, mineral acid
Iodide	Copper iodine	Nat. marshite. CuI (or Cu_2I_2)	HCl, KI, KCN, NH_3
Oxygen/Nitrogen	Copper hydroxide	$Cu(OH)_2$	acid, NH_2OH, KCN
Nitrogen	Copper nitride	Cu_3N	H_2O, acid
Oxygen	Copper oxide	Nat. cuprite. Cu_2O; Nat. tenorite, CuO	HCl, NH_4Cl, NH_4OH acid, NH_4Cl, KCN, NH_4F
Oxygen	Copper peroxide	$CuO_2 \cdot H_2O$	acid
Oxygen	Copper suboxide	Cu_4O	acid
Selenium	Copper selenide	Cu_2Se; CuSe	HCl HCl, NH_4OH
Sulfur/Oxygen	Copper sulfate	Cu_2SO_4	HCl, NH_3
Sulfur	Copper sulfide	Nat. chalcocite, Cu_2S; Nat. covellite, CuS	NH_4OH KCN, HCl
Tellurium	Copper telluride	Cu_2Te	$Br+H_2O$

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Tellurium/Oxygen	Copper tellurite	$CuTeO_3$	HCl
Sulfur/Carbon/Nitrogen	Copper thiocyanate	CuSCN; $Cu(SCN)_2$	NH_4OH, acetic acid· acid, NH_4OH

TABLE IV

GOLD COMBINATIONS

IONS	GOLD-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Bromine	Gold bromide	AuBr $Aubr_3$	acid; NaCN H_2O; ether, alcohol
Chlorine	Gold chloride	AuCl $AuCl_3$ or Au_2Cl_4	HCl, HBr H_2O; alcohol, ether, NH_3
Carbon/nitrogen	Gold cyanide	AuCN Cyanoauric acid. $Au(CN)_3.3H_2O$ or $HAu(CN_4).3H_2O$	NH_4OH H_2O; alcohol, ether
Iodine	Gold iodide	AuI AUI_3	H_2O; KI H_2O; iodides
Hydrogen/oxygen/ nitrogen	Gold nitrate, hydrogen	Nitratoauric acid. $AuH(NO_3)_4.3H_2O$ or $H[Au(NO_3)_4].3H_2O$	H_2O; HNO_3
Oxygen	Gold oxide	Au_2O_3 $Au_2O_3.xH_2O$	HCl, concentrated HNO_3, NaCN HCl, NaCN, concentrated HNO_3
Sulfur	Gold sulfide	Au_2S_3	Na_2S

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TABLE V

ALUMINUM COMBINATIONS

IONS	ALUMINUM-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon/hydrogen/ oxygen	Aluminum triacetate	$Al(C_2H_3O_2)_3$	H_2O
Carbon/hydrogen/ oxygen	Aluminum acetylacetonate	$Al(C_5H_7O_2)_3$	alcohol; ether, benzene
Arsenic/oxygen	Aluminum orthoarsenate	$AlAsO_4.8H_2O$	acid
Boron	Aluminum Boride	AlB_{12}	HNO_3
Bromine/oxygen	Aluminum bromate	$Al(BrO_3)_3.9H_2O$	H_2O; acid
Bromine	Aluminum bromide	$AlBr_3$ (or Al_2Br_6)	H_2O; alcohol, acetone, CS_2
Bromine	Aluminum hexabromide hydrate	$AlBr_3.6H_2O$	H_2O; alcohol, acid, CS_2
Bromine	Aluminum pentabromide decylhydrate	$AlBr_3.15H_2O$	H_2O; alcohol
Carbon/hydrogen/ oxygen	Aluminum tertbutoxide	$Al(C_4H_2O)_3$	organic solvents
Carbon	Aluminum carbide	Al_4C_3	H_2O; acid
Chlorine/oxygen	Aluminum chlorate	$Al(ClO_3)_3.6H_2O$	H_2O
Chlorine/oxygen	Aluminum perchlorate	$Al(ClO_4)_3.6H_2O$	H_2O
Chlorine	Aluminum chloride	$AlCl_3$ (or Al_2Cl_6)	H_2O; $100^{12.5}$ alcohol; 0.072^{25} chloroform; CCl_4, ether
Chlorine	Aluminum hexachloride hydrate	$AlCl_3.6H_2O$	H_2O; 50 alcohol; ether
Chlorine/nitrogen/ hydrogen	Aluminum hexammine	$AlCl_3.6NH_3$	H_2O
Carbon/hydrogen/ oxygen	Aluminum diethylmalonate derivative	$Al(C_7H_{11}O_4)_3$	organic solvents
Carbon/hydrogen/ oxygen	Aluminum ethoxide	$Al(C_2H_5O)_2$	H_2O
Carbon/hydrogen/ oxygen	Aluminum α-ethylacetoacetate derivative	$Al(C_4H_9O_3)_3$	H_2O; ligroin
Iron/carbon/nitrogen	Aluminum ferrocyanide	$Al_4[Fe(CN)_6]_3.17H_2O$	H_2O; acid

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Fluorine	Aluminum fluoride	AlF3 $AlF3.3^1/_2H_2O$	H_2O H_2O; acetic acid
Fluorine	Aluminum monofluoride hydrate	Nat. fluelite. $AlF_3.H_2O$	H_2O
Oxygen/hydrogen	Aluminum hydroxide	Nat. boehmite. AlO(OH) Nat. diaspore. AlO(OH) $Al(OH)_3$	acid acid acid
Iodine	Aluminum iodide	AlI_3 (or Al_2I_6)	H_2O; alcohol, ether, CS_2, NH_3
Iodine	Aluminum hexaiodide hydrate	$AlI_3.6H_2O$	H_2O; alcohol, CS_2
Carbon/hydrogen/ oxygen	Aluminum isopropoxide	$Al(C_3H_7O)_3$	H_2O; alcohol, benzene, chloroform
Carbon/hydrogen/ oxygen	Aluminum lactate	$Al(C_3H_5O_3)_3$	H_2O
Nitrogen/oxygen	Aluminum nitrate	$Al(NO_3)_3.9H_2O$	H_2O; 100 alcohol; acetone, HNO_3. acid
Nitrogen	Aluminum nitride	AlN	H_2O; acid,
Hydrogen/oxygen	Aluminum oleate (com'l)	$Al(_{18}H_{33}O_2)_3$(?)	H_2O
Carbon/oxygen	Aluminum oxalate	$Al_2(C_2O_4)_3.4H_2O$	acid
Oxygen	Aluminum oxide	γ-Alumina. Al_2O_3	acid
Oxygen	Aluminum trihydrate oxide	Nat. gibbsite, hydra-argilite. $Al_2O_3.3H_2O$ Nat. bayerite. $Al_2O_3.3H_2O$	acid acid
Carbon/hydrogen/ oxygen	Aluminum monopalmitate (com'l)	$Al(OH)_2C_{16}H_{31}O_2$	hydrocarbon
Carbon/hydrogen/ oxygen/sulfur	Aluminum 1-phenol-4-sulfonate	$Al(C_6H_5O_4S)_3$	H_2O; alcohol, glycerin
Carbon/hydrogen/ oxygen	Aluminum phenoxide	$Al(C_6H_5O)_3$	H_2O; alcohol, ether, chloroform
Phosphorous/oxygen	Aluminum orthophosphate	$AlPO_4$	acid, alcohol
Carbon/hydrogen/ oxygen	Aluminum propoxide	$Al(C_3H_7O)_3$	H_2O; alcohol
Selenium	Aluminum selenide	Al_2Se_3	H_2O; acid
Oxygen/silicon	Aluminum silicate	Nat. sillimanite, andalusite, cyanite. $Al_2O_3.SiO_2$	HF

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Carbon/hydrogen/ oxygen	Aluminum tritearate	$Al(C_{18}H_{35}O_2)_3$	alcohol, benzene, turpentine
Sulfur/oxygen	Aluminum sulphate	$Al_2(SO_4)_3$	acid; alcohol
Sulfur	Aluminum sulfide	Al_2S_3	H_2O; acid

