Thin Films

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Low-Temperature Atomic Layer Deposition of Copper Metal Thin Films: Self-Limiting Surface Reaction of Copper Dimethylamino-2-propoxide with Diethylzinc**

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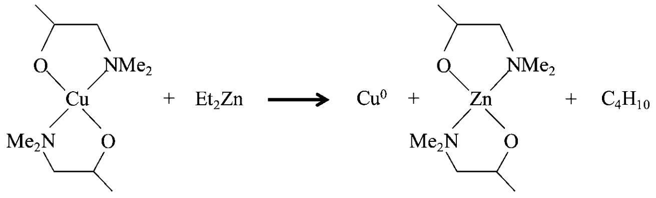
Copper has been of great interest as a conducting material to replace aluminum in device manufacturing, because of its good conductivity and superior resistance to electromigration and stress migration compared with aluminum.[1–3] In addition, copper has good thermal stability and a low temperature coefficient of resistance.[4] Typically, copper films have been prepared by using electrodeposition, physical vapor deposition (PVD), and chemical vapor deposition (CVD). However, the increasing complexity and decreasing dimensions of devices for microelectronic, data storage, and other applications are placing stringent demands on these deposition technologies that have not yet been fully satisfied. The demands include reductions in the deposition temperature, conformal coverage of complex surfaces, and complete filling of narrow, high-aspect-ratio structures.[1] For example, copper-interconnected structures for integrated circuits must be no wider than 100 nm and have aspect ratios less than 3:1.

One method particularly suitable for making uniform and conformal thin films is atomic layer deposition (ALD). ALD is a gas-phase thin film deposition method related to CVD. During the past decade, ALD has attracted considerable attention as a method of manufacturing high-quality thin films and producing tailored molecular structures.[5–11] The ALD method relies on sequential saturated surface reactions, which result in the formation of a monolayer in each sequence. In contrast to CVD, the successive self-terminating growth mechanism in ALD inherently eliminates gas-phase reactions and produces uniform thin films not only over flat substrate surfaces, but also in very narrow holes and trenches. There have been a few reports on ALD of copper metal thin films, such as $CuCl/Zn$,[12] $CuCl/H_2$,[13] $[Cu(tmhd)_2]/H_2$ (tmhd = tetramethyl-3,5-heptanedionate),[14,15] $[Cu(hfac)_2]/H_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate),[16,17] $[Cu(acetylacetone)_2]/H_2$,[18] and $[Cu(dialkyl\ acetamidinate)_2]/H_2$[19,20] as the reactant precursors. All these reports, however, lacked self-terminating behavior, purity, conformality, reproducibility, low temperature, and selectivity.

Recently, binary Cu/ZnO nanocatalysts for methanol synthesis were prepared by metal–organic precursor routes inspired by CVD techniques. Scheme 1 shows the key step of the process, which is a ligand-exchange reaction of $[Cu(dmap)_2]$ (dmap = dimethylamino-2-propoxide)[22,23] with diethylzinc (Et_2Zn) taking place either at the internal surface of periodic mesoporous silica supports (MCM-41/48)[21] or in colloidal solution.[22] The stoichiometric by-product $[Zn(dmap)_2]$ itself serves as a precursor for nanoscale ZnO species, which are subsequently formed during annealing at temperatures above 200 °C under inert conditions. Such a highly selective and quantitative ligand-replacement reaction involving chemical reduction of one component to the pure metal can be applicable to atomic layer deposition of metal thin films. Below, we describe a new ALD process that yields high-quality copper metal thin films using the reaction of $[Cu(dmap)_2]$ with Et_2Zn (Scheme 1).

In this ALD process, the Cu thin films were formed by two sequential saturated surface reactions. First, a monolayer of $[Cu(dmap)_2]$ was adsorbed on a substrate through dipole–dipole interactions between the precursor and the substrate surface at temperatures of 100–120 °C. The dosing of diethylzinc molecules in the second ALD step leads to the reaction of Scheme 1 at the surface and the formation of Cu species. The by-products ($[Zn(dmap)_2]$ and butane) were desorbed from the substrate without decomposition at these low temperatures. The metallic Cu species provide active adsorption sites for the next monolayer of $[Cu(dmap)_2]$. The advantages of this ALD process include accurate control of film thickness, large-scale uniformity, excellent conformality,



Scheme 1. Reaction between $[Cu(dmap)_2]$ and Et_2Zn.

