Growth of Cu Metal Films at Room Temperature Using Catalyzed Reactions

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Integrated circuits (IC) technology aims to realize higher integration densities using optimum submicrometer design rules. Further, continuous advances in IC technology require innovations in the metallization schemes, both in the materials and processes.

Today, Cu interconnects in semiconductor devices are manufactured by an electroplating technique with a thin physical vapor deposited (PVD) Cu seed layer. Electroplating requires a conductive substrate, and in principle, electrodeposition could proceed directly on top of the diffusion barrier; however, in practice, a thin Cu seed layer is first deposited on the barrier layer. This seed layer is important because in addition to improving adhesion, it also influences the nucleation and crystallographic texture of the electrodeposited Cu.[1]

Conventionally, Cu seed layers are deposited using PVD methods. However, the deposition of conformal films by PVD methods is difficult. Further, as the device aspect ratios increase, it will become increasingly difficult to deposit a continuous and uniform seed layer using PVD. Hence, atomic layer deposition (ALD) of Cu has attracted considerable attention as an alternative. ALD is based on sequential self-limiting surface reactions and is therefore ideally suited for producing highly conformal layers of thin films with single-atomic-layer thickness control.[2] Although ALD is promising, its potential applications in growing pure Cu films have been limited by the lack of efficient precursors with high volatility, thermal stability, and reactivity. In Cu ALD, many Cu(I) and Cu(II) precursors have been used, such as metal organics[3−6] and halides.[7] Cu(I) precursors cannot be used in ALD because the Cu film will grow via thermally induced disproportional reactions on the substrate surface,[8] resulting in a loss of the self-limiting nature of the process. Hence, Cu (II) precursors are more appropriate. Among the Cu(II) precursors, $Cu(hfac)_2$, where hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate, has been widely studied because of its high volatility. However, the use of $Cu(hfac)_2$ typically requires process temperatures greater than 423 K. The ability to deposit Cu at lower temperatures would make ALD even more attractive for use in combination with low-k dielectric materials, which have limited thermal stability. Cu growth at low temperatures is also very desirable for thermally sensitive applications such as in electronic equipments or as protective coatings.

In this paper, we report a method for growing Cu metal films even at room temperature by catalyzing the surface reactions. The organic base pyridine (C_5H_5N) was chosen as the catalyst because it strongly interacts with the Cu metal atoms in the Cu precursor molecules adsorbed on the surface and it is a stable molecule; this decreases the incorporation of impurities such as N or C into the deposited Cu film. H_2 was used as a reducing agent. We also performed density-functional calculations with ultrasoft pseudopotentials,[9] as implemented in the Vienna Ab initio Simulation Package (VASP) code,[10] for a complete understanding of the theoretical bonding state or structural changes when a Cu metal in $Cu(hfac)_2$ interacts with pyridine (Lewis base) on the surface. The plane-wave cutoff voltage was 450 eV, and the cubic supercell contained a molecule with a volume of 16 × 16 × 16 Å^3. Generalized gradient approximation (GGA) was used to describe the electron-correlation energy.[11] Structure optimization was performed by reducing the Hellmann−Feynman forces to less than 0.01 eV/Å.

The experiments were performed in a normal thermal ALD system operated at a pressure of 1 Torr. The substrates for the growth of Cu thin films were Si wafers coated with PVD titanium nitride (TiN). $Cu(hfac)_2$ (Strem, 99.99%) and pyridine (Aldrich, 99.9%) were evaporated from a stainless steel bubbler maintained at a temperature of 333 and 298 K, respectively. The depositions were performed using $Cu(hfac)_2$ and pyridine with H_2 pulse lengths of 3 s each, purge lengths of 10 s each between the respective pulses, and 500 deposition cycles.

No uncatalyzed growth of Cu thin films was observed on TiN wafers at 298 K after 500 cycles in the case of

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(1) Rosenberg, R.; Edelstein, D. C.; Hu, C. K.; Rodbell, K. P. *Annu. Rev. Mater. Sci.* **2000**, *30*, 229.
(2) Ritala, M.; and Leskelä, M. *Handbook of Thin Film Materials*; Academic Press: San Diego, 2001.
(3) Kim, S.; Choi, D. J.; Yoon, K. R.; Kim, K. H.; Koh, S. K. *Thin Solid Films* **1997**, *311*, 218.
(4) Huo, J.; Solanki, R.; McAndrew, J. *J. Mater. Res.* **2002**, *17*, 2394.
(5) Awaya, N.; Ohno, K.; Arita, Y. *J. Electrochem. Soc.* **1995**, *142*, 3173.
(6) Jin, H. J.; Shiratani, M.; Kawasaki, T.; Fukuzawa, T.; Kinoshita, T.; Watanabe, Y.; Kawasaki, H.; Toyofuku, M. *J. Vac. Sci. Technol., A* **1999**, *17*, 726.
(7) Mårtensson, P.; Carlsson, J. O. *Chem. Vapor Deposition* **1997**, *3*, 45.

