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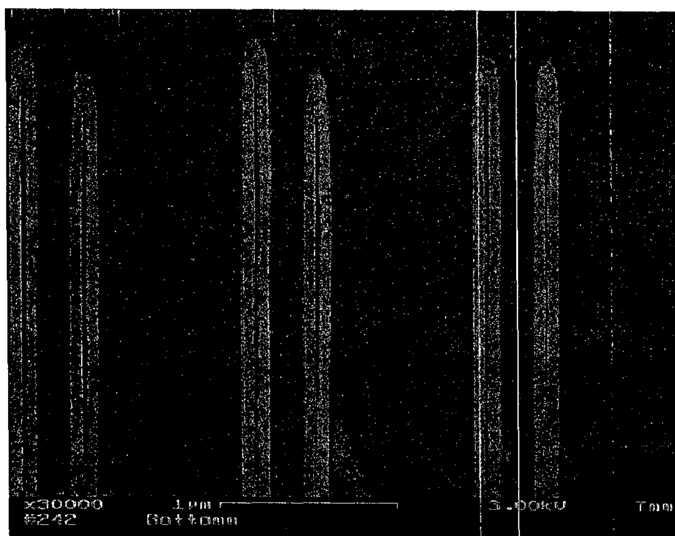
(54) Title: VAPOR DEPOSITION OF TUNGSTEN NITRIDE



(57) **Abstract:** Tungsten nitride films were deposited on heated substrates by the reaction of vapors of tungsten bis(alkylimide)bis(dialkylamide) and a Lewis base or a hydrogen plasma. For example, vapors of tungsten bis(*tert*-butylimide)bis(dimethylamide) and ammonia gas supplied in alternate doses to surfaces heated to 300 °C produced coatings of tungsten nitride having very uniform thickness and excellent step coverage in holes with aspect ratios up to at least 40:1. The films are metallic and good electrical conductors. Suitable applications in microelectronics include barriers to the diffusion of copper and electrodes for capacitors. Similar processes deposit molybdenum nitride, which is suitable for layers alternating with silicon in X-ray mirrors.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

VAPOR DEPOSITION OF TUNGSTEN NITRIDE

Background of the Invention

1. Field of the Invention

5 This invention relates to materials and processes for deposition of thin films on solid substrates. In particular, this invention relates to materials and processes for deposition of tungsten-containing thin films on solid substrates. This invention also relates to methods and materials for making electrically conducting, conformally deposited films for fabrication of devices in the areas of microelectronics.

10 2. Description of the Related Art

Tungsten nitride, WN_x, is considered to be a good barrier against diffusion of copper in microelectronic circuits. WN_x can also be used in electrodes for thin-film capacitors and field-effect transistors. WN_x has been made by reactive sputtering, but the uniformity of film thickness inside narrow features ("step coverage") is not expected to 15 be adequate for use in future microelectronic devices having narrow features with high aspect ratios.

Atomic layer deposition (also known as atomic layer epitaxy) is a process for depositing thin layers of solid materials from two vapor precursors. The surface of a substrate onto which a film is to be deposited is exposed to a dose of vapor from one 20 precursor. Then any excess unreacted vapor from that precursor is pumped away. Next, a vapor dose of the second precursor is brought to the surface and allowed to react. This cycle of steps can be repeated to build up thicker films. Typically, each precursor contributes a portion of the atoms to the deposited film. One particularly important

aspect of this process is that the ALD reactions are self-limiting, in that only a certain maximum thickness can form in each cycle, after which no further deposition occurs during that cycle, even if excess reactant is available. Because of this self-limiting character, ALD reactions produce coatings with highly uniform thicknesses. Uniformity
5 of ALD film thickness extends not only over flat substrate surfaces, but also into very narrow holes and trenches. This ability of ALD to make conformal films is called "excellent step coverage."

Coatings of WN_x made by ALD from WF_6 and NH_3 have good step coverage. A disadvantage of this process is that WF_6 and/or its reaction byproduct, HF, can attack
10 substrates made of Si or SiO_2. This reaction can also generate unwanted particles of ammonium fluoride byproduct that may cause defects in a semiconductor product. Also, this process can leave the WN_x surface with a fluorine residue that may impede adhesion of copper to the surface. In particular, adhesion of Cu deposited by CVD is often considered to be poor in part because of fluorine contamination at the interface between
15 the tungsten nitride and the copper. Loss of adhesion can cause severe loss of yield in manufacturing or reliability problems during operation of a semiconductor device.

Molybdenum nitride layers may be used along with alternating layers of silicon to make mirrors for X-rays. ALD would be an ideal method for depositing the MoN_x and silicon layers with the required highly uniform thicknesses needed in an X-ray mirror.

20

Summary of the Invention

The present invention provides a highly efficient process for depositing conformal coatings, particularly those containing tungsten, on solid substrates. These coatings comprise tungsten, nitrogen, and optionally, may contain oxygen, silicon, carbon and/or hydrogen, and relatively small amounts of other elements. As used herein, the coatings of the present invention are referred to as "tungsten nitride." Tungsten nitride layers with extremely uniform thicknesses and/or tungsten nitride coatings with extremely smooth surfaces are obtained.

One aspect of the present invention is a process for depositing a thin film on the surface of a substrate by a sequential process including one or more cycles, wherein at least one cycle comprises:

(a) exposing the substrate to a vapor of a first material containing at least two elements of the thin film, wherein at least a portion of the first material's vapor adsorbs on the surface of the substrate by a self-limiting process;

(b) removing un-adsorbed vapor of the first material from the vicinity of the substrate;

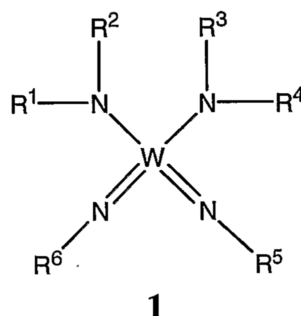
(c) exposing the substrate to the vapor of a second material that activates the surface so that the surface is prepared to react with additional quantities of said first material; and

(d) removing residual vapor of the second material from the vicinity of the substrate.

In one aspect of the invention vapors of bis(alkylimido)bis(dialkylamido) tungsten(VI) are reacted with a Lewis base, such as ammonia or pyridine, on the heated

surface of a substrate to form coatings of tungsten nitride. In other embodiments, the tungsten nitride precursor vapor is exposed to an activating plasma.

In at least some embodiments, tungsten compounds have the general formula **1**, in which R^n represents alkyl groups, fluoroalkyl groups or alkyl groups substituted with
5 other atoms or groups, preferably selected to enhance the volatility of the compound, where R^n is any one of R^1 through R^6. The R^n may be the same or different from each other.