TABLE VI

MOLYBDENUM COMBINATIONS

IONS	MOLYBDENUM-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Bromine	Molybdenum dibromide	$MoBr_2$ (or Mo_2Br_4)	alkali
Bromine	Molybdenum tetrabromide	MoBr4	H_2O, alkali
Bromine	Molybdenum tribromide	MoBr3	alkali, NH3
Carbon	Molybdenum monocarbide	MoC	HF, HCl
Carbon	Molybdenum dicarbide	Mo_2C	HF, HCl
Carbon/oxygen	Molybdenum carbonyl	$Mo(CO)_6$	benzene; ether
Chlorine	Molybdenum dichloride	$MoCl_2$ (or Mo_2Cl_6)	HCl, alkali, NH_4OH, alcohol, acetone
Chlorine	Molybdenum pentachloride	$MoCl_5$	mineral acid, liquid, NH_3, CCl_4, chloroform; alcohol, ether
Chlorine	Molybdenum tetrachloride	$MoCl_4$	concentrated mineral acid; alcohol, ether
Chlorine	Molybdenum trichloride	$MoCl_3$	H_2O
Fluorine	Molybdenum hexafluoride	MoF6	H_2O; NH_4OH, alkali
Oxygen/hydrogen	Molybdenum hydroxide	$Mo(OH)_3$ (or $Mo_2O_3.3H_2O$);	HCl; 30% H_2O_2
		$MoO(OH)_3$ (or $Mo_2O_5.3H_2O$);	acid, alkali, carbon
		$MoO_3.2H_2O$	H_2O_2, alkali, hydrogen; acid
Bromine/oxygen/ hydrogen	Molybdenum hydroxytetra-dibromide	$Mo_3Br_4(OH)_2$	alkali
Bromine/oxygen/ hydrogen	Molybdenum hydroxytetra-dioctabromide hydrate	$Mo_3Br_4(OH)_2.8H_2O$	HCl; alkali

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Chlorine/oxygen/ hydrogen	Molybdenum hydroxytetra-dichloride	$Mo_2Cl_4(OH)_2.2H_2O$	concentrated acid
Iodine	Molybdenum di-iodide	MoI_2	H_2O
Oxygen/hydrogen	Molybdenum pentoxide	Mo_2O_5; "Molybd. blue" $Mo_2O_5.xH_2O$ (variations in Mo and O)	HCl H_2O; acid, MeOH
Oxygen	Molybdenum trioxide	Molybdic anhydride. Nat. Molybdite. MoO_3	acid, alkali, sulfur, NH_4OH
Oxygen/bromine	Molybdenum dioxydibromide	MoO_2Br_2	H_2O
Oxygen/chlorine	Molybdenum oxytetrachloride	$MoOCl_4$	H_2O
Oxygen/chlorine	Molybdenum oxytrichloride	$MoOCl_3$	H_2O
Oxygen/chlorine	Molybdenum dioxydichloride	MoO_2Cl_2	H_2O; alcohol, ether
Oxygen/chlorine/ hydrogen	Molybdenum dioxydichloride hydrate	$MoO_2Cl_2.H_2O$	H_2O; alcohol, acetone, ether
Oxygen/chlorine	Molybdenum trioxyhexachloride	$Mo_2O_3Cl_6$	H_2O; ether
Oxygen/chlorine	Molybdenum trioxypentachloride	$Mo_2O_3Cl_5$	H_2O
Oxygen/hydrogen/ chlorine	Molybdenum oxychloride acid	$MoO(OH)_2Cl_2$	H_2O; alcohol, ether, acetone
Oxygen/fluorine	Molybdenum dioxydifluoride	MoO_2F_2	H_2O; alcohol, MeOH
Oxygen/fluorine	Molybdenum oxytetrafluoride	$MoOF_4$	H_2O; alcohol, ether, CCl_4
Silicon	Molybdenum silicide	$MoSi_2$	$HF+HNO_3$
Silicon/oxygen/ hydrogen	Molybdenum pentasulfide	$Mo_2S_5.3H_2O$	NH_4OH, alkali, sulfides
Sulfur	Molybdenum tetrasulfide	MoS_4	alkali sulfide
Sulfur	Molybdenum trisulfide	MoS_3	H_2O; alkali, sulfur, concentrated KOH

While the present invention has been described in conjunction with the preferred embodiment and several examples, it is evident that

numerous alternatives, depictions, variations and uses will be apparent to those skilled in the art in light of the foregoing description. Specifically, the metal films 3 used in the present invention may comprise any of a variety of metals or a combination thereof, while the specific ions 9, metal compounds 8 and removal means are not limited to any specific type as they are to be selected in accordance with the metal compounds to be formed.

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CLAIMS:

1. In the fabrication of a semiconductor device, a method for etching a metal film formed on a semiconductor substrate comprising the steps of:

forming a mask on the metal film to define an exposed region of the metal film;

converting the exposed region of the metal film into a converted layer of the metal film, the converted layer comprising metal compounds of the metal film; and

selectively removing the converted layer without substantial etching of the metal film.

2. The method of Claim 1, wherein the mask comprises a hard mask selected from the group consisting of dielectric films, metal films and tightly bonded metal oxide films.

3. The method of Claim 1, wherein the mask comprises a photoresist layer.

4. The method of Claim 1, wherein the method further comprises the step of removing the mask after the converted layer is formed.

5. The method of Claim 1, wherein the step of converting the exposed region is performed by introducing ions into the exposed region to form the metal compounds.

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6. The method of Claim 1, wherein the step of converting the exposed region is performed by implanting ions into the exposed region of the metal film by an ion implantation system.

7. The method of Claim 6, wherein the method further comprises the step of forming an implant barrier layer beneath the metal film to prevent the ions from penetrating into layers beneath the implant barrier layer.

8. The method of Claim 7, wherein the implant barrier comprises a material that is electrically and chemically stable with respect to the ions implanted.

9. The method of Claim 6, wherein the method further comprises the step of thermally treating the semiconductor substrate after the exposed region is converted to assist in formation of the metal compounds.

10. The method of Claim 6, wherein the metal film comprises copper, the ions comprise chlorine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

11. The method of Claim 6, wherein the metal film comprises copper, the ions comprise bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

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12. The method of Claim 6, wherein the step of removing the metal compounds is performed by applying an etchant to etch the metal compounds.

13. The method of Claim 12, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

14. The method of Claim 12, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

15. The method of Claim 12, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

16. The method of Claim 12, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

17. The method of Claim 12, wherein the metal film comprises copper, the ions comprise Iodine ions and the etchant is selected from the group consisting of HCl, KI, KCN and NH_3.

18. The method of Claim 12, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

19. The method of Claim 12, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

20. The method of Claim 12, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

21. The method of Claim 1 wherein the step of converting the exposed region is performed by exposing the semiconductor substrate to a plasma comprising ions under an electric potential to reactively form metal compounds within the exposed regions of the metal film.

22. The method of Claim 21, wherein the step of exposing the semiconductor substrate to a plasma is performed in a reactive ion etch system.

23. The method of Claim 22, wherein the method further comprises the step of heating the semiconductor substrate to at least 200º Celsius during exposure of the integrated circuit to the plasma.

24. The method of Claim 22, wherein the metal film comprises copper, the plasma comprises chlorine ions and the step of removing the

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metal compounds is performed by evaporating the metal compounds in a ligand ambient.

25. The method of Claim 22, wherein the metal comprises copper, the plasma comprises bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

26. The method of Claim 22, wherein the step of removing the metal compounds is performed by applying an etchant to etch the metal compounds.

27. The method of Claim 26, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

28. The method of Claim 26, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

29. The method of Claim 26, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

30. The method of Claim 26, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the

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group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

31. The method of Claim 26, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, KI, KCN and NH_3.

32. The method of Claim 26, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

33. The method of Claim 26, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

34. The method of Claim 26, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

35. In the fabrication of a semiconductor device, a method is provided for etching a metal film formed on a semiconductor substrate comprising the steps of:

forming a mask on the metal film to define an exposed region of the metal film;

implanting ions into the exposed region of the metal film to form a converted layer of metal compounds within the exposed region; and

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selectively removing the converted layer without substantial etching of the metal film.

36. The method of Claim 35, wherein the method further comprises the step of forming an implant barrier layer beneath the metal film to prevent the ions from penetrating into layers beneath the implant barrier layer.

37. The method of Claim 36, wherein the implant barrier comprises a material that is electrically and chemically stable with respect to the ions implanted.

38. The method of Claim 35, wherein the mask comprises a hard mask selected from the group consisting of dielectric films, metal films and tightly bonded metal oxide films.

39. The method of Claim 35, wherein the mask comprises a photoresist layer.

40. The method of Claim 35, wherein the method further comprises the step of removing the mask after the converted layer is formed.

41. The method of Claim 35, wherein the method further comprises the step of thermally treating the semiconductor substrate after the ions are implanted into the exposed region to assist in the formation of the metal compounds.

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42. The method of Claim 35, wherein the metal film comprises copper, the ions comprise chlorine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

43. The method of Claim 35, wherein the metal film comprises copper, the plasma comprises bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

44. The method of Claim 35, wherein the step of removing the converted layer is performed by applying an etchant to etch the metal compounds.