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good reproducibility, and excellent copper film quality at low deposition temperatures.

In a true ALD process, the surface reactions must be self-terminating and complementary in order to yield a uniform, conformal, and high-quality copper metal thin film. To verify that the surface reaction for [Cu(dmap)$_2$] is really self-terminating, the dose time was varied between 0.5 and 10 s at growth temperatures of 100–120 °C. The film thickness per cycle for [Cu(dmap)$_2$] is saturated when the pulse time exceeds 2 s, as shown in Figure 1 a. This result indicates that [Cu(dmap)$_2$] undergoes a self-terminating reaction with the copper metal surface prepared by reaction with diethylzinc. Figure 1 b shows that the growth rate as a function of the Et_2Zn dose time is quickly saturated when the pulse time exceeds 0.5 s. This result suggests that Et_2Zn undergoes a fast self-terminating replacement reaction with [Cu(dmap)$_2$] adsorbed on Si substrates. All the self-terminating growth experiments were undertaken with 1000 cycles and resulted in the deposition of 20 nm thick films. The thickness of the copper thin films versus the number of ALD cycles is shown in Figure 1 c. The growth is extremely linear with respect to the number of cycles, showing that the surface reactions for this ALD process are complementary and complete. The measured growth rate was 0.2 Å per cycle.

XPS analysis was performed to determine the composition of the copper films grown by this ALD process as a function of ALD temperature. Figure 2 a–c show the survey and high-resolution spectra of the copper films grown at 100–120 °C. The XP spectra of the copper films cleaned by Ar^+ ion sputtering display only the photoelectron and Auger electron peaks for pure copper metal without contamination from other materials. Also, the peak positions of Cu(2p) and Cu(LMM) (LMM: transition between inner shells L and M) clearly demonstrate that the films are pure copper metals.[25,26] The peaks in the XP spectra show almost constant intensities and shapes between 100 and 120 °C. These observations indicate that ALD surface reactions similar to that of Scheme 1 allow the deposition of a high-quality copper metal thin film at temperatures in the range 100–120 °C, which appears to be an ALD process window. When the ALD temperature is raised to 130 °C, Zn peaks suddenly appear with oxygen and carbon peaks (Figure 2 d). The Zn(2p) peak then rapidly increases in intensity with further increase of the substrate temperature. These changes indicate that zinc compounds, that is, [Zn(dmap)$_2$] and Et_2Zn, are decomposed and incorporated into the copper films above 120 °C. Also, at a temperature below 100 °C, the growth rate decreases (Figure 1 d) and the deposited copper films are contaminated with zinc, carbon, and oxygen. It is possible that the evaporation of zinc compounds (i.e. [Zn(dmap)$_2$] and Et_2Zn) is incomplete at these low ALD temperatures. The process window for this ALD process is very narrow; the lower limit is dictated by desorption of the zinc compounds and the upper limit by their decomposition.

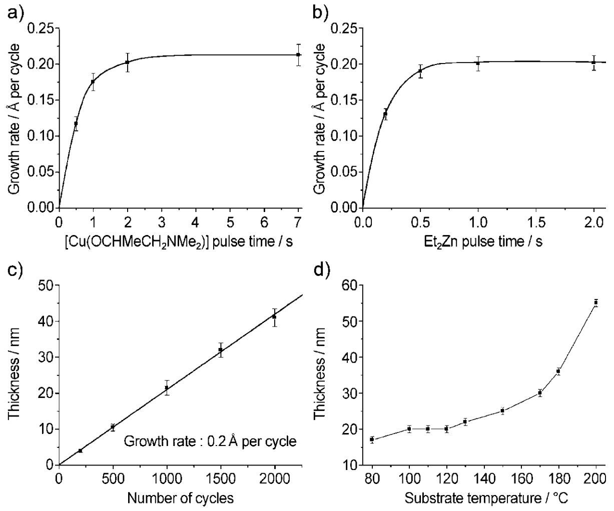

Figure 1. Growth rate a) as a function of [Cu(dmap)$_2$] pulse time, b) as a function of Et_2Zn pulse time for copper films grown at 100–120 °C. Thickness of the copper films c) versus the number of ALD cycles at 100–120 °C, d) versus the substrate temperature.