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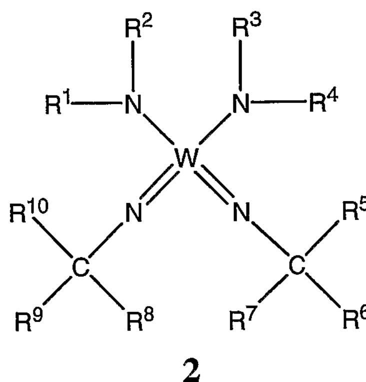
10 In one or more embodiments corresponding to formula **1**, the alkyl groups R^5 and R^6 have a tertiary carbon attached to the imido nitrogen. In one or more embodiments, the compounds have the general structure **2**:



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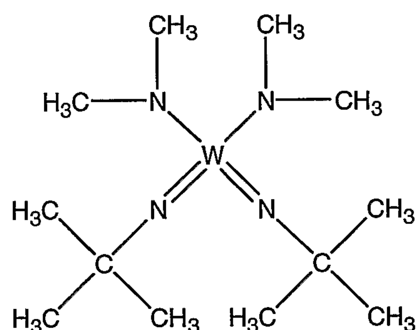
This structure is believed to facilitate deposition of films with low carbon content because

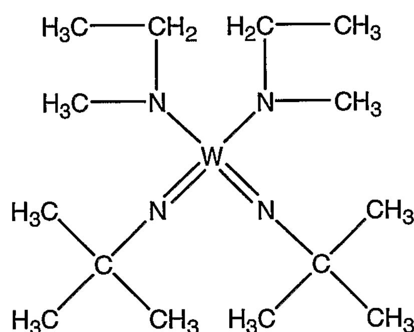
of the facile beta-hydrogen elimination reactions for alkyl groups with tertiary carbon.

In at least some embodiments methyl groups are selected for all the R^n in the general formula **2** given above, obtaining the compound bis(*tert*-butylimido)bis(dimethylamido) tungsten(VI) having formula **3**:



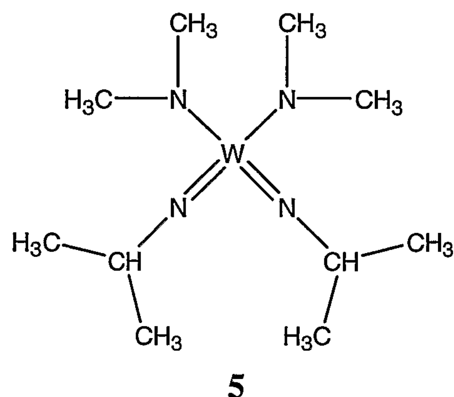
5 **3**

In one or more embodiments of the present invention, the compound is obtained by selecting in formula **2** R^1, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} to be methyl groups, and R^2 and R^3 to be ethyl groups, to obtain bis(ethylmethylamido)bis(*tert*-butylimido)tungsten(VI) having formula **4**:



10 **4**

Another compound of the invention is obtained by selecting in formula **1** the groups R^1, R^2, R^3 and R^4 to be methyl groups, and R^5 and R^6 to be isopropyl groups, to obtain bis(dimethylamido)bis(isopropylimido)tungsten(VI) having formula **5**:



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5 In the foregoing compounds, it is also understood that two or more alkyl groups may be linked to form cyclic compounds, and that the groups may contain some degree of unsaturation, e.g., aryl, alkenyl or alkynyl groups.

In one or more embodiments of the present invention, tungsten nitride films are deposited. The films are deposited under conditions that produce good adhesion between 10 the deposited tungsten nitride film and a substrate onto which it is deposited.

In one or more embodiments strongly adherent films are deposited on top of the tungsten nitride films of the invention. In particular, an adherent copper layer can be deposited on the tungsten nitride layer.

In one or more embodiments, vapor deposition of highly uniform tungsten nitride 15 films is accomplished over a range of conditions such as concentrations of reactants and position of the substrate inside the reactor. In one or more embodiments of the present invention, substrates are coated at relatively low temperatures, e.g., from about 200 °C to 400 °C.

The method of the present invention also provides conformal coatings of tungsten nitride over substrates with narrow holes, trenches or other structures. This ability is commonly known as "good step coverage." Tungsten nitride coatings that are substantially free of pinholes or other mechanical defects can also be prepared. Coatings
5 may also be placed on powders or wires, or around and within complicated mechanical structures. The coating can be used in an electrical capacitor or as a barrier to diffusion of metals in microelectronic devices.

The tungsten source is a non-corrosive liquid at room temperature, and the process for atomic layer deposition proceeds without etching or damaging structures (mainly
10 because HF is not a byproduct of the deposition process). Thus, the uniform tungsten nitride films are deposited without fluorine impurity in the film and without toxic fluorine components in the precursor or in the effluent from the process.

In one or more embodiments, an electrically conducting film is provided that is a good barrier to diffusion of copper. The present invention includes a process for
15 depositing electrically conductive tungsten nitride for use as a barrier against diffusion of copper in microelectronic devices, having useful mechanical properties as hard coatings, or useful as protection against diffusion, oxidation or corrosion.

Molybdenum nitride, MoN_x, can be deposited by use of analogous compounds with molybdenum in place of tungsten.

20

Brief Description of the Drawings

The foregoing and various other aspects, features, and advantages of the present invention, as well as the invention itself, may be more fully appreciated with reference to the following detailed description of the invention when considered in connection with
5 the following drawings. The drawings are presented for the purpose of illustration only and are not intended to be limiting of the invention, in which:

FIG. 1 is a cross-sectional illustration of an atomic deposition layer apparatus used in the practice of at least one embodiment of the invention;

FIG. 2 is a cross-sectional scanning electron micrograph of holes in a silicon
10 wafer uniformly coated with tungsten nitride using one embodiment of the invention; and

FIG. 3 is a graphical representation illustrating that the thickness of the layer deposited per cycle depends on the temperature of the substrate during deposition.

Detailed Description of the Invention

1. Summary of processes for ALD of tungsten nitride.

The present invention provides a method for preparing materials comprising tungsten and nitrogen, which we will refer to as "tungsten nitride" even if it contains smaller amounts of other elements such as carbon, oxygen or hydrogen. In a conventional chemical vapor deposition (CVD) method, a vapor of a tungsten precursor is reacted with a Lewis base such as ammonia on the surface of a substrate. The tungsten nitride may be formed as a film on a heated substrate. In an alternating layer deposition (ALD) process, a substrate is alternately exposed to the vapor of a tungsten precursor and then to ammonia or to another Lewis base, such as pyridine. In a plasma-assisted ALD process, a substrate is alternately exposed to the vapor of a tungsten precursor and then to a hydrogen-containing plasma. As is discussed in greater detail below, the ALD method provides highly conformal films and is suitable for use in a wide range of reaction conditions and reactant reactivity.

