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

(71) Applicant *(for JP only)*: TOKYO ELECTRON ARIZONA, INC. [US/US]; 2120 W. 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).

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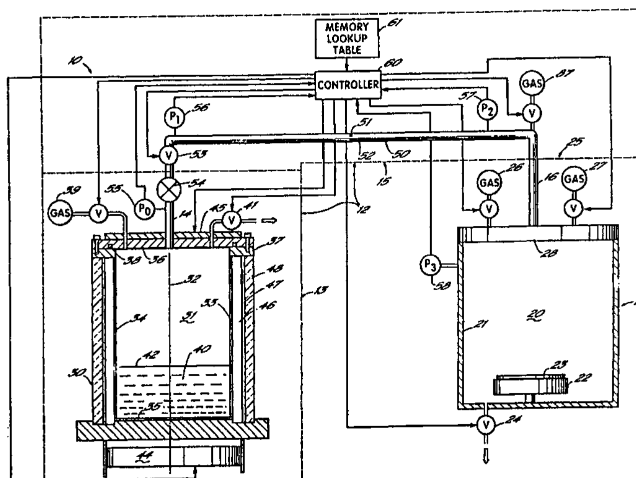

(57) Abstract

Plasma treated chemical vapor deposition (PTTCVD) method for depositing high quality tantalum nitride (TaN_x) films from inorganic tantalum halide (TaX_5) precursors and a nitrogen containing gas for filling small contacts having high aspect ratio features with TaN_x film and eliminating copper deposition step. The inorganic tantalum halide precursors are tantalum pentafluoride (TaF_5), tantalum pentachloride ($TaCl_5$) and tantalum pentabromide ($TaBr_5$). In a thermal CVD process, TaX_5 vapor is delivered into heated chamber (11). The vapor is combined with process gas containing nitrogen to deposit TaN_x film in feature. In one embodiment, hydrogen gas is introduced in radiofrequency generated plasma to plasma treat TaN_x film. Plasma treatment is performed periodically until the feature is filled with TaN_x film. Deposited TaN_x film is useful for integrated circuits containing copper. The method produces seamless TaN plug fill in high aspect ratio structures.

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CVD TANTALUM NITRIDE PLUG FORMATION FROM TANTALUM HALIDE PRECURSORS

This invention relates to the formation of integrated circuits, and specifically to filling electrical contacts with tantalum nitride films deposited by chemical vapor deposition from tantalum halide precursors.

5 **Background of the Invention**

Integrated circuits provide the pathways for signal transport in an electrical device. An integrated circuit (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
10 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 features such as holes, vias or trenches that are cut into a substrate. The particular point of the metal interconnection which actually makes
15 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 IC, the diameter of the contact plug must decrease to allow for the increased number of interconnects, multilevel metalization structures and higher aspect ratio vias.

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

As the shift occurs from aluminum to copper as an interconnect element of choice, new materials are required to serve as a barrier, preventing copper diffusion into the underlying dielectric layers of the substrate and to form
15 an effective "glue" layer for subsequent copper deposition. 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
20 deposited either by physical vapor deposition (PVD) such as sputtering and/or chemical vapor deposition (CVD), are ineffective as diffusion 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
5 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 μm) and small aspect ratio contacts and vias. CVD offers the inherent advantage over PVD of
10 better conformality, even in small structures (< 0.25 μm) 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 (diethylanmino) tantalum (PDEAT) yields mixed results. Additional problems are that all resulting films have relatively high
15 concentrations of oxygen and carbon impurities and require the use of a carrier gas.

A contact plug makes an electrical connection between doped silicon and metal wires that connect transistors, both with each other and with the outside world. Contact plugs involving Cu lines currently require the depositions
20 as follows. A liner of about 100 Å Ta is first deposited using PVD. This Ta layer enhances the electrical contact to the silicon base layer. A liner of about 500 Å TaN is then deposited on the Ta layer by PVD. A seed layer of 100 Å Cu is then

deposited by PVD, and the remainder of the plug is filled with electroplated Cu. The TaN layer serves as a metal diffusion barrier to protect the dielectric layer from Cu diffusion. TaN also serves as an adhesion layer for the Cu.

As transistor densities continue to increase and structures become
5 narrower, the proportion of Cu in the plug becomes smaller. Since the probable TaN barrier layer may remain at greater than about 200 Å for robust performance as a diffusion barrier and the Ta thickness is still required to be 100 Å, it follows that the portion of the contact plug that is filled with Cu is diminished. For example, a structure with a diameter of 0.13 μm would have a Cu film or "core"
10 in the center of the plug that is only about 700 Å. Therefore, the effective plug resistance becomes dominated more by the higher resistivity Ta and TaN and, more importantly, the resistance of the interface between the TaN and Cu layers.

Subsequent filling of the contact plugs with Cu, then, provides an extra procedural step with no significant effect on the overall resistance of the
15 contact plug. Accordingly, a process step in the formation of an IC could be eliminated, manufacturing efficiency could be increased, and significant savings for the fabrication of these devices could be realized by filling a via with a contact plug of TaN only, rather than with TaN and Cu. Therefore, what is needed is a method of forming a TaN contact plug by CVD and eliminating a Cu layer in the
20 contact plug in the formation of an IC.

While the absolute thickness of the Cu layer may vary according to the size of the via to be filled, its relative thickness is about 80% of the via

diameter. This is because the deposited film must not only fill the volume of the via with a contact plug, but it must also fill the "dimple" above the contact plug. The "dimple," defined as an indentation in the TaN that is formed during filling of the via, is eliminated by depositing more TaN on top of the plug, resulting in a

5 capping layer. Thus, for a 0.2 μm feature, a TaN film having a thickness of 1600 Å (0.8 x 2000 Å) is required. For a good plug fill it is also critical that these thick films be continuous, completely conformal, and seamless.

Thus, what is needed is a method for depositing TaN_x films to fill a contact plug in and eliminating a copper deposition step. The method would

10 require deposition temperature less than about 500°C to protect the integrity of underlying materials such as low k dielectrics, a deposition rate of more than 100 Å/minute for reasonable throughput, a cracking threshold larger than 2000 Å, sufficiently low electrical resistivities for low interconnect impedances, 100% conformality in high aspect ratio features, no attack or corrosion of subsequently

15 deposited films such as copper films, minimal impurities in the film, and the film would provide a good barrier to copper diffusion.

