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Chemical Vapor Deposition of Cobalt Nitride and its Application as an Adhesion-Enhancing Layer for Advanced Copper Interconnects

Harish B. Bhandari,a,b Jing Yang,c Hoon Kim,a,c Youbo Lin,a,c Roy G. Gordon,a,c,z Qing Min Wang,c Jean-Sébastien M. Lehn,e Huazhi Li,e and Deo Shenaie

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An interlayer of face centered cubic (fcc) Co4N has demonstrated significant improvements in adhesion between copper and diffusion barrier layers. This fcc phase of Co4N was prepared by chemical vapor deposition (CVD) using bis(N-tert-butyl-N′-ethylpropionamidinato)cobalt(II) and a reactant mixture of NH3 and H2 at substrate temperatures from 100 to 180 °C. The Co/N atomic ratio and the phase of cobalt nitride film can be modified by adjusting the ratio of NH3 and H2 in the gas feedstock. The cobalt nitride films prepared by CVD are smooth, highly conformal, and stable against intermixing with copper up to at least 400 °C. This fcc cobalt nitride material has very strong adhesion to copper due to the small lattice mismatch (−1 to 2%) between fcc-Co4N and fcc Cu. Copper wires should be stabilized against failure by electromigration when fcc cobalt nitride interlayers are placed between the copper and surrounding diffusion barriers.

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Cobalt thin films are used widely in the microelectronic industry for numerous applications. Co is used to form CoSi2 by Co/Si interfacial reactions to make source, drain and gate electrodes for CMOS structures. Although NiSi offers lower resistivity,1 the greater interfacial reactions to make source, drain and gate electrodes for presumably thereby increasing the lifetime of the copper wires.3 Other barriers such as TaN, WN or TiN increased adhesion at the interface, thermodynamic stability of CoSi2 makes it more suitable for DRAM applications of Co films include magnetic devices4 and nano-catalysts try for numerous applications. Co is used to form CoSi2 by Co/Si interfacial reactions to make source, drain and gate electrodes for CMOS structures. Although NiSi offers lower resistivity,1 the greater interfacial reactions to make source, drain and gate electrodes for presumably thereby increasing the lifetime of the copper wires.3 Other barriers such as TaN, WN or TiN increased adhesion at the interface, thermodynamic stability of CoSi2 makes it more suitable for DRAM applications of Co films include magnetic devices4 and nano-catalysts4 and nano-catalysts for carbon nanotube synthesis.5

As the feature sizes in integrated circuits shrink to smaller sizes, conventional techniques such as physical vapor deposition (PVD) may not provide adequate step coverage owing to their non-conformal deposition. The problem gets especially challenging for three-dimensional CMOS devices and very narrow copper interconnects. In this article we report the deposition of a novel material, cobalt nitride, using a conformal technique of chemical vapor deposition (CVD). We discuss its potential application as an adhesion-enhancing interlayer for advanced copper interconnect technology.

Copper has successfully replaced aluminum for ultra-large-scale integration (ULSI) because of its low resistivity and superior resistance against electromigration. In the damascene structure, copper is deposited using electroplating due to its low cost, high throughput and via-filling capability. However, the electro-deposition of thick copper is initiated on a pre-existing tri-layer stack which consists of a thin and continuous Cu, an adhesion promoter and a barrier. The current technology utilizes physical vapor deposition (PVD) to make Cu (seed)/Ta (adhesion)/TaN (barrier) in the damascene structure. The International Technology Roadmap for Semiconductors (ITRS) projects that as the features shrink, these multilayer stacks have to be thinner and more conformal to maintain effective interconnect resistivity while avoiding any pinholes. It is becoming increasingly challenging for PVD to meet all these requirements and therefore there is a need for a conformal deposition technique such as CVD or atomic layer deposition (ALD). Metal depositions using ALD have slower growth rates than their CVD counterparts and in most cases, longer deposition leads to rougher morphology due to agglomeration. CVD of Cu has been extensively studied because of its fast deposition rate compared to ALD and its ability to minimize agglomeration in a kinetically driven process.6 However, CVD Cu is known to exhibit weak adhesion to Ta-based adhesion/barrier layers due to the formation of Ta oxide or Ta fluoride during the CVD process.7 Ta’s high affinity to oxygen and fluorine can extract these elements from a copper precursor during the CVD process. Trace amounts of oxygen or oxygen-containing impurities in the carrier gas can also oxidize the tantalum surface. The presence of an oxide or fluoride layer on Ta facilitates electromigration at the copper/oxide interface, because of the weaker adhesion. Cu can now be deposited by ALD8 or CVD9 from precursors that contain neither oxygen nor fluorine, thus providing a possible way to provide strong adhesion of CVD Cu to Ta. However, at present, there is no way to deposit conformal tantalum layers, either by CVD or by ALD. Thus alternative materials for adhesion layers have been sought.

Various studies have been conducted to examine different metals such as Ru,10,11 Pd,12 Pt,13 Rh,13 Ir,13 Ag,13 Os,14 or Co17 as possible candidates for an adhesion layer to replace Ta. These more noble metals bind oxygen and fluorine less strongly than Ta does, so they are expected to adhere better to CVD Cu than Ta does. Recently Ru has received much attention and has been widely studied.11 Ru is a stable metal with low resistivity (7.4 μΩ · cm) and strong adhesion to Cu, but Ru is expensive and in short supply, making it a poor choice for large-scale use.

There are reports suggesting that the adhesion energy at the interface between two metals is larger if their lattices match in size and structure.1,18,19 Hoon et al.18 have demonstrated that a smaller lattice mismatch of Cu with Ru compared to with Ta leads to a lower interface energy and enhanced adhesion of Cu onto Ru. According to this mismatch principle, the strongest adhesion to copper should be found for a metal with the same face-centered cubic (fcc) structure and the same lattice constant. The lattice misfits between Cu and Co, Co4N and Ru are summarized in Table I, which suggests that Co4N has cobalt atoms arranged in the same fcc structure as Cu and with almost exactly the same lattice constant (mismatch only −0.8%). Therefore, Co4N should have a strong adhesion to copper.

In this report we demonstrate successful CVD of cobalt nitride as an interlayer between CVD WN (barrier) and CVD Cu (seed), all of which is performed in a single CVD reactor without breaking the vacuum. The cobalt nitride exhibits the fcc Co4N structure that closely matches the Cu lattice and hence demonstrates the expected strong adhesion to CVD copper grown on top of it. Strong adhesion is preserved during CVD also because the copper precursor contains no oxygen or fluorine that could contaminate the surface of the Co4N. During the CVD processes of various layers the carbon and hydrogen that accompany the metalorganic precursors are completely removed as...
vapor byproducts resulting in pure films. The CVD Cu grows epitaxially on all orientations of the polycrystalline Co3N films, as shown by high-resolution transmission electron microscopy (TEM). Such a CVD cobalt nitride can also be used to make conformal CoSi2.20

Experimental

The chemical vapor deposition of Co3N was carried out in a hot wall, tube-furnace reactor. The schematic of the CVD system is as shown in Figure 1. The substrate holder is a half cylinder made of aluminum which was inserted into a stainless steel reactor tube. A cartridge heater and a thermocouple (not shown) are embedded in the substrate holder in order to heat the substrate to a temperature higher than the reactor wall by 10–20°C. This arrangement favors deposition of desired film on the substrate rather than the wall and is suitable for a CVD process with a thermally activated rate. The reactor pressure during deposition was controlled automatically by a throttle valve (MKS Instruments) located downstream to the substrate holder. The metal precursors were loaded in U-shaped bubblers and ultra high purity N2 was used as a carrier gas. The bubblers and their associated gas lines were plumbed inside ovens with suitable temperature set points for efficient vaporization and delivery of precursor vapors to the reactor tube. The gas flow rates were established using metal-sealed mass flow controllers (MKS Instruments).

CVD of Co3N was carried out from bis(N-tert-butyl-N'-ethylpropionamidinato)cobalt(II), Co[Bu'NC(Et)NEt]2, precursor. The synthesis of Co[Bu'NC(Et)NEt]2 has been described elsewhere.21 This Co precursor is a dark green liquid at room temperature with melting point of 17°C. The vapor pressure of this precursor may be approximated by log10(P, torr) = 5.424 – 2151/T, giving 0.14 torr at 70°C. This result showed that no significant decomposition occurs within time periods of minutes even at temperatures as high as 200°C. Another test of thermal stability was done by heating the neat liquid in contact with various surfaces: glass (presumably with little or no surface catalytic activity); oxidized stainless steel (to mimic a typical bubbler surface); and stainless steel from which the native oxide had been removed by acid etching. The viscosity of the precursor was also measured with flow tubes inside a glove box, in order to protect it from oxidation. Accelerated rate calorimetry (ARC) testing involves heating a closed sample at a series of increasing temperatures 10 K apart, with a dwell time of 50 minutes at each temperature. During this heating the pressure was measured to see if any gases are being generated by decomposition. If a significant pressure rise is detected, the dwell time is lengthened to see if the pressure rise is transient or if a self-sustained exotherm occurs.

The ranges of CVD conditions in which Co3N films were deposited are shown in Table II. NH3 gas was used as the nitrogen source and H2 as the reducing agent. Although the ratio of NH3 to H2 gas flow was varied, the total flow rate of the mixture was always maintained at 60 sccm. 60 sccm of N2 carrier gas passed through the bubbler to carry the precursor vapor into the deposition chamber. We assumed that an equilibrium vapor pressure of the Co precursor was achieved while the N2 bubbled up through about 10 cm of the liquid. A total pressure drop of 6.3 torr was estimated between the bubbler and the reactor tube, most of it arising from the pressures required to open the three spring-loaded check valves installed downstream to the bubbler. The check valves (not shown in Fig. 1) were used to separate multiple precursors installed in two ovens and to avoid back flow of vapor to cooler parts of the system. The high total pressure in the bubbler reduces the partial pressure of the precursors in the reactor, thereby limiting the overall growth rate and the step coverage inside features with high-aspect ratios. The estimated partial pressures for the reacting species are presented in Table III.

Table I. Percentage difference between the lattice constants of copper and of various metals. For the hcp metals, alignment of the hexagonal axis (002) with the Cu(111) axis is assumed. (All the lattice constant values are quoted from Powder Diffraction File (PDF) from ICDD (International Center for Diffraction Data)).

<table>
<thead>
<tr>
<th>Candidate material</th>
<th>Structure type</th>
<th>Lattice mismatch with Cu</th>
<th>Lattice constant (Å)</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>0%</td>
<td>a = b = c = 3.615</td>
</tr>
<tr>
<td>Co3N</td>
<td>fcc</td>
<td>−0.8%</td>
<td>a = b = c = 3.586</td>
</tr>
<tr>
<td>α-Co</td>
<td>fcc</td>
<td>−1.9%</td>
<td>a = b = c = 3.545</td>
</tr>
<tr>
<td>ε-Co</td>
<td>hcp</td>
<td>−2.0%</td>
<td>2/3a = 3.544</td>
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<tr>
<td>Ru</td>
<td>hcp</td>
<td>+5.9%</td>
<td>2/3a = 3.827</td>
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Table II. CVD conditions explored in this work.

<table>
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<tr>
<th>CVD Parameters</th>
<th>Cobalt Nitride</th>
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<td>Temperature:</td>
<td>100–180°C</td>
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<tr>
<td>Pressure:</td>
<td>1–5 torr</td>
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<tr>
<td>Co source temp:</td>
<td>70–85°C</td>
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<tr>
<td>N2 carrier gas:</td>
<td>60 sccm</td>
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<tr>
<td>Reactant Gas (NH3:H2):</td>
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<tr>
<td></td>
<td>10 + 50, 0 + 60 sccm</td>
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<tr>
<td>Pressure Drop:</td>
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<td>Bubbler Pressure:</td>
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<td>Partial Pressures:</td>
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<tr>
<td>P(N2):</td>
<td>0.16 torr</td>
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<tr>
<td>P(NH3):</td>
<td>0.33 torr</td>
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<tr>
<td>P(H2):</td>
<td>0.02 torr</td>
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<tr>
<td>Step Coverage:</td>
<td>&gt;10:1</td>
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<tr>
<td>Growth Rate (on SiO2 and WN):</td>
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</table>