2. Synthesis of tungsten precursors.

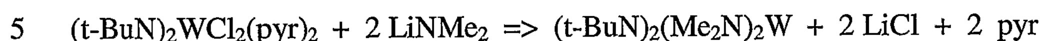
An exemplary tungsten precursor, bis(*tert*-butylimido)bis(dimethylamido) tungsten(VI), $(t\text{-}BuN)_2(Me_2N)_2W$, can be synthesized according to the following reaction sequence:

$$WCl_6 + 4\ HN(t\text{-}Bu)SiMe_3 \Rightarrow (t\text{-}BuN)_2WCl_2NH_2(t\text{-}Bu) + 3\ Me_3SiCl + (t\text{-}Bu)(Me_3Si)NH_2Cl$$

(1)

$$(t\text{-}BuN)_2WCl_2NH_2(t\text{-}Bu) + 2\ pyr \Rightarrow (t\text{-}BuN)_2WCl_2(pyr)_2 + (t\text{-}Bu)NH_2$$

(2)



$$(t\text{-}BuN)_2WCl_2(pyr)_2 + 2\ LiNMe_2 \Rightarrow (t\text{-}BuN)_2(Me_2N)_2W + 2\ LiCl + 2\ pyr$$

(3)

In these formulas, “t-Bu” stands for *tertiary*-butyl and “pyr” stands for pyridine.

As would be appreciated by one of ordinary skill in the art, other similar tungsten precursors may be prepared by similar reactions, by substituting other amines for *tert*-butyltrimethylsilylamine and other lithium alkylamides for lithium dimethylamide. The tungsten precursors generally react with moisture in the ambient air, and should be stored under an inert, dry atmosphere such as pure nitrogen gas.

3. Detailed description of ALD process.

The process according to one or more embodiments of the invention may be carried out using an atomic layer deposition (ALD) apparatus. Alternating doses of first and second reactant vapors are introduced into the deposition chamber to form a layer of controlled composition and thickness on a substrate. The apparatus introduces a metered amount of a first reactant vapor into a deposition chamber having a substrate therein to be coated. A thin layer of the first reactant is deposited on the substrate. After a preselected time period, a metered amount of a second reactant vapor is then introduced into the deposition chamber and allowed to interact with the layer already deposited by the first reactant. The time period may be on the order of a few seconds and is selected to provide

adequate time for the just-introduced component to react on the substrate and for any excess vapor to be removed from the headspace above the substrate. It has been determined that the surface reactions are self-limiting so that a reproducible layer of predictable composition is deposited. As will be appreciated by one of ordinary skill in
5 the art, deposition processes utilizing more than two reactant components are within the scope of the invention.

In one embodiment of the invention, 6-port sampling valves (Valco model EP4C6WEPH, Valco Instruments, Houston, TX) normally used for injecting samples into gas chromatographs may be used to deliver pulses of reactant gases, liquids or solutions
10 into a suitable carrier gas. Each time that a valve is opened, a defined volume of reactant flows into a heated tube in which liquids or solutions are vaporized. Carrier gas moves the reactant gas or vapor from the tube into the zone containing the substrate.

In another embodiment, a layer is deposited by ALD using an apparatus such as that illustrated in FIG. 1. A liquid or solid precursor **20** is placed in vessel **10** and heated
15 by oven **40** to temperature T_1 at which temperature it has equilibrium vapor pressure P_{eq} chosen to be less than the chamber pressure. Measured doses of tungsten precursor vapor **30** are introduced into the heated deposition chamber **110** by the use of three air-actuated diaphragm valves, **3**, **50** and **70** (Titan II model made by Parker-Hannifin, Richmond, CA). The chamber **5** is first pressurized with carrier gas delivered through tube **1** and
20 valve **3** from a pressure controller (not shown). Valve **3** is then closed and valve **50** opened to allow the carrier gas to pressurize precursor reservoir **10** to pressure P_{tot}, which pressure is chosen to be larger than the chamber pressure P_{dep}, and then valve **50** is closed.

The mole fraction of precursor vapor in the vapor space **30** of reservoir **10** then becomes P_{eq}/P_{tot}. Valve **70** is then opened in order to let a dose of the precursor vapor and carrier gas flow into the reaction zone. The number of moles delivered in this dose can be estimated from the equation

5

$$n = (P_{eq}/P_{tot})(P_{tot} - P_{dep})(V/RT_1),$$

where V is the volume of the vapor space **30** in chamber **10.** If some carrier gas from tube **95** enters the volume **30** during the time that the valve **70** is open, then a dose somewhat larger than this estimate may be delivered. By making the volume V large enough, a precursor dose may be made large enough to cause the surface reactions to go
10 to completion (also called "saturation"). If the vapor pressure P_{eq} is so low that the required volume V would be impracticably large, then additional doses from volume V may be delivered before delivering a dose of the other reactant.

Carrier gas (such as nitrogen or hydrogen gas) flows at a controlled rate into inlets **90** and **95** in order to speed the flow of the reactants into the deposition chamber and the
15 purging of reaction byproducts and un-reacted reactant vapor. A static mixer may be placed in the tubing **100** leading into the reactor to provide a more uniform concentration of the precursor vapor in the carrier gas as it enters the deposition chamber **110** heated by furnace **120** and containing one or more substrates **130.** The reaction byproducts and un-reacted reactant vapors may be removed by trap **140** before passing into a vacuum pump
20 **150.** Carrier gas exits from exhaust **160.**

Gaseous reactants, such as ammonia or hydrogen, are introduced into the tube **180** from a source tank and a pressure regulator and/or flow controller (not shown). The gas flows through 3-way valve **170** into the mixing zone **100** and then over the substrate **130**

inside chamber **110** in heated zone **120**. When a sufficient dose has been delivered, the 3-way valve **170** is turned into its other position so that carrier gas flows from mass-flow controller **90** into the deposition chamber **110**, sweeping away any excess reactant vapor. The size of the dose is controlled by the length of time during which the 3-way valve **170**
5 is held in the delivery position.

In an isothermal deposition zone **110**, material is generally deposited on all surfaces exposed to the precursor vapors, including substrates and the interior chamber walls. Thus it is appropriate to report the precursor doses used in terms of moles divided by the total area of the substrates and exposed chamber walls. In some cases, deposition
10 also occurs on part or all of the back side of the substrates, in which case that area should also be included in the total area.

The invention may be understood with reference to the following examples which are presented for the purpose of illustration only and which are not limiting of the invention, the full scope of which is set forth in the claims which follow.