45. The method of Claim 44, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

46. The method of Claim 44, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

47. The method of Claim 44, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

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48. The method of Claim 44, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

49. The method of Claim 44, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, KI, KCN and NH_3.

50. The method of Claim 44, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

51. The method of Claim 44, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

52. The method of Claim 44, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

53. In the fabrication of a semiconductor device, a method is provided for etching a metal film formed on a semiconductor substrate comprising the steps of:

forming a mask on the metal film to define an exposed region of the metal film;

exposing the semiconductor substrate to a plasma comprising ions under an electric potential to reactively form metal compounds within the exposed region of the metal film; and

selectively removing the converted layer without substantial etching of the metal film.

54. The method of Claim 53, wherein the mask comprises a hard mask selected from the group consisting of dielectric films, metal films and tightly bonded metal oxide films.

55. The method of Claim 53, wherein the mask comprises a photoresist layer .

56. The method of Claim 53, wherein the method further comprises the step of removing the mask after the converted layer is formed.

57. The method of Claim 53, wherein the step of exposing the semiconductor substrate to a plasma is performed in a reactive ion etch system.

58. The method of Claim 57, wherein the method further comprises the step of heating the semiconductor substrate to at least 200º Celsius during the exposure of the semiconductor substrate to the plasma.

59. The method of Claim 57, wherein the metal film comprises copper, the plasma comprises chlorine ions and the step of removing the

metal compounds is performed by evaporating the metal compounds in a ligand ambient.

60. The method of Claim 57, wherein the metal comprises copper, the plasma comprises bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

61. The method of Claim 57, wherein the step of removing the converted layer is performed by applying an etchant to etch the metal compounds.

62. The method of Claim 57, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

63. The method of Claim 57, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

64. The method of Claim 57, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

65. The method of Claim 57, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the

group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

66. The method of Claim 57, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, KI, KCN and NH_3.

67. The method of Claim 57, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

68. The method of Claim 57, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

69. The method of Claim 57, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

70. In the fabrication of a semiconductor device, a method for etching a metal film formed on a semiconductor substrate, substantially as herebefore described with reference to the accompanying drawings.

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FIG 1A

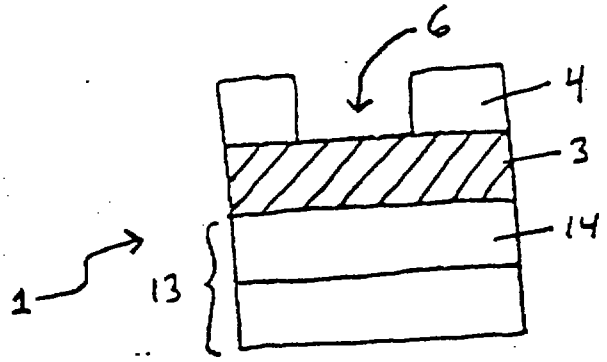


FIG. 1B

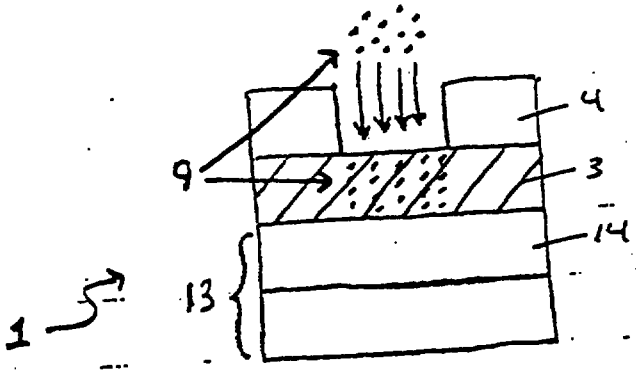


FIG. 1C

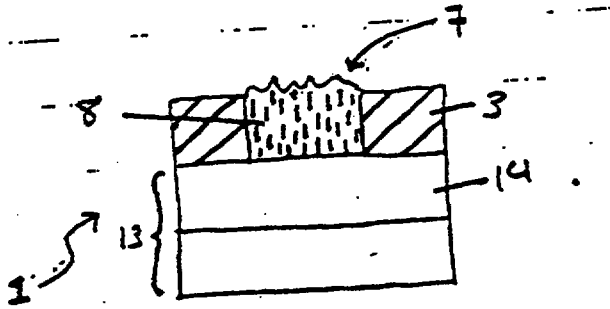
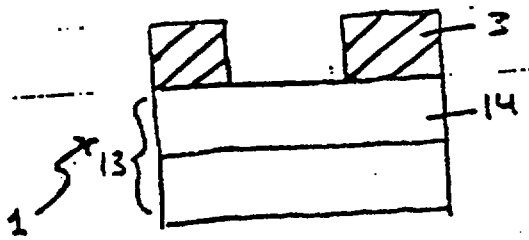


FIG 1D



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FIG. 2A

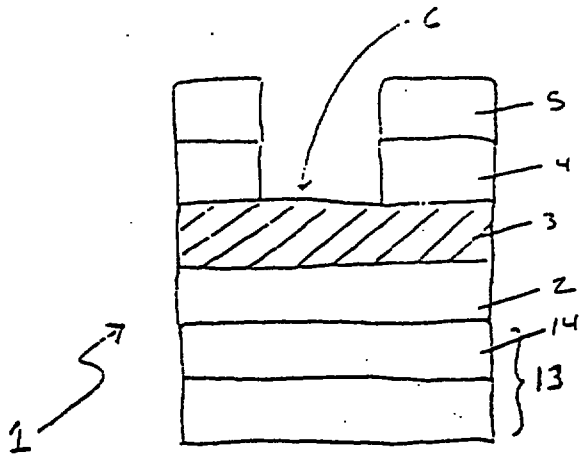


FIG. 2B

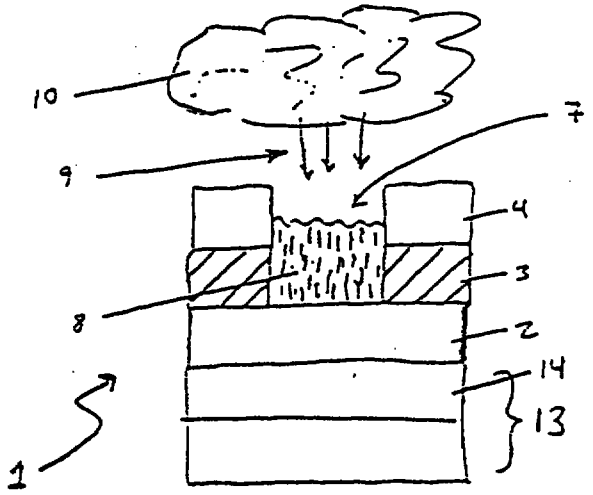
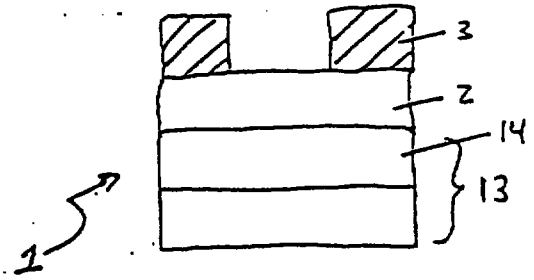


FIG. 2C



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FIG 3A

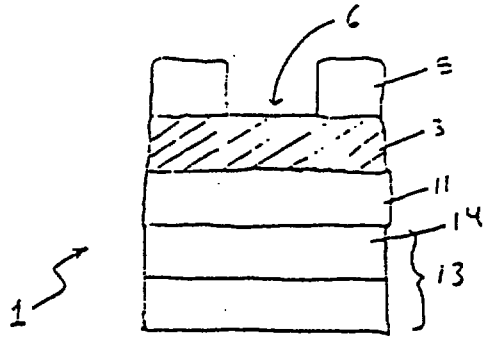


FIG 3B

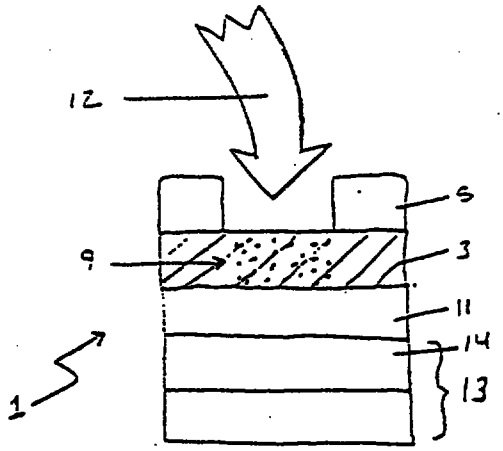


FIG 3C

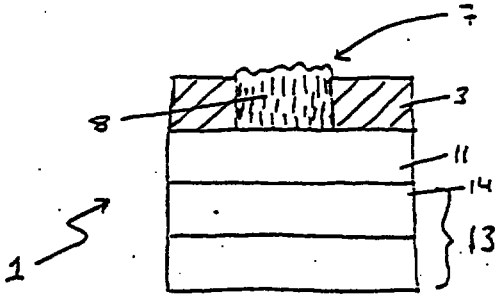
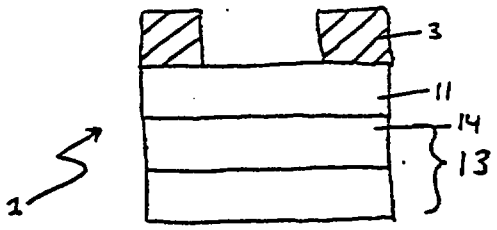