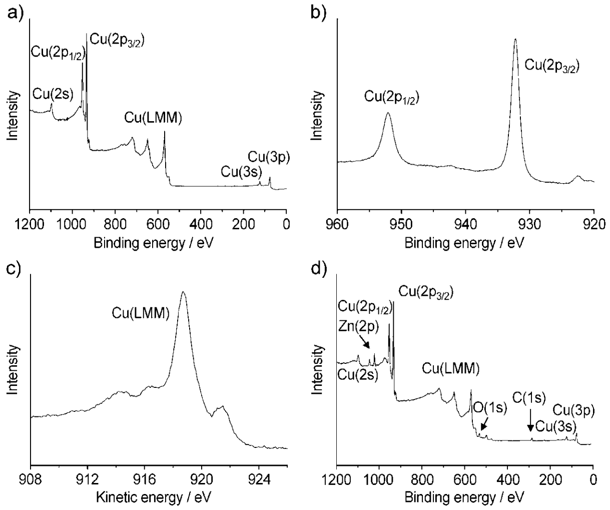

Figure 2. Spectra of the copper films grown at 100–120 °C: a) Survey XP spectrum; b) high-resolution XP spectrum of the Cu(2p) regions; c) Auger spectrum of the Cu(LMM) regions. d) Survey XP spectrum for the copper films grown at 130 °C.

Figure 3 a shows a typical XRD pattern for 50 nm thick Cu thin films grown at temperatures of 100–120 °C on Si substrates. A strong XRD peak attributed to Cu(111) and weak Cu(200) and Cu(220) peaks appear, indicating predominantly [111] oriented film growth with co-deposition of the [100] and [110] oriented crystallites. The morphology of the copper thin films was examined by scanning electron microscopy (SEM). A typical surface morphology of the 50 nm thick Cu films is characterized by 10 nm granular crystallites

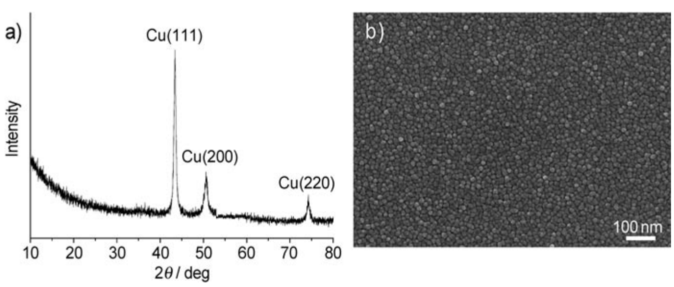

Figure 3. a) XRD pattern, b) SEM image of the copper thin films grown at 100–120 °C.

(Figure 3b). The electrical resistivity of the 50 nm thick Cu thin films was determined by measuring the sheet resistivity using a four-point probe. The resistivity was about 2.78 μΩ cm, which is approximately 2.1 times greater than the bulk Cu resistivity (1.68 μΩ cm).

Patterned deposition of Cu is a very important aspect for integration of copper metallization schemes into device processing. To demonstrate the suitability of the described Cu-ALD process, Cu thin films were deposited selectively onto patterned alkyl siloxane self-assembled monolayers (SAMs). Patterned SAMs of octadecylsiloxane on Si substrates were made using microcontact printing according to standard protocols.[27–29] Figure 4a shows an AFM image of patterned SAMs fabricated using the masters with 3.1 μm parallel lines and 2.7 μm spaces. The image clearly shows that the patterned monolayers retain the dimensions of the masters without noticeable line spreading. Additionally, the height of the patterned monolayer is about 24 Å, which is close to that of a densely packed octadecylsiloxane monolayer (ca. 25 Å). The regions covered by OTS-SAMs (OTS = octadecyltrichlorosilane) are nonpolar, low-free-energy surfaces, whereas the regions exposing the silanol groups of the Si substrates are polar, high-free-energy surfaces. The selective ALD of Cu films was performed at 100 °C, and the number of ALD cycles in a run was kept to 600. The thickness of the copper thin films, measured by AFM, is about 12 nm. Figure 4b illustrates an AFM image of micropatterned Cu thin films that were selectively deposited onto the monolayer-patterned Si substrate by ALD. The patterns of the copper thin films were defined and directed by the patterned SAMs generated by microcontact printing. The copper thin films are selectively deposited only on the regions exposing the polar silanol groups of the Si substrates because the regions covered with the octadecylsiloxane monolayers do not have any polar group to interact with the ALD precursors.[30] The AFM image clearly shows that the patterned copper thin films retain the dimensions of the patterned SAMs with no noticeable line spreading.