Figure 1. Schematic diagram of the CVD system. (a) deposition chamber; (b) furnace; (c) substrate holder; (d) throttle valve; (e) mass flow controllers; (f) bubbler; (g) pneumatically controlled valves; (h) bypass gas line. Precursors: (1) Cu precursor; (2) Co precursor; (3) W precursor.
CVD WN was deposited from bis(tert-butylimido)bis(dimethylamido)tungsten(VI) vaporized from a bubbler at 85°C and NH₃ gas. The deposition conditions for WN were 390°C substrate temperature and 1 torr total pressure. The N₂ carrier gas and NH₃ flow rates were both set at 20 sccm. Cu metal or CuON was deposited from (N₂,N₂-di-sec-butylacetamidimino)copper(I). For Cu deposition, 40 sccm of H₂ was used as the reducing agent and 40 sccm of N₂ was bubbled through the molten precursor at 95°C. The Cu deposition was carried out at 180°C and 1 torr total pressure. An alternate route adopted to make smoother Cu films was to deposit CuON and reduce it after deposition at room temperature by hydrogen plasma. This process is discussed in detail elsewhere. Multilayer films were deposited without air break in order to prevent any oxidation of the films.

Substrates used in these experiments were 300 nm of thermally oxidized SiO₂ supported on Si wafers. Before deposition, the substrates were exposed to a mercury UV lamp in air for 10 min to remove any organic contamination. The substrates were then dipped briefly in 5% HF solution and rinsed in distilled water to expose fresh oxide surface by etching 20–30 nm of SiO₂.

The surface morphologies of the films were characterized by an atomic force microscope (AFM, Asylum MFP-3D). The thicknesses of smooth films were measured by X-ray reflection (XRR, Scintag XDS 2000). For metals with rough surfaces, the films were patterned into stripes using photolithography and etching techniques, and the resulting thickness profiles were measured using AFM. The film composition and density were measured using 2 Mev He⁺ Rutherford backscattering spectroscopy (RBS). The areal density of individual elements was determined by using a reference of Harwell Bi standard.

Results and Discussion

Properties of the liquid cobalt precursor.—Some additional properties of the cobalt precursor were measured. The viscosity as a function of temperature is given by ln μ(η°C) = 3365.5/T(K) − 8.1694 and plotted in Fig. 2. Within the range of bubbler temperatures used, 70 to 85°C, the viscosity is low, just 3 to 5 times that of water. Thus bubbling is not impeded by the viscosity of this precursor.

Heating the neat precursor at 120°C in contact with glass, etched stainless steel or oxidized stainless steel for 60 hours did not generate any diamagnetic decomposition products in the NMR spectrum, indicating that thermal stability is not compromised by contact with these surfaces. An ARC test of stability was carried out. Slow, non-sustaining, transient exotherms were observed at 180, 210, and 219°C. This test shows that little or no decomposition takes place at temperatures below 180°C over periods of hours. These thermal stability tests have important implications for the vaporization of this cobalt precursor in a direct liquid injection (DLI) system. In such a system, vaporization takes place within seconds, so that temperatures up to about 180°C could be used without significant decomposition of the precursor. Thus much higher vapor pressures can be produced in a DLI system than in a traditional bubbler. Much higher precursor partial pressures translates into the ability to coat much narrower features conformally.

Chemical vapor deposition of Co₄N.—Co₄N films were deposited without an air-break on freshly-deposited WN in order to increase the adhesion energy of the films to substrates. Table IV shows RBS data for the composition of Co₄N films deposited at 180°C with various feed rates of NH₃ and H₂. The area density of nitrogen atoms in Co₄N was found by subtracting the area density of N in control samples of WN from the total number of N atoms per unit area detected by RBS in Co₄N/WN/C. It is clear that N was incorporated into the as-deposited films only when NH₃ was introduced, irrespective of its flow rate. All of the films show metallic conduction, with resistivity increasing with nitrogen content.

When Co₄N was deposited with just NH₃ and no H₂ gas, a composition Co₃.5N was obtained. Figure 3 shows an electron diffraction pattern for a Co₂.5N film that corresponds to a Co₄N phase with a hexagonal close packed (hcp) structure. The only phase that resulted from NH₃ alone as a co-reactant is the hcp (Co₃N) phase.