FIG 3D



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FIG. 4A

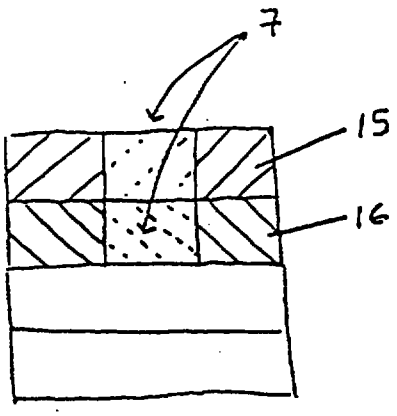


FIG. 4B

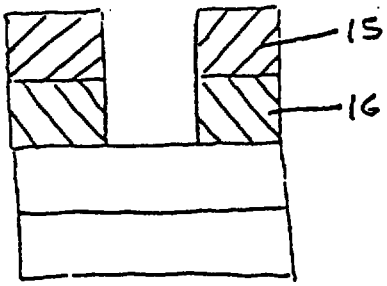


FIG 5A

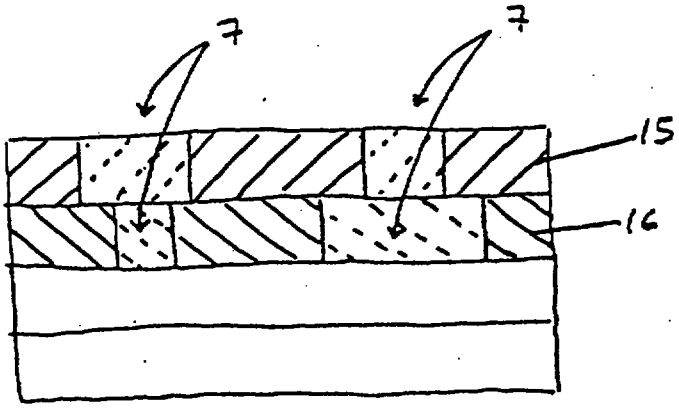
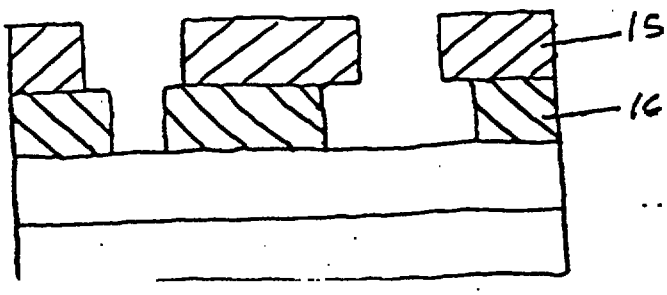


FIG. 5B



ABSTRACT

A METHOD FOR THE ANISOTROPIC ETCHING OF METAL FILMS IN THE FABRICATION OF INTERCONNECTS

The present invention discloses a method for anisotropically etching metal interconnects in the fabrication of semiconductor devices, especially ULSI interconnects having high aspect ratios. A metal film is first deposited on the appropriate layer of a semiconductor substrate by techniques well-known in the art. A mask layer is deposited over the metal film with openings defined in the mask layer for patterning of the metal film. Ions are then introduced into an exposed region of the metal film to anisotropically form a converted layer of the metal film comprising compounds of the metal. The introduction of the ions into the metal film can be performed by conventional methods, such as through the use of a reactive ion etch system or an ion implantation system, or by any other method which anisotropically forms the metal compounds. The mask layer is then removed by conventional means to leave behind the metal film having a converted layer of metal compounds. Finally, the metal compounds are selectively removed by a suitable removal means chosen for its properties in removing the metal compounds without causing significant etching or degradation of the metal film itself.

(Fig. 1B & 1C)

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REPLACEMENT SHEETS SG
☑ Description : paged 10, 15 to paged 24
☑ Claim(s) : paged 26 to paged 33
☑ Drawing(s) : paged 1 to paged 4
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focused on the substrate 1 to directionally implant the ions 9 into the metal film 3. In the present invention, a high-current Extrion (RTM) implanter manufactured by Varian Associates-Extrion is used for implanting the ions 9 into the metal film 3, although the particular ion implantation system used need not be limited to an implanter of this type. Similarly, a medium-current or a high-energy implanter can be used in the present invention depending upon the density of the metal film 3, the type of ions 9 to be implanted and the volume of the metal film 3 to be implanted.

An important consideration in the use of an ion implantation system is the possible use of a implant barrier 11 beneath the metal film 3 for protection of the underlying layers 13 from the ion implants 9. This implant barrier 11 may also be used as a diffusion barrier during the actual conversion of the exposed region 6 to prevent diffusion of the metal film 3 into the underlying layers 13. During ion implantation, the profile of the implants 9 exhibits an implant tail that may reach beyond the metal film 3 and into the underlying layers 13. In order to avoid charging and/or conversion of the underlying layers 13 into an unstable material, the implant barrier 11 is placed beneath the metal film 3 for absorption and neutralization of the ion implants 9. This implant barrier 11 should be formed from a material that is electrically and chemically stable with respect to the ion implants 9. For example, if oxygen ions were implanted into the metal film 3, a silicon oxide layer could be used to receive the implant tail so as to prevent any ionic contamination of the underlying layers 13.

As shown in Figs. 3B and 3C, after the exposed region 6 of the metal film 3 is thoroughly saturated with the ions 9, the mask layer 5 can then be removed by dissolution in a solvent or by other techniques well-known in the art. Following the removal of the mask layer 5, the substrate 1

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An advantage of this new method over the prior art method of etching copper is that the ULSI interconnect is anisotropically formed in a conventional reactive ion etch system without the usual high temperature requirement. Therefore, the present invention avoids the formation of the undesired copper chloride compounds which eliminates the problem of copper chloride condensation and particle formation.

EXAMPLE II

In the second case, shown in Fig. 3, an ion implantation system is utilized to implant chlorine ions 9 into a copper film 3 to form copper chloride compounds 8. To prevent contamination of the layers 13 underlying the copper film 3 resulting from the implantation of chlorine ions 9 beyond the film 3, an implant barrier layer 11 of Molybdenum is first deposited on the substrate 1. After the copper film 3 is deposited as described above, a mask layer 5, comprising a photoresist in this case, is formed thereon and lithographically developed for patterning of the copper film 3. The conversion step is then performed using a high-current Extrion (RTM) implanter with an accelleration potential of approximately 50-250 Kev to implant a large dose ($10^{18}/cm^2$) of the chlorine ions 9 into the copper film 3 at an angle of approximately 90° to the surface of the copper film 3.

If the implant is performed at a lower temperature than that required to react the chlorine ions 9 with the copper atoms, the substrate 1 is then heated to assist in the reaction. Once copper chloride compounds 8 are formed throughout the exposed region 6 of the metal film 3, the converted layer 7 can be removed by either evaporating the compounds 8 in a ligand ambient at a temperature of 100°C or by using a wet clean comprised of $(NH_4)Cl$.

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In addition to the foregoing examples, the following tables are provided to illustrate more clearly the various combinations of metals, ions, metal compounds and removal means that can be selected to form the metal interconnects as described above. However, it is noted that the combinations which may properly be used in the method of the present invention are not limited to the particular metals, ions, metal compounds and removal means listed below.