Summary of the Invention

The invention is directed to a method of filling a via with a TaN plug and eliminating a copper (Cu) deposition step by depositing a tantalum nitride

20 (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 greater than about 3 Torr. The vapor is combined with a process gas containing nitrogen and TaN_x is deposited by a thermal chemical vapor deposition (thermal CVD) process. The deposition is halted to plasma treat the film, then deposition is resumed. The
5 plasma treatments are performed at regular intervals in the thermal CVD process (PTTCVD) until a desired film thickness is obtained. 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
10 about 300°C-500°C.

The present invention is also directed to a method of completely filling a high aspect ratio via which is less than about 0.16 μm in diameter with a TaN_x layer from a TaF_5 or $TaCl_5$ precursor by elevating the precursor temperature sufficient to vaporize the precursor to provide a pressure to deliver
15 the vapor. The vapor is combined with a process gas containing nitrogen and TaN_x is deposited in the feature by a thermal chemical vapor deposition (thermal CVD) process. The deposition is halted to plasma treat the film surface, then deposition is resumed. The plasma treatments are performed at regular intervals in the thermal CVD process until a desired film thickness is obtained.

20 The invention is further directed to a method of filling a high aspect ratio via which is less than about 0.16 μm in diameter with 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 TaN_x is deposited in the feature by a thermal chemical vapor deposition (thermal CVD) process. The deposition is halted to plasma treat the film surface, then deposition is resumed.
5 The plasma treatments are performed at regular intervals in the thermal CVD process until a desired film thickness is obtained.

The films deposited by the method of the invention can completely fill a feature and eliminate the need for a copper deposition step. The films are deposited at temperature less than about 500°C, thereby protecting the integrity
10 of the underlying material. The films have a cracking threshold greater than 2000 Å, have sufficiently low electrical resistivities, have 100% conformality in high aspect ratio features, and show no attack or corrosion of integral copper films. The films have minimal impurities and are good barriers to copper diffusion. The films can be deposited at a rate sufficient for throughput considerations. It will
15 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 Drawings

FIG. 1 is a schematic of an apparatus for plasma treated thermal
20 chemical vapor deposition (PTTCVD).

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

FIG. 3 is a schematic representation of a structure fabricated using standard plug fills.

FIG. 4 is a scanning electron micrograph (SEM) image of a plug fill by TaN_x deposited by TaF_5 based thermal CVD.

5 FIG. 5 is a SEM image of a plug fill by TaN_x deposited by TaF_5 based plasma treated thermal CVD (PTTCVD).

FIG. 6 is a SEM image of a plug fill by TaN_x deposited by $TaBr_5$ based thermal CVD.

FIG. 7 is a SEM image of a plug fill by TaN_x deposited by $TaBr_5$ based

10 PTTCVD.

FIG. 8 is a SEM image of a 1150 Å TaF_5 based CVD TaN_x film.

FIG. 9 is a SEM image of a 3700 Å $TaCl_5$ based CVD TaN_x film.

FIG. 10 is a SEM image of a 1350 Å $TaBr_5$ based CVD TaN_x film.

FIG. 11 is a SEM image of TaF_5 based CVD Ta/TaN_x film deposited

15 on a copper (Cu) layer.

FIG. 12 is a SEM image of $TaCl_5$ based CVD TaN_x film deposited on a Cu layer.

FIG. 13 is a SEM image of $TaBr_5$ based CVD Ta/TaN_x film deposited on a Cu layer.

20 FIG. 14 is an Auger spectrum of a $TaBr_5$ based CVD TaN_x film deposited on a Cu layer.

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
5 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
10 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
15 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

20

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 reaction chamber 11 and a precursor delivery system 12. In the reaction chamber, 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). The TaN film is not limited to any particular stoichiometry (TaN_x). Thus, as used herein, TaN_x encompasses a tantalum nitride film of any stoichiometry.

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, 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 at a rate that is sufficient to maintain a commercially viable CVD process in the reaction chamber.

5 The reaction chamber 11 is a generally conventional CVD reactor 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 10 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 to 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 15 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 20 substrate 23.

The precursor gas source 13 includes a sealed evaporator 30 that includes a cylindrical evaporation vessel 31 having a vertically oriented axis 32.

The vessel 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 materials requiring lower temperatures, such as $TaCl_5$ and TaF_5, a conventional elastomeric O-ring seal 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 chamber with the solid mass of Ta_x 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
5 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
10 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
15 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,
20 preferably above its melting point, that will produce a vapor pressure greater than 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 and so on. In a direct 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
5 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 contemplated as a being tantalum or titanium halide compound.

10 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
15 it connects at its upstream end to the outlet 14, to the reaction chamber 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.

20 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
5 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. The pressure sensors include
10 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
15 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 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 is achieved by the controller 60 in response to the pressures
20 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.

5 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 10 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 15 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 vessel 31 20 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 reaction chamber 11. The reaction chamber 11 was heated to a temperature of at least about 100°C to
5 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
10 vaporize the precursor 40 to provide a vapor pressure to deliver the tantalum halide vapor to the reaction chamber 11. Thus, a carrier gas was not necessary and preferably was not used. A sufficient vapor pressure was in the range of about 3-10 Torr. This pressure was required to maintain a constant pressure drop across a defined orifice in a high conductance delivery system while delivering up
15 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
20 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
5 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
10 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
15 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.

The thermal CVD is stopped at regular intervals to plasma treat the
20 film surface. The flow of tantalum halide precursor gas and process gas is turned off or is directed around the reaction chamber 11 and a plasma treatment is then performed on the surface of the film. For the plasma treatment a parallel plate RF

discharge is used where the driven electrode is the gas delivery showerhead and the wafer stage is the RF ground. H_2 was used to plasma treat the film at a flow of 7 slm, after which thermal CVD was resumed. The depositing, plasma treating and resumed depositing steps continued until the desired film thickness was obtained. The plasma treatment of films deposited by thermal CVD, that is, the plasma treated thermal CVD (PTTCVD) process, could decrease the film's electrical resistivity by a factor of greater than ten thousand. In addition, PTTCVD improves the film's morphology from a relatively rough structure to a smooth dense film.

Process conditions for deposition of good quality PTTCVD TaN_x films are given in Table 2.

