Deposition of Cu seed layer film by supercritical fluid deposition for advanced interconnects*

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The deposition of a Cu seed layer film is investigated by supercritical fluid deposition (SCFD) using H_2 as a reducing agent for Bis(2,2,6,6-tetramethyl-3,5- heptanedionato) copper in supercritical CO_2 ($scCO_2$). The effects of deposition temperature, precursor, and H_2 concentration are investigated to optimize Cu deposition. Continuous metallic Cu films are deposited on Ru substrates at 190 °C when a 0.002 mol/L Cu precursor is introduced with 0.75 mol/L H_2. A Cu precursor concentration higher than 0.002 mol/L is found to have negative effects on the surface qualities of Cu films. For a H_2 concentration above 0.56 mol/L, the root-mean-square (RMS) roughness of a Cu film decreases as the H_2 concentration increases. Finally, a 20-nm thick Cu film with a smooth surface, which is required as a seed layer in advanced interconnects, is successfully deposited at a high H_2 concentration (0.75 mol/L).

Keywords: supercritical CO_2, Cu film, seed layer, Cu interconnects

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1. Introduction

As device feature shrinