Ultrathin CVD Cu Seed Layer Formation Using Copper Oxynitride Deposition and Room Temperature Remote Hydrogen Plasma Reduction

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Cu seed layers for future interconnects must have conformal step coverage, smooth surface morphology, and strong adhesion. Conformal deposition had been achieved by chemical vapor deposition (CVD), but CVD Cu films have rough surfaces and poor adhesion. In this paper, conformal, smooth, adherent, continuous, and thin (<9 nm) Cu films were made by CVD. CuON was deposited from a Cu-amidinate precursor, H₂O, and NH₃ at 140–180°C on Ru. Crystallites in the deposited film have either a Cu₂O or Cu₃N structure depending on the ratio of H₂O to NH₃. As-deposited CuON films have a smooth surface morphology (~0.5 nm root-mean-square (rms) roughness) and are highly conformal (~95% step coverage in 40:1 aspect ratio holes). The CuON films were then reduced with remote hydrogen plasma near room temperature to minimize agglomeration of the thin Cu films during reduction. After reduction, CuON films having a Cu₂O crystal structure showed a higher density Cu film (95%) than those having a Cu₃N crystal structure (84%). Both reduced Cu films had a smooth morphology (~1 nm rms roughness). Thus, deposition of a CuON film having a Cu₂O crystal structure and then reduction with remote hydrogen plasma can make Cu layers that conformally cover Cu seed layers of future Cu interconnects.

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the overall deposition rate of the film is mainly determined by the 
H2O flow rate. CuON film shows a smooth surface morphology 
[root-mean-square (rms) roughness < 1 nm]. CuON films having 
CuO structure have higher density than films having Cu3N struc-
ture. After 1 min reduction with H2 remote plasma at room temper-
ature, both films are fully reduced to Cu metal that has smooth mor-
phology (rms roughness ~ 1 nm) and low resistivity (12 μΩ cm 
at 9 nm thickness). CVD CuON films having CuO structure form 
Cu with higher density after reduction than CuON films having 
Cu3N structure do. Room temperature remote hydrogen plasma re-
duction is the best method to maintain smooth surface morphology.
Thus, this process can be a promising candidate of thin CVD Cu seed layer deposition for future Cu interconnects.

**Experimental**

The deposition of CuON was done in a tube-furnace type reactor 
which has 36 mm inner diameter (i.d.). Copper (I) 
N,N’-di-sec-butylacetamidinate ([Cu(“Bu-Me-amd)]2) was used as 
a Cu precursor, which was delivered by bubbling with 40 sccm of 
N2 carrier gas. The bubbler temperature was 130°C, which main-
tained the Cu precursor as a liquid phase because its melting point is 
77°C. All the gas lines, bubbler, and valves were located in an oven 
which maintained a good temperature uniformity. H2O was used as 
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**Results and Discussion**

Cu oxynitride deposition with [Cu(“Bu-Me-amd)]2, H2O, and 
NH3—Temperature effect on CuON film deposition—CuON was 
deposited from [Cu(“Bu-Me-amd)]2 vapor and a mixture of H2O 
vapor and NH3 gas. Figure 1 shows the deposition rate of Cu ox-
ynitride at different deposition temperatures. The ratio of H2O flow 
to NH3 flow was 30:10 in these depositions. The deposition rate 
increased with increasing deposition temperature, up to a value over 

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Figure 2. (Color online) AFM images of CuON films grown from \([\text{Cu('Bu-Me-amd)}]_2\) vapor and a mixture of 30 sccm of H\(_2\)O and 10 sccm of NH\(_3\) at (a) 140, (b) 160, (c) 180, and (d) 220°C, which have about 20 nm thickness.

Figure 3. (Color online) The composition of CuON films deposited on carbon substrates from \([\text{Cu('Bu-Me-amd)}]_2\) vapor and a mixture of 30 sccm of H\(_2\)O and 10 sccm of NH\(_3\) at different temperatures, as measured by RBS.

Figure 4. (Color online) Deposition rate of CuON film at different H\(_2\)O and NH\(_3\) ratios at 140°C, 8 Torr working pressure. Total flow rate of H\(_2\)O and NH\(_3\) is maintained at 40 sccm. Thus, the NH\(_3\) flow rate is equal to 40 sccm minus the H\(_2\)O flow rate.
Compositions of CuON films deposited with different H₂O to NH₃ ratios at 140°C are shown in Fig. 5. The oxygen content of the films exceeds the nitrogen content, even for the film grown from an excess of ammonia (H₂O to NH₃ flow ratio of 10:30). This is another indicator that water vapor is more reactive with the copper precursor than ammonia is. If we assign the conventional oxidation states to O (−2) and N (−3), these compositions all correspond closely to copper in the +1 oxidation state. Because the copper in the precursor is also in the +1 oxidation state, the reactions with H₂O and NH₃ do not produce any oxidation or reduction of the copper during CVD of the films.

The “Cu ratio” is defined by the ratio of Cu thickness to physical thickness of CuON. The physical thickness of CuON film was measured by AFM after etching a stripe pattern. Cu thickness was measured by RBS as if it were pure copper with bulk density. From Fig. 6 the Cu ratio in the CuON films reached a maximum for the conditions of 30 sccm of H₂O and 10 sccm of NH₃. Films with a high Cu ratio contain more Cu that may be obtained by the reduction of a given thickness of CuON.

All the CuON films have a very smooth surface morphology. The morphology of deposited CuON depends on the ratio of H₂O to NH₃ as shown in Fig. 7. With increasing the H₂O ratio, the grain size increased, but the rms roughness value decreased, so the grains became wider, flatter, and less tall.

The crystal structure of CuON film depended on the ratio of flow rates of H₂O to NH₃. The structure was evaluated by electron diffraction in a TEM image (Fig. 8). The diffraction patterns were obtained from CuON films deposited in three different conditions: Fig. 8a for 10 sccm H₂O and 30 sccm NH₃, Fig. 8b for 30 sccm H₂O and 10 sccm NH₃, and Fig. 8c for 40 sccm H₂O. The electron diffraction pattern of Fig. 8a (high NH₃) matches with the Cu₃N structure. Those of Fig. 8b and c (high H₂O) coincide with the crystal structure of Cu₅O₂. The peak assignments are summarized in Tables I and II for the Cu₃N and Cu₅O₂ structures, respectively. Although the CuON films have similar compositions, the films show different crystal structures. The high ratio of NH₃ only makes a Cu₃N structure, even though that film contains 24 atom % oxygen. The high ratio of H₂O makes CuON films having only the crystal structure of Cu₅O₂. We find no additional diffraction peaks that could arise from a crystalline mixed oxynitride phase, nor did we find any such phases reported. Thus, it seems likely that these films contain a significant amount of amorphous copper oxynitride that only has broad diffraction patterns and a smooth surface morphology.

It is thought that H₂O reacts with the Cu precursor on a surface, followed by the reaction of NH₃ with Cu–O on the surface because CuON film is not deposited without H₂O. Thus, a high NH₃ flow and low H₂O flow make a low deposition rate of Cu₅O₂, causing a longer time for NH₃ reaction on the surface, which results in the formation of a Cu₃N structure containing oxygen. This result coincides with ald Cu₃N deposition using a pulse sequence of Cu precursor/H₂O/NH₃. Torndahl et al. made Cu oxide, first using Cu(hfac)₂ and H₂O; then it was nitrified by a NH₃ pulse, which resulted in the formation of Cu₃N. Thus, Cu$_2$O and Cu$_3$N can be formed by controlling the reaction gas ratio because the kinetic competition between H₂O and NH₃ with Cu atoms on the surface can make both structures.

The step coverage of CVD CuON was tested by depositing films on a silicon substrate with holes having aspect ratios of 40:1. The scanning electron microscopy (SEM) image of a cleared cross section in Fig. 9 shows a step coverage of about 95% at the bottom of these very narrow holes.

Reduction of CuON with remote H₂ plasma at room temperature.— CuON films can be deposited with different crystal structures and Cu densities depending on the ratio of H₂O to NH₃. The CuON film (high H₂O CuON) with high H₂O ratio (H₂O:30 sccm, NH₃:10 sccm) has the Cu₅O₂ crystal structure and a high Cu ratio (53%). Low H₂O CuON from low H₂O ratio (H₂O:10 sccm, NH₃:30 sccm) has the crystal structure of Cu₃N and a low Cu ratio (41%). Thus, these two films were used to compare the reduction behavior because these can represent high or low density films. High H₂O CuON has about a 12% higher Cu ratio than that of low H₂O CuON.