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
NH_3 flow	0.1-5 slm
H_2 flow	0.0-5 slm
Ar, N_2 flow	0-5 slm
Process Pressure	0.1-5.0 Torr
RF Power	0-1000 W/cm^2

Typical initial film results for TaN_x films deposited by thermal CVD are given in Table 3. Depositions were on 200 mm Si and SiO_2 substrates. 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)	NH_3 flow (slm)	Pressure (Torr)	Temp. (°C)	Dep. Rate (Å/min)	Resistivity ($\mu\Omega$cm)	Step Coverage	Halide Conc. (atomic %)
TaN	TaF_5	6	1	0.3	415	850	$> 1X10^7$	0.2	Not determined
TaN	TaF_5	10	1	0.3	415	1000	$7X10^6$	1	0.2
TaN	TaF_5	28	1	0.3	415	1115	$4X10^5$	1	Not determined
TaN	$TaBr_5$	10	1	1	425	200	$> 1X10^7$	0.6	< 2

5

Typical initial film results for TaN_x films deposited by PTTCVD are given in Table 4. Depositions were on 200 mm Si and SiO_2 substrates. The properties of the deposited TaN_x films as listed in Table 4 were uniform within plus or minus 20% across the wafer.

Table 4

Film	Precursor	TaX_5 flow (sccm)	NH_3 flow (slm)	Pressure (Torr)	Temp. (°C)	# cycles	Thick/ cycle	H_2 flow (slm)	RF (Watts)	Resistivity ($\mu\Omega$cm)	Step Coverage	Halide Conc. (atomic %)
TaN	TaF_5	14	0.4	0.2	440	0				$> 1X10^7$	1	< 0.2
TaN	TaF_5	14	0.4	0.2	440	10	70	7	200	3600	1	< 0.2
TaN	TaF_5	14	0.4	0.2	440	15	45	7	200	1100	1	< 0.2
TaN	$TaBr_5$	20	1	1	430	0				$> 1X10^7$	0.6	< 1
TaN	$TaBr_5$	20	1	1	430	6	105	7	200	32000	1	< 1
TaN	$TaBr_5$	20	1	1	430	10	20	7	200	5800	1	< 1

5

As shown in Table 4, the results of the initial tests indicate that plasma treatment of the TaN_x film deposited by thermal CVD makes this process potentially viable for $TaBr_5$ and TaF_5 based TaN_x films. The $TaCl_5$ based film is expected to perform similarly because the $TaCl_5$ based films had
5 properties that were effectively between the $TaBr_5$ and TaF_5 based TaN_x films.

The improvement of TaN_x electrical resistivity by application of the H_2 plasma can be seen in Table 4. Resistivities of the films that did not undergo the plasma treatment were high, greater than $1X10^7$ $\mu\Omega$cm, which was the limit of the measurement tool. As thinner layers of TaN_x films
10 deposited by thermal CVD were treated by the hydrogen RF discharge, lower resistivities were obtained. The electrical resistivity of the PTTCVD TaF_5 based film decreased from greater than $1X10^7$ $\mu\Omega$cm in the untreated state to 3600 $\mu\Omega$cm when a 70 Å thick TaN_x film per cycle was subjected to plasma treatment. The resistance further decreased to 1100 $\mu\Omega$cm when a 45 Å thick
15 TaN_x film per cycle was subjected to plasma treatment. Similarly, the electrical resistivity of the PTTCVD $TaBr_5$ based film decreased from greater than $1X10^7$ $\mu\Omega$cm for untreated films to 32,000 $\mu\Omega$cm when a 105 Å TaN_x film per cycle was subjected to plasma treatment. A further decrease to 5800 $\mu\Omega$cm was obtained when a 20 Å thick TaN_x film per cycle was subjected to
20 plasma treatment. A TaN_x film deposited using a $TaCl_5$ precursor would be expected to perform similarly since other TaN_x based films had properties that were effectively between TaF_5 and $TaBr_5$ precursors.

The H_2 plasma treatment process appeared to cause a fundamental change in the electrical and/or morphological properties of the

TaN_x films. Plasma treatment times in the range of between 10 seconds and 240 seconds have been evaluated. It has been determined that, within this range, longer treatment times yield films with lower resistivities for the material. The microstructure of the TaN_x film also changed from a rough to a
5 smooth surface with the cycled deposition and plasma treatment.

For a plug fill application, seamless fill of the structure requires a nearly perfect conformality and a 100% step coverage. A conformal film is one that exactly reproduces the surface topography of the underlying substrate. A seamless film is one that contains no cracks. The step coverage
10 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. As shown in FIG. 4 and FIG. 5 for TaF_5 based TaN_x films, and FIG. 6 and FIG. 7 for $TaBr_5$ based TaN_x films, the thermal CVD
15 and PTTCVD TaN_x processes using these tantalum halide precursors meet these criteria. $TaCl_5$ based films would be expected to exhibit the same desired conformality and step coverage as the TaF_5 and $TaBr_5$ precursors since all of the other measured properties appeared very similar.

With reference to FIGS. 8-10, thick TaN_x films deposited by CVD
20 are shown. FIG. 8 is a scanning electron micrograph (SEM) image of a 1150 Å thick crack-free TaF_5 based CVD TaN_x film. FIG. 9 is a SEM image of a 3700 Å thick crack-free $TaCl_5$ based CVD TaN_x film. FIG. 10 is a SEM image of a 1350 Å crack-free $TaBr_5$ based CVD TaN_x film. A continuous, completely conformal film with no cracks is required for a good plug fill. Cracking would

be problematic for adhesion of the film to the underlying layers, to prevent flaking off of the film that would compromise subsequent processes. Cracking would also be problematic because it would be expected to increase the electrical resistivity of the plug. As shown in each of FIGS. 8-10, each film from the three precursors were free of cracks.

The compatibility of the precursor chemistries of the TaN_x plug fills 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 reaction chamber 11. A TaN_x film was deposited by CVD 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. 11-13. FIG. 11 shows a TaF_5 based Ta/TaN_x film deposited directly on the Cu surface. FIG. 12 shows a $TaCl_5$ based TaN_x film on deposited directly on the Cu surface. FIG. 13 shows a $TaBr_5$ based Ta/TaN_x film deposited directly on the Cu surface. For each of FIGS. 11-13, the tantalum pentahalide based Ta and TaN_x based films deposited directly on the Cu layer showed no visible evidence of etching or attack of Cu.

With reference to FIG. 14, a $TaBr_5$ based TaN_x film deposited by thermal CVD directly on a Cu layer was analyzed by Auger analysis. The Auger spectrum confirms a clean interface between the TaN_x film and the other

layers. FIG. 14 indicates that the thermal TaN_x film is nitrogen rich ($x > 1.0$), which was consistent with the results shown in Table 3. Nitrogen rich TaN_x films ($x > 1$) are expected to have a relatively high electrical resistivity. FIG. 14 also shows a good sharp interface between the TaN_x layer and Cu, which
5 suggests little or no attack of the Cu surface during TaN_x deposition. The bromide concentration was determined to be less than 2 atomic percent.

