Highly Conformal Thin Films of Tungsten Nitride Prepared by Atomic Layer Deposition from a Novel Precursor

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Highly uniform, smooth, and conformal coatings of tungsten nitride were synthesized by atomic layer deposition (ALD) from vapors of a novel precursor, bis(tert-butylimido)-bis(dimethylamido)tungsten, (BuN)2(Me2N)2W, and ammonia at low substrate temperatures (250–350 °C). This tungsten precursor is a low-viscosity, noncorrosive liquid with sufficient volatility at room temperature to be a vapor source for ALD. These vapors were alternately pulsed into a heated reactor, yielding up to 0.1 nm of tungsten nitride film for every cycle, with no initial delay or induction period. The films were uniform in thickness along the 20-cm length of the deposition zone, as determined by scanning electron microscopy. Successful depositions were carried out on all substrates tested, including silicon, glass, quartz, glassy carbon, stainless steel, aluminum, gold, and copper. The films are shiny, silver-colored, and electrically conducting. All of the films showed good adhesion to the substrates, were acid-resistant, and did not oxidize over time. The stoichiometry of the WN films was determined to be 1:1 by Rutherford backscattering spectrometry. The films were amorphous as-deposited, as shown by X-ray diffraction and high-resolution transmission electron microscopy. 100% step coverage was obtained inside holes with aspect ratios greater than 200:1. Annealing for 30 min at temperatures above 725 °C converted the WN to pure, polycrystalline tungsten metal. WN films as thin as 1.5 nm proved to be good barriers to diffusion of copper for temperatures up to 600 °C. ALD of copper onto the surface of the WN produced strongly adherent copper films that could be used as “seed” layers for chemical vapor deposition (CVD) or electrodeposition of thicker copper coatings.

I. Introduction

Shrinking dimensions in integrated circuits without increasing device delay times has forced a move away from aluminum toward copper interconnects.1 Copper has a lower resistivity than aluminum, 1.7 versus 2.7 μΩ·cm, respectively (bulk values). This property of copper enables the signal to move faster by reducing the RC (resistance × capacitance) time delay. Another major advantage of copper is its superior resistance to electromigration, a common reliability problem with aluminum lines.2 Narrower copper metal lines can carry the same amount of current as aluminum. This means that a greater density of interconnections can be achieved. Copper interconnects also require a very thin and efficient barrier to prevent the copper from diffusing into neighboring silicon or dielectric layers, causing device failure. A diffusion barrier is also needed as a passivating layer to protect the copper interconnect from corrosion and oxidation and to promote the adhesion of copper. Transition metal nitrides, such as titanium nitride, tantalum nitride, and tungsten nitride are currently the most intensively studied barrier materials. There are many requirements to be met by a diffusion barrier. The process demands and desired properties of a diffusion barrier are listed as follows:3,4 (1) Prevention of copper diffusion; (2) effective barrier thickness <5 nm; (3) resistivity < 500 × 10⁻⁶ Ω·cm; (4) halide-free; (5) excellent step coverage in high aspect ratio holes and trenches; (6) chemical mechanical polishing (CMP) compatible; (7) deposition temperatures under 350 °C (due to the thermal instability of low-k materials); (8) good growth and adhesion on, and lack of reaction with (a) SiO₂ and low-k insulators, (b) Si₃N₄, SiC, or other etch-stop and barrier materials, and (c) Cu; (9) amorphous structure; (10) crack- and pinhole-free films.

Titanium nitride may fail to meet all these demands due to its polycrystalline nature, allowing leakage along grain boundaries.5 Another candidate, sputtered tantalum nitride, is amorphous and conductive, but sputtering deposition methods can lead to poor surface coverage of high aspect ratio structures such as trenches.

and vias due to shadowing. Chemical vapor deposition (CVD) TaN produces better step coverage, but its electrical resistance is too high.

Tungsten nitride is a promising barrier material for copper metallization because of its refractory nature and excellent thermal, chemical (acid-resistant), and mechanical properties. Compared to the other transition metal nitrides, WN has the lowest electrical resistivity (single crystal). Copper forms no known compounds with tungsten nitride, indicating its stability as a barrier.