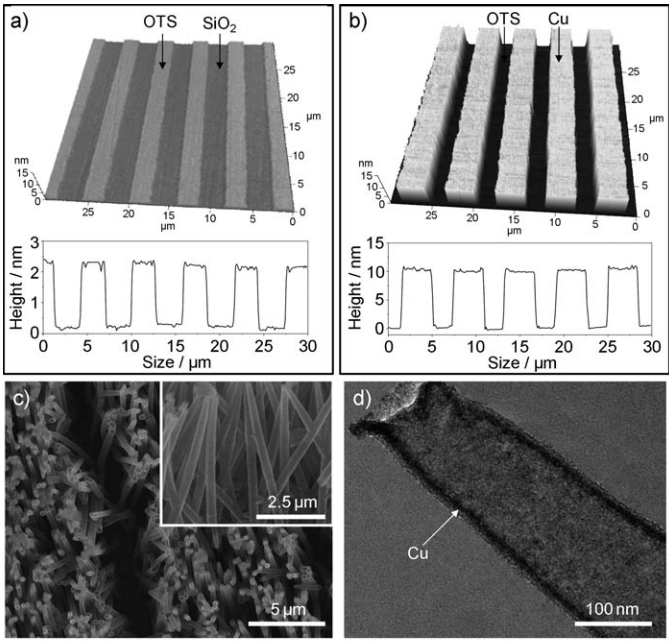

Figure 4. AFM image and cross-section a) of the patterned OTS-SAMs fabricated by microcontact printing on Si substrates, b) of the patterned Cu thin film produced using selective ALD on SAMs-patterned Si substrates. c) Field-emission SEM images of Cu nanotubes. d) HR-TEM image of a Cu nanotube.

Such highly selective deposition features of an excellent ALD processes allow the fabrication of unusual nanostructures. This application is demonstrated by the fabrication of Cu nanotubes. We used nanoporous membranes as templates for Cu ALD and removed them subsequently, leaving behind the Cu nanostructures. The membranes used in this study are commercially available polycarbonate (PC) filters with a pore diameter of approximately 150 nm.[9,31] To avoid any subsequent processing step during fabrication of freestanding Cu nanotubes (e.g., etching of unwanted films deposited onto both sides of PC templates), ALD was used for selective area depositions only onto the inner wall of the PC holes using microcontact-printed OTS-SAMs as passivation layers. OTS-SAMs were deposited onto both sides of the PC membranes by microcontact printing. Subsequent ALD produced conformal copper coats only on the inner walls of the PC templates. Coatings on the inner wall of the PC membranes were carried out using ALD at 100 °C. In a typical experiment the number of ALD cycles in a run was kept to 900. After 900 cyclic ALD processes, the PC membranes were etched away using chloroform. Figures 4c,d show FE-SEM and high-resolution TEM micrographs of the Cu nanotubes, respectively. The wall thickness and length of the tubes were about 18 nm and 12 μm, respectively. The length of the tubes corresponded to the thickness of the PC template, implying excellent conformality of our ALD process. A very high aspect ratio of 80:1 was achieved, and even higher aspect ratios of nanotubes might be formed with thicker templates.