15 Example 1. Synthesis of bis(*tert*-butylimido)bis(dimethylamido) tungsten(VI), $(t\text{-}BuN)_2(Me_2N)_2W$.

1) To a purple suspension of WCl_6 (30.0g, 75.6mmol) in toluene (300 mL) a solution of $HN(t\text{-}Bu)SiMe_3$ (50g, 344 mmol) in toluene (65 mL) was added dropwise over a period of 2 h. The suspension was stirred for a total of 24 h. The dark green suspension
20 was filtered through Celite to remove the solid $(t\text{-}Bu)(Me_3Si)NH_2Cl$ and any unreacted WCl_6. The dark brown filtrate was dried under vacuum in a warm water bath. 50 mL of hexane was added to the resulting dark brown solid and stirred in order to dissolve some impurities. The brown suspension was cooled in the freezer for overnight, and then the

dark brown supernatant solution containing the impurities was decanted. NMR for [(t-BuN)$_2$WCl$_2$ NH$_2$(t-Bu)]$_2$

^{1}H NMR (CDCl$_3$): δ 4.3 (br, 4, H_2NMe$_3$), 1.45(s, 18, μ-NCMe_3), 1.40(s, 18, NCMe_3), 1.33(s, 18, H$_2$NCMe_3). (Reference for this first reaction: A. J. Nielson, *Polyhedron*,
5 volume *6*, page 1657, 1987)

2) The solid product from the first step was suspended in 200 mL of ether. To this yellowish brown suspension excess pyridine (30 mL, 371 mmol) was added. The suspension turned black immediately. The suspension was stirred for 30 min and then placed under vacuum to remove ether, *tert*-butylamine and excess pyridine, leaving a
10 black solid. NMR for (t-BuN)$_2$WCl$_2$ (pyr)$_2$ ^{1}H NMR (CDCl$_3$): δ 8.93 (m, 4 , *o*-py) 7.62 (m, 2, *p*-py), 7.42 (m, 4, *m*-py) 1.40 (s, 18, NCMe_3). (Reference for this second reaction: J. Sundermeyer, *Chem. Ber.*, volume *124*, page 1977, 1991.)

3) 300 mL of ether was added to the solid, and then LiNMe$_2$ (12.0g, 235.2 mmole) was added very slowly to the suspension. (Caution! The reaction is very vigorous
15 and exothermic.) The addition of the lithium dimethylamide can be carried out from a solid addition funnel through a reflux column. The resulting brown suspension was stirred overnight and then dried under vacuum to remove ether and pyridine. The sticky black residue was extracted with portions of hexanes (total 300 mL) and filtered over Celite to remove LiCl and excess LiNMe$_2$. The black filtrate was dried under vacuum, and then
20 the black residue was distilled twice under reduced pressure (bp. 77-78 °C at 23 mTorr) to afford the product as a pale yellow liquid (12.3g, yield 39%). ^{1}H NMR (C$_6$D$_6$): δ 3.50 (s, 12, NMe_2), 1.40 (s, 18, NCMe_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 66.4 (2, NCMe$_3$), 53.8 (4,

N*Me*$_2$), 34.1 (6, NC*Me*$_3$). Elemental composition for $C_{12}H_{30}N_4W$, found (calculated): 35.07 (34.79)%C, 7.22 (7.30)%H, 13.14 (13.53)%N, (44.38)%W.

Example 2. Synthesis of bis(tert-butylimido)bis(ethylmethylamido)tungsten(VI).

To synthesize bis(tert-butylimido)bis(ethylmethylamido)tungsten(VI), (*t*-
5 BuN)2(EtMeN)2W, the $LiNMe_2$ is replaced with LiNEtMe. The product is a pale yellow liquid (17.1g, yield: 50%)(bp 79-81 °C at 20 mTorr). ^1H NMR (C_6D_6): δ 3.70 (q, 4, ^3J = 7.0 Hz, N(C*H*$_2$CH$_3$)*Me*), 3.50 (s, 12, NEt*Me*), 1.40 (s, 18, NC*Me*$_3$), 1.18 (t, 6, ^3J = 7.0 Hz, N(CH$_2$C*H*$_3$)*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6): 66.2 (2, NCMe$_3$), 59.7 (2, N(*C*H$_2$CH$_3$)Me), 50.1 (2, NEt*Me*), 34.0 (6, NC*Me*$_3$), 16.3 (2, N(CH$_2$*C*H$_3$)Me).
10 Elemental composition for $C_{14}H_{34}N_4W$, found (calculated): 37.74 (38.01)%C, 7.90 (7.75)%H, 12.51 (12.67)%N, (41.57)%W.

Example 3. ALD of tungsten nitride.

The apparatus of FIG. 1 was used to deposit tungsten nitride coatings. Bis(*tert*-butylimido)bis(dimethylamido)tungsten (VI) was placed in a stainless steel container **10**
15 having vapor volume of 0.6 liter and heated to 30°C, at which temperature the tungsten precursor has a vapor pressure of about 6 milliTorr. Ammonia was held in a compressed gas cylinder at 20 °C, and passed through a pressure regulator so that its pressure was reduced to 2.4 atmospheres. A silicon substrate **130** was prepared by dissolving its native oxide by placing it in dilute hydrofluoric acid solution for a few seconds. Next the
20 substrate was irradiated by ultraviolet light (e.g. UV mercury lamp) in air until the surface became hydrophilic (about 3 minutes). Then the substrate **130** was placed on a half-round substrate holder 25 cm long in chamber **110** having diameter 2.4 cm and heated

over a length 30 cm to a temperature of 300 °C. Another silicon substrate with narrow holes (0.1 microns by 0.2 microns wide and 7.3 microns deep) was also cleaned and placed in the chamber **110**.

Using the apparatus of FIG. 1, the deposition cycle began by introducing nitrogen

5 at 0.5 atmosphere pressure into the gas volume **5** containing 12 cm^3. After pressurizing volume **30** with this nitrogen, opening valve **70** for 1 second released a dose of about 4 x 10^{-10} moles/cm^2 of the tungsten precursor vapor into the deposition chamber **110.** A vacuum pump moved the tungsten precursor through the chamber in about 20 milliseconds. Then nitrogen flowed for 10 seconds to purge the chamber of excess

10 tungsten precursor as well as volatile byproducts of the reaction. The carrier gas also flowed through valve **170** during this tungsten vapor dose and purge step. To deliver a pulse of ammonia gas, the three-way valve **170** with inner channels 0.4 mm inner diameter, was opened to ammonia for 1 second, during which time about 5 x 10^{-6} moles/cm^2 of ammonia flowed into the deposition chamber. Then the three-way valve

15 **170** was turned to allow the flow of nitrogen carrier gas for 10 seconds to purge the chamber of residual ammonia gas. This cycle was then repeated 999 more times.

After these 1000 cycles were completed, the substrate **130** was removed from the reactor. The substrate was examined by scanning electron microscopy and found to have a film of tungsten nitride with a uniform thickness of 50 nm along the length of the

20 deposition zone. Each of the cycles deposited about 0.05 nm of film. Rutherford Backscattering was used to determine the chemical composition of the film to be $WN_{1.1\pm0.1}$. The density of the films was measured to be about 12 g/cm^2.

