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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : **C23C 16/34, H01L 21/285**	**A1**	**(11) International Publication Number:** **WO 00/65125** **(43) International Publication Date:** 2 November 2000 (02.11.00)

(21) International Application Number: PCT/US00/11278

(22) International Filing Date: 26 April 2000 (26.04.00)

(30) Priority Data:
09/300,658 27 April 1999 (27.04.99) US

(71) Applicant: TOKYO ELECTRON LIMITED [JP/JP]; TBS Broadcast Center, 3–6 Akasaka 5–chome, Minato–ku, Tokyo 107 (JP).

(71) Applicant *(for JP only)*: TOKYO ELECTRON ARIZONA, INC. [US/US]; 2120 West Guadalupe Road, Gilbert, AZ 85233–8205 (US).

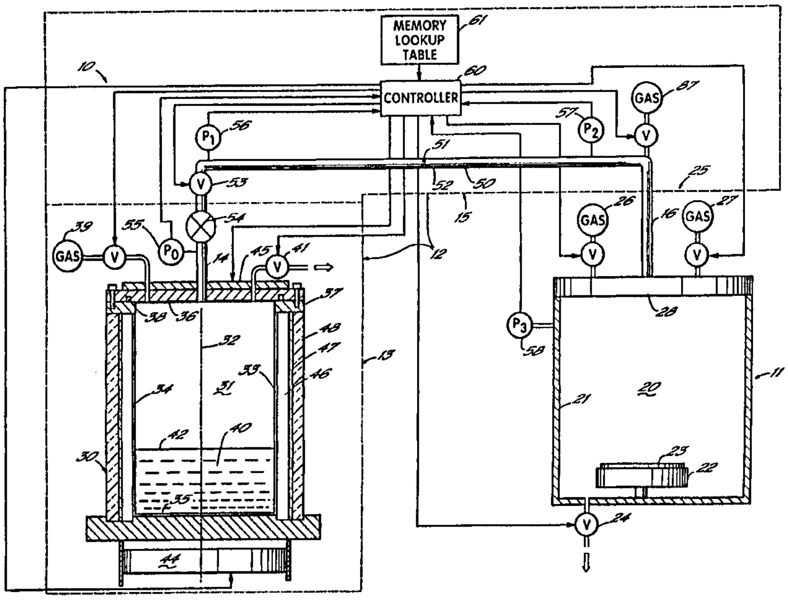
(72) Inventors: HAUTALA, John, J.; 8 Baker Avenue, Beverly, MA 01915 (US). WESTENDORP, Johannes, F., M.; 9 Woodbury Lane, Rockport, MA 01966 (US).

(74) Agents: FREI, Donald, F. et al.; Wood, Herron & Evans, L.L.P., 2700 Carew Tower, Cincinnati, OH 45202 (US).

(81) Designated States: CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PECVD OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS



(57) Abstract

A plasma enhanced chemical vapor deposition (PECVD) method for depositing high quality conformal tantalum nitride (TaN_x) films from inorganic tantalum pentahalide (TaX_5) precursors and nitrogen is described. The inorganic tantalum halide precursors are tantalum pentafluoride (TaF_5), tantalum pentachloride ($TaCl_5$) and tantalum pentabromide ($TaBr_5$). A TaX_5 vapor is delivered into a heated chamber. The vapor is combined with a process gas containing nitrogen to deposit a TaN_x film on a substrate that is heated to 300 °C–500 °C. The deposited TaN_x film is useful for integrated circuits containing copper films, especially in small high aspect ratio features. The high conformality of these films is superior to films deposited by PVD.

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PECVD OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS

Field of the Invention

The invention relates to the formation of integrated circuits, and specifically to chemical vapor deposition of tantalum nitride films from tantalum halide precursors.

Background

Integrated circuits (IC) provide the pathways for signal transport in an electrical device. An IC in a device is composed of a number of active transistors contained in a silicon base layer of a semiconductor substrate. To increase the capacity of an IC, large numbers of interconnections with metal "wires" are made between one active transistor in the silicon base of the substrate and another active transistor in the silicon base of the substrate. The interconnections, collectively known as the metal interconnection of a circuit, are made through holes, vias or trenches that are cut into a substrate. The particular point of the metal interconnection which actually makes contact with the silicon base is known as the contact. The remainder of the hole, via or trench is filled with a conductive material, termed a contact plug. As transistor densities continue to increase, forming higher level integrated circuits, the diameter of the contact plug must decrease to allow for the increased number of interconnections, multilevel metalization structures and higher aspect ratio vias.

Aluminum has been the accepted standard for contacts and interconnections in integrated circuits. However, problems with its electromigration and its high electrical resistivity require new materials for newer structures with submicron dimensions. Copper holds promise as the interconnect material for the next generation of integrated circuits in ultra large scale integration (ULSI) circuitry, yet its formation of copper silicide (Cu-Si) compounds at low temperatures and its electromigration through a silicon oxide (SiO_2) are disadvantages to its use.

As the shift from aluminum to copper as an interconnect element of choice occurs, new materials are required to serve as a barrier, preventing copper diffusion into the underlying dielectric layers of the substrate. New materials are also required to serve as a liner, adhering subsequently deposited copper to the substrate. The liner must also provide a low electrical resistance interface between copper and the barrier material. Barrier layers that were previously used with aluminum, such as titanium (Ti) and titanium nitride (TiN) barrier layers deposited either by physical vapor deposition (PVD) methods such as sputtering and/or chemical vapor deposition (CVD), are ineffective as barriers to copper. In addition, Ti reacts with copper to form copper titanium compounds at the relatively low temperatures used with PVD and/or CVD.

Sputtered tantalum (Ta) and reactive sputtered tantalum nitride (TaN) have been demonstrated to be good diffusion barriers between copper and a silicon substrate due to their high conductivity, high thermal stability and resistance to diffusion of foreign atoms. However, the deposited Ta and/or TaN film has inherently poor step coverage due to its shadowing effects. Thus the sputtering process is limited to relatively large feature sizes ($> 0.3\ \mu m$) and small aspect ratio contact vias. CVD offers the inherent advantage over PVD of better conformality, even in small structures ($< 0.2\ \mu m$) with high aspect ratios. However, CVD of Ta and TaN with metal-organic sources such as tertbutylimidotris (diethylamido)tantalum TBTDET, pentakis (dimethylamino) tantalum (PDMAT) and pentakis (diethylamnio) tantalum (PDEAT) yields mixed results. Additional problems with Ta and TaN are that all resulting films have relatively high concentrations of oxygen and carbon impurities and require the use of a carrier gas.

The need to use a carrier gas presents the disadvantage that the concentration of the precursor gas in the carrier is not precisely known. As a result, accurate metering of a mixture of a carrier gas and a precursor gas to the CVD reaction chamber does not insure accurate metering of the precursor gas alone to the reactor. This can cause the reactants in the CVD chamber to be either too rich or too lean. The use of a carrier gas also presents the disadvantage that particulates are frequently picked up by the flowing carrier gas and delivered as contaminants to the CVD reaction chamber. Particulates on the surface of a semiconductor wafer during processing can result in the production of defective semiconductor devices.

Thus, a process to deposit TaN at the relatively low temperatures used in PECVD (< 500°C) would provide an advantage in the formation of copper barriers in the next generation of IC. Ideally, the deposited film will have a high step coverage (the ratio of the coating thickness at the bottom of a feature to the thickness on the sides of a feature or on the top surface of the substrate or wafer adjacent the feature), good diffusion barrier properties, minimal impurities, low resistivity, good conformality (even coverage of complex topography of high aspect ratio features) and ideally the process will have a high deposition rate.

Summary of the Invention

The invention is directed to a method of depositing a tantalum nitride (TaN_x) film from a tantalum halide precursor on a substrate. The tantalum halide precursor is delivered at a temperature sufficient to vaporize the precursor to provide a vaporization pressure to deliver the tantalum vapor to a reaction chamber containing the substrate. The vaporization pressure is at least about 3 Torr. The vapor is combined with a process gas containing nitrogen and TaN_x is deposited on the substrate by a plasma enhanced chemical vapor deposition (PECVD) process. The tantalum halide precursor is tantalum fluoride (TaF), tantalum chloride (TaCl) or tantalum bromide (TaBr), preferably tantalum pentafluoride (TaF_5), tantalum pentachloride ($TaCl_5$) or tantalum pentabromide ($TaBr_5$). The substrate temperature is in the range of about 300°C-500°C.