In conclusion, we described the atomic layer deposition of copper metal thin films using a new precursor concept involving ligand exchange reaction of $[Cu(dmap)_2]$ with Et_2Zn. In this ALD process, the surface reactions were found to be self-terminating and complementary enough to make a uniform, conformal, high-quality copper metal thin film. The ALD process yields a predominantly [111] oriented thin film without any contaminants at very low substrate temperatures of 100–120 °C. We also demonstrated a selective ALD of Cu thin films on patterned octadecylsiloxane self-assembled monolayers formed by microcontact printing. Cu nanotubes with 150 nm diameter and 12 μm length were fabricated by ALD at 100 °C, followed by chemical etching of the PC template. The very high aspect ratio of 80:1 implies excellent conformality of this copper ALD process. Metal ALD in general[32] and copper ALD in particular are challenging problems.[12–20] Typically, hydrogen is used as a reducing component, as cited in the introduction. Alternative reducing agents, such as elementary zinc vapor, are largely undesirable because of the high process temperature and possible contamination. Our results show that subtle adjustment of the reactivity of the two components, the metal precursor and the reducing agent, together with engineering of the metal precursor and by-product, allows the design of excellent ALD processes. Using organometallic alkyl compounds as reducing agents for metal–organic complexes is not limited to the Cu/Zn case presented herein. For example, the reactions of [M(dmap)$_2$] with ZnR$_2$[33,34] (M = Cu, Ni, Pd) and more general [M(acac)$_2$] (M = Cu, Ni, Pd; acac = acetylacetonate) with ZnR$_2$ or AlR$_3$ follow the principle of Scheme 1, which is alkylation of the transition-metal ion with subsequent reductive elimination of hydrocarbons to deposit the pure metal. This concept has been used extensively for the preparation of nonaqueous metal colloids.[35] Finally, we suggest that low-temperature ALD processes similar to our Cu case study may be relevant for the fabrication of superior metal contacts on top of functional SAMs.[36]

Experimental Section

Materials: Et$_2$Zn (Aldrich; 96 %), CH$_3$(CH$_2$)$_{17}$SiCl$_3$ (Aldrich; 97 %), and hexane (Aldrich; anhydrous, 99 %) were used as received. Polydimethylsiloxane (Sylgard 184) was ordered from Dow Corning. Polycarbonated filters (Whatman Co., UK) were used as templates in this study. Deionized water was purified with a Millipore Milli Q plus system, distilled over KMnO$_4$, and then passed through the Millipore Simplicity system. [Cu(OCHMeCH$_2$NMe$_2$)$_2$] was prepared by the previously reported procedures.[22,23]

Preparation of substrates: The Si substrates used in this study were cut from n-type (100) wafers (LG Siltron) with a resistivity in the range 1–5 Ω cm. The Si substrates were initially treated by a chemical cleaning process proposed by Ishizaka and Shiraki which involves degreasing, boiling in HNO$_3$, boiling in NH$_3$/H$_2$O (alkali treatment), boiling in HCl (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants and grow a thin protective oxide layer on the surface.[24]

ALD: The oxidized Si(100) substrates were introduced into the ALD system Cyclic 4000 (Genitech, Taejon, Korea). The Cu thin films were deposited onto the substrate using [Cu(dmap)$_2$] and Et$_2$Zn as ALD precursors. Argon served as both a carrier and a purging gas. [Cu(dmap)$_2$] and Et$_2$Zn were evaporated at 70 and 5 °C, respectively. The cycle consisted of exposure to [Cu(dmap)$_2$] for 2 s, purging with Ar for 5 s, exposure to Et$_2$Zn for 0.5 s, and purging with Ar for 5 s. The total Ar flow rate was 50 cm^3 min^{-1}. The Cu thin films were grown at temperatures of 80–200 °C under a pressure of 0.3 Torr.

Sample characterization: All XP spectra were recorded on a VG Scientific ESCALAB MK II spectrometer using an Al$_{K\alpha}$ source run at 15 kV and 10 mA. The binding-energy scale was calibrated to 284.6 eV for the main C(1s) peak. Each sample was analyzed at a 90° angle relative to the electron analyzer. X-ray diffraction (XRD, Rigaku RU-200BH) was carried out to determine the crystallinity of the copper films. Atomic force microscopy images of the samples were obtained on a PSIA XE-100 microscope operating in tapping mode. The morphology and thickness of the copper thin films were observed by scanning electron microscopy (SEM, JEOL) and transmission electron microscopy (TEM, JEOL). The electric resistivity of the Cu thin films on the Si substrate was measured by the linear four-probe method at room temperature.

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