Copper diffusion barrier properties of the resulting TaN_x films are expected to be good. One contributing factor may be the nitrogen rich process, since this is known to improve barrier performance. Another factor
10 may be the generally amorphous structure of the material, since it is known that an amorphous material, defined as having a low fraction of crystalline structure, provides a better barrier.

Therefore, a method of producing high quality PTTCVD TaN_x films suitable for integration with IC interconnect elements that contain Cu has been
15 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 demonstrated excellent step coverage, low residual impurity concentrations, sufficiently high deposition rates and no signs of TaN_x etching of Cu. The introduction of a H_2 RF plasma treatment between thermal CVD cycles resulted in a greater than
20 ten thousand times reduction in the electrical resistivity of the TaN_x film. The H_2 RF plasma treatment also significantly improved the microstructure of the film with no change in step coverage. The TaF_5 based films initially appear to be the most promising due to their lower resistivities and smoother microstructure.

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, and TaN films may be deposited by either thermal CVD, PECVD, or 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, PECVD 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, 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 as disclosed in the copending application CVD INTEGRATED Ta AND TaN_x FILMS FROM TANTALUM HALIDE PRECURSORS, invented by Hautala and Westendorp, assigned to Tokyo Electron Limited, filed on the same date as the present application and expressly incorporated by reference herein in its 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 filling a feature in a substrate comprising depositing a tantalum nitride (TaN_x) film in said feature by 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
5 combining said vapor with a process gas containing nitrogen, depositing said TaN_x film in said feature by a thermal chemical vapor deposition (CVD) process and plasma treating said deposited TaN_x.

2. The method of claim 1 further comprising repeating said depositing by thermal CVD and said plasma treating to produce a desired thickness of said film in said feature.

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

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

5. The method of claim 1 wherein said precursor is tantalum pentafluoride and said temperature is about 95 °C.

6. The method of claim 1 wherein said precursor is tantalum pentachloride and said temperature is about 145 °C.

7. The method of claim 1 wherein said precursor is tantalum pentabromide and said temperature is about 205 °C.

8. 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.

9. The method of claim 1 wherein said feature has an aspect ratio greater than 8.0.

10. The method of claim 1 wherein said feature has a diameter less than about 0.16 μm.

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

12. The method of claim 1 wherein said precursor is provided at a rate in the range of about 1-50 sccm.

13. The method of claim 1 wherein said nitrogen containing gas is ammonia.

14. The method of claim 13 wherein said ammonia is at a flow rate in the range of about 0.1-5.0 slm.

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

16. 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.

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

18. The method of claim 1 wherein said depositing is stopped prior to beginning said plasma treatment.

19. The method of claim 18 wherein said depositing is stopped by halting a flow of said precursor gas and said process gas in said chamber.

20. The method of claim 18 wherein said depositing is stopped by redirecting a flow of said precursor gas and said process gas in said chamber.

21. The method of claim 1 wherein said plasma treatment is generated by a radiofrequency energy source.

22. The method of claim 1 wherein a hydrogen gas is used for said plasma treatment.

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

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

25. A method of filling a feature in a substrate comprising providing a vapor of 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
5 vapor of said precursor to provide a pressure to deliver a tantalum vapor, combining said vapor with a process gas containing nitrogen, depositing a tantalum nitride (TaN_x) film in said feature by a thermal chemical vapor deposition (CVD) process and plasma treating said deposited TaN_x film.

26. The method of claim 25 further comprising repeating said depositing by thermal CVD and said plasma treating to produce a desired thickness of said film in said feature.

27. The method of claim 25 wherein said elevated temperature is less than a temperature that would cause a reaction between said precursor vapor and said process gas.

28. The method of claim 25 wherein said pressure to deliver said tantalum vapor is at least about 3 Torr.

29. The method of claim 25 wherein said precursor is tantalum pentafluoride and said temperature is about 95 °C.

30. The method of claim 25 wherein said precursor is tantalum pentachloride and said temperature is about 145°C.

31. The method of claim 25 wherein said thermal CVD is stopped prior to beginning said plasma treatment.

32. A method of filling a feature in a substrate comprising providing a vapor of 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
5 with a process gas containing nitrogen, depositing a tantalum nitride (TaN_x) film in said feature by a thermal chemical vapor deposition (CVD) process and plasma treating said deposited TaN_x film.

33. The method of claim 32 wherein said precursor is tantalum pentabromide and said temperature is in the range of about 190° to about 208°C.

34. The method of claim 33 wherein said precursor is tantalum pentabromide and said temperature is about 205°C.

35. The method of claim 32 further comprising repeating said depositing by thermal CVD and said plasma treating to produce a desired thickness of said film in said feature.