The invention is also directed to a method of depositing a TaN_x film from a TaF_5 or $TaCl_5$ precursor on a substrate by elevating the precursor temperature sufficient to vaporize the precursor. The vapor is combined with a process gas containing nitrogen and the TaN_x film is deposited by PECVD.

The invention is further directed to method of depositing a TaN_x film from a $TaBr_5$ precursor on a substrate without a carrier gas. The temperature of the precursor is elevated sufficient to produce a tantalum vapor. The vapor is combined with a process gas containing nitrogen and the TaN_x film is deposited on the substrate by PECVD.

The invention is still further directed to a substrate integral with a copper layer and a TaN_x layer in which diffusion of copper is prevented by the TaN_x layer.

The TaN_x layer deposited according to the invention has minimal impurities and low resistivity. The film provides good step coverage, good conformality in high aspect ratio features and is a good diffusion barrier to a copper film.

It will be appreciated that the disclosed method and substrates of the invention have an array of applications. These and other advantages will be further understood with reference to the following drawings and detailed description.

Brief Description of the Figures

FIG. 1 is a schematic of an apparatus for plasma enhanced chemical vapor deposition (PECVD).

FIG. 2 is a graph of vapor pressure versus temperature for tantalum halides.

FIG. 3 is a photograph of a scanning electron micrograph (SEM) of a tantalum nitride (TaN_x) film deposited using a tantalum pentafluoride (TaF_5) precursor.

FIG. 4 is a photograph of a SEM of a TaN_x film deposited using a tantalum pentachloride ($TaCl_5$) precursor.

FIG. 5 is a photograph of a SEM of a TaN_x film depositedusing a tantalum pentabromide ($TaBr_5$) precursor.

FIG. 6 is a photograph of a SEM of a TaF_5 based film stack.

FIG. 7 is a photograph of a SEM of a $TaCl_5$ based film stack.

FIG. 8 is an Auger spectrum tracing of a TaN_x film deposited using a $TaBr_5$ precursor deposited on SiO_2.

FIG. 9 is an Auger spectrum tracing of a TaN_x film deposited using a $TaBr_5$ precursor deposited on a PECVD tantalum film.

Detailed Description

Refractory transition metals such as tantalum (Ta) and their nitride films (TaN) are effective diffusion barriers to copper (Cu). Their effectiveness is due to their high thermal stability, high conductivity and resistance to diffusion of foreign elements or impurities. Ta and TaN are especially attractive due to their chemical inertness with Cu; no compounds form between Cu and Ta or Cu and N.

Tantalum halides provide a convenient inorganic source for Ta and TaN. Specifically, the inorganic precursor is a tantalum pentahalide (TaX_5) where X represents the halides fluorine (F), chlorine (Cl) and bromine (Br). Table 1 shows relevant thermodynamic properties of the tantalum halide precursors, specifically tantalum pentafluoride (TaF_5), tantalum pentachloride ($TaCl_5$) and tantalum bromide ($TaBr_5$), with tantalum pentaiodide (TaI_5) included for comparison. The TaF_5, $TaCl_5$ and $TaBr_5$ precursor materials are all solids at room temperature (18°C-22°C).

Table 1

PRECURSOR	MELTING POINT	BOILING POINT	CHANGE IN HEAT OF FORMATION (ΔHf)
TaF_5	97°C	230°C	-455 kcal/mole
$TaCl_5$	216°C	242°C	-205 kcal/mole
$TaBr_5$	265°C	349°C	-143 kcal/mole
TaI_5	367°C	397°C	-82 kcal/mole

In chemical vapor deposition (CVD) processes, gas precursors are activated using either thermal energy or electrical energy. Upon activation, the gas precursors react chemically to form a film. A preferred method of CVD is illustrated in FIG 1 and is disclosed in a copending application entitled APPARATUS AND METHODS FOR DELIVERY OF VAPOR FROM SOLID SOURCES TO A CVD CHAMBER by Westendorp et al. filed on the same date as the present application and assigned to Tokyo Electron Limited and incorporated by reference herein in its entirety. A chemical vapor deposition (CVD) system 10 includes a CVD reactor 11 and a precursor delivery system 12. In the reactor 11, a reaction is carried out to convert a precursor gas of, for example, tantalum chloride (TaCl) or other tantalum halide compound, into a film such as a barrier layer film of tantalum (Ta) or tantalum nitride (TaN_x). The TaN film is not limited to any particular stoichiometry (TaN_x), since TaN_x can be continuously varied by changing the ratios of the gases in any given deposition. Thus, as used herein, TaN_x encompasses a tantalum nitride film of any stoichometry.

The precursor delivery system 12 includes a source 13 of precursor gas having a gas outlet 14, which communicates through a metering system 15 with a gas inlet 16 to the CVD reaction chamber 11. The source 13 generates a precursor gas, for example a tantalum halide vapor, from a tantalum halide compound. The compound is one that is in a solid state when at standard temperature and pressure. The precursor source is maintained, preferably by controlled heating, at a temperature that will produce a desired vapor pressure of precursor. Preferably, the vapor pressure is one that is itself sufficient to deliver the precursor vapor to the reaction chamber 11, preferably without the use of a carrier gas. The metering system 15 maintains a flow of the precursor gas vapor from the source 13 into the reaction chamber 11 at a rate that is sufficient to maintain a commercially viable CVD process in the reaction chamber 11.

The reaction chamber 11 is a generally conventional CVD reaction chamber and includes a vacuum chamber 20 that is bounded by a vacuum tight chamber wall 21. In the chamber 20 is situated a substrate support or susceptor 22 on which a substrate such as a semiconductor wafer 23 is supported. The chamber 20 is maintained at a vacuum appropriate for the performance of a CVD reaction that will deposit a film such as a Ta/TaN_x barrier layer on the semiconductor wafer substrate 23. A preferred pressure range for the CVD reaction chamber 11 is in the range of from 0.2-5.0 Torr. The vacuum is maintained by controlled operation of a vacuum pump 24 and of inlet gas sources 25 that include the delivery system 12 and may also include reducing gas sources 26 of, for example, hydrogen (H_2), nitrogen (N_2) or ammonia (NH_3) for use in carrying out a tantalum reduction reaction, and an inert gas source 27 for a gas such as argon (Ar) or helium (He). The gases from the sources 25 enter the chamber 20 through a showerhead 28 that is situated at one end of the chamber 20 opposite the substrate 23, generally parallel to and facing the substrate 23.

The precursor gas source 13 includes a sealed evaporator 30 that includes a cylindrical evaporation chamber 31 having a vertically oriented axis 32. The chamber 31 is bounded by a cylindrical wall 33 formed of a high temperature tolerant and non-corrosive material such as the alloy INCONEL 600, the inside surface 34 of which is highly polished and smooth. The wall 33 has a flat circular closed bottom 35 and an open top, which is sealed by a cover 36 of the same heat tolerant and non-corrosive material as the wall 33. The outlet 14 of the source 13 is situated in the cover 36. When high temperatures are used, such as with TiI_4 or $TaBr_5$, the cover 36 is sealed to a flange ring 37 that is integral to the top of the wall 33 by a high temperature tolerant vacuum compatible metal seal 38 such as a HELICOFLEX seal, which is formed of a C-shaped nickel tube surrounding an INCONEL coil spring. With$TaCl_5$ and TaF_5, a conventional elastomeric O-ring seal 38 may be used to seal the cover.