WN can also act as an adhesion promoter for copper and for tungsten. WN has been made by reactive sputtering and by CVD methods, but the uniformity of film thickness inside narrow features ("step coverage") is not expected to be adequate for use in future microelectronic devices having narrow features with high aspect ratios. WN has also been made by metal–organic chemical vapor deposition (MOCVD) from the precursor bis(tert-butylimido)-bis(dimethylamido)tungsten, \((\text{BuN})_2\text{W}-(\text{NH}_2\text{Bu})_2\), where it was used as a single-source precursor to grow W,N films. These films contained carbon due to thermal decomposition of the precursor and were not conformal.

The shrinkage of integrated circuits puts great demands on thin film processing techniques. Atomic layer deposition (ALD), characterized by excellent conformality, and thickness control, is receiving attention for applications in the deposition of diffusion barriers, nucleation layers, and high-k dielectric materials. ALD (also known as atomic layer epitaxy) is a process for depositing thin layers of solid materials from two or more vapor precursors. The surface of a substrate onto which film is to be deposited is exposed to a dose of vapor from one 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 then be repeated to build up thicker films. One particularly important aspect of this process is that the ALD reactions must be 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 of ALD film thicknesses extends not only over flat substrate surfaces but also into narrow holes and trenches. This ability of ALD to make conformal films is called "good step coverage."

Coatings of WN made by ALD from WF6 and NH3 have good step coverage. A disadvantage of this process is that WF6 and/or its reaction byproduct, HF, attacks substrates made of Si or SiO2. Also, this process can leave the WN surface with a fluorine residue that may impede adhesion of copper to the surface. In particular, adhesion of Cu deposited by ALD or CVD is often considered to be poor in part because of fluorine contamination at the interface between the tungsten nitride and the copper.

In the present work, we studied the deposition of WN barrier films by ALD using a novel precursor, bis(tert-butylimido)-bis(dimethylamido)tungsten-(VI), \((\text{BuN})_2\text{Me}_2\text{W}\), and ammonia at low substrate temperatures (250–350 °C). The basic properties of these films were investigated, as well as their performance as a barrier to the diffusion of copper.

### II. Experimental Section

#### General Procedures

All reactions and manipulations were conducted under a pure nitrogen atmosphere using either an inert atmosphere box or standard Schlenk techniques. Solvents were dried using an Innovative Technology solvent purification system. Reagents were used as-received from Aldrich. NMR spectra were recorded with a Bruker AM-500 spectrometer. Cryoscopic measurements of molecular weight were carried out by temperature measurements using a thermistor in a paraxylene solution cooling in an ice bath.

#### A. Synthesis of Tungsten Precursor

The tungsten precursor, bis(tert-butylimido)-bis(dimethylamido)tungsten-(VI), \((\text{BuN})_2\text{Me}_2\text{W}\), is readily synthesized from commercially available reactants, by the following three chemical reactions:

\[
\text{WCl}_6 + 4\text{HN(}\text{Bu})\text{SiMe}_3 \rightarrow \frac{1}{2}[(\text{BuN})_2\text{WCl}_2(\text{NH}_2\text{Bu})_2] + 3\text{Me}_3\text{SiCl} + (\text{Bu})(\text{Me}_2\text{Si})\text{NH}_2\text{Cl} \quad (1)
\]

\[
\frac{1}{2}[(\text{BuN})_2\text{WCl}_2(\text{NH}_2\text{Bu})_2] + 2\text{pyridine} \rightarrow (\text{BuN})_2\text{WCl}_2(\text{py})_2 + (\text{Bu})\text{NH}_2 \quad (2)
\]

\[
(\text{BuN})_2\text{WCl}_2(\text{py})_2 + 2\text{LiMe}_2\text{N} \rightarrow (\text{BuN})_2\text{Me}_2\text{W} + 2\text{LiCl} + 2\text{pyridine} \quad (3)
\]

(1) To a purple suspension of WCl6 (30.0 g, 75.6 mmol) in toluene (300 mL) a solution of HN(\text{Bu})\text{SiMe}_3 (50 g, 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 was filtered through Celite to remove the solid (Bu(Me)3Si)2NH2Cl and any unreacted WCl6. The dark brown filtrate was dried under vacuum in a water bath; 50 mL of hexane was added to the resulting dark brown solid and stirred to dissolve some impurities. The brown suspension was cooled in the freezer overnight, and then the dark brown suspension containing the impurities was dried under vacuum for (W/NBu2(N-Bu)Cl(NH2Bu)2). 1H NMR (CDCl3) δ 4.3 (br, 4, H, NMe2), 1.45 (s, 18, μ-NCMe), 1.40 (s, 18, NCMe), 1.33 (s, 18, H2NCMe).

(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 black solid. NMR for (Bu(N)₂-WCl₂(py)₂): 1H NMR (CDCl3) 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) Ether (300 mL) was added to the solid, and then LiNMe2 (12.0 g, 235.2 mmol) was added very slowly to the suspension. (CAUTION! The reaction is very vigorous and exothermic.) The black suspension was stirred overnight and then dried under vacuum. The sticky black residue was stirred for a total of 24 h. The dark green supernatant solution containing the impurities was decanted. The dark brown suspension was filtered through Celite to remove the solid.


20 mTorr, 17.1 g, yield: 50%). 1H NMR (C6D6) (Model WPMV200SM) before passing through a pressure controller so that its pressure was 20 psi before entering a three-way, two-position gas chromatography (GC) valve purchased from Valco Instruments (Model DC6WHE). Silicon substrates were prepared by removing the native oxide by dipping them in (48%) hydrofluoric acid solution for -5 s and then rinsing them with distilled water, creating a hydrophobic surface. Next, the substrates were irradiated by ultraviolet light from a mercury lamp in air (forming ozone) until the surface became hydrophilic (normally 3 min). Then the substrate was placed in the stainless steel chamber on an aluminum substrate holder via a removable flange. The chamber has a diameter of 2.4 cm and length of 30 cm and was heated to a temperature of 300 °C. The substrate holder is 25 cm long, half-round 2.1 cm in diameter. The deposition zone of the reactor was 20 cm long and was defined by the isothermal zone of the tube furnace (the surface area of the reactor wall in this region is 160 cm² and of the substrate holder it is 111 cm²). The total surface area in the deposition zone is 271 cm². Under ideal deposition conditions, film was deposited on all surfaces in this region.

Using the apparatus shown in Figure 1, the deposition cycle begins by introducing nitrogen at 380 Torr into the gas volume, V, containing 12 cm³ by opening the two-way diaphragm valve, "fill nitrogen" for 1 s. This gas was then introduced into the "ALD bubbler" by opening the two-way diaphragm valve, "empty nitrogen". After pressurization of the volume above the tungsten precursor with this nitrogen at a pressure of 30 Torr, the on-off diaphragm valve, "empty precursor", was opened for 1 s. Then nitrogen flowed for 10 s to purge the chamber of excess tungsten precursor as well as volatile byproducts of the reaction. The carrier gas also flowed during this tungsten vapor dose and the purge step through the nitrogen feed line. To deliver a pulse of ammonia gas, the two-position valve, with inner channels 0.4-mm inner diameter, was opened to ammonia for 1 s, releasing a dose of about 0.3 nmol/cm², which provided an exposure of 6.9 × 10⁸ Langmuirs of the tungsten precursor to the surfaces of the substrates. A rotary vane vacuum pump (Edwards RV3) moved the tungsten precursor through the chamber in about 0.2 s. Then nitrogen flowed for 10 s to purge the chamber of residual ammonia gas. This cycle was then repeated until the desired thickness was obtained. At the end of the prescribed number of cycles (typically 20–3000), substrates of silicon, glass, and glassy carbon were removed from the reactor and analyzed.

C. Film Characterization. Roughness measurements were made by atomic force microscopy (AFM) (Nanoscope III
Surface morphology, step coverage (on cleaved samples), and thickness measurements were made by scanning electron microscopy (SEM) (Leo 982; resolution of 3 nm). Composition and number of atoms per unit area were determined by Rutherford backscattering spectroscopy (RBS) (General Ionics Model 4117, 1.7 MeV Tandetron) of samples grown on glassy carbon substrates. RBS was also used to determine the thickness of very thin films, using the number of atoms per unit area and the density measured for thicker films. Composition was also verified by X-ray photoelectron spectroscopy (XPS) (Surface Science Lab SSX-100) and energy-dispersive X-ray spectroscopy (EDS) (JEOL 2010F equipped with an energy-dispersive X-ray spectrometer). Thickness and density were also found by low-angle X-ray reflection (XRR) (Scintag Model XDS2000). X-ray diffraction (XRD) (Scintag Model XDS2000) and electron diffraction by transmission electron microscopy (TEM) (JEOL 2010F) determined that the films are amorphous. Electrical resistivities were obtained on glass substrates using a four-point probe (Veeeco Model No. FPP-100). Step coverage was measured by deposition in fused silica capillary tubes with inner diameter 20 μm (Restek Corporation). After deposition, the polyimide coating on the outside of the tubing was burned off. Refractive index fluid matching fused silica (Cargille Laboratories) was placed in the tubing, and the film was imaged in a low-power (10×) optical microscope.