(8) Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Roberts, D. A.; Hochberg, A. K. *J. Phys. IV* **1991**, *1*, C2–271.
(9) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
(10) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
(11) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
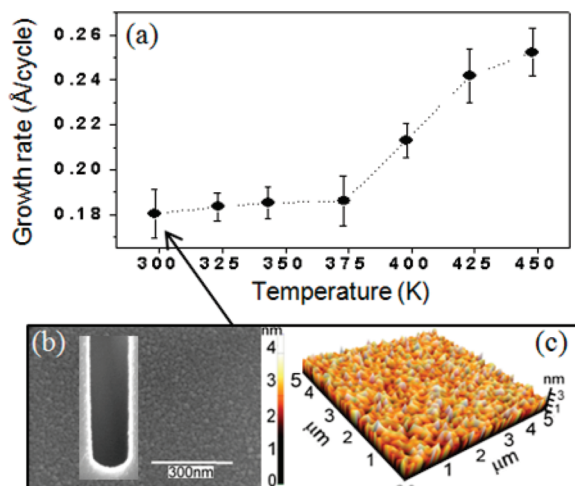
Figure 1. (a) Growth rate of Cu films as a function of deposition temperature. (b) Top-view SEM image of Cu films deposited at 298 K over 500 cycles. (c) AFM image of Cu films deposited at 298 K over 500 cycles. $Cu(hfac)_2$ and H_2 pulse lengths were maintained at 3 s, and all the purge lengths were maintained at 10s.

reactant exposures during $Cu(hfac)_2$ and H_2 half reactions. In contrast, the addition of pyridine with H_2 initiated immediate growth of the Cu thin films. The growth rate observed from room temperature to 373K (Figure 1) was approximately 0.185 Å/cycle, which is similar to the value obtained by radical-enhanced Cu ALD in the literature.[12] The thickness of the Cu thin films was evaluated with X-ray reflectivity (Philips-MRD). When the deposition temperature was increased until 373 K, there was no change in the growth rate, which indicates these conditions were sufficient for a complete catalytic reaction. However, when the temperature became greater than 373 K, the growth rate exhibited a sudden increase because of the thermal self-decomposition of $Cu(hfac)_2$ on the surface. The copper film quality was evaluted with 4-point probe and X-ray photoelectron spectroscopy (XPS, PHI 5400 ESCA). The resistivity of films deposited at 298−373 K was in the range of 19 $\mu\Omega$ cm for about 15 nm thick films. When the films thickness is less than the mean-free path of electrons in copper (30 nm), the resistivity of as-deposited films is possible to increase the smallest obtainable resistivity value by scattering from interfaces.[12] The impurity concentration of films was measured by XPS. The films deposited at 298K contained 5 atom % oxygen and 16 atom % carbon and it is decreased with the increase in deposition temperature. The film deposited at 373K contained 4 atom % oxygen and 5 atom % carbon. The film resistivity grown in the range of 298−373 K was similar even though the impurity concentration was lowered. We believe that is because the surface roughness and scattering from grain boundaries are increased with the increased deposition temperature.

The surface morphology of Cu films was studied using an AFM in contact mode. Figure 1c shows a $5 \times 5 \ \mu m^2$ scan for a Cu film deposited over 500 cycles at 298 K. The micrographs of the deposited Cu films indicate a

(12) Niskanen, A.; Rahtu, A; Sajavaara, T.; Arstila, K.; Ritala, M.; Leskela, M. *J. Electrochem. Soc.* **2005**, *152*, G25.
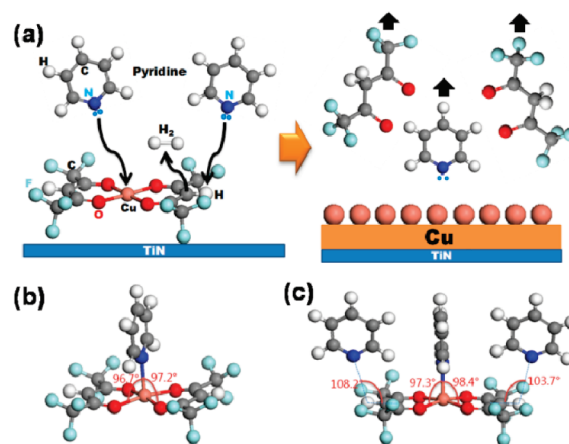
Figure 2. (a) Proposed mechanism of catalytic reaction of pyridine; (b) bond angles (deg) for Cu in $Cu(hfac)_2$−pyridine; (c) bond angles (deg) for Cu in $Cu(hfac)_2$−pyridine and H in $Cu(hfac)_2$−pyridine.