TABLE II

SILVER COMBINATIONS

IONS	SILVER-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon	Silver acetylide	Ag_2C_2	acid,alcohol
Arsenic/oxygen	Silver orthoarsenate	Ag_3As0_4	NH_4OH, Acetic acid
Arsenic/oxygen	Silver orthoarsenite	Ag_3As0_3	acetic acid NH_4OH
Nitrogen	Silver azide	AgN_3	NH_4OH
Carbon/hydrogen/ oxygen	Silver benzoate	$AgC_7H_50_2$	0.017 alcohol
Boron/oxygen	Silver tetraborate	$Ag_2B_40_7.2H_20$	H_20; acid
Bromine/oxygen	Silver bromate	$AgBr0_3$	NH_4OH
Bromine	Silver bromide	Bromyrite;AgBr	NaClsol;NH_4OH
Carbon/oxygen	Silver carbonate	$Ag_2C0_3NH_4OH$,	$Na_2S_20_3$
Chlorine/oxygen	Silver chlorate	$AgC10_3$	Alcohol
Chlorine/oxygen	Silver perchlorate	$AgC10_4$	H_20;alcohol;101 toluene; 5.28 benzene
Chlorine	Silver chloride	Nat.cerargyrite.	$AgC1NH_4OH$, $Na_2S_20_3$
Chromium/oxygen	Silver chromate	Ag_2Cr0_4	NH_4OH
Chromium/oxygen	Silver dichromate	$Ag_2Cr_2O_7$	H_2O;acid,NH_4OH
Carbon/hydrogen/ oxygen	Silver citrate	$Ag_3C_6H_50_7$	H_20;NH_4OH,$Na_2S_20_3$
Oxygen/carbon/ nitrogen	Silver cyanate	AgOCN	H_20;NH_40H
Carbon/nitrogen	Silver cyanide	AgCN	NH_40H,$Na_2S_20_3$
Iron/carbon/nitrogen	Silver ferricyanide	$Ag_3Fe(CN)_6$	NH40H,$(NH_4)_2C0_3$
Gallium/fluorine	Silver fluogallate	$Ag_3[GaF_6].10H_20$	H_20
Fluorine	Silver Fluoride	AgF	NH_40H
Fluorine	Silver difluoride	AgF_2	H_20

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Fluorine	Silver (di-)fluoride	Ag_2F	H_20
Silicon/fluorine	Silver fluosilicate	$Ag_2SiF_6.4H_20$	H_20
Carbon/nitrogen/oxygen	Silver fulminate	$Ag_2C_2N_20_2$	H_20; NH_40H
Iodine/oxygen	Silver iodate	$AgI0_3$	NH_40H,KI
Iodine/oxygen	Silver periodate	$AgI0_4$	H_20
Iodine	Silver iodide (α)	Nat.iodyrite.AgI	Na2S203,KI;NH40H
Iodine/mercury	Silver iodomercurate(α)	Ag2HgI4	KI
Iodine/mercury	Silver iodomercurate(β)	AG_2HgI_4	KI
Carbon/hydrogen/ oxygen	Silver laurate	$AgC_{12}H_{23}0_2$	0.007^{25}alcohol;0.008^{15} ether
Carbon/hydrogen/ oxygen	Silver levunilate	$AgC_5H_70_3$	H_20
Manganese/oxygen	Silver permanganate	$AgMn0_4$	alcohol
Carbon/hydrogen/ oxygen	Silver myristate	$AgC_{14}H_{27}0_2$	0.006^{25}alcohol;0.007^{15} ether
Nitrogen/oxygen	Silver nitrate	$AgN0_3$	ether,glycerin
Nitrogen/oxygen	Silver nitrite	$AgN0_2$	acetic acid,NH_40H
Platinum/nitrogen/ oxygen	Silver nitroplatinite	$Ag_2[P1(N0_2)_4]$	H_20
Iron/nitrogen/oxygen/ carbon	Silver nitroprusside	$Ag_2[FeN0(CN)_5]$	NH_40H
Carbon/oxygen	Silver oxalate	$Ag_2C_20_4$	NH_40H, acid
Oxygen	Silver oxide	Ag_20	acid, NH_40H, alcohol
Oxygen	Silver peroxide	Ag_20_2 (or Ag0)	NH_40H
Carbon/hydrogen/ oxygen	Silver palmitate	$AgC_{16}H_{31}0_2$	0.007^{15} ether; 0.006^{25} alcohol
Phosphorous/oxygen	Silver metaphosphate	$AgPO_3$	NH_40H
Phosphorous/oxygen	Silver orthophosphate	Ag_3P0_4	acid,NH_40H,NH_3
Phosphorous/oxygen	Silver pyrophosphate	$Ag_4P_20_7$	acid,NH_40H, acetic acid
Carbon/hydrogen/ oxygen	Silver salicylate	$AgC_7H_50_3$	H_20, alcohol
Selenium	Silver selenide	Ag_2Se	NH_40H
Carbon/hydrogen/ oxygen	Silver stearate	$AgC_{18}H_{35}0_2$	0.006^{25} alcohol; 0.006^{25} ether
Sulfur/oxygen	Silver sulfate	Ag_2S0_4	acid, NH_40H
Sulfur	Silver sulfide	Nat.argentite. Ag_2S	acid
Sulfur/oxygen	Silver sulfite	Ag_2S0_3	acid, NH_40H
Carbon/hydrogen/ oxygen	Silver d-tartrate	$Ag_2C_4H_40_6$	acid,NH_40H

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Helium/tellurium/ oxygen	Silver orthotellurate, tetra-H	$Ag_2H_4TeO_6$	NH_4OH
Tellurium	Silver telluride	Nat.Hessite, Ag_2Te	NH_4OH
Tellurium/oxygen	Silver tellurite	Ag_2TeO_3	NH_3
Sulfur/carbon/oxygen	Silver thiocyanate	AgSCN	NH_4OH
Sulfur/oxygen	Silver thiosulfate	$Ag_2S_2O_3$	H_2O;$Na_2S_2O_3$,NH_4OH
Tungsten/oxygen	Silver tungstate	Ag_2WO_4	NH_4OH

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TABLE III

COPPER COMBINATIONS

IONS	COPPER-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon	Copper acetylide	CuC_2	H_20,acid,KCN
Arsenic	Copper arsenide	Cu_5As_2	acid,NH_40H
Nitrogen	Copper azide	$Cu(N_3)2$	acid
Bromine	Copper bromide	CuBr(or Cu_2Br_2)	H_20,HBr,HC1,NH_40H,acetone
		$CuBr_2$	H_20,alcohol,acetone,NH_3,pyridine
Carbon/0xygen	Copper carbonate	Cu_2Co_3	acid, NH_40H
Chlorine/0xygen	Copper perchlorate	$Cu(C10_4)_2$	H_20
Chlorine	Copper chloride	CuC1(or Cu_2C1_2)	HC1,NH_40H,ether
		$CuC1_2$	alcohol,Me0H,acetone
Carbon/Nitrogen	Copper cyanide	CuCn;	HC1, KCN, NH_40H
		$CU(CN)_2$	acid,alkali, KCN,pyridine
Fluorine	Copper fluoride	CuF(or Cu_2F_2);	HC1,HF
		CuF_2	H_20,mineral acid
Iodide	Copper iodine	Nat.marshite. CuI(or Cu_2I_2)	HC1,KI,KCN,NH_3
0xygen/Nitrogen	Copper hydroxide	$Cu(0H)_2$	acid, NH_40H,KCN
Nitrogen	Copper nitride	Cu_3N	H_20,acid
0xygen	Copper oxide	Nat.cuprite.Cu_20;	HC1,NH_4C1,NH_40H
		Nat.tenorite,	acid,NH_4C1,KCN,NH_4F
		Cu0	
0xygen	Copper peroxide	$Cu0_2 \cdot H_20$	acid
0xygen	Copper suboxide	Cu_40	acid
Selenium	Copper selenide	Cu_2Se;	HC1
		CuSe	HC1,NH_40H
Sulfur/0xygen	Copper sulfate	Cu_2S0_4	HC1,NH_3
Sulfur	Copper sulfide	Nat.chalcocite,Cu_2S;	NH_40H
		Nat.covellite,CuS	KCN,HC1
Tellurium	Copper telluride	Cu_2Te	$Br+H_20$
Tellurium/0xygen	Copper tellurite	$CuTe0_3$	HC1
Sulfur/Carbon/Nitrogen	Copper thiocyanate	CuSCN;	NH_40H,acetic acid
		$Cu(SCN)_2$	acid, NH_40H

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TABLE IV

GOLD COMBINATIONS

IONS	GOLD-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Bromine	Gold bromide	AuBr	acid;NaCN
		$Aubr_3$	H_20;ether,alcohol
Chlorine	Gold chloride	AuC1	HC1,HBr
		$AuC1_3$ or Au_2C1_4	H_20;alcohol,ether,NH_3
Carbon/nitrogen	Gold cyanide	AuCN	NH_40H
		Cyanoauric acid.	H_20;alcohol,ether
		$Au(CN)_3.3H_20$ or	
		$HAu(CN_4).3H_20$	
Iodine	Gold iodide	AuI	H_20;KI
		AUI_3	H_20;iodides
Hydrogen/oxygen/ nitrogen	Gold nitrate,hydrogen	Nitratoauric acid.	H_20;$HN0_3$
		$AuH(N0_3)_4.3H_20$ of	
		$H[Au(N0_3)_4].3H_20$	
0xygen	Gold oxide	Au_20_3	HC1,concentrated $HN0_3$,NaCN
		$Au_20_3.xH_20$	HC1,NaCN,concentrated $HN0_3$
Sulfur	Gold sulfide	Au_2S_3	Na_2S