The film developed according to the foregoing possessed very desirable, smooth surface characteristics. Atomic force microscopy confirmed that the surface roughness of the deposited layer was very similar, if not equal to that of the substrate on which it was deposited. X-ray diffraction showed that the layer was mostly amorphous along with small amounts of extremely small crystallites shown by the presence of weak, broad diffraction peaks corresponding to the known cubic, crystalline phase of WN. This structural information was confirmed by transmission electron microscopy (TEM), which showed some crystallites up to 3 nm in size in an amorphous matrix.

A scanning electron micrograph (SEM) was taken of a wafer with narrow holes having aspect ratio 40:1 coated with WN_x by the process described in the first paragraph of this example and then cleaved to show a cross-section of the coated holes. The SEM in FIG. 2 shows that the walls of the narrow hole are covered with a perfectly conformal coating. In other similar samples, good step coverage for holes having aspect ratios of over 200:1 were observed. These results demonstrate the excellent step coverage achieved by the process of the invention.

The electrical resistivity of the tungsten nitride coating is about 1.5×10^{-3} ohm-cm. The resistivity was reduced to less than 4×10^{-4} ohm-cm by annealing in forming gas at 800 °C for 30 minutes. The annealed film had crystallized to the cubic tungsten structure and lost its nitrogen to become pure tungsten metal.

Example 4. Example 3 was repeated, except that the tungsten nitride film was deposited directly on silicon without an oxide interlayer produced by the UV-ozone treatment. Annealing the WN_x to a temperature of 1000 °C produced a coating of tungsten silicide.

Example 5. Example 3 was repeated, except that the exposure time to tungsten precursor vapor was increased from 10 seconds to 60 seconds. Identical results were obtained, showing that the chemical reactions of the tungsten precursor were completed within 10 seconds.

5 Example 6. Example 3 was repeated, except that the sizes of the tungsten doses were doubled. The film thickness and its properties were unchanged from those of Example 3. These results show that the surface reactions of the tungsten precursor are self-limiting.

Example 7. Example 3 was repeated, except that the sizes of the ammonia doses

10 were doubled. The film thickness and its properties were unchanged from those of Example 3. These results show that the surface reactions of the ammonia are self-limiting.

Example 8. Example 3 was repeated, except that the substrate temperatures were varied within the range from 250 °C to 350 °C. Similar tungsten nitride films were

15 obtained, except that the thicknesses of the films varied with the substrate temperature as shown in FIG. 3. No films were formed at temperatures below 250 °C. Films formed at temperatures above 350 °C, but they contained carbon in addition to tungsten and nitrogen, and their step coverage was not as good as for the films made in the range 250 °C to 350 °C.

20 Example 9. Example 3 was repeated with hydrogen plasma in place of the ammonia. 250 Watts of RF power (13.56 MHz) was capacitatively coupled to form the hydrogen plasma. Similar results that those of Example 3 were obtained, except that the

resistivity of the as-deposited film was much lower, about 4 x 10^{-4} ohm-cm, and the carbon content was higher.

Example 10. Example 3 was repeated using substrates of fused silica, quartz, soda-lime glass, glassy carbon, stainless steel, aluminum, copper and gold. Identical
5 results were obtained.

Comparative Example 1. Example 1 was repeated using only the tungsten precursor and no ammonia. No film was deposited.

Example 11. The ALD tungsten nitride films were shown to be good barriers to the diffusion of copper by the following tests. 100 nm of copper was sputtered on top of
10 various films of tungsten nitride ranging in thickness from 1 nm to 100 nm on silicon substrates, including films with thicknesses of 1 nm, 2 nm, 5 nm, 10 nm, 20 nm, 50 nm and 100 nm. Samples of these Si/WN/Cu structures were annealed in forming gas for 30 minutes at various temperatures. The copper on the surface was dissolved in nitric acid solution, and then the tungsten nitride was dissolved in ammonia/hydrogen peroxide
15 solution. Examination of the silicon by SEM showed no change in samples annealed at 450, 500 or 550 °C. A sample annealed at 600 °C showed a few bright crystals of copper silicide due to isolated breakdown of the tungsten nitride barrier. A sample annealed at 650 °C showed numerous crystals of copper silicide due to complete breakdown of the barrier. These results are conventionally interpreted to mean that the tungsten nitride is
20 stable to 550 °C and is an excellent barrier to diffusion of copper, even for films only about 1 nm or 2 nm thick.

Example 12. Copper oxide was deposited on tungsten nitride films by ALD from 100 cycles of alternating exposure to copper(II)bis(sec-butylacetoacetate) vapor and an

ozone/oxygen gas mixture at a substrate temperature of 200 °C using an apparatus described by FIG. 1 with the copper precursor in chamber **10** and the ozone/oxygen mixture from an ozone generator passing into tube **180**. Copper oxide, CuO, was deposited at a rate of about 0.05 nm per cycle. The copper oxide was reduced to copper
5 metal by heating the sample to 500 °C in a hydrogen atmosphere for 1 hour. The resulting shiny copper layer adhered strongly to the tungsten nitride, and could not be removed by adhesive tape.

Example 13. The thin ALD copper layer produced in Example 12 can be used as a "seed" layer to initiate the CVD of copper using the process described by E. S. Hwang
10 and J. Lee in Chemistry of Materials, volume 12, page 2076, 2000.

Example 14. The thin ALD copper layer produced in Example 12 can be used as a "seed" layer to initiate the electrochemical plating of copper by well-known methods.

Example 15. The ALD process of the invention can be used to make a capacitor having the structure $WN_x/HfO_2/WN_x$, in which the WN_x layers are the electrically
15 conducting electrodes and the HfO_2 is the insulating dielectric layer. The HfO_2 can be made by ALD reaction of tetrakis(dimethylamido)hafnium and water vapor as described in Example 12 of WO 0227063.

Example 16. The ALD process of the invention can be used to make a capacitor having the structure $WN_x/Ta_2O_5/WN_x$, in which the WN_x layers are the electrically
20 conducting electrodes and the Ta_2O_5 is the insulating dielectric layer. The Ta_2O_5 can be made by ALD reaction of ethylimidotris(diethylamido)tantalum and water vapor as described in Example 15 of WO 0227063.

Example 17. Example 3 was repeated, using isotopically labeled $^{15}NH_3$ in place of the normal $^{14}NH_3$. The tungsten nitride film was analyzed by Rutherford Backscattering, which showed that the nitrogen in the film is normal nitrogen ^{14}N, not ^{15}N. Thus the nitrogen in the film arises from the nitrogen in the tungsten precursor, not from the
5 ammonia.

Example 18. Example 3 was repeated with pyridine vapor in place of the ammonia. Similar results were obtained. The effectiveness of pyridine in producing tungsten nitride films is consistent with the proposition that the second component of the ALD process serves to activate the deposition process, but that it itself is not
10 incorporated into the deposited film. Pyridine cannot undergo transamination, yet it nonetheless deposits tungsten nitride films. This suggests that the second component of the ALD process acts as a base catalyst in the reaction.

Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention
15 described specifically herein. Such equivalents are intended to be encompassed within the scope of the following claims.

What is claimed is:

1. A process for depositing a thin film on the surface of a substrate by a sequential process including one or more cycles, wherein at least one cycle comprises:

exposing the substrate to a vapor of a first material containing at least two
5 elements of the thin film, wherein at least a portion of the first material's vapor adsorbs on the surface of the substrate by a self-limiting process;

removing un-adsorbed vapor of the first material from the vicinity of the substrate;

exposing the substrate to the vapor of a second material that activates the surface so that the surface is prepared to react with additional quantities of said first material, said
10 activation characterized in that elements of the second material are not incorporated into the thin film; and

removing residual vapor of the second material from the vicinity of the substrate.

2. A process as in claim 1 for forming a thin film comprising tungsten and nitrogen.

15

3. A process for depositing a thin film on the surface of a substrate by a sequential process including one or more cycles, wherein at least one cycle comprises:

exposing the substrate to a vapor of a first material comprising an element selected from the group consisting of tungsten and molybdenum and containing at least
20 two elements of the thin film, wherein at least a portion of the first material's vapor adsorbs on the surface of the substrate by a self-limiting process;

removing un-adsorbed vapor of the first material from the vicinity of the substrate;

exposing the substrate to the vapor of a second material that activates the surface

so that the surface is prepared to react with additional quantities of said first material; and

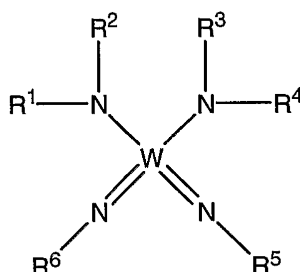
removing residual vapor of the second material from the vicinity of the substrate.

4. A process as in claim 3 in which said first material comprises one or more compounds

5 comprising tungsten-nitrogen bonds.

5. A process as in claim 3 in which said first material comprises one or more compounds comprising molybdenum-nitrogen bonds.

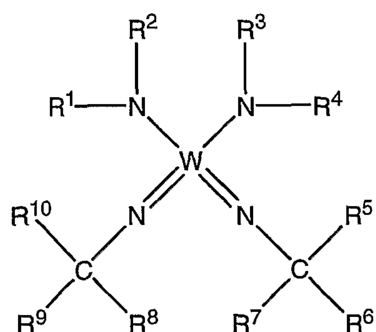
10 6. A process as in claim 4 in which said compounds comprising tungsten-nitrogen bonds have the general formula



in which R^n represents alkyl groups, arylalkyl groups, alkenylalkyl groups, alkynylalkyl groups, fluoroalkyl groups or alkyl groups substituted with other atoms or

15 groups selected to enhance the volatility of the compound, where R^n is any one of R^1 through R^6 and where the R^n may be the same or different from each other.

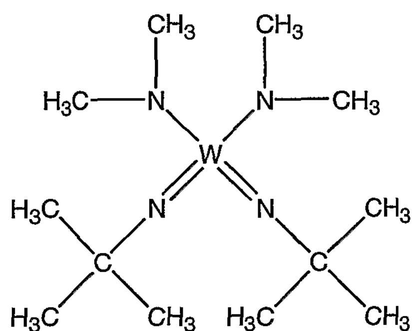
7. A process as in claim 4 in which said compounds comprising tungsten-nitrogen bonds have the general formula



in which R^n represents alkyl groups, arylalkyl groups, alkenylalkyl groups, alkynylalkyl groups, fluoroalkyl groups or alkyl groups substituted with other atoms or groups selected to enhance the volatility of the compound, where R^n is any one of R^1

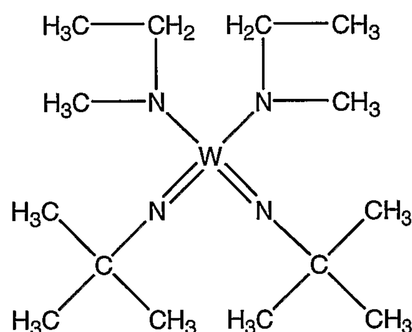
5 through R^{10} and where the R^n may be the same or different from each other.

8. A process as in claim 7 in which said compounds comprising tungsten-nitrogen bonds comprise bis(*tert*-butylimido)bis(dimethylamido)tungsten(VI) having the formula



10

9. A process as in claim 7 in which said compounds comprising tungsten-nitrogen bonds comprise bis(ethylmethylamido)bis(*tert*-butylimido)tungsten(VI) having formula:



10. A process as in claim 3 in which said second material is a Lewis base.

5 11. A process as in claim 10 in which said Lewis base is ammonia.

12. A process as in claim 10 in which said Lewis base is pyridine

13. A process as in claim 3 in which said second material comprises a hydrogen plasma.

10

14. A process as in claim 3 in which said second material comprises hydrogen atoms

15. A process as in claim 3 in which the substrate is maintained at a temperature in the range of about 200 °C to about 400 °C.

15

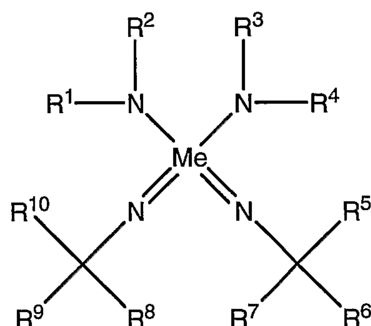
16. An electrical capacitor comprising one or more electrically conducting electrodes formed using the process of claim 1 or 6.

17. A barrier to diffusion of metals in microelectronic devices formed by the process of

claim 1 or 6.

18. The diffusion barrier of claim 17 having a thickness within the range 1 to 100 nm.

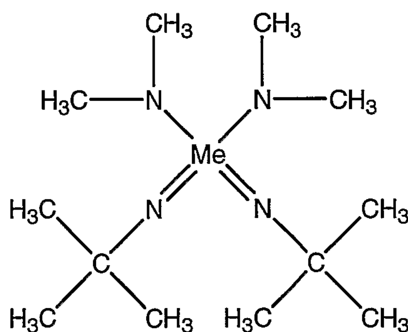
5 19. A composition of matter corresponding to the chemical compound described by the formula



in which Me is W or Mo, R^n represent alkyl groups, arylalkyl groups, alkenylalkyl groups, alkynylalkyl groups, fluoroalkyl groups or alkyl groups substituted

10 with other atoms or groups selected to enhance the volatility of the compound, where R^n is any one of R^1 through R^6 and the R^n may be the same or different from each other.

20. A composition of matter corresponding to the chemical compound described by the formula



15

in which Me is W or Mo.

21. The composition of claim 19 or 20, wherein Me is W.

5 22. A process for depositing material from a vapor phase comprising contacting the compound of claim 19 or 20 to a surface.