III. Results and Discussion

A new ALD reaction for WN is reported in eq 4.

\[(\text{tBuN})_2\text{W(NMe)}_2 + \text{excess NH}_3 \rightarrow \text{WN} + \text{gaseous byproducts (4)}\]

Control experiments using only the tungsten precursor and no ammonia showed no deposition on substrates previously deposited with WN or on bare substrates at temperatures from 250 to 350 °C.

After the desired number of cycles was completed, the substrates were removed from the reactor. The substrates were examined by SEM (looking at the cross sections) and found to have a film with uniform thickness along the 20-cm length of the deposition zone (see Figure 2). This was uniform across the 20 cm length of the deposition zone at 300 °C for 1000 cycles.

The thickness was linear in the number of cycles. This is illustrated in Figure 3. The film growth started right within the first few cycles and no "initiation" period was observed. Successful depositions were carried out on all substrates tested, including silicon, glass, quartz, glassy carbon, stainless steel, aluminum, gold, and copper. We attempted unsuccessfully to prevent deposition on copper. The native oxide on copper substrates was first reduced in situ using 2-propanol and then exposed to ethyl iodide to adsorb a layer of iodine onto the freshly reduced copper surface. However, even very thin films of WN grew on the iodized copper substrates.

The films were pure tungsten nitride. RBS analyses showed that there was no appreciable oxygen in the film (see Figure 4). Carbon was less than the detectable limit, <0.5 at. %. XPS confirmed that no carbon was detectable in the film (detection limit < 0.25 at. %). The films were silver and shiny. The density of the material was found to be about 12 g/cm³ by combining RBS and SEM data. The density of bulk WN is 18.656 g/cm³.22 RBS determined the chemical composition of the film to be WN\(_{1.1\pm0.1}\). XRD confirmed that once the as-deposited amorphous films were annealed for 30 min at temperatures of 700 °C, they contained the diffraction peaks corresponding to the known cubic, crystalline phase of WN.22

The WN films possessed very smooth surfaces. AFM confirmed that the surface roughness of the deposited layer (root-mean-square (RMS) roughness = 0.33 nm) was very similar, if not equal, to that of the substrate (RMS roughness = 0.2–0.3 nm) on which it was deposited. The RMS roughness was independent of film thickness....

(22) Khitrova, V. I.; Pinsker, Z. G. Krystallografiya 1959, 4, 545.
thickness. SEM also showed that the films were smooth
and featureless. XRD showed that the as-deposited layer
was amorphous. This structural information was con-
firmed by high-resolution transmission electron micros-
copy (HRTEM), which showed the film to be amorphous
(Figure 5).

An SEM picture was taken of a wafer with narrow
holes having an aspect ratio greater than 40:1 coated
with WN and then cleaved to show a cross section of
the coated holes. The SEM showed that the walls of the
narrow hole are covered with a perfectly conformal
coating.23

To answer the question of how high an aspect ratio
can be coated with tungsten nitride, a 2-cm-long fused
silica capillary tube with 20-μm inner diameter was
used as the test structure. This length of tubing gives
an aspect ratio of 1000:1. The transport down the hole
is by molecular diffusion, the same as down the small
features in the wafer mentioned above because the
mean free path is much larger than the 20-μm diameter.

An optical microscope was used to image the film inside
of the tube. Figure 6 shows an ALD WN coating
extending 4.2 mm from the open end of the fused silica
tube, demonstrating a coating inside a hole with an
aspect ratio of 210:1.