When H₂ was introduced along with NH₃ in different proportions, while maintaining the total flow rate of the two gases at 60 sccm, the as-deposited Co₄N films became richer in cobalt (x > 2.3). Co precursor and H₂ gas alone (no NH₃) showed no reactivity at 180°C because no film growth was detected at that temperature. Thus H₂ acts as a reducing agent during some stage of the reaction of the Co precursor with NH₃ at 180°C even though it shows no direct reactivity with the Co precursor itself. The Co/N atomic ratio increases as the H₂/NH₃ feed-ratio is increased.

These cobalt-rich films exhibit a fcc structure as shown in Figure 3 for the NH₃/H₂ = 20/40 sccm condition. A fcc Co₄N phase has been reported by other groups using sputtering. This is the first report of Co₄N material with the fcc phase prepared using CVD. The crystal geometry of the Co₄N phase can be considered to be made of Co atoms placed in a fcc lattice and a nitrogen atom trapped interstitially in the center of a unit cell. As a result, the introduction of N atoms should show expansion from the fcc Co lattice (a = 3.545 Å). Theoretical studies of the Co₄N phase have shown that lattice expands as a function of interstitial nitrogen trapped per unit cell. Therefore it might be possible to adjust the lattice parameter of Co₄N experimentally by controlling the amount of nitrogen in the film. The polycrystalline Co₄N films have a relatively smooth morphology even when deposited on SiO₂ without WN underneath. The AFM image shown in Fig. 4a for a 20 nm Co₄N film has a root-mean-square (RMS) surface roughness

![Figure 2. Viscosity of the cobalt precursor as a function of temperature.](image-url)
of 1.3 nm. In comparison, the AFM image shown in Fig. 4b showed CVD Co films of the same thickness 20 nm deposited at a higher temperature (240 °C) with H₂ as the only co-reactant are rougher (RMS roughness = 2.7 nm).

**Hetero-epitaxial relation between Co₄N and Cu.**— During the processing of copper interconnects, it is critical for Cu to adhere strongly to the underlying barrier material. The minimum adhesion energy recommended between Cu and the barrier material in order to survive the chemical mechanical planarization (CMP) is 5 J × m⁻². Amorphous WN is a well-studied barrier material for copper interconnects application but exhibits poor adhesion with CVD copper (<2 J × m⁻²). In order to improve adhesion between Cu and WN, an interlayer of Co₄N was tested. A stack of CVD Cu/Co₄N/WN was deposited on SiO₂/Si without breaking the vacuum. Fig. 5 shows the TEM cross section of the as-deposited film stack with sharp interfaces between the film stacks. The four-point bend test evaluation of the stack revealed adhesion energy of 10–13 J × m⁻² between Cu and Co₄N, which is stronger than the reported adhesion energy 6 J × m⁻² of Ru glue layer. The high resolution TEM image (Fig. 5) shows that Cu grew epitaxially on the Co₄N. The lattice spacing seen in Figure 6 matches the (111) planes. The hetero-epitaxial relation between the two polycrystalline metals was discontinuous along the interface but was sufficient to promote strong adhesion.

The lattice parameters of Co₄N films with different amounts of nitrogen were evaluated by carrying out selected area electron diffraction (SAD) on thin films deposited on Si₃N₄ TEM grids. Measurement of absolute lattice parameters from SAD diffraction patterns involved careful elimination of the instrumental errors. Cu was deposited on top of Co₄N film to form a Cu/Co₄N stack, where the lattice parameter of Cu (a = 3.615 Å) served as an internal standard. For comparison, copper was also deposited directly on the TEM grids. Fig. 7 shows the comparison of diffraction patterns from Cu/Co₄N stack, Cu and Co₄N on TEM grids. The diffraction pattern on all three samples show three major rings that correspond to the (111), (200), (220) and (311)
planes of fcc lattice. It is especially convincing that the diffraction signals from the bi-layer stack of Co$_4$N and Cu closely overlap with each other. This re-confirms the close match between the Cu and Co$_4$N lattice parameters, because both films are exactly the same distance from the detector. The only diffraction ring that does not show any overlap is that of the Cu$_2$O along with the Cu sample, resulting from surface oxidation of copper. The diffraction rings from the Cu/Co$_4$N film stack were carefully resolved to measure the lattice parameter of Co$_4$N using Cu as the internal standard. The resulting lattice parameters of the Co$_4$N are 1 to 2% smaller than Cu, as expected from the literature values of the lattice constants of bulk single crystals. The precision of these values was not high enough to resolve any variation of the lattice constant of Co$_4$N with variations in the nitrogen content.

