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<th>Citation</th>
<th>Bhandari, Harish B., Jing Yang, Hoon Kim, Youbo Lin, Roy G. Gordon, Qing Min Qang, Jean-Sebastien Lehn, Huazhi Li, Deo Shenai. 2012. ECS Journal of Solid State Science and Technology 1(5): N79-N84.</th>
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<td>Published Version</td>
<td>doi:10.1149/2.005205jss</td>
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<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:9925419">http://nrs.harvard.edu/urn-3:HUL.InstRepos:9925419</a></td>
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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, Jing Yang, Hoon Kim, Youbo Lin, Roy G. Gordon, Qing Min Wang, Jean-Sébastien M. Lehn, Huazhi Li and Deo Shenai

An interlayer of face centered cubic (fcc) Co$_4$N has demonstrated significant improvements in adhesion between copper and diffusion barrier layers. This fcc phase of Co$_4$N was prepared by chemical vapor deposition (CVD) using bis(N-tert-butyl-N'-ethyl-propionamidinato)cobalt(II) and a reactant mixture of NH$_3$ and H$_2$ 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 NH$_3$ and H$_2$ 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-Co$_4$N 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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vapor byproducts resulting in pure films. The CVD Cu grows epitaxially on all orientations of the polycrystalline Co3N grains, 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 high total pressure in the bubbler 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 Co precursor in the reactor.

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>
</thead>
<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(1/2)a = 3.544</td>
</tr>
<tr>
<td>Ru</td>
<td>hcp</td>
<td>+5.9%</td>
<td>2(1/2)a = 3.827</td>
</tr>
</tbody>
</table>

Table II. CVD conditions explored in this work.

<table>
<thead>
<tr>
<th>CVD Parameters</th>
<th>Cobalt Nitride</th>
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<tr>
<td>Temperature:</td>
<td>100–180°C</td>
</tr>
<tr>
<td>Pressure:</td>
<td>1–5 torr</td>
</tr>
<tr>
<td>Co source temp:</td>
<td>70–85°C</td>
</tr>
<tr>
<td>N2 carrier gas:</td>
<td>60 sccm</td>
</tr>
<tr>
<td>Reactant gas (NH3+H2):</td>
<td>60 + 0.40 + 20, 20 + 40, 10 + 50, 0 + 60 sccm</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of the CVD system. (a) deposition chamber; (b) furnace; (c) substrate holder; (d) throttle valve; (e) mass flow controller; (f) bubbler; (g) pneumatically controlled valves; (h) bypass gas line. Precursors: (1) Cu precursor; (2) Co precursor; (3) W precursor.
CVD VN was deposited from bis(tert-butylimido)bis(dimethylamido)tungsten(VI) vaporized from a bubbler at 85°C and NH3 gas. The deposition conditions for VN 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 (N,N-di-sec-butylacetamidinato)cooper(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.6

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 thickness of smooth films was 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 standard23 and by using a glassy carbon substrate. The phases of as-deposited films were evaluated by electron diffraction in a transmission electron microscope (JEOL, JEL2100) and SEM (Zeiss Supra55VP) to study epitaxy and step coverage, respectively, of as-deposited thin films. The sheet resistance was measured by a four point probe station (Miller Design & Equipment, FPP-500). The atomic concentrations of elements were analyzed by X-ray photoelectron spectroscopy (XPS, ESCA SXX-100). The interfacial adhesion energies were evaluated by the four-point bend test, as described elsewhere.23

**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 \( \mu (cP) = 3365.5/T(\text{K}) - 8.1694 \) 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.

<table>
<thead>
<tr>
<th>NH3 sccm</th>
<th>H2 sccm</th>
<th>CoN_x</th>
<th>Phase</th>
<th>Resistivity (( \mu \Omega \text{cm} ))</th>
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<tbody>
<tr>
<td>40</td>
<td>20</td>
<td>1.0</td>
<td>CoN, hcp</td>
<td>~150</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>1.0</td>
<td>CoN, fcc</td>
<td>~100</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>1.0</td>
<td>CoN, fcc</td>
<td>~100</td>
</tr>
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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.24 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.25

**Chemical vapor deposition of CoN.**—CoN 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 CoN films deposited at 180°C with various feed rates of NH3 and H2. The area density of nitrogen atoms in CoN 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 CoN/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 CoN was deposited with just NH3 and no H2 gas, a composition Co2N was obtained. Figure 3 shows an electron diffraction pattern for a Co2N film that corresponds to a CoN phase with a hexagonal close packed (hcp) structure. The only phase that resulted from NH3 alone as a co-reactant is the hcp (CoN) 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 CoN 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 CoN 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 CoN phase has been reported by other groups26,27 using sputtering. This is the first report of CoN material with the fcc phase prepared using CVD. The crystal geometry of the CoN 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 CoN phase27 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 CoN experimentally by controlling the amount of nitrogen in the film. The polycrystalline CoN 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 CoN film has a root-mean-square (RMS) surface roughness.
Figure 3. Electron diffraction patterns of polycrystalline Co$_3$N (a) $\langle 002 \rangle$, (b) $\langle 101 \rangle$, (c) $\langle 103 \rangle$, (d) $\langle 201 \rangle$ and Co$_4$N (a') $\langle 111 \rangle$, (b') $\langle 200 \rangle$, (c') $\langle 220 \rangle$, (d') $\langle 311 \rangle$.