The electrical resistivity of the tungsten nitride coating
is about $1.5 \times 10^{-3} - 4.0 \times 10^{-3}$ Ω-cm. The resistivity
was reduced to $4.8 \times 10^{-4} - 9.6 \times 10^{-4}$ Ω-cm by anneal-
ing in forming gas at 700 °C for 30 min to form the
polycrystalline WN phase. The resistivities were even
further reduced to $1.2 \times 10^{-4} - 5.0 \times 10^{-4}$ Ω-cm when
the films were annealed at temperatures greater than
725 °C for 30 min. Films annealed at temperatures
greater than 725 °C had lost their nitrogen to become
pure tungsten metal and crystallized to the cubic
tungsten structure. RBS and XPS confirmed the loss of
nitrogen, as well as did EDS. XRD too confirmed that
once the as-deposited amorphous films were annealed
at temperatures greater than 725 °C, they contained
the diffraction peaks corresponding to the known cubic,
crystalline phase of W.24 A decrease in thickness (30%)
occurred as the films turned from WN into the more
dense W films as verified by HRTEM. The polycrystal-
line W films remained smooth, as was seen by AFM
(RMS roughness = 0.4 nm). There was no loss of
adhesion even after annealing.

When a tungsten nitride film was deposited directly
on silicon, without an oxide interlayer produced by the
UV-ozone treatment, annealing the WN to a tempera-
ture of 1000 °C produced a coating of tungsten silicide.
This was confirmed by RBS.

When the exposure time to tungsten precursor vapor
was increased from 10 to 60 s, identical results were
obtained, showing that the chemical reactions of the
tungsten precursor were completed within 10 s.

A series of WN films were grown under identical
conditions, except that the sizes of the tungsten doses
were increased. Figure 7 shows the average film thick-
ness per cycle versus bubbler temperature. As the
temperature increases by 10 °C, the W dose is roughly
doubled. At bubbler temperatures of 30 °C and higher,
the film thickness is constant and is also uniform over
the whole length of the 20-cm substrate. These results
demonstrate that the surface reaction of the tungsten
precursor is self-limiting. The saturating dose at 30 °C
was estimated from the vapor pressure to be about $3 \times
10^{-10}$ mol/cm². The 20 °C point corresponds to films that
were uniform in thickness only for the first 15 cm from
the gas inlet, with a growth rate of 0.5 nm/cycle.


matching the saturated value. Then the film growth stopped abruptly in the region beyond 15 cm because the amount of vapor supplied from the bubbler at room temperature completely reacted in the first 15 cm of the reactor. This underdosed thickness profile demonstrates that the W precursor is highly reactive to the surface because the film growth is so abruptly cut off when the precursor is used up.

Similarly, the ammonia dose was varied using differently sized sample loops for a gas chromatography valve. Figure 8 shows how the sample loop is filled in position A and emptied in position B. Using 500-μL, 1-mL, 2-mL, and 10-mL sample loops at 20 psig and a 10-mL sample loop at 30, 40, and 50 psig, doses up to 6.6 μmol/cm² were supplied. Figure 9 plots the growth rate per cycle as a function of the ammonia dose. Saturation occurs at doses above 4.4 μmol/cm², showing that the surface reactions of the ammonia are self-limiting. The saturation value for ammonia is about 3 orders of magnitude higher than that for the W precursor, suggesting that the ammonia surface reaction is much slower. The films made with underdosed ammonia were quite uniform in thickness along the length of the gas flow, giving another indication that the reaction probability of ammonia with the surface is quite low.

Three experiments were run to determine the source of the nitrogen in the films. In the first experiment isotopically labeled ammonia, 15NH3, was used in place of normal 14NH3 to grow a WN film. The tungsten nitride film was analyzed by RBS, which showed that the nitrogen in the film is normal nitrogen 14N, not 15N. Thus, the nitrogen in the film arises from the nitrogen in the tungsten precursor, not from the ammonia.25 Presumably, the nitrogen arises from the imido groups, which have strong WN bonds.

Similarly, tert-butylimidotris(diethylamido)tantalum, (t-BuN)(NEt₂)₃Ta, was used to grow tantalum nitride films under ALD conditions with isotopically labeled ammonia, 15NH₃, and the resulting films contained mainly 14N, suggesting that the strong Ta–N double bond is preserved.26 A slight amount of 15N was found in the films, suggesting that at least one of the Ta–N single bonds does undergo some transamination reaction. In contrast, the isotopic experiment showed that no transamination occurs in the case of the W precursor.