Cu/Co$_4$N bilayers were also deposited on thin Si$_3$N$_4$ TEM grids. Plane-view TEM pictures this film stack in Fig. 8a show the grain size and nucleation density of copper on Co$_4$N. For comparison, Fig. 8b shows a CVD Cu film grown under the same conditions on a thin Co layer. The Cu grains are larger on the Co$_4$N substrate than on the Co substrate. Larger grains should translate into higher electrical conductivity.

**Thermal stability of Cu/Co$_4$N structure.**—The thermal stability of the interface between Co$_4$N and Cu is crucial in keeping the resistivity of the Cu wires low. The thermal stability can be determined by annealing a stack containing the interface. A stack of Cu/Co$_4$N/WN was deposited on Si$_3$N$_4$/Si using CVD. A 90 nm thick Cu was sputtered on top of the 10 nm Cu to avoid agglomeration of free surface of Cu. The stack was then annealed in forming gas (N$_2$/H$_2$: 95/5 vol%) for 30 min at 400°C. The sheet resistances of the film before and after the annealing step were 0.33 ohms/sq and 0.28 ohms/sq, respectively. Post-annealing of this PVD Cu/ CVD Cu/Co$_4$N/WN stack in N$_2$ for 30 min at 400°C showed a decrease in the sheet resistance as well. The sheet resistances of the film stack before and after the annealing were 0.33 ohm/sq and 0.27 ohm/sq. The sheet resistance of the Cu would have increased sharply if there were any migration of Co, N or Co-N species into the bulk of Cu. The lowering of the sheet resistance indicates re-crystallization of Cu, and an overall stability of the Co$_4$N and Cu interface.

**Step coverage of Co$_4$N.**—The step coverage of CVD Co$_4$N was tested by depositing film on a silicon substrate with holes having an aspect ratio of 30:1 with a diameter 336 nm. The CVD conditions tested are tabulated in Table III. In the initial design of the system, there were 3 check valves between the cobalt bubbler and the reactor tube. The Co$_4$N deposition with three check valves in the system had low step coverage, even with aspect ratio lower than 10:1, the step coverage was not satisfactory. After removal of two check valves, it is found that step coverage on structures with aspect ratio of 30:1 is achieved with only a 20% reduction in film thickness on the bottom of the hole.
the hole (∼23.5 nm) compared with the top of the hole (∼30 nm). The step coverage tends to be poor when the CVD reaction is operating in transport-limited conditions of low partial pressure of the precursor inside the reactor and high surface reaction rate. Table III presents the partial pressures of different gases before and after removal of check valves. After the removal of two check valves, the partial pressure of cobalt precursor is 0.04 torr compared to 0.02 torr before the system optimization. The growth rate of the cobalt nitride film increased to 1nm/min from 0.5nm/min. Fig. 9 shows an SEM image of nearly conformal deposition of Co4N down to an aspect ratio of 30:1 in a hole. The overall step coverage can be improved by eliminating the back pressure from the check valves, increasing the vaporization temperature of the Co bubbler or by using DLI to make higher partial pressures of the precursor vapor.25

Conclusions

In this article we report Chemical Vapor Deposition synthesis of smooth, continuous and conformal Co4N thin films using a cobalt amide, Co[Bu’N(CEt)NEt]2, as the cobalt source and a combination of NH3 and H2 gases. Although H2 shows no reactivity with the Co precursor at 180°C, it stabilizes Co4N into a face centered cubic structure in the presence of NH3 feed. In the absence of H2, the reaction between Co precursor and NH3 yields the Co3N phase, which has a hexagonal close packed structure. The fcc structure of the Co4N phase exhibits low (∼1%) mismatch with that of Cu and therefore shows a strong bonding (adhesion energy: 10–13 Joules m−2) at the Co4N/Cu interface. The stability of the interface was tested up to 400°C with no evidence of intermixing. Thus Co4N, which has a fcc structure, is a good choice for an adhesion-promoting under-layer for conformal methods of forming the Cu seed layers for advanced copper interconnects.

Acknowledgment

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References