TABLE V

ALUMINUM COMBINATIONS

IONS	ALUMINUM-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Carbon/hydrogen/ oxygen	Alumimum triacetate	$Al(C_2H_30_2)_3$	H_20
Carbon/hydrogen/ oxygen	Aluminum acetylacetonate	$Al(C_5H_70_2)_3$	alcohol;ether,benzene
Arsenic/oxygen	Aluminum orthoarsenate	$A1As0_4.8H_20$	acid
Boron	Aluminum Boride	AlB_{12}	$HN0_3$
Bromine/oxygen	Aluminum bromate	$Al(Br0_3)_3.9H_20$	H_20;acid
Bromine	Aluminum bromide hydrate	$AlBr_3$(or Al_2Br_6)	H_20;alcohol,acetone,CS_2
Bromine	Aluminum hexabromide hydrate	$A1Br_3.6H_20$	H_20;alcohol, acid,CS_2

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Bromine	Aluminum pentabromide decylhydrate	$AlBr_3.15H_2O$	H_2O;alcohol
Carbon/hydrogen/ oxygen	Aluminum tertbutoxide	$Al(C_4H_2O)_3$	organic solvents
Carbon	Aluminum carbide	Al_4C_3	H_2O;acid
Chlorine/oxygen	Aluminum chlorate	$Al(ClO_3)_3.6H_2O$	H_2O
Chlorine/oxygen	Aluminum perchlorate	$Al(ClO_4)_3.6H_2O$	H_2O
Chlorine	Aluminum chloride	$AlCl_3$(or Al_2Cl_6)	H_2O;$100^{12.5}$alcohol;0.072^{25} chloroform; CCl_4,ether
Chlorine	Aluminum hexachloride hydrate	$AlCl_3.6H_2O$	H_2O;50 alcohol; ether
Chlorine/nitrogen/ hydrogen	Aluminum hexammine	$AlCl_3.6NH_3$	H_2O
Carbon/hydrogen/ oxygen	Aluminum diethylmalonate derivative	$Al(C_7H_{11}O_4)_3$	organic solvents
Carbon/hydrogen/ oxygen	Aluminum ethoxide	$Al(C_2H_5O)_2$	H_2O
Carbon/hydrogen/ oxygen	Aluminum α-ethylacetoacetate derivative	$Al(C_4H_9O_3)_3$	H_2O; ligroin
Iron/carbon/nitrogen	Aluminum ferrocyanide	$Al_4[Fe(CN)_6]_3 17H_2O$	H_2O;acid
Fluorine	Aluminum fluoride	AlF3	H_2O
		$AlF3.3^1/_2H_2O$	H_2O;acetic acid
Fluorine	Aluminum monofluoride hydrate	Nat.fluelite. $AlF_3.H_2O$	H_2O
Oxygen/hydrogen	Aluminum hydroxide	Nat.boehmite. A10(0H)	acid
		Nat.diaspore. A10(0H)	acid
		$Al(0H)_3$	acid
Iodine	Aluminum iodide	AlI_3 (or Al_2I_6)	H_2O;alcohol,ether,CS_2NH_3
Iodine	Aluminum hexaiodide hydrate	$AlI_3.6H_2O$	H_2O;alcohol, CS_2
Carbon/hydrogen/ oxygen	Aluminum isopropoxide	$Al(C_3H_7O)_3$	H_2O;alcohol,benzene chloroform
Carbon/hydrogen/ oxygen	Aluminum lactate	$Al(C_3H_5O_3)_3$	H_2O
Nitrogen/oxygen	Aluminum nitrate	$Al(NO_3)_3.9H_2O$	H_2O; 100 alcohol;acetone, HNO_3. acid
Nitrogen	Aluminum nitride	AlN	H_2O;acid,
Hydrogen/oxygen	Aluminum oleate(com'l)	$Al(_{18}H_{33}O_2)_3$(?)	H_2O
Carbon/oxygen	Aluminum oxalate	$Al_2(C_2O_4)_3.4H_2O$	acid

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Oxygen	Aluminum oxide	γ-Alumina. Al_2O_3	acid
Oxygen	Aluminum trihydrate oxide	Nat.gibbsite,hydra-argilite.$Al_2O_3.3H_2O$	acid
		Nat.bayerite $Al_2O_3.3H_2O$	acid
Carbon/hydrogen/oxygen	Aluminum monopalmitate (com'l)	$Al(OH)_2C_{16}H_{31}O_2$	hydrocarbon
Carbon/hydrogen/oxygen/sulfur	Aluminum 1-phenol-4-sulfonate	$Al(C_6H_5O_4S)_3$	H_2O;alcohol,glycerin
Carbon/hydrogen/oxygen	Aluminum phenoxide	$Al(C_6H_5O)_3$	H_2O;alcohol,ether,chloroform
Phosphorous/oxygen	Aluminum orthophosphate	$AlPO_4$	acid,alcohol
Carbon/hydrogen/oxygen	Aluminum propoxide	$Al(C_3H_7O)_3$	H_2O;alcohol
Selenium	Aluminium selenide	Al_2Se_3	H_2O;acid
Oxygen/silicon	Aluminum silicate	Nat. sillimanite, andalusite, cyanite $Al_2O_3.SiO_2$	HF
Carbon/hydrogen/oxgyen	Aluminum tritearate	$Al(C_{18}H_{35}O_2)_3$	alcohol,benzene,turpentine
Sulfur/oxygen	Aluminum sulphate	$Al_2(SO_4)_3$	acid;alcohol
Sulfur	Aluminum sulfide	Al_2S_3	H_2O;acid

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TABLE VI

MOLYBDENUM COMBINATIONS

IONS	MOLYBDENUM-BASED COMPOUNDS	SYMBOLS	ETCHANTS
Bromine	Molybdenum dibromide	$MoBr_2$(or Mo_2Br_4	alkali
Bromine	Molybdenum tetrabromide	MoBr4	H_20,alkali
Bromine	Molybdenum tribromide	MoBr3	alkali, NH3
Carbon	Molybdenum monocarbide	MoC	HF, HC1
Carbon	Molybdenum dicarbide	Mo_2C	HF, HC1
Carbon/oxygen	Molybdenum carbonyl	$Mo(C0)_6$	benzene; ether
Chlorine alcohol	Molybdenum dichloride	$MoC1_2$(or Mo_2C1_6)	HC1,alkali, NH_40H, acetone
Chlorine	Molybdenum pentachloride	$MoC1_5$	mineral acid, liquid NH_3 $CC1_4$,chloroform;alcohol ether
Chlorine	Molybdenum tetrachloride	$MoC1_4$	concentrated mineral acid; alcohol, ether
Chlorine	Molybdenum trichloride	$MoC1_3$	H_20
Fluorine	Molybdenum hexafluoride	MoF6	H_20;NH_40H,alkali
Oxygen/hydrogen	Molybdenum hydroxide	$Mo(0H)_3$ (or $M0_20_3.3H_20$);	HC1;30% H_20_2
		$Mo0(0H)_3$ (or $Mo_20_5.3H_20$);	acid,alkali,carbon
		$Mo0_3.2H_20$	H_20_2,alkali,hydrogen;acid
Bromine/oxygen/ hydrogen	Molybdenum hydroxytetra dibromide	$M0_3Br_4(0H)_2$	alkali
Bromine/oxygen/ hydrogen	Molybdenum hydroxytetra dioctabromide hydrate	$MO_3BR_4(0H)_2.8H_20$	HC1;alkali
Chlorine/oxygen/ hydrogen	Molybdenum hydroxytetra-dichloride	$Mo_2C1_4(0H)_2.2H_20$	concentrated acid
Iodine	Molybdenum di-iodide	MoI_2	H_20
Oxygen/hydrogen	Molybdenum pentoxide	Mo_20_5;	HC1
		"Molybd.blue" $M0_20_5.xH_20$ (variations in Mo and 0)	H_20;acid,Me0H
Oxygen	Molybdenum trioxide	Molybdic anhydride. Nat.Molybdite. $Mo0_3$	acid,alkali,sulfur,NH_40H