23. A microelectronic device comprising copper features, said device characterized in that a layer of tungsten nitride deposited according to the process of claim 3 or 6 is
10 interposed between the device substrate and the copper feature.

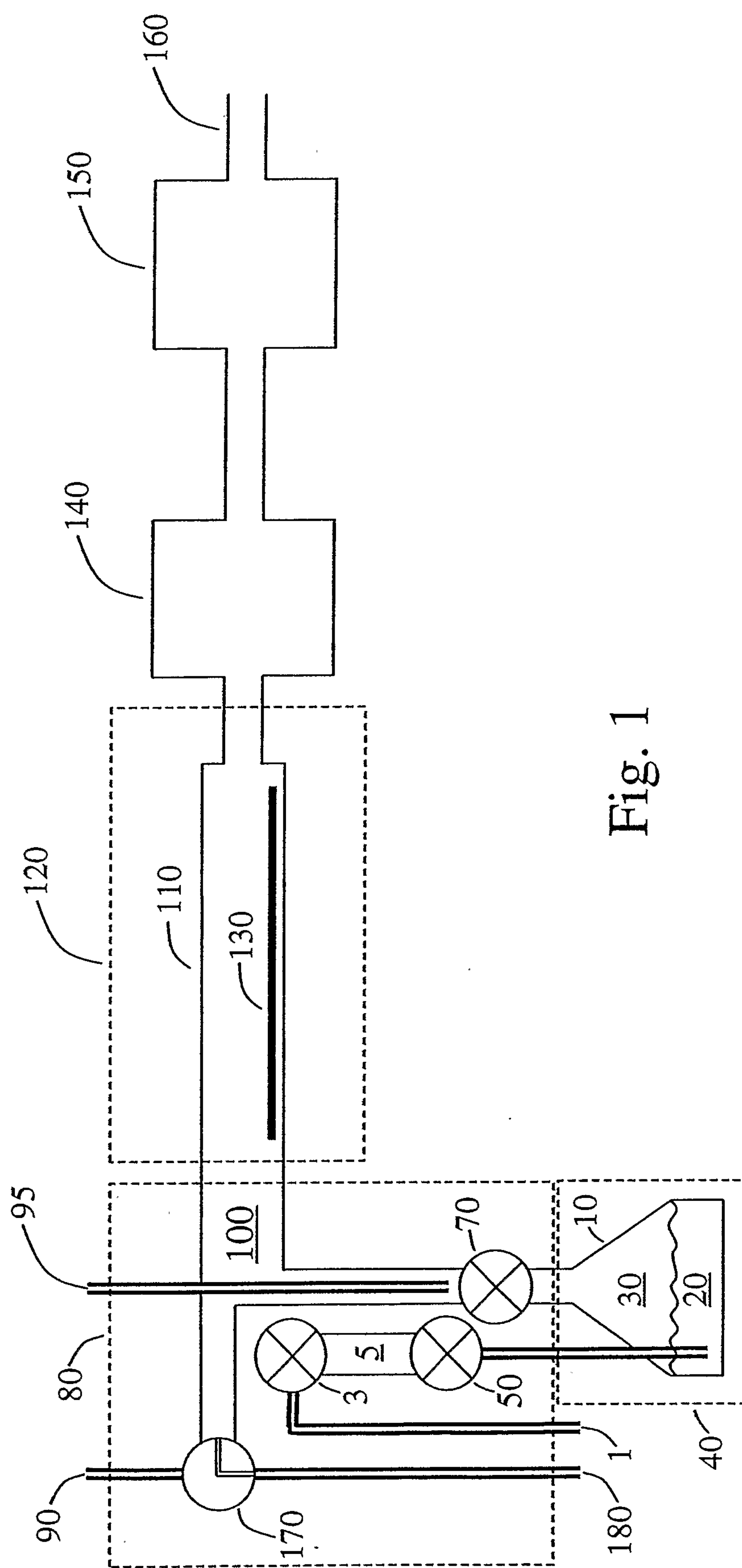


Fig. 1

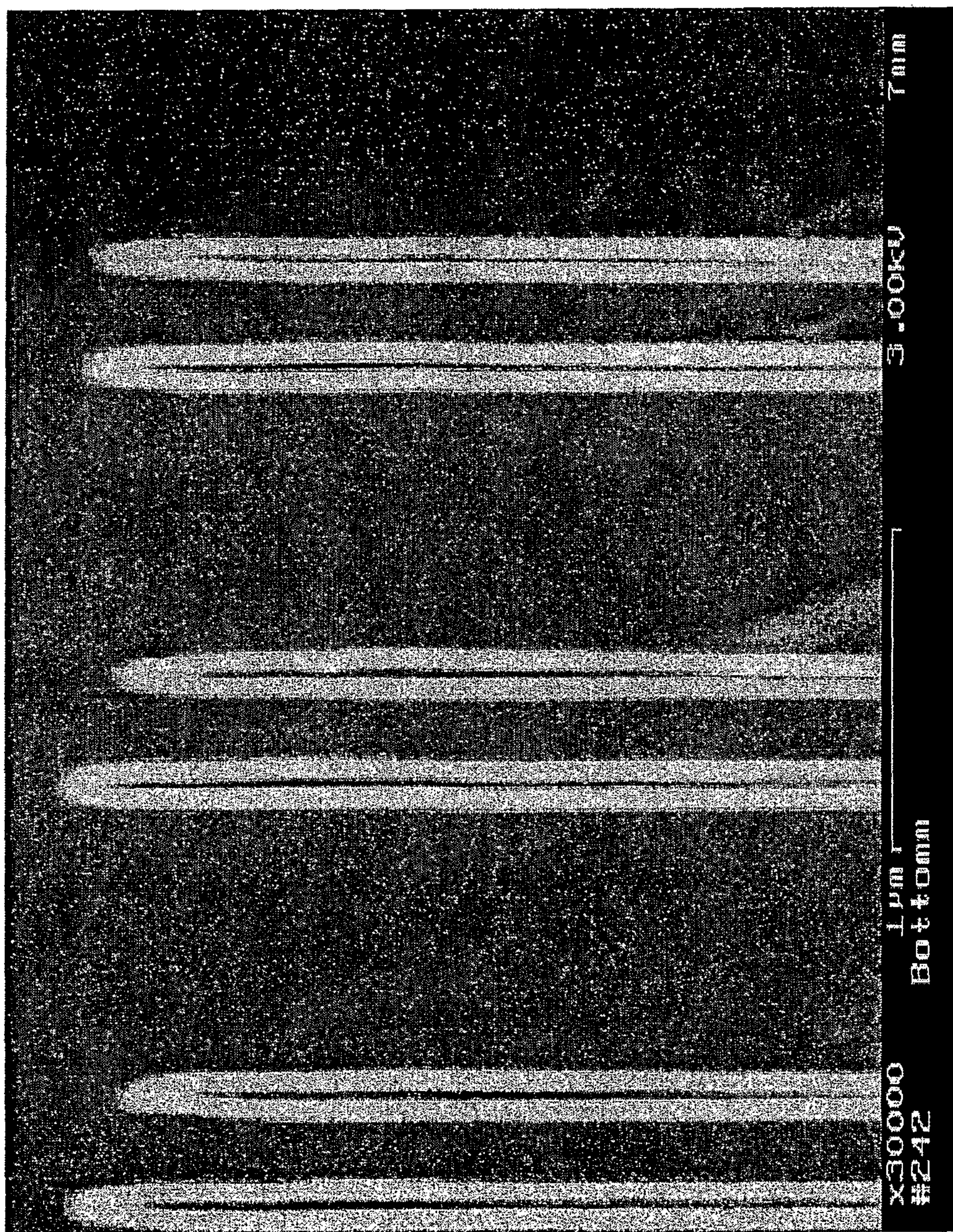
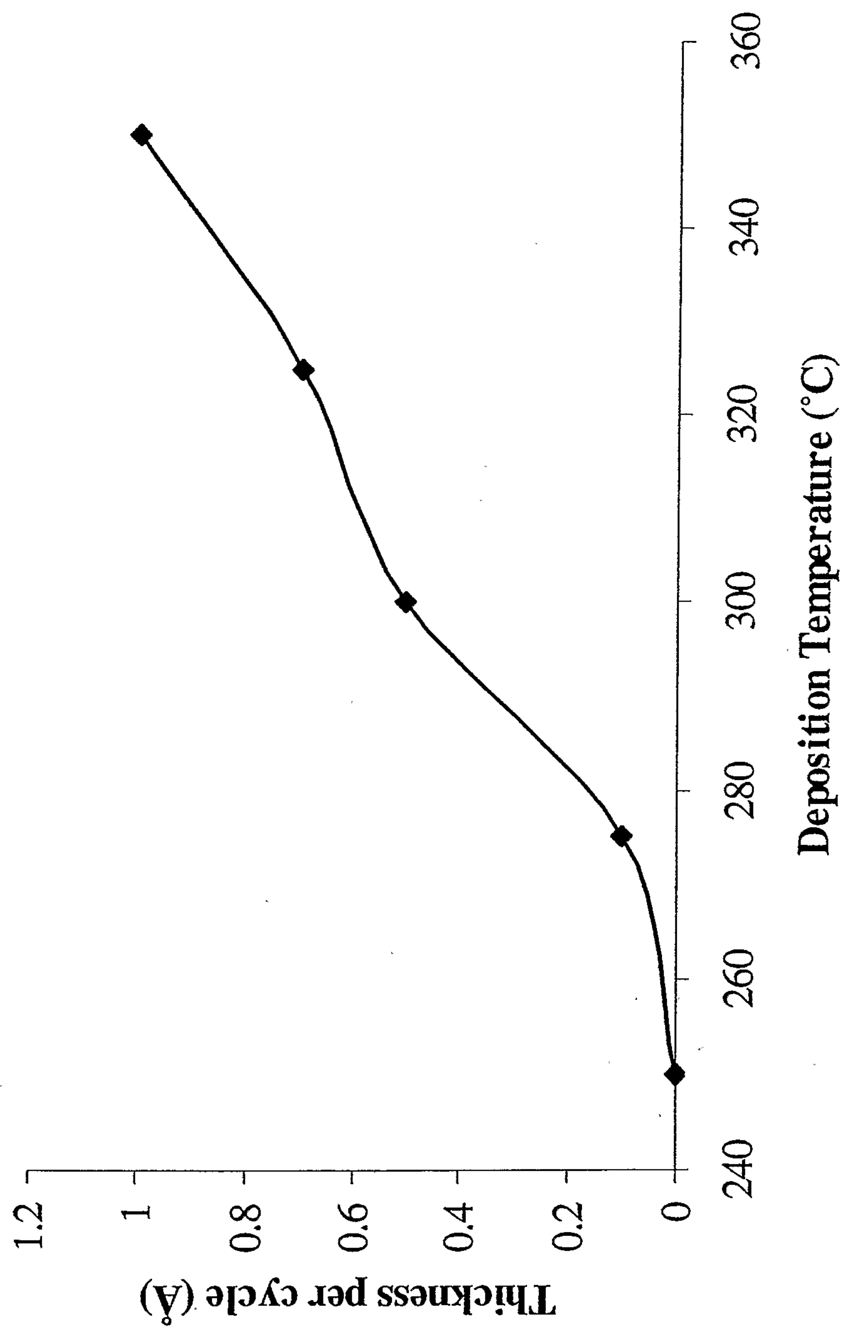


FIG. 2

FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/21281

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/34 C07F11/00 H01L21/768 H01L21/02

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 C07F H01L

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, CHEM ABS Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	BECKER J S ET AL: "DIFFUSION BARRIER PROPERTIES OF TUNGSTEN NITRIDE FILMS GROWN BY ATOMIC LAYER DEPOSITION FROM BIS(TERT-BUTYLIMIDO)BIS(DIMETHYLAMIDO)TUNGSTEN AND AMMONIA" APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 82, no. 14, 7 April 2003 (2003-04-07), pages 2239-2241, XP001166649 ISSN: 0003-6951 the whole document ---	1-11,14, 15,17-23
X	US 6 359 160 B1 (SUN SHI-CHUNG ET AL) 19 March 2002 (2002-03-19) column 2, line 66 -column 3, line 56; claims ---	1-23
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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

"E" earlier document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 November 2003	26/11/2003