Connected to the vessel 31 through the cover 36 is a source 39 of a carrier gas, which is preferably an inert gas such as He or Ar. The source 13 includes a mass of precursor material such as tantalum fluoride, chloride or bromide (TaX), preferably as the pentahalide (TaX_5), at the bottom of the vessel 31, which is loaded into the vessel 31 at standard temperature and pressure in a solid state. The vessel 31 is filled with tantalum halide vapor by sealing the vessel with the solid mass of TaX therein. The halide is supplied as a precursor mass 40 that is placed at the bottom of the vessel 31, where it is heated, preferably to a liquid state as long as the resulting vapor pressure is in an acceptable range. Where the mass 40 is liquid, the vapor lies above the level of the liquid mass 40. Because wall 33 is a vertical cylinder, the surface area of TaX mass 40, if a liquid, remains constant regardless of the level of depletion of the TaX.

The delivery system 12 is not limited to direct delivery of a precursor 40 but can be used in the alternative for delivery of precursor 40 along with a carrier gas, which can be introduced into the vessel 31 from gas source 39. Such a gas may be hydrogen (H_2) or an inert gas such as helium (He) or argon (Ar). Where a carrier gas is used, it may be introduced into the vessel 31 so as to distribute across the top surface of the precursor mass 40 or may be introduced into the vessel 31 so as to percolate through the mass 40 from the bottom 35 of the vessel 31 with upward diffusion in order to achieve maximum surface area exposure of the mass 40 to the carrier gas. Yet another alternative is to vaporize a liquid that is in the vessel 31. However, such alternatives add undesired particulates and do not provide the controlled delivery rate achieved by the direct delivery of the precursor, that is, delivery without the use of a carrier gas. Therefore, direct delivery of the precursor is preferred.

To maintain the temperature of the precursor 40 in the vessel 31, the bottom 35 of the wall 33 is maintained in thermal communication with a heater 44, which maintains the precursor 40 at a controlled temperature, preferably above its melting point, that will produce a vapor pressure in the range of about 3 Torr in the absence of a carrier gas (i.e., a direct delivery system), and a lower vapor pressure such as about 1 Torr when a carrier gas is used. The exact vapor pressure depends upon other variables such as the quantity of carrier gas, the surface area of the substrate 23, and so on. In a direct delivery system for tantalum, a vapor pressure can be maintained at the preferred pressure of 5 Torr or above by heating the a tantalum halide precursor in the 95°C to 205°C range as shown in FIG. 2. For TaX_5 the desired temperature is at least about 95°C for TaF_5, the desired temperature is at least about 145°C for $TaCl_5$, and the desired temperature is at least about 205°C for $TaBr_5$. The melting points of the respective fluoride, chloride and bromide tantalum pentahalide compounds are in the 97°C to 265°C range. A much higher temperature is required for tantalum pentaiodide (TaI_5) to produce a sufficient vapor pressure in the vessel 31. Temperatures should not be so high as to cause premature reaction of the gases in the showerhead 28 or otherwise before contacting the wafer 23.

For purposes of example, a temperature of 180°C is assumed to be the control temperature for the heating of the bottom 35 of the vessel 31. This temperature is appropriate for producing a desired vapor pressure with a titanium tetraiodide (TiI_4) precursor. Given this temperature at the bottom 35 of the vessel 31, to prevent condensation of the precursor vapor on the walls 33 and cover 36 of the vessel 31, the cover is maintained at a higher temperature than the heater 44 at the bottom 35 of the wall 33 of, for example, 190°C, by a separately controlled heater 45 that is in thermal contact with the outside of the cover 36. The sides of the chamber wall 33 are surrounded by an annular trapped air space 46, which is contained between the chamber wall 33 and a surrounding concentric outer aluminum wall or can 47. The can 47 is further surrounded by an annular layer of silicon foam insulation 48. This temperature maintaining arrangement maintains the vapor in a volume of the vessel 31 bounded by the cover 36, the sides of the walls 33 and the surface 42 of the precursor mass 40 in the desired example temperature range of between 180°C and 190°C and the pressure greater than about 3 Torr, preferably at greater than 5 Torr. The temperature that is appropriate to maintain the desired pressure will vary with the precursor material, which is primarily contamplated as a being a tantalum or titanium halide compound.

The vapor flow metering system 15 includes a delivery tube 50 of at least ½ inch in diameter, or at least 10 millimeters inside diameter, and preferably larger so as to provide no appreciable pressure drop at the flow rate desired, which is at least approximately 2 to 40 standard cubic centimeters per minute (sccm). The tube 50 extends from the precursor gas source 13 to which it connects at its upstream end to the outlet 14, to the reaction chamber 11 to which it connects at its downstream end to the inlet 16. The entire length of the tube 50 from the evaporator outlet 14 to the reactor inlet 16 and the showerhead 28 of the reactor chamber 20 are also preferably heated to above the evaporation temperature of the precursor material 40, for example, to 195°C.

In the tube 50 is provided baffle plate 51 in which is centered a circular orifice 52, which preferably has a diameter of approximately 0.089 inches. The pressure drop from gauge 1 56 to gauge 2 57 is regulated by control valve 53. This pressure drop after control valve 53 through orifice 52 and into reaction chamber 11 is greater than about 10 milliTorr and will be proportional to the flow rate. A shut-off valve 54 is provided in the line 50 between the outlet 14 of the evaporator 13 and the control valve 53 to close the vessel 31 of the evaporator 13.

Pressure sensors 55-58 are provided in the system 10 to provide information to a controller 60 for use in controlling the system 10, including controlling the flow rate of precursor gas from the delivery system 15 into the chamber 20 of the CVD reaction chamber 11. The pressure sensors include sensor 55 connected to the tube 50 between the outlet 14 of the evaporator 13 and the shut-off valve 54 to monitor the pressure in the evaporation vessel 31. A pressure sensor 56 is connected to the tube 50 between the control valve 53 and the baffle 51 to monitor the pressure upstream of the orifice 52, while a pressure sensor 57 is connected to the tube 50 between the baffle 51 and the reactor inlet 16 to monitor the pressure downstream of the orifice 52. A further pressure sensor 58 is connected to the chamber 20 of the reaction chamber 11 to monitor the pressure in the CVD chamber 20.

Control of the flow of precursor vapor into the CVD chamber 20 of the reaction chamber 11 is achieved by the controller 60 in response to the pressures sensed by the sensors 55-58, particularly the sensors 56 and 57 which determine the pressure drop across the orifice 52. When the conditions are such that the flow of precursor vapor through the orifice 52 is unchoked flow, the actual flow of precursor vapor through the tube 52 is a function of the pressures monitored by pressure sensors 56 and 57, and can be determined from the ratio of the pressure measured by sensor 56 on the upstream side of the orifice 52, to the pressure measured by sensor 57 on the downstream side of the orifice 52.

When the conditions are such that the flow of precursor vapor through the orifice 52 is choked flow, the actual flow of precursor vapor through the tube 52 is a function of only the pressure monitored by pressure sensor 57. In either case, the existence of choked or unchoked flow can be determined by the controller 60 by interpreting the process conditions. When the determination is made by the controller 60, the flow rate of precursor gas can be determined by the controller 60 through calculation.

Preferably, accurate determination of the actual flow rate of precursor gas is calculated by retrieving flow rate data from lookup or multiplier tables stored in a non-volatile memory 61 accessible by the controller 60. When the actual flow rate of the precursor vapor is determined, the desired flow rate can be maintained by a closed loop feedback control of one or more of the variable orifice control valve 53, the CVD chamber pressure through evacuation pump 24 or control of reducing or inert gases from sources

26 and 27, or by control of the temperature and vapor pressure of the precursor gas in chamber 31 by control of heaters 44, 45.

As shown in FIG. 1, the solid TaF_5, $TaCl_5$ and $TaBr_5$ precursor material 40 is sealed in a cylindrical corrosion resistant metal vessel 31 that maximizes the available surface area of the precursor material. Vapor from either TaF_5, $TaCl_5$ or $TaBr_5$ was delivered directly, that is, without the use of a carrier gas, by a high conductance delivery system into a chamber 11. The chamber 11 was heated to a temperature of at least about 100°C to prevent condensation of vapor or deposition by-products.