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Oxygen/bromine	Molybdenum dioxydibromide	MoO_2Br_2	H_2O
Oxygen/chlorine	Molybdenum oxytetrachloride	$MoOCl_4$	H_2O
Oxygen/chlorine	Molybdenum oxytrichloride	$MoOCl_3$	H_2O
Oxygen/chlorine	Molybdenum dioxydichloride	MoO_2Cl_2	H_2O; alcohol,ether
Oxygen/chlorine/ hydrogen	Molybdenum dioxydichloride hydrate	$MoO_2Cl_22_0$	H_2O;alcohol, acetone,ether
Oxygen/chlorine	Molybdenum trioxyhexachloride	$Mo_2O_3Cl_6$	H_2O;ether
Oxygen/chlorine	Molybdenum trioxypentachloride	$Mo_2O_3Cl_5$	H_2O
Oxygen/hydrogen/ chlorine	Molybdenum oxychloride acid	$MoO(OH)_2Cl_2$	H_2O;alcohol,ether,acetone
Oxygen/fluorine	Molybdenum dioxydifluoride	MoO_2F_2	H_2O;alcohol,MeOH
Oxygen/fluorine	Molybdenum oxytetrafluoride	$MoOF_4$	H_2O;alcohol,ether,CCl_4
Silicon	Molybdenum silicide	$MoSi_2$	$HF+HNO_3$
Silicon/oxygen/hydrogen	Molybdenum pentasulfide	$Mo_2S_5.3H_2O$	NH_4OH,alkali,sulfides
Sulfur	Molybdenum tetrasulfide	MoS_4	alkali sulfide
Sulfur	Molybdenum trisulfide	MoX_3	H_2O;alkali,sulfur,concentrated KOH

While the present invention has been described in conjunction with the preferred embodiment and several examples, it is evident that

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CLAIMS

1. A method for use in the fabrication of a semiconductor device, said method for etching a metal film formed over a semiconductor substrate comprising the steps of:

forming a mask on the metal film to define a preselected region of the metal film;

implanting ions into a preselected region of the metal film to form a converted layer of metal compounds in the preselected region; and

selectively removing the converted layer by etching the metal compounds at low temperatures with an etchant chosen to prevent substantial etching of the metal film.

2. The method of claim 1, wherein the mask comprises a hard mask selected from the group consisting of dielectric films, metal films and tightly bonded metal oxide films.

3. The method of claim 1, wherein the mask comprises a photoresist layer.

4. The method of claim 1, wherein the method further comprises the step of removing the mask after the converted layer is formed.

5. The method of claim 1, wherein the method further comprises the step of forming an implant barrier layer beneath the metal film to prevent the ions from penetrating into layers beneath the implant barrier layer.

6. The method of claim 5, wherein the implant barrier comprises a material that is electrically and

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chemically stable with respect to the ions implanted.

7. The method of claim 1, wherein the method further comprises the step of thermally treating the semiconductor substrate after the preselected region is converted to assist in formation of the metal compounds.

8. The method of claim 1, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

9. The method of claim 1, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

10. The method of claim 1, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

11. The method of claim 1, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

12. The method of claim 1, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, K1, KCN and NH_3.

13. The method of claim 1, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

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14. The method of claim 1, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

15. The method of claim 1, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

16. A method for use in the fabrication of a semiconductor device, said method for etching a metal film formed over a semiconductor substrate comprising the steps of:

forming an implant barrier layer on the semiconductor substrate;

forming the metal film on the implant barrier layer;

forming a mask on the metal film to define a preselected region of the metal film;

implanting ions into the preselected region of the metal film to form a converted layer of metal compounds within the preselected region, the implant barrier layer preventing the ions from penetrating into layers beneath the implant barrier layer; and

selectively removing the converted layer without substantial etching of the metal film.

17. The method of claim 16, wherein the implant barrier comprises a material that is electrically and chemically stable with respect to the ions implanted.

18. The method of claim 16, wherein the method further comprises the step of thermally treating the

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semiconductor substrate after the ions are implanted into the preselected region to assist in the formation of the metal compounds.

19. The method of claim 16, wherein the metal film comprises copper, the ions comprise chlorine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

20. The method of claim 16, wherein the metal film comprises copper, the plasma comprises bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

21. The method of claim 16, wherein the step of removing the converted layer is performed by applying an etchant to etch the metal compounds.

22. The method of claim 21, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

23. The method of claim 21, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

24. The method of claim 21, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

25. The method of claim 21, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the group consisting of HCl,

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NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

26. The method of claim 21, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, Kl, KCN and NH_3.

27. The method of claim 21, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

28. The method of claim 21, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

29. The method of claim 21, wherein the metal film comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

30. A method for use in the fabrication of a semiconductor device, said method for etching a metal film formed on a semiconductor substrate comprising the steps of:

forming a mask on the metal film to define a preselected region of the metal film;

exposing the semiconductor substrate to a plasma comprising ions under an electric potential to reactively form metal compounds within the preselected region of the metal film; and

selectively removing the converted layer with an etchant chosen to prevent substantial etching of the metal film.

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31. The method of claim 30, wherein the mask comprises a hard mask selected from the group consisting of dielectric films, metal films and tightly bonded metal oxide films.

32. The method of claim 30, wherein the mask comprises a photoresist layer.

33. The method of claim 30, wherein the method further comprises the step of removing the mask after the converted layer is formed.

34. The method of claim 30, wherein the step of exposing the semiconductor substrate to a plasma is performed in a reactive ion etch system.

35. The method of claim 34, wherein the method further comprises the step of heating the semiconductor substrate to at least 200° Celsius during the exposure of the semiconductor substrate to the plasma.

36. The method of claim 34, wherein the metal film comprises copper, the plasma comprises chlorine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

37. The method of claim 34, wherein the metal comprises copper, the plasma comprises bromine ions and the step of removing the metal compounds is performed by evaporating the metal compounds in a ligand ambient.

38. The method of claim 34, wherein the step of removing the converted layer is performed by applying an etchant to etch the metal compounds.

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39. The method of claim 34, wherein the metal film comprises copper, the ions comprise chlorine ions and the etchant is selected from the group consisting of HCl, NH_4OH, MeOH, ether, alcohol, acetone and water.

40. The method of claim 34, wherein the metal film comprises copper, the ions comprise oxygen ions and the etchant is selected from the group consisting of HCl, NH_4OH, NH_4Cl, KCN, NH_4F and acid.

41. The method of claim 34, wherein the metal film comprises copper, the ions comprise fluorine ions and the etchant is selected from the group consisting of HCl, HF, H_2O and mineral acid.

42. The method of claim 34, wherein the metal film comprises copper, the ions comprise bromine ions and the etchant is selected from the group consisting of HCl, NH_4OH, HBr, H_2O, NH_3, acetone, alcohol and pyridine.

43. The method of claim 34, wherein the metal film comprises copper, the ions comprise iodine ions and the etchant is selected from the group consisting of HCl, K1, KCN and NH_3.

44. The method of claim 34, wherein the metal film comprises molybdenum, the ions comprise oxygen ions and the etchant is selected from the group consisting of H_2O, NH_4OH, acid, alkali and sulfer.

45. The method of claim 34, wherein the metal film comprises silver, the ions comprise fluorine ions and the etchant is selected from the group consisting of H_2O and NH_4OH.

46. The method of claim 41, wherein the metal film

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comprises silver, the ions comprise oxygen ions and the etchant is selected from the group consisting of NH_4OH, acid and alcohol.

47. A method for use in the fabrication of a semiconductor device, the method for etching a metal film formed over a semiconductor substrate, said method substantially as hereinbefore described with reference to the accompanying drawings.