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	Mauger, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/21281

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 02 27063 A (BECKER JILL ;SUH SEIGI (US); GORDON ROY G (US); HARVARD COLLEGE (U) 4 April 2002 (2002-04-04) cited in the application claim 28; table 1	19-22
X	EP 1 067 595 A (AIR PROD & CHEM) 10 January 2001 (2001-01-10) paragraph '0049!; claims	19,21,22
X	US 2001/041250 A1 (HAUKKA SUVI P ET AL) 15 November 2001 (2001-11-15) paragraph '0114! - paragraph '0131!	17,18,23
X	US 2001/054730 A1 (KIM JIN-WON ET AL) 27 December 2001 (2001-12-27) paragraph '0031! - paragraph '0033!	16
A	US 2001/002280 A1 (SNEH OFER) 31 May 2001 (2001-05-31) claim 30	1-23
A	WO 01 27347 A (ASM MICROCHEMISTRY OY ;HAUKKA SUVI PAEIVIKKI (FI); KAIPIO SARI JOH) 19 April 2001 (2001-04-19) claim 1	1-23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/21281

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1 and 3 relate to an extremely large number of possible processes. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the processes claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the processes in which tungsten or molybdenum nitrides are formed from precursors containing tungsten or molybdenumn and nitrogen.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/21281

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
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