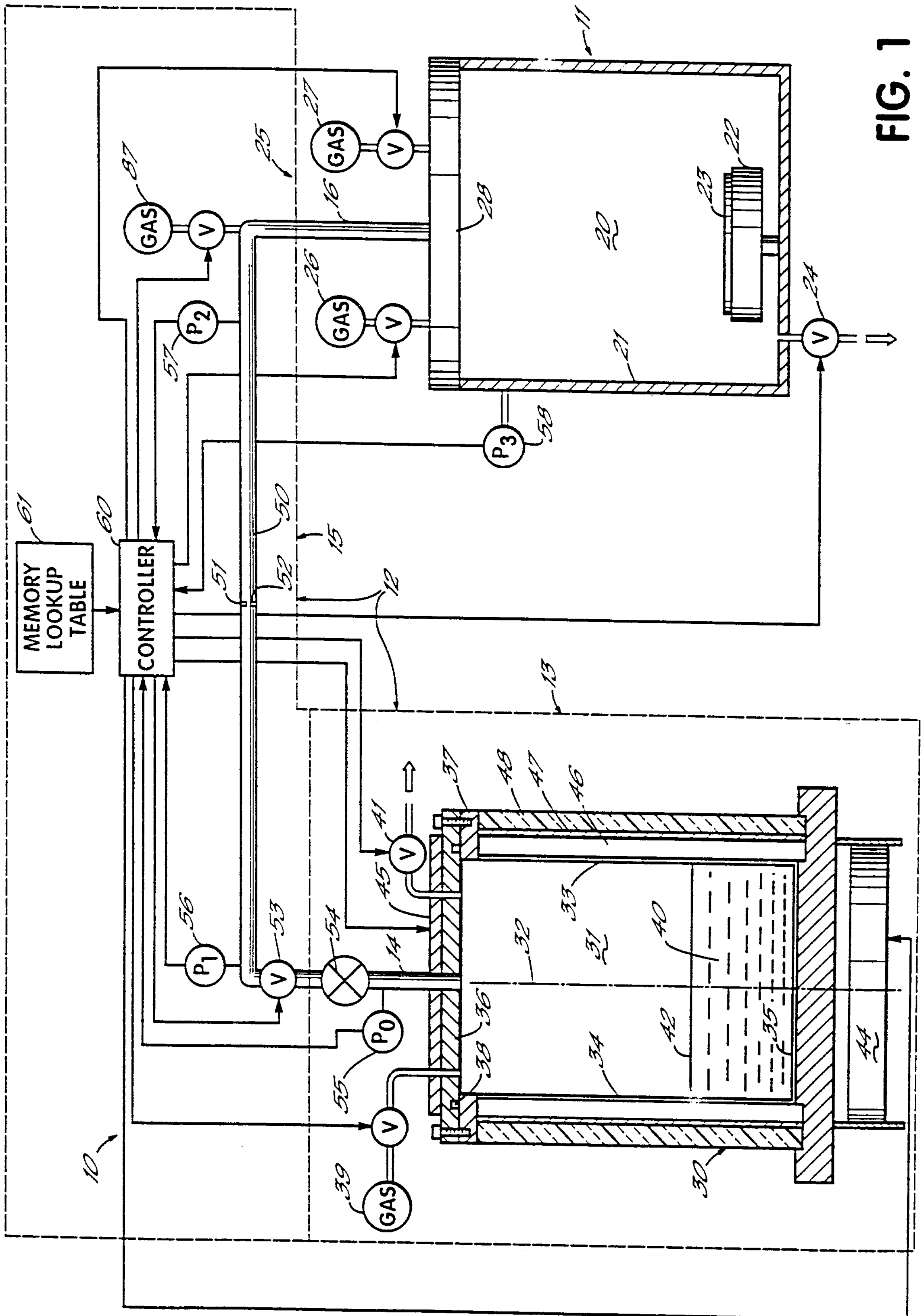

FIG. 1

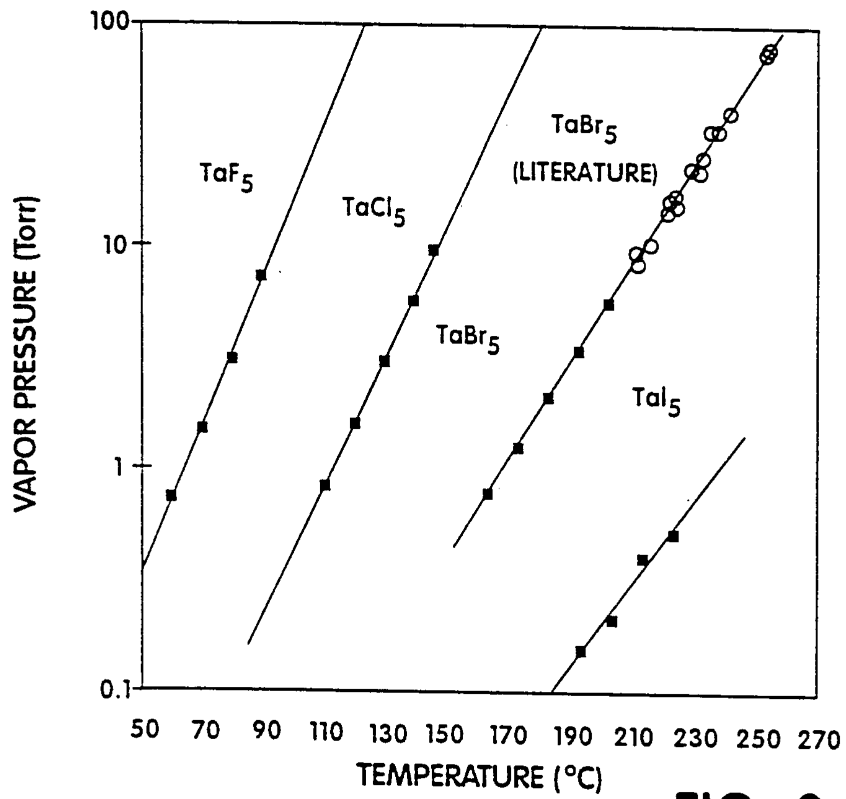

FIG. 2

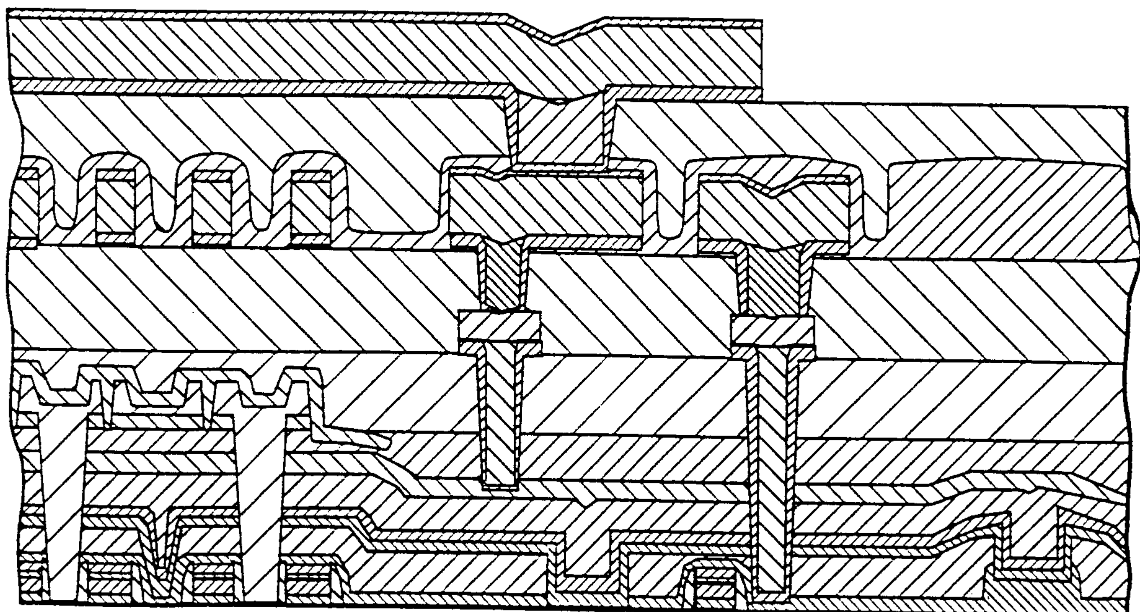

FIG. 3

FIG. 4

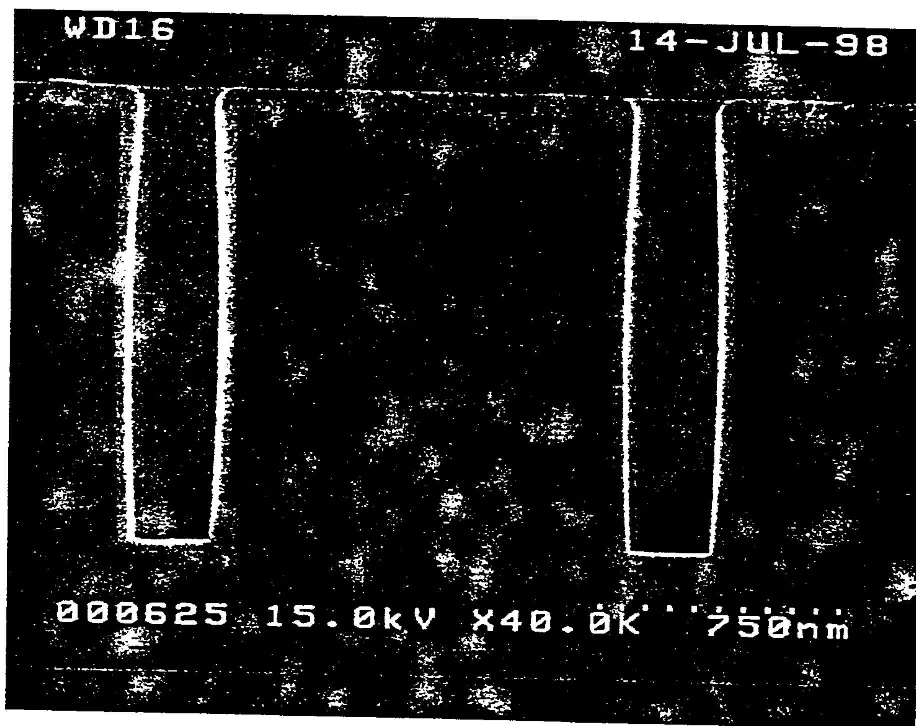

FIG. 5

FIG. 6

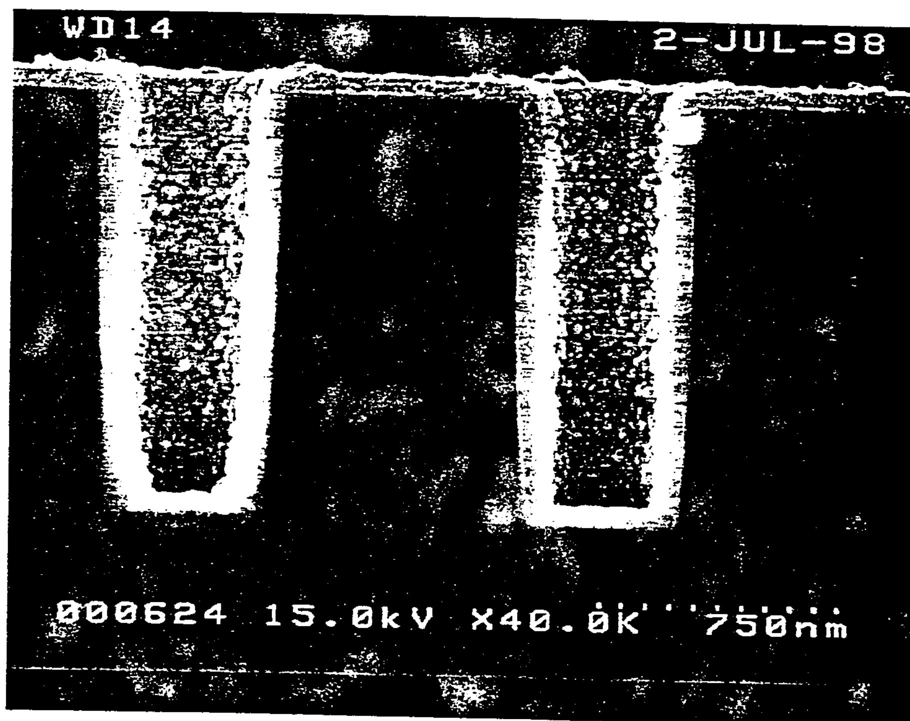

FIG. 7

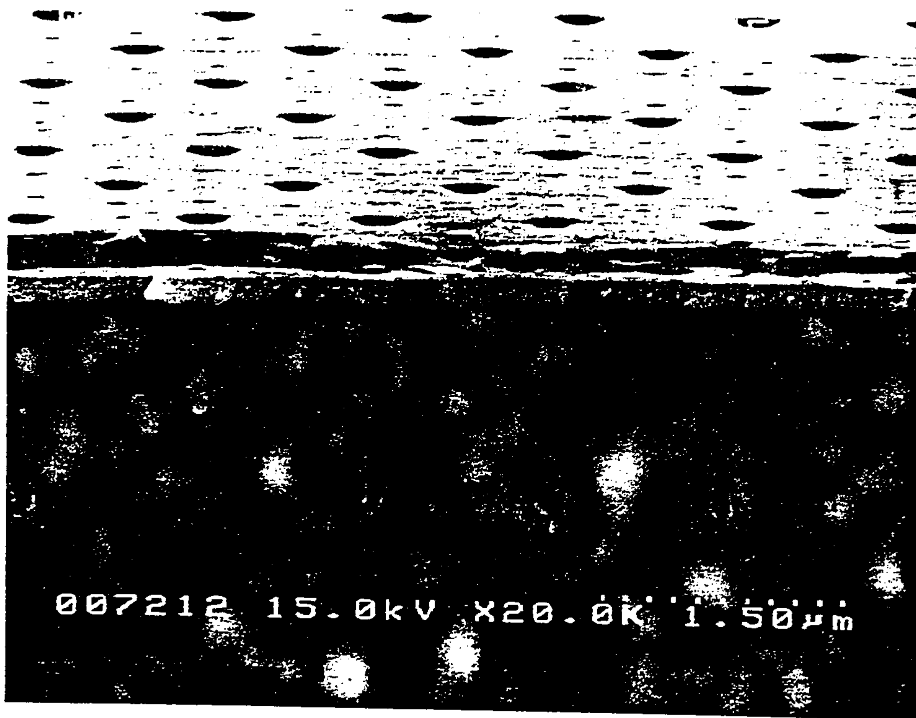

FIG. 8

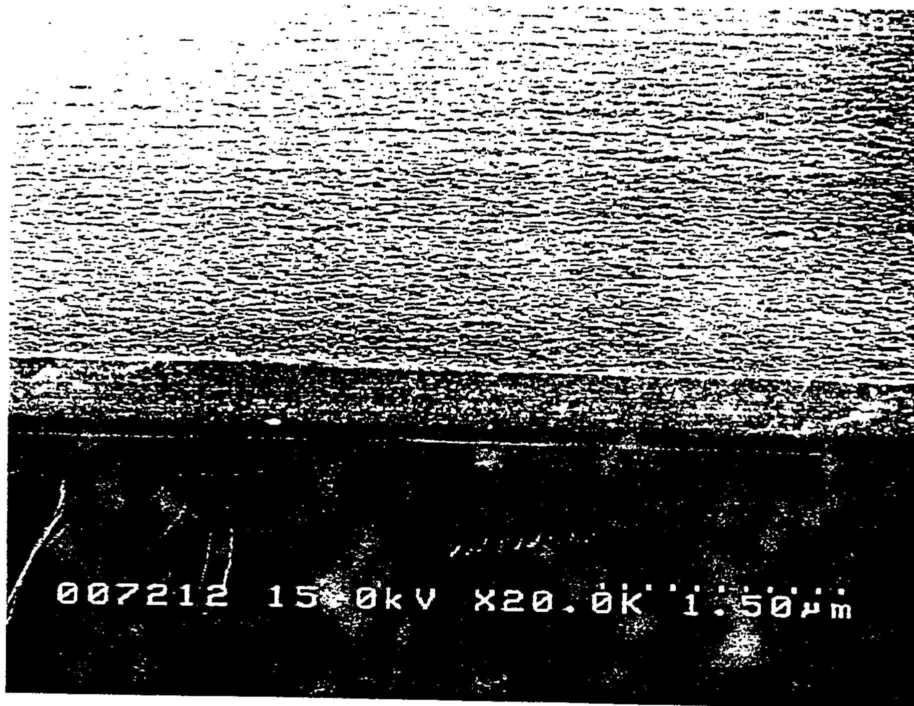

FIG. 9