The controlled direct delivery of tantalum halide vapor into the reaction chamber 11 was accomplished by heating the solid tantalum halide precursor 40 to a temperature in the range of about 95°C-205°C, the choice depending upon the particular precursor. The temperature was sufficient to vaporize the precursor 40 to provide a vapor pressure to deliver the tantalum halide vapor to the chamber 11. Thus, a carrier gas was not necessary and preferably was not used. A sufficient vapor pressure was greater than about 3 Torr. This pressure was required to maintain a constant pressure drop across a defined orifice in a high conductance delivery system while delivering up to about 50 sccm tantalum halide precursor to a reaction chamber 11 operating in the range of about 0.1-2.0 Torr. The temperatures to obtain the desired pressures in a direct delivery system were in the range of about 83°C-95°C and preferably about 95°C with TaF_5, in the range of about 130°C-150°C and preferably about 145°C with $TaCl_5$, and in the range of about 202°C-218°C and preferably about 205°C with $TaBr_5$. Under these conditions, TaF_5 is a liquid while $TaCl_5$ and $TaBr_5$ remain solid.

FIG. 2 shows the relationship between the measured vapor pressure and temperature for the precursors TaF_5, $TaCl_5$ and $TaBr_5$, with TaI_5 included for comparison. As previously stated, the desired pressure was greater than about 3 Torr and preferably greater than 5 Torr. Also as previously stated, the vapor pressure for TaF_5, $TaCl_5$ and $TaBr_5$ was desirably low enough to be able to deposit tantalum in the absence of a carrier gas but yet sufficient to maintain a constant pressure drop across a defined orifice in a high conductance delivery system and still be able to deliver up to 50 sscm TaX_5 to a reaction chamber 11 operating at 0.1-2.0 Torr. The vapor pressure for TaI_5 was determined to be too low for practical implementation in the described apparatus. For $TaBr_5$ the open circles represent published values, while closed squares for $TaBr_5$, TaF_5, $TaCl_5$ and TaI_5 represent the inventors' experimental data.

A parallel plate RF discharge was used where the driven electrode was the gas delivery showerhead and the susceptor 22 or stage for the wafer or substrate 23 was the RF ground. The selected TaX_5 vapor was combined with other process gases such as H_2 above the substrate, which had been heated to a temperature between about 300°C-500°C. Ar and He could also be used, either singularly or in combination, as process gases in addition to H_2.

Process conditions for deposition of good quality PECVD TaN_x films are given in Table 2, where slm is standard liters per minute and W/cm^2 is watts per centimeter squared.

Table 2

Substrate Temperature	300°C-500°C
TaX_5 temperature	95°C (TaF_5), 145°C ($TaCl_5$), 205°C ($TaBr_5$)
TaX_5 flow	1-50 sccm
H_2 flow	1-10 slm
N_2 flow	0.1-10 slm
Ar, He flow	0-10 slm
Process Pressure	0.2-5.0 Torr
RF Power	0.1-5.0 W/cm^2

The TaF_5, $TaCl_5$ and $TaBr_5$ based PECVD TaN_x film properties for process conditions using the method of the invention are given in Table 3. Representative values were selected from among the PECVD of TaN_x from a TaX_5 precursor (TaF_5 number of experiments $(n) = 15$, $TaCl_5$ $n=8$, $TaBr_5$ $n=8$) on 200 mm Si and SiO_2 substrates. In addition, PECVD of Ta/TaN_x bilayers was also performed (TaF_5 $n=3$, $TaCl_5$ $n=1$, $TaBr_5$ $n=1$). The properties of the deposited TaN_x films as listed in Table 3 were uniform within plus or minus 20% across the wafer.

Table 3

Film	Precursor	TaX_5 flow (sccm)	N_2 flow (slm)	H_2 flow (slm)	Pressure (Torr)	Temp. (°C)	RF (Watts)	Dep. rate (Å/min.)	Resistivity ($\mu\Omega$cm)	Step Coverage
TaN	TaF_5	14	0.5	7	1.1	430	200	305	505	0.2
TaN	TaF_5	14	2.5	7	1.4	400	200	755	1120	0.2
TaN	TaF_5	14	5	5	1.6	400	200	1900	2160	0.2
TaN	$TaCl_5$	14	0.5	7	1.1	350	200	525	945	0.2
TaN	$TaCl_5$	14	2.5	7	1.4	400	500	613	1564	0.25
TaN	$TaCl_5$	14	5	5	1.6	400	500	953	7865	0.13
TaN	$TaBr_5$	2.5	0.5	7	1.1	375	100	107	1177	0.5
TaN	$TaBr_5$	2.5	1.5	7	1.3	375	100	200	2300	0.2

The film deposited by the method of the invention displays characteristics important to the formation of an IC. The film is in the range of low enough electrical resistivity for low interconnect impedances (less than 1000 μΩcm and preferably less than 500 μΩcm), and the film has good conformality and good step coverage (greater than 0.3). In addition, the level of impurities are low (less than 2 atomic percent). Also, the deposition rates are sufficient for throughput considerations (greater than 100 Å/min) and the process uses a low wafer temperature (less than 450°C) and thus is compatible with other thin film materials used within the device including materials with dielectric constants lower than that of SiO_2.

The dependence of the film resistivities on the deposition temperature differed among the three precursors. At a temperature of 430°C and at a N_2 flow of 0.5 slm, TaF_5 based films had a resistivity of 505 μΩcm. At a temperature of 400°C and a N_2 flow of 2.5 slm, the resistivity increased to 1120 μΩcm. When the N_2 flow rate was increased to 5 slm while a temperature of 400°C was maintained the resistivity further increased to 2160 μΩcm. Resistivity for PECVD TaN_x films deposited using $TaCl_5$ as the precursor also increased as the N_2 flow rate increased. At a temperature of 350°C and a N_2 flow rate of 0.5 slm, the resistivity was 945 μΩcm. At a temperature of 400°C and a N_2 flow of 2.5 slm, the resistivity increased to 1564 μΩcm. When the N_2 flow rate increased to 5 slm while a temperature of 400°C was maintained, the resistivity further increased to 7865 μΩcm. Resistivity for TaN_x films deposited using $TaBr_5$ as the precursor increased from 1177 μΩcm to 2300 μΩcm with a temperature maintained at 375°C when the N_2 flow increased from 0.5 slm to 1.5 slm. Thus, for all three precursors, the resistivity of the TaN_x film increased when the N_2 flow in the gas mix was increased. The increased resistivity is assumed to be due to the increase of nitrogen concentration in the film. This is consistent with previous results from TaN_x films deposited either by PVD such as sputtering, or by organic-metal CVD (OMCVD), where increasing the ratio of nitrogen to tantalum dramatically increased the resistivity of the TaN_x film.

Scanning electron micrographs (SEM) of TaN_x films deposited by PECVD according to the invention were obtained and are shown in FIGS 3-5. FIG 3 is a SEM of a TaN_x film using TaF_5 as the precursor, FIG 4 is a SEM of a TaN_x film using $TaCl_5$ as the precursor and FIG 5 is a SEM of a TaN_x film using $TaBr_5$ as the precursor.

Each of FIGS 3-5 shows a 3:1 aspect ratio structure with representative bottom step coverage and side wall coverage for each of the three precursors. The step coverage represents the film thickness on the bottom of the feature divided by the film thickness on the surface of the substrate adjacent the feature, also called the field. An ideal step coverage is 1.0 or 100%, representing identical thickness on the bottom as on the field. The $TaBr_5$ and $TaCl_5$ based PECVD TaN_x films appeared to have better step coverage than the TaF_5 based PECVD TaN_x films. As shown in Table 3, for $TaBr_5$ the step coverage was 0.50 and 0.20, for $TaCl_5$ the step coverage was 0.20, 0.25 and 0.13 and for TaF_5 the step coverage was consistently 0.2.

As shown in FIGS 3-5, the TaN_x films generally appeared to have good dense morphologies. The TaN_x films using $TaBr_5$ and $TaCl_5$ as the precursors generally appeared to be smoother and TaN_x films using TaF_5 as the precursor generally appeared rougher.