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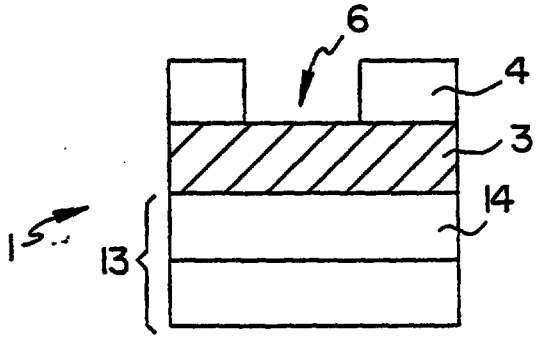


FIG. 1A

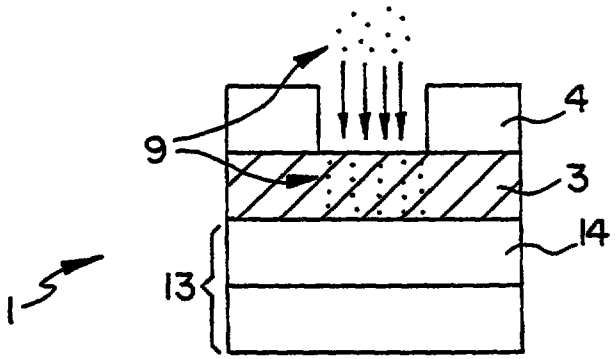


FIG. 1B

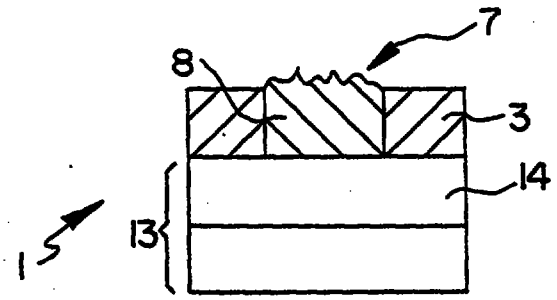


FIG. 1C

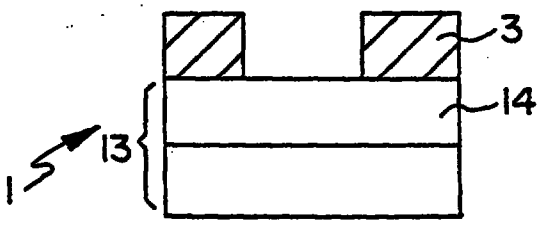


FIG. 1D

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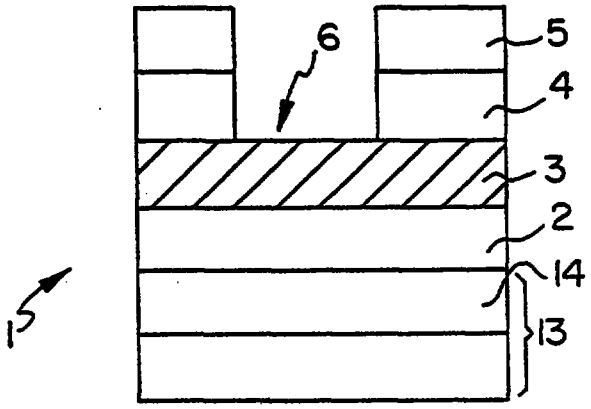


FIG. 2A

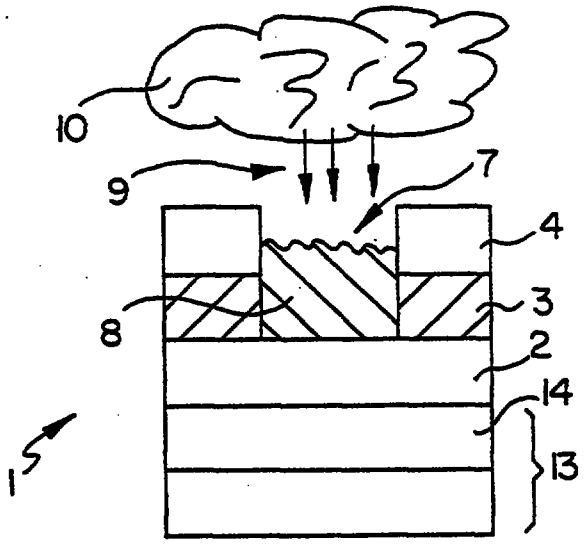


FIG. 2B

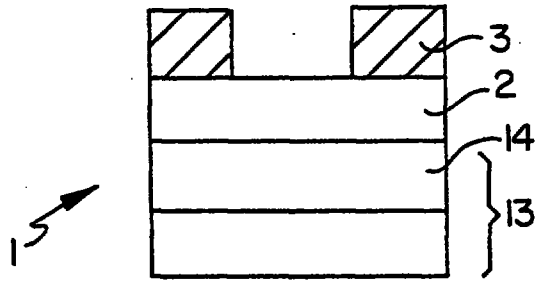


FIG. 2C

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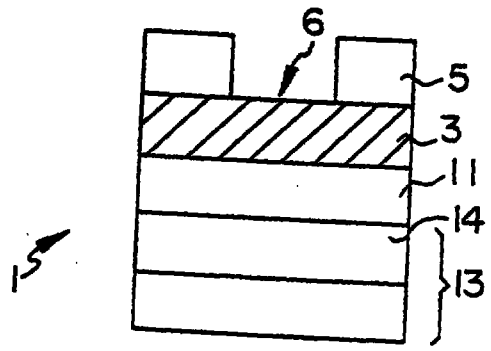


FIG. 3A

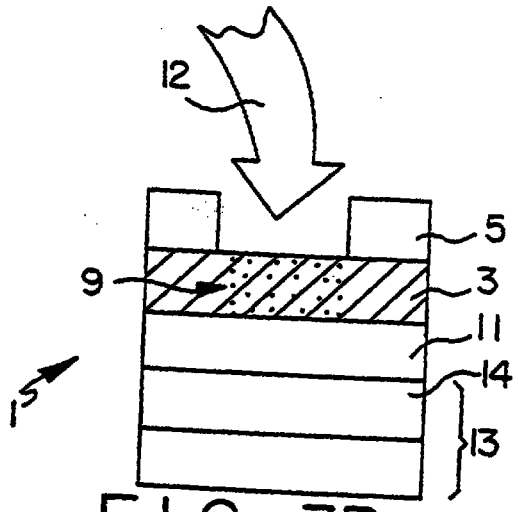


FIG. 3B

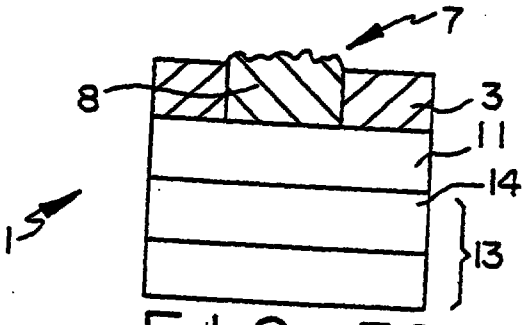


FIG. 3C

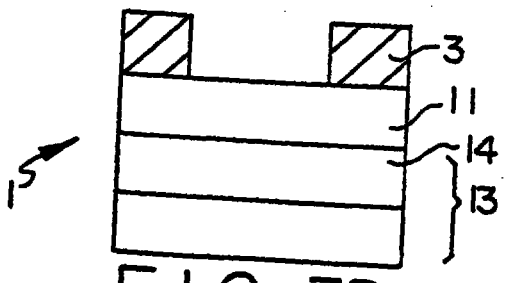


FIG. 3D

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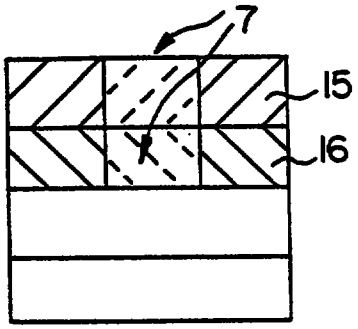


FIG. 4A

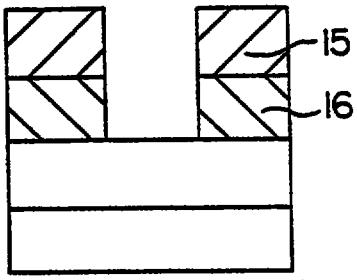


FIG. 4B

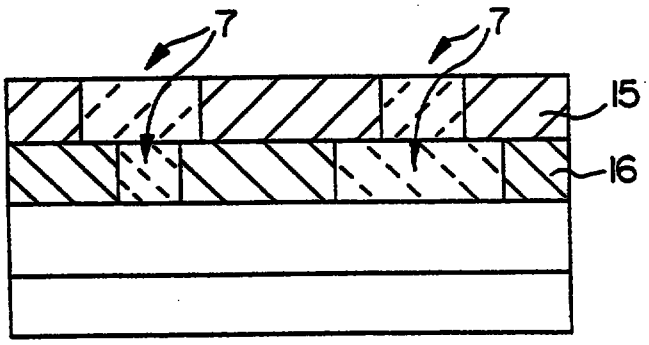


FIG. 5A

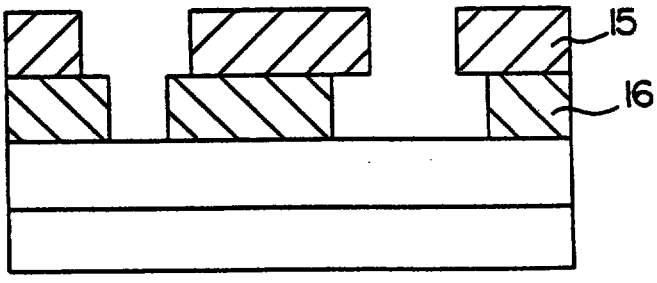


FIG. 5B