If the ammonia is acting as a basic catalyst, not a reactant, in this deposition reaction, then another base, pyridine, could also be used, even though pyridine cannot undergo transamination. In agreement with this prediction, an ALD experiment with pyridine vapor in place of the ammonia also grew WN films. In a third experiment probing the mechanism, we attempted to grow tungsten oxide by using the tungsten precursor and water vapor. RBS showed films of tungsten oxynitride. The ratio of W to N was 1:1 in all of the films and in the WO₃N films the ratio x of oxygen to tungsten was greater than 1. WO₃N made by this ALD reaction is a dielectric. The nitrogen in this film also comes from the W precursor itself, probably from one of the imido groups.

The following mechanism for the ALD growth of tungsten nitride is proposed (Figure 10). First, the precursor vapor reacts in a self-limiting manner with the substrate eliminating dimethylamine. Then the two tert-butyl groups decompose via α-hydrogen elimination catalyzed by ammonia, giving off isobutene. This second reaction returns the surface to a state in which it is ready to react with the first reactant again. The resulting WN₂ is apparently unstable since no compound is known that corresponds to this stoichiometry. According to Prybyla, J. A.; Chiang, C. M.; Dubois, L. H. J. Electrochem. Soc. 1993, 140, 2695.

25) This result is an interesting contrast with CVD of TiN in which the nitrogen in the film comes from the ammonia, rather than the titanium alkylamide precursor. See Prybyla, J. A.; Chiang, C. M.; Dubois, L. H. J. Electrochem. Soc. 1993, 140, 2695.

26) Tsai, M. H.; Sun, S. C.; Chiu, H. Y.; Tsai, C. E.; Chuand, S. H. Appl. Phys. Lett. 1995, 67, 1128, suggested that the Ta–N in tert-butylimidotris(diethylamido)tantalum was preserved during the pyrolysis process and ended up in the tantalum nitride films that were grown under low-pressure MOCVD conditions.
ingly, the WN₂ thermally decomposes by losing gaseous N₂ to form the known stable phase WN. RBS and XPS both confirmed the stoichiometry of this product. To test the plausibility of this mechanism, quantum chemistry calculations 27 were performed for a simple model 28 for the ammonia-catalyzed β-hydrogen elimination step. The results showed that the presence of the ammonia reduced the activation energy for this reaction by more than 47 kJ/mol, thereby greatly increasing its reaction rate. In the transition state, the nitrogen atom of the ammonia temporarily comes close to the tungsten atom.

To determine the temperature range over which this ALD process operates, experiments were repeated with substrate temperatures varied from 200 to 400 °C. Similar tungsten nitride films were obtained within the range 250–350 °C, except that the thicknesses of the films increased with the substrate temperature as shown in Figure 11. Films formed at temperatures above 350 °C contained carbon in addition to tungsten and nitrogen, and their step coverage was not as good as that for the films made in the range 250–350 °C. Another decomposition pathway is apparently becoming significant above 350 °C. The films formed at 400 °C were more conductive, 4.2 × 10⁻⁴ Ω-cm, and were also as smooth as the films made at lower temperatures.

No films were formed at temperatures below 250 °C. Evidently, even with ammonia catalysis, below 250 °C the reaction is too slow to be completed within the cycle time. This lack of film growth at low temperatures is a distinct practical advantage in preventing unwanted growth on chamber walls kept at temperatures below 250 °C.

WN films as thin as 1.5 nm proved to be good barriers to diffusion of copper for temperatures up to 600 °C. 23 ALD of copper onto the surface of the WN produced strongly adherent copper films that could not be removed by adhesive tape applied to the copper. These copper films could be used as "seed" layers for chemical vapor deposition (CVD) or electrodeposition of thicker copper coatings. 23

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(28) The system was simplified by using hydrogen atoms to terminate bonds more than two bonds away from the reaction center. The structures and energies of the reactants, products, and transition state were calculated by the Gaussian program with the MP2 method using a LanL2DZP basis set.
IV. Conclusions

Tungsten nitride films were synthesized from vapors of a novel precursor, tungsten bis(tert-butylimide)-bis-(dimethylamide) and ammonia gas supplied in alternate doses to surfaces heated to temperatures from 250 to 350 °C. This process produced coatings of tungsten nitride having very uniform thickness and excellent step coverage in holes with aspect ratios up to over 200:1. The films are metallic electrical conductors. Suitable applications in microelectronics include barriers to the diffusion of copper and electrodes for capacitors.

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