The compatibility of the PECVD TaN_x film process of the present invention with copper was determined. Since in practice the TaN_x film will be integral, that is, in direct contact with copper, little or no attack or etching of the copper should take place during TaN_x deposition. TaN_x compatibility with copper was tested by placing a Si wafer containing a 500 Å layer of TaN_x deposited by PVD and a 2000 Å layer of copper deposited by PVD into the deposition chamber 11. A TaN_x film was deposited by PECVD on top of the copper layer using the process of the invention with either a TaF_5 or $TaCl_5$ precursor.

Photographs of SEM of the resulting films are shown in FIGS 6 and 7. FIG 6 shows a TaF_5 based TaN_x film on a stack having layers of $SiO_2/TiN/Cu/TaN_x$. FIG 7 shows a $TaCl_5$ based TaN_x film on a stack having layers of $SiO_2/TiN/Cu/TaN_x$. The Cu layers have the same thicknesses of about 2000 Å as deposited. FIGS 7-8 also show films having a relatively sharp interface for all layers. It can therefore be concluded that very little or no attack or etching occurs during PECVD of either TaF_5 or $TaCl_5$ precursor-based films. Based on these results, a $TaBr_5$ based TaN_x film would also be expected to show compatibility with copper.

Selected films were also evaluated by Auger electron spectroscopy. Auger analysis spectra are shown in FIGS 8-9 with $TaBr_5$ used as the precursor for depositing TaN_x on either a SiO_2 layer (FIG 8) or on a PECVD $TaBr_5$ based Ta film (FIG 9). Analysis of the Auger spectra confirmed the clean interface and the minimal diffusion between the copper and TaN_x layers. The analysis also confirmed the low level of impurities present in the films. The figures indicate that these TaN_x films were nitrogen poor ($x < 1.0$), which is consistent with the results shown in Table 2. These films were deposited with the low N_2:H_2 ratio of 0.5:7, which was expected to result in a lower nitrogen-containing film. The normally exponentially rising electrical resistivity of TaN_x when $x > 1.0$ is observed in TaN_x films deposited by both PVD and CVD. The figures show relatively sharp interfaces between all layers including with Cu. The bromide concentration was determined to be less than 2 atomic percent.

Therefore, a method of producing high quality PECVD TaN_x films suitable for integration with IC interconnect elements that contain Cu has been demonstrated. The method is based on the vapor delivery of either TaF_5, $TaCl_5$ or $TaBr_5$ precursors. All of the resulting TaN_x films from the three precursors demonstrated reasonable step coverage, low residual impurity concentrations, sufficiently high deposition rates and no signs of TaN_x etching of Cu.

It should be understood that the embodiments of the present invention shown and described in the specification are only preferred embodiments of the inventors who are skilled in the art and are not limiting in any way. For example, Ta films may be deposited by PECVD, TaN_x films may be deposited by thermal CVD, TaN_x films may be deposited by plasma treated thermal CVD as disclosed in, respectively, PECVD OF Ta FILMS FROM TANTALUM HALIDE PRECURSORS, THERMAL CVD OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS and PLASMA TREATED THERMAL CVD

OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS all of which are invented by Hautala and Westendorp and assigned to Tokyo Electron Limited, are copending applications filed on the same date as the present application and are expressly incorporated by reference herein in their entirety. As another example, TiN from titanium halide precursors deposited by CVD can be used for plug formation as disclosed in the copending application entitled CVD TiN PLUG FORMATION FROM TITANIUM HALIDE PRECURSORS, invented by Hautala et al., assigned to Tokyo Electron Limited, filed on the same date as the present application and expressly incorporated by reference herein in its entirety. Furthermore, Ta/TaN$_x$ bilayers may be deposited by CVD and TaN$_x$ may be used for plug fill according to the inventions as disclosed in, respectively, CVD INTEGRATED Ta AND TaN$_x$ FILMS FROM TANTALUM HALIDE PRECURSORS and CVD TaN$_x$ PLUG FORMATION FROM TANTALUM HALIDE PRECURSORS, both of which are invented by Hautala and Westendorp and assigned to Tokyo Electron Limited, are copending applications filed on the same date as the present application and are expressly incorporated by reference herein in their entirety. Therefore, various changes, modifications or alterations to these embodiments may be made or resorted to without departing from the spirit of the invention and the scope of the following claims.

What is claimed is:

1. A method of depositing a tantalum nitride (TaN_x) film on a substrate comprising providing a vapor of a tantalum halide precursor to a reaction chamber containing said substrate by heating said precursor to a temperature sufficient to vaporize said precursor, then combining said vapor with a process gas containing nitrogen to deposit said TaN_x on said substrate by a plasma enhanced chemical vapor deposition (PECVD) process.

2. The method of claim 1 wherein said tantalum halide precursor is selected from the group consisting of tantalum fluoride, tantalum chloride and tantalum bromide.

3. The method of claim 1 wherein said providing of said vapor includes producing said vapor at a pressure of at least about 3 Torr.

4. The method of claim 3 wherein said precursor is tantalum pentafluoride and said temperature is about 95°C.

5. The method of claim 3 wherein said precursor is tantalum pentachloride and said temperature is about 145°C.

6. The method of claim 3 wherein said precursor is tantalum pentabromide and said temperature is about 205°C.

7. The method of claim 1 wherein said heating of said precursor is to a temperature sufficient to provide a vapor pressure of said tantalum halide precursor of at least 3 Torr.

8. The method of claim 1 wherein said substrate is heated to a temperature in the range of about 300°C-500°C.

9. The method of claim 1 wherein said delivery of said tantalum halide precursor is in the range of about 1-50 sccm.

10. The method of claim 1 wherein said process gas is selected from the group consisting of hydrogen, argon, helium and combinations thereof.

11. The method of claim 10 wherein said hydrogen gas is at a flow of about 1-10 slm.

12. The method of claim 1 wherein said nitrogen containing gas is at a flow in the range of about 0.1-10 slm.

13. The method of claim 1 wherein said depositing occurs at a pressure of said chamber in the range of about 0.2-5.0 Torr.

14. The method of claim 1 wherein said film is integral with a copper layer of said substrate.

15. The method of claim 1 wherein said TaN_x is deposited at a rate of at least about 100 Å/min.

16. The method of claim 1 wherein said substrate comprises an integrated circuit containing a high aspect ratio feature.

17. The method of claim 1 wherein said tantalum halide precursor is delivered to said reaction chamber without a carrier gas.

18. The method of claim 1 further comprising depositing said TaN_x film sequentially with a tantalum film.

19. A method of depositing a tantalum nitride (TaN_x) film on a substrate comprising delivering a tantalum halide precursor selected from the group consisting of tantalum fluoride and tantalum chloride to a reaction chamber containing said substrate by elevating a temperature of said precursor sufficient to produce a vapor of said precursor to provide a pressure to deliver a tantalum vapor, combining said vapor with a process gas containing nitrogen, and depositing said TaN_x on said substrate by a plasma enhanced chemical vapor deposition (PECVD) process.

20. The method of claim 19 wherein said elevated temperature is less than a temperature that would cause a reaction between said precursor vapor and said process gas.

21. The method of claim 19 wherein said pressure to deliver said tantalum vapor is at least about 3 Torr.

22. The method of claim 20 wherein said precursor is tantalum pentafluoride and said temperature is about 95 °C.

23. The method of claim 20 wherein said precursor is tantalum pentachloride and said temperature is about 145 °C.

24. A method of depositing a tantalum nitride (TaN_x) film on a substrate comprising delivering a tantalum pentabromide precursor to a reaction chamber containing said substrate without a carrier gas by elevating a temperature of said precursor sufficient to produce a vapor of said precursor, combining said vapor with a process gas containing nitrogen, and depositing said TaN_x on said substrate by a plasma enhanced chemical vapor deposition process.

25. The method of claim 24 wherein said precursor is tantalum pentabromide and said temperature is in the range of about 190° to about 208°C.