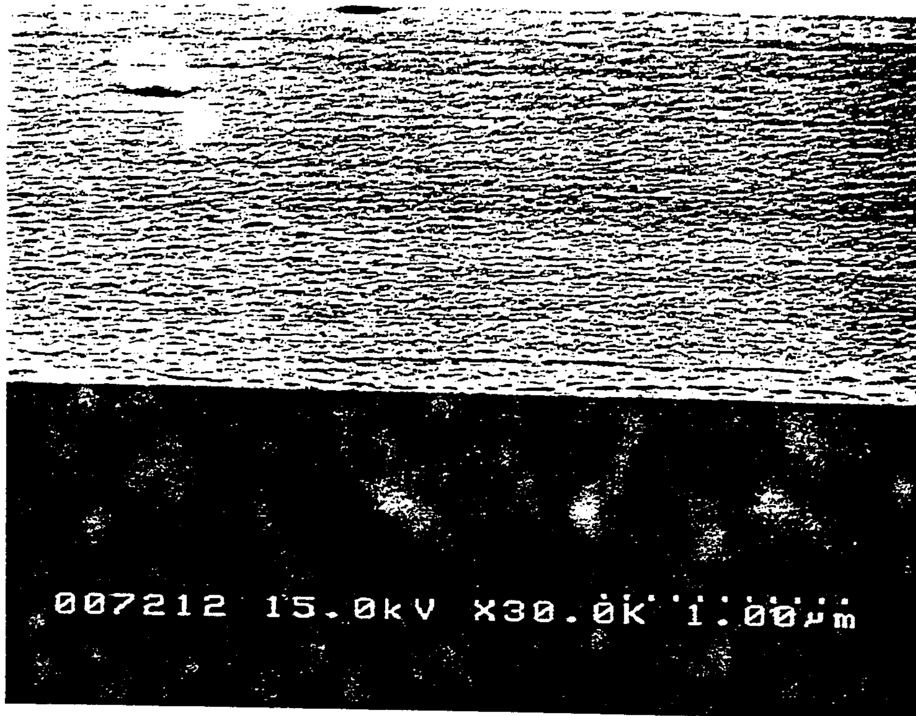

FIG. 10

FIG. 11

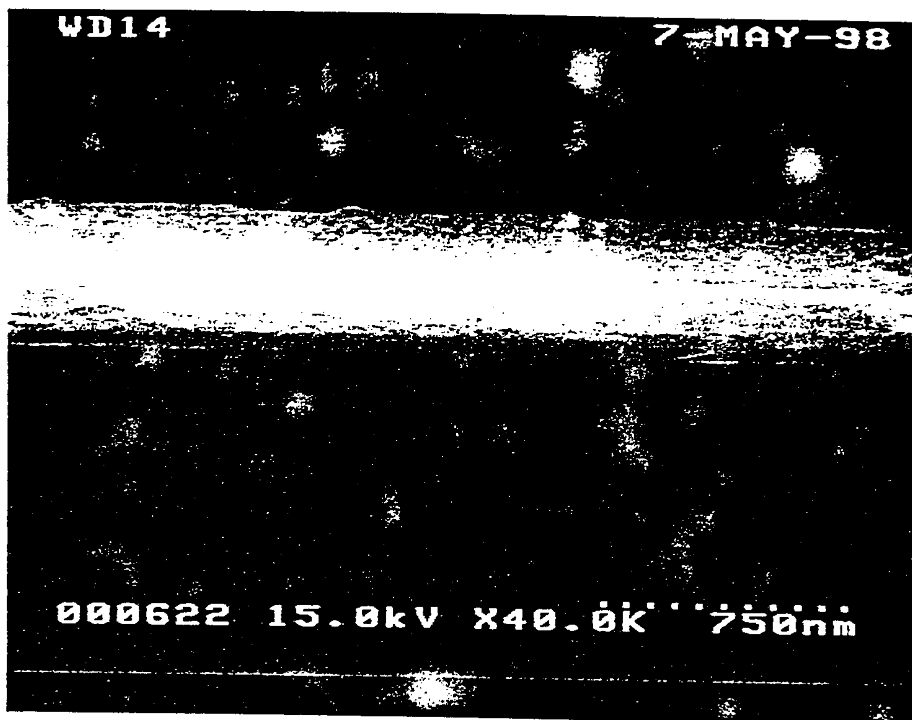

FIG. 12

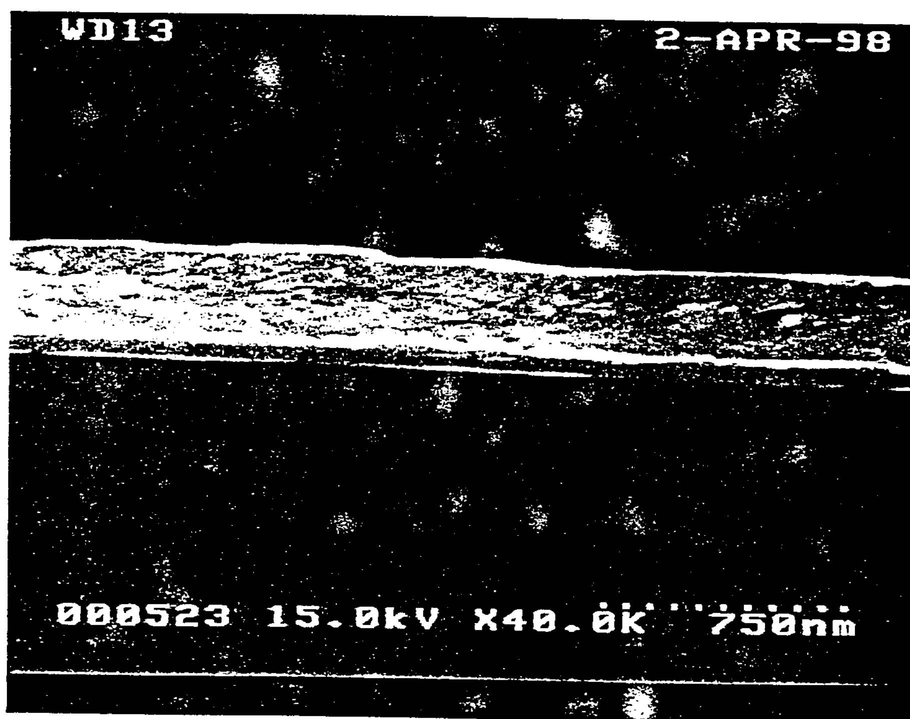

FIG. 13

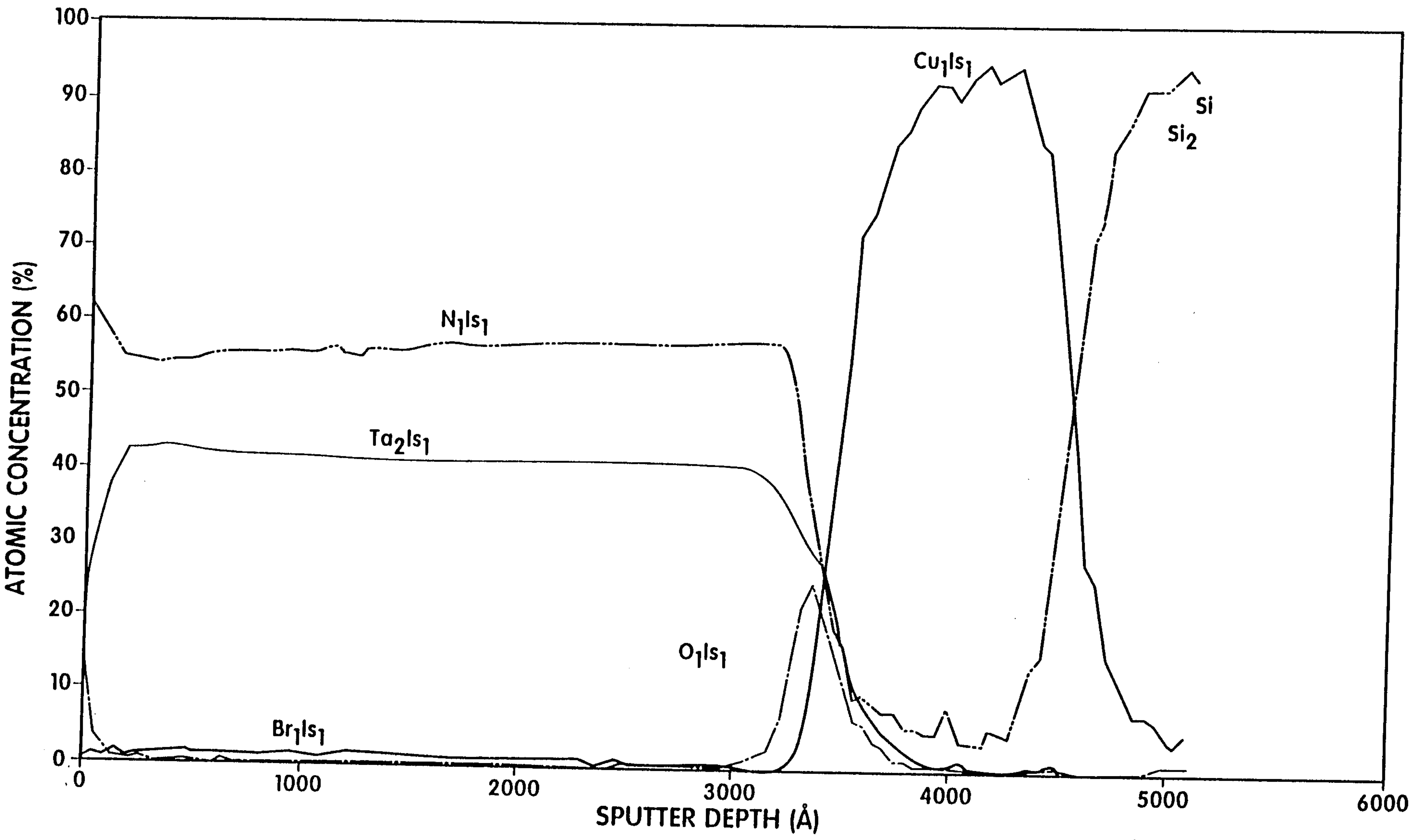

FIG. 14

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/11281

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.
Y	EP 0 818 560 A (APPLIED MATERIALS INC) 14 January 1998 (1998-01-14) page 4, line 49 - line 53; claims 21,25,28-30,36,38,39 page 4, line 4 - line 11; figure 1 page 12, line 38 -page 18, line 57 ---	1-3,11, 13-18, 20-22, 24-28, 31,32,35

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 2000	07/09/2000

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

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

International Application No
PCT/US 00/11281

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	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 171, left-hand column; table I ---	1-3,11, 13-18, 20-22, 24,32,35
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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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