Figure 4. AFM images of (a) an Co$_4$N film 20 nm thick, RMS roughness = 1.3 nm; (b) a Co film 20 nm thick, RMS roughness 2.7 nm.

of 1.3 nm. In comparison, the AFM image shown in Fig. 4b showed CVD Co films of the same thickness 20nm deposited at a higher temperature (240$^\circ$C) with H$_2$ as the only co-reactant are rougher (RMS roughness = 2.7 nm).

Hetero-epitaxial relation between Co$_4$N 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 $5 \text{ J} \times \text{m}^{-2}$. Amorphous WN is a well-studied barrier material for copper interconnects application but exhibits poor adhesion with CVD copper ($<2 \text{ J} \times \text{m}^{-2}$). In order to improve adhesion between Cu and WN, an interlayer of Co$_4$N was tested. A stack of CVD Cu/Co$_4$N/WN was deposited on SiO$_2$/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 $10-13 \text{ J} \times \text{m}^{-2}$ between Cu and Co$_4$N, which is stronger than the reported adhesion energy $6 \text{ J} \times \text{m}^{-2}$ of Ru glue layer. The high resolution TEM image (Fig. 5) shows that Cu grew epitaxially on the Co$_4$N. The lattice spacing seen in Figure 6 matches the $\langle 111 \rangle$ planes. The hetero-epitaxial relation between the two poly crystalline metals was discontinuous along the interface but was sufficient to promote strong adhesion.

Figure 5. Cross-sectional TEM of SiO$_2$/WN/Co$_4$N/Cu.
Figure 6. High-resolution cross-sectional TEM of the Co4N/Cu interface showing the epitaxial relation between the materials.

planes of fcc lattice. It is especially convincing that the diffraction signals from the bi-layer stack of Co4N and Cu closely overlap with each other. This re-confirms the close match between the Cu and Co4N 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 Cu2O along with the Cu sample, resulting from surface oxidation of copper. The diffraction rings from the Cu/Co4N film stack were carefully resolved to measure the lattice parameter of Co4N using Cu as the internal standard. The resulting lattice parameters of the Co4N 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 Co4N with variations in the nitrogen content.

Cu/Co4N bilayers were also deposited on thin Si3N4 TEM grids. Plane-view TEM pictures this film stack in Fig. 8a show the grain size and nucleation density of copper on Co4N. 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 Co4N substrate than on the Co substrate. Larger grains should translate into higher electrical conductivity.

Figure 7. Electron diffraction patterns of a single layer of Co4N (upper left), a bilayer film of Cu/Co4N (right side), and an oxidized Cu film (lower left).

Figure 8. Comparison of Cu nucleation on (a) Co4N and (b) Co underlayers. The average Cu grain size on Co is ~19 nm, whereas the grain size on Co4N is ~38 nm.

Figure 9. Cross-sectional SEM of a Co4N film inside a narrow hole with an aspect ratio of about 30:1.

Thermal stability of Cu/Co4N structure.— The thermal stability of the interface between Co4N 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/Co4N/WN was deposited on SiO2/Si using CVD. A 90 nm thick Cu was sputtered on top of the 10 nm Co to avoid agglomeration of free surface of Cu. The stack was then annealed in forming gas (N2/H2: 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/Co4N/WN stack in N2 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-crystalization of Cu, and an overall stability of the Co4N and Cu interface.

Step coverage of Co4N.— The step coverage of CVD Co4N 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 Co4N 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 (~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 1 nm/min from 0.5 nm/min. Fig. 9 shows an SEM image of nearly conformal deposition of Co3N 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 Co3N thin films using a cobalt amidinate, Co[ButNC(Et)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 Co3N 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 Co3N phase exhibits low (~1%) mismatch with that of Cu and therefore shows a strong bonding (adhesion energy: 10–13 Joules m−2) at the Co3N/Cu interface. The stability of the interface was tested up to 400 °C with no evidence of intermixing. Thus Co3N, 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

This work was performed in part at the Center for Nanoscale Systems (CNS) at Harvard University, a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by NSF award no. ECS-0335765.

References