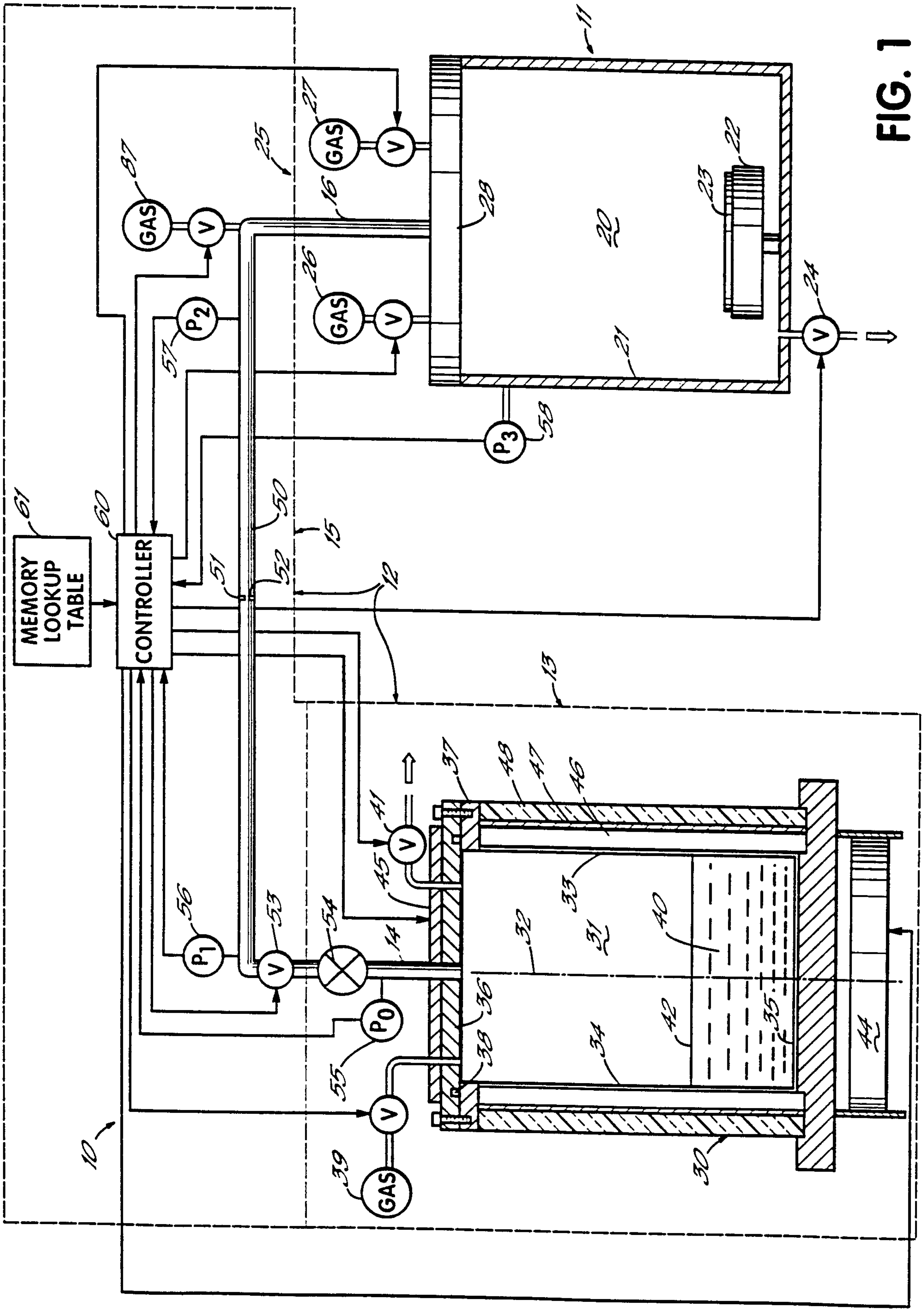
26. The method of claim 25 wherein said precursor is tantalum pentabromide and said temperature is about 205°C.

27. A substrate having an underlying dielectric layer and comprising a copper (Cu) layer and a tantalum nitride (TaN_x) layer wherein said TaN_x prevents diffusion of said Cu into said underlying dielectric layer and has less than about 2 atomic percent impurities.

28. The substrate of claim 27 wherein said TaN_x layer provides conformal coverage of a high aspect ratio feature.

29. The substrate of claim 27 wherein said TaN_x layer has a resistivity less than about 1000 $\mu\Omega$cm.

30. The substrate of claim 27 wherein said TaN_x layer is deposited by delivering a tantalum halide precursor selected from the group consisting of tantalum pentafluoride, tantalum pentachloride and tantalum pentabromide to a reaction chamber containing said substrate with said precursor heated to a temperature sufficient to vaporize said precursor, combining said vapor with a process gas containing nitrogen, and depositing said TaN_x on said substrate by a plasma enhanced chemical vapor deposition process.


MEMORY LOOKUP TABLE
CONTROLLER
GAS
V
P0
P1
P2
P3
10
11
12
13
14
15
16
20
21
22
23
24
25
26
27
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41
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56
57
58
60
61
87

FIG. 1

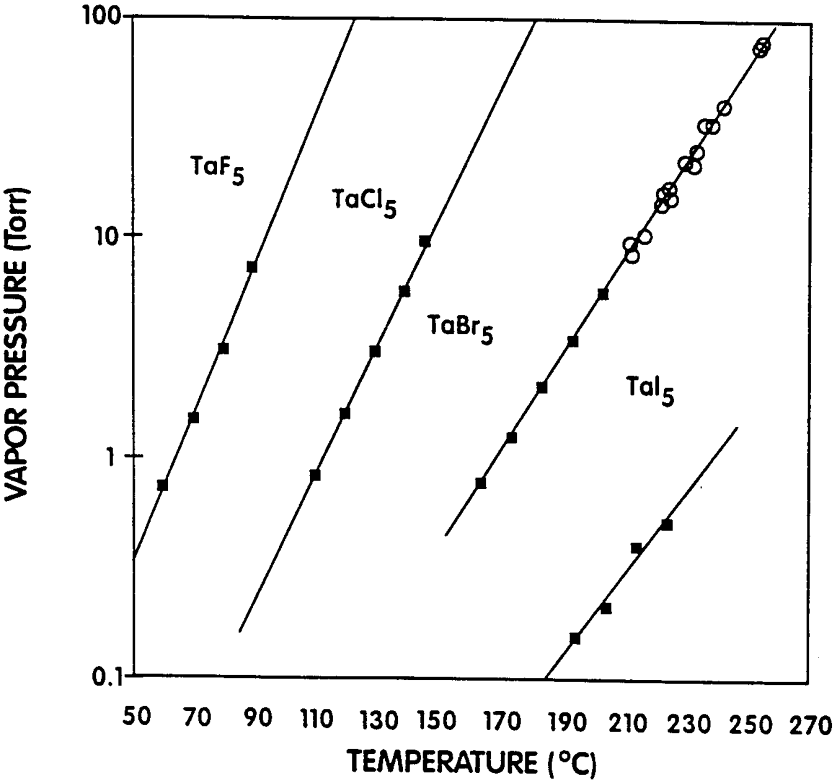
100
10
1
0.1
VAPOR PRESSURE (Torr)
TaF5
TaCl5
TaBr5
TaI5
50
70
90
110
130
150
170
190
210
230
250
270
TEMPERATURE (°C)