surface roughness of 0.44 nm (root-mean-square). In comparison, the surface roughness of the initial TiN wafer was 0.66 nm. A Cu film deposited at 393 K showed a roughness of 0.65 nm, which was higher than that deposited at 298 K. These results confirm that the films were conformal. Conformality, in turn, supports the premise that the film growth occurs in the ALD mode.

Catalysis of the Cu film growth lowers the reaction temperature from greater than 423 K to room temperature. The proposed mechanism for the catalytic activation along with two catalytic pathways is shown in Figure 2a. One mechanism is the direct interaction between the lone-pair donating molecule, pyridine, and a Cu metal atom in $Cu(hfac)_2$. The Cu metal atom on the surface is known to have strong interactions with Lewis bases such as pyridine.[13] The other mechanism is the hydrogen-bonding interactions of the N lone-pair electrons with hydrogen in an hfac ligand. The N lone-pair electrons in amines are well-known to form very strong hydrogen-bonds with C−H σ-orbitals.[14,15] Such interactions can weaken the Cu−O bonds and facilitate Cu film growth by H_2 reduction reaction. Before calculating the effect of N lone-pair electrons on pyridine, we determined the ab initio structure of $Cu(hfac)_2$-NH_3 to estimate the accuracy of our experimental results. Our theoretical optimized atomic structure is very consistent with previous experimental results. The calculated bond lengths of Cu−N, Cu−O, C−O, and C−C in $Cu(hfac)_2$-NH_3 are 1.96, 1.95, 1.27, and 1.40 Å, respectively, which are within 1.00% of the experimental values of 1.93, 1.94−2.07, 1.24−1.26, and 1.37−1.40 Å.[16]

As shown in Table 1, the catalytic behavior of pyridine causes a remarkable change in the atomic structure of the reactants. In particular, the interaction results in an

(13) Antusek, A.; Urban, M.; Sadlej, A. J. *J. Chem. Phys.* **2003**, *119*, 7247.
(14) Mui, C.; Wang, G. T.; Bent, S. F.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *114*, 10170.
(15) Rodriguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Phys. Chem. C* **2007**, *111*, 4800.
(16) Pinkas, J.; Huffman, J. C.; Chisholm, M. H.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 5314.

Table 1. Variations in Bond Distances (Å) as a Result of the Interaction between Cu(hfac)$_2$ and Pyridine

	Cu(hfac)$_2$	Cu−pyridine	Cu−pyridine H−pyridine	Cu−pyridine 2 × (H−pyridine)
d (Cu−O)	1.95	1.99	2.01	1.99
d (C−O)	1.27	1.27	1.27	1.27
d (C−C)	1.40	1.40	1.40	1.40
d (Cu−N)		2.26	2.23	2.26
d (H−N)			3.03	right, 3.02 left, 2.98

increase in the Cu−O bond length. When only a Cu metal atom interacts with the N lone-pair electrons, the bond length of Cu−O increases from 1.95 to 1.99 Å. However, when pyridine interacts with both a Cu metal atom and a right-side hydrogen atom of Cu(hfac)$_2$, the calculated bond length of Cu−O, 2.01 Å, becomes significantly greater than the length of Cu(hfac)$_2$ without any interaction. However, when an interaction with a left-side hydrogen atom is added, the bond length has the same value as when the pyridine molecule interacts only with a Cu metal atom. From these results, we find that the interaction of pyridine with a Cu metal atom is highly effective in decreasing the Cu−O bond strength. Further, asymmetric interactions (one-sided interactions of pyridine) are more effective than symmetric interactions.

In conclusion, we have presented a new method for improving the reactivity between Cu(hfac)$_2$ and H$_2$ by employing a catalyst gas (pyridine). The addition of pyridine with H$_2$ initiated immediate growth of Cu thin films even at room temperature. The reasons for such deposition at room temperature are confirmed by density-functional theory calculations; further, the variations in the theoretical bonding states are also investigated.