The CuON films were reduced with remote H₂ plasma. The films were not heated deliberately, but their temperature did rise from room temperature to about 50°C because of the heat released by the recombination of hydrogen atoms to form H₂ and by reaction with oxygen and nitrogen on CuON surfaces. The as-deposited thicknesses of these high H₂O CuON and low H₂O CuON films were 16 and 14 nm, respectively. The sheet resistance of the films depends on reduction time as shown in Fig. 10. After 1 min reduction treatment, both CuON films were reduced to Cu. The sheet resistance is not changed further after 3 min reduction, which means that reduction for 1 min is sufficient to reduce 14–16 nm thick CuON films with either crystal structure. The morphology of reduced CuON was evaluated by AFM, shown in Fig. 11. Both high H₂O and low H₂O CuON showed smooth surface morphology (1.1–1.2 nm rms roughness) even after 3 min reduction. Thus, the reduced Cu films were not agglomerated even at a longer reduction time. Because the films retain their smooth morphology even after over-reduction for longer times, we expect that films can also be reduced successfully inside the whole length of deep trenches. Film near the top of a trench will be reduced before film deeper in the trench, which only receives a smaller flux of hydrogen atoms depleted by reactions at the walls during their diffusion down the trench.

Because these films were reduced at nearly room temperature, they can maintain their smooth surface morphology by avoiding diffusion of the Cu over the Ru surface to form agglomerates. How-
ever, CuON films deposited on SiO$_2$ underlayers were agglomerated under the same reduction condition, as shown by the increase in rms roughness from 0.7 to $\sim$3.5 nm (Fig. 12). Any surface oxide on ruthenium can be reduced during the CuON reduction because the stabilities of Cu$_2$O and RuO$_2$ are similar. The Gibbs energies of the reduction reactions for these oxides are similar,$^2$ which implies both metal oxides can be reduced under similar reduction conditions. The Cu is bonded strongly to the reduced metallic surface of Ru. However, Cu on Si having a native oxide can be agglomerated during reduction even at room temperature due to the high mobility of Cu atoms on oxide surfaces$^9$ and the difficulty of reducing silicon oxides. Thus, an easily reducible underlayer like Ru is essential for maintaining a smooth surface morphology during the reduction of CuON.

The volume shrinkage of two CuON films was evaluated by comparing the thickness of CuON film before and after reduction. The physical thickness of high H$_2$O CuON is changed from 16 to 9 nm, which is a shrinkage of volume by 45%. Low H$_2$O CuON showed that the thickness is changed from 14 to 7 nm, which means a 50% volume shrinkage. These samples are evaluated by RBS to measure the density of reduced Cu film. The RBS result shows that the thickness of high or low H$_2$O CuON would be 8.5 or 5.9 nm, respectively, if they had bulk Cu density. Thus, comparing these values with the physical thicknesses, the density of the reduced copper from high Cu$_2$O CuON or low H$_2$O CuON is 95 or 84%, respectively, of the bulk value. Summarizing the density of the CuON films, high Cu$_2$O CuON has a higher density not only in the as-deposited film but also after reduction. Thus, high Cu$_2$O CuON film should be used as the most suitable Cu compound for reduction to deposit a dense, reduced Cu film.

The resistivity of reduced high Cu$_2$O CuON is 12 $\mu\Omega$ cm at a thickness of 9 nm. That of low H$_2$O CuON film has 15 $\mu\Omega$ cm at a thickness of 7 nm. These values are similar to the resistivity of sputtered Cu at the corresponding thicknesses.$^{15}$ Thus, the reduced Cu film has a high density and high purity.

All the reduced copper films on ruthenium pass the tape test for adhesion, whereas the ones on silica are easily pulled off by tape. More quantitative 4-point bend tests of adhesion are underway.

Conclusions

Smooth, continuous, dense, and conformal Cu films with $\sim$1 nm rms roughness and thickness <10 nm were fabricated by
CVD of CuON followed by reduction with remote hydrogen plasma at room temperature. The crystal structure of CuON can be controlled by the ratio of H₂O and NH₃, although the elemental composition of the film was not changed significantly. A high H₂O ratio makes the CuON film having a Cu₂O crystal structure. A low H₂O ratio, meaning high NH₃ partial pressure, makes CuON films having a Cu₃N crystal structure. The reduction rate of the films does not show any difference depending on the crystal structure. CuON film with a Cu₂O structure produces a higher density of Cu after reduction. Thus, CuON having a Cu₂O structure is the best Cu compound

### Table I. Electron diffraction results for low H₂O CuON film from TEM. The index of plane (hkl) and interplanar spacing (d) shown in this table represents the Cu₃N crystal structure. Error means the difference between reference data and measured data.

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<th>Error (%)</th>
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### Table II. Electron diffraction result for high H₂O CuON film from TEM. The index of plane (hkl) and interplanar spacing (d) shown in this table represents the Cu₂O crystal structure. Error means the difference between reference data and measured data.

<table>
<thead>
<tr>
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for this deposition and reduction process, which is a promising method for Cu seed layer deposition for future Cu interconnects.

Acknowledgments

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References