FIG. 2

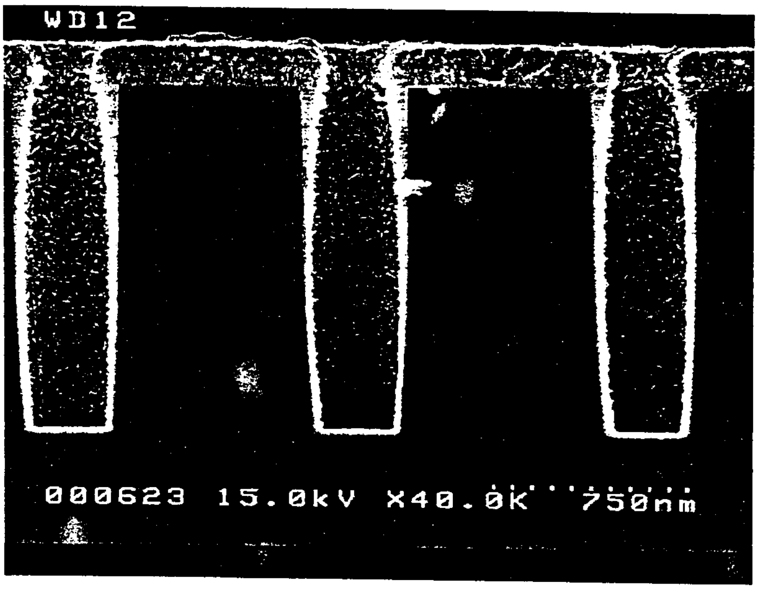

FIG. 3

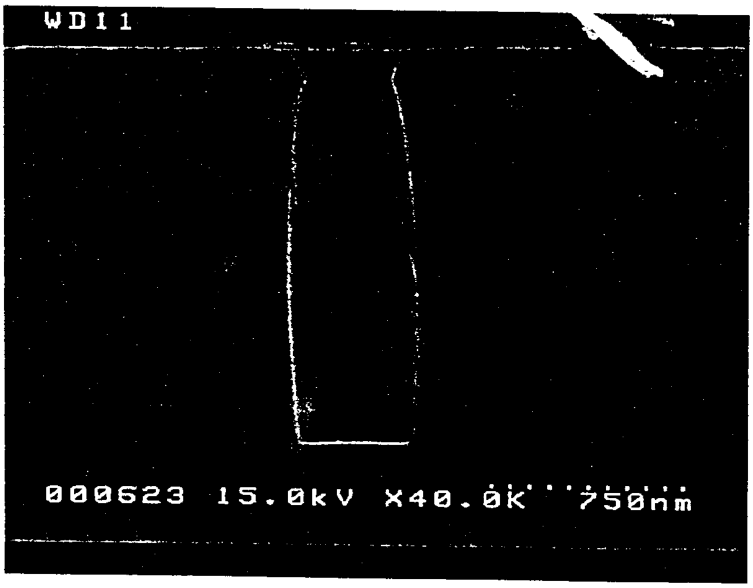

FIG. 4

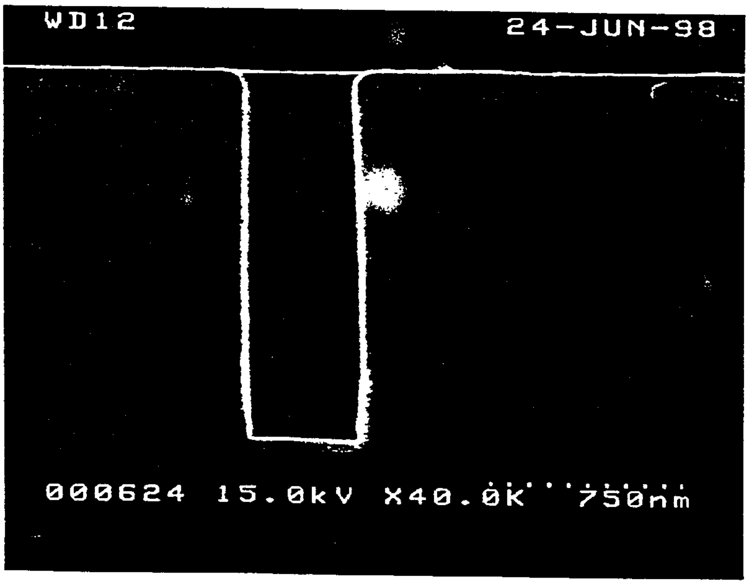

FIG. 5

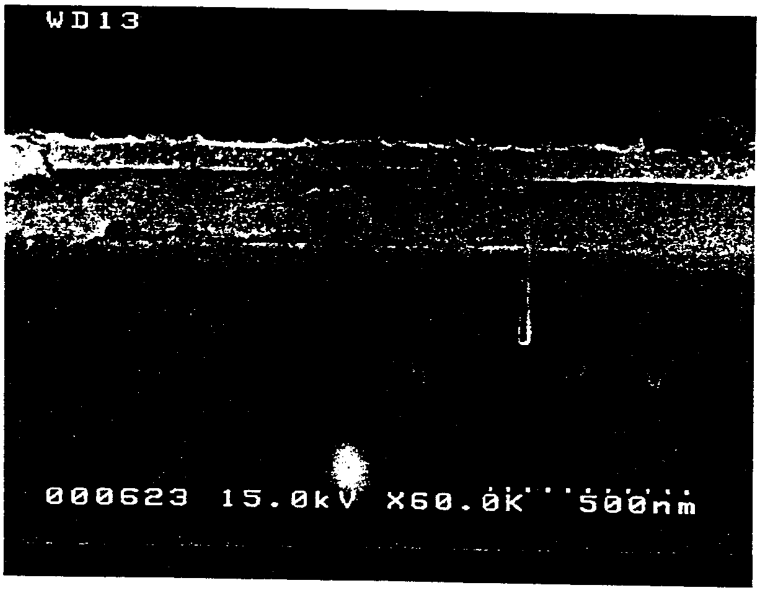
WD13
000623 15.0kV X60.0K 500nm

FIG. 6

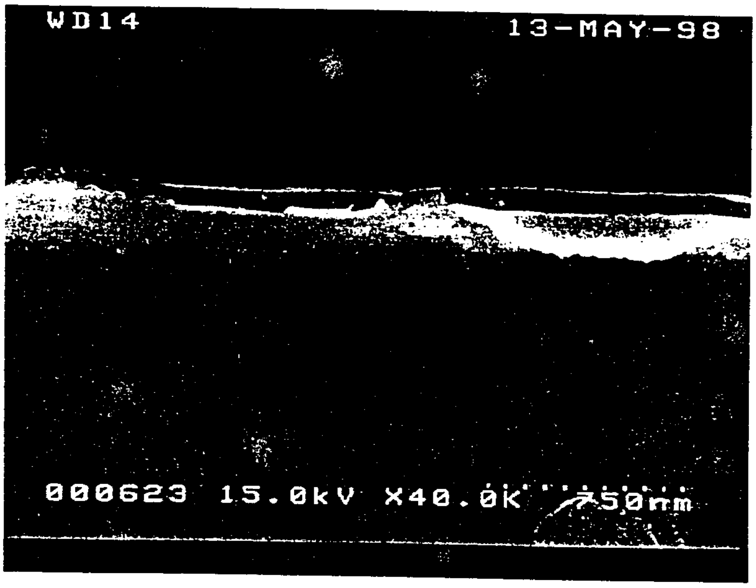
WD14
13-MAY-98
000623 15.0kV X40.0K 750nm

FIG. 7

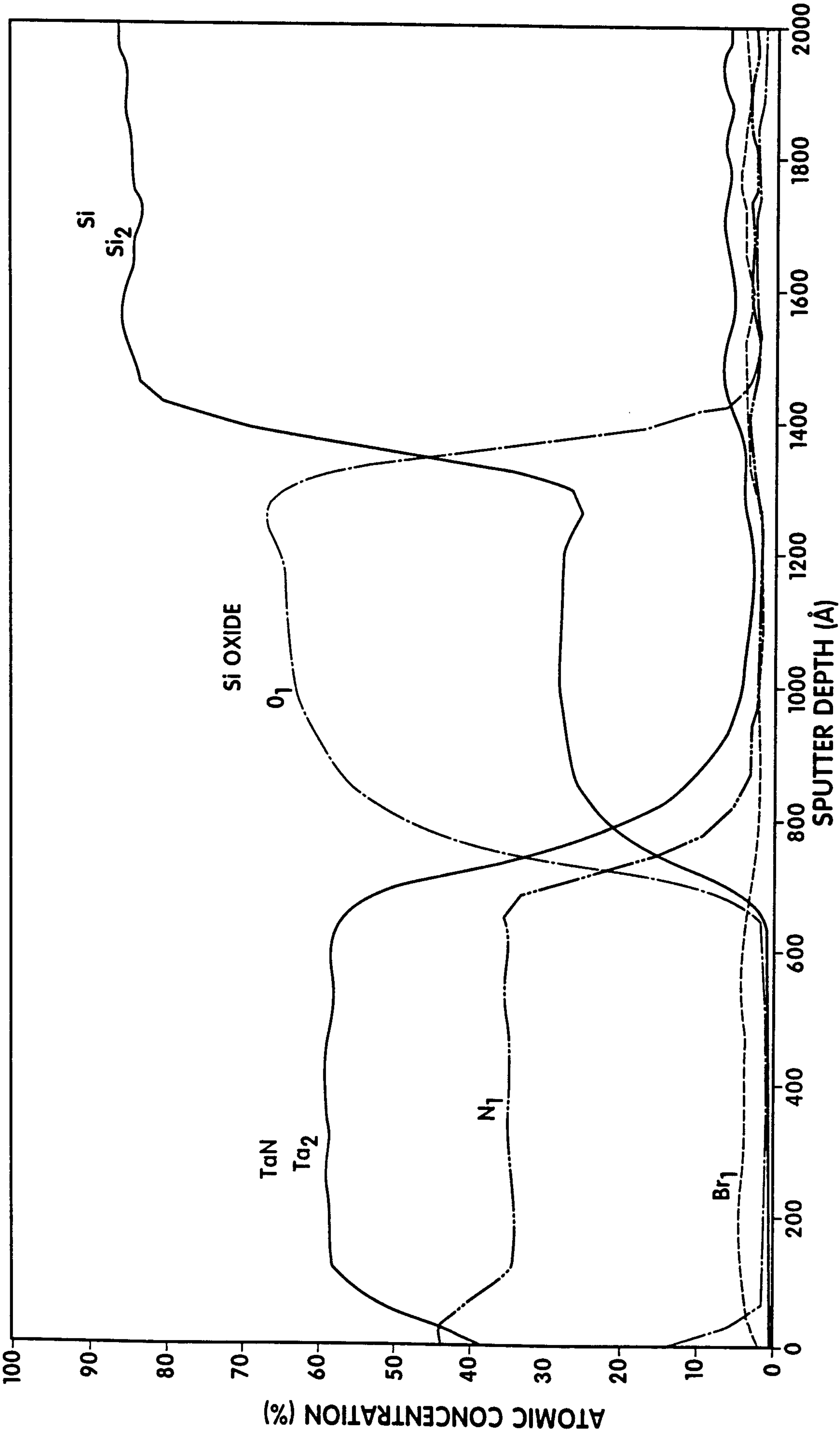
Si
Si2
Si OXIDE
O1
TaN
Ta2
N1
Br1
ATOMIC CONCENTRATION (%)
100
90
80
70
60
50
40
30
20
10
0
SPUTTER DEPTH (Å)
0
200
400
600
800
1000
1200
1400
1600
1800
2000

FIG. 8

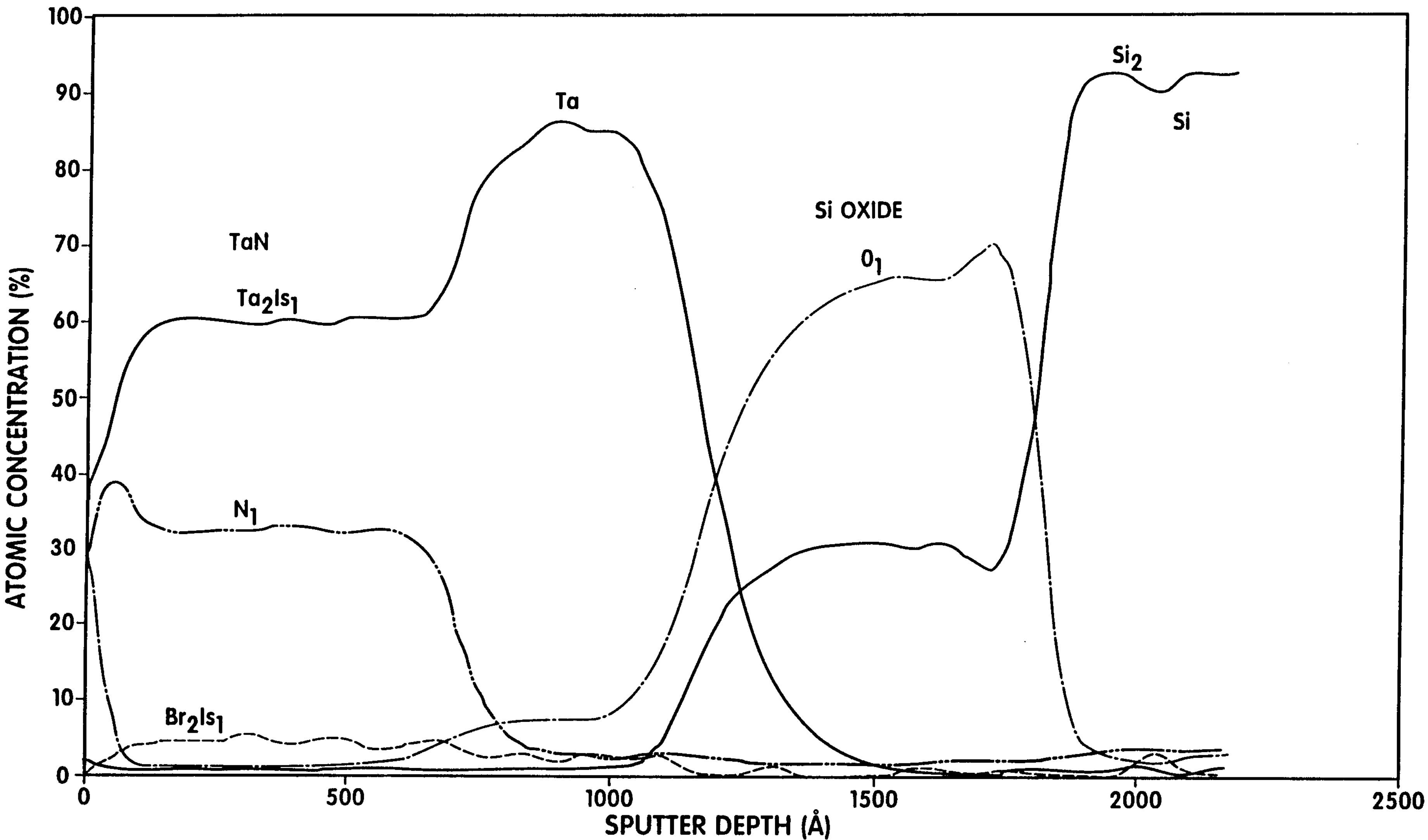
ATOMIC CONCENTRATION (%)
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
SPUTTER DEPTH (Å)
TaN
Ta2ls1
N1
Br2ls1
Ta
Si OXIDE
01
Si2
Si

FIG. 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/11278

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/34 H01L21/285

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEN, XIAOMENG ET AL: "Low temperature plasma-assisted chemical vapor deposition of tantalum nitride from tantalum pentabromide for copper metalization" J. VAC. SCI. TECHNOL., B (1999), 17(1), 182-185 , 1999, XP002145175 the whole document	1,2,8, 10-14,24
A		27-30

X	JP 03 209869 A (NEC CORP) 12 September 1991 (1991-09-12) abstract	1,2,19

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search
17 August 2000

Date of mailing of the international search report
07/09/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL – 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer
Patterson, A

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/11278

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	KALOYEROS A E ET AL: "Tantalum nitride films grown by inorganic low temperature thermal chemical vapor deposition-diffusion barrier properties in copper metallization" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, JAN. 1999, ELECTROCHEM. SOC, USA, vol. 146, no. 1, pages 170-176, XP002145088 ISSN: 0013-4651 page 170, final paragraph page 171 -page 173 ---	27,28
P,X	US 5 919 531 A (KALOYEROS ALAIN E ET AL) 6 July 1999 (1999-07-06) examples 1,3,5 -----	1,2,8, 10-13, 18,24,25

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intc .ational Application No

PCT/US 00/11278

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 03209869 A	12-09-1991	JP 2611466 B	21-05-1997
US 5919531 A	06-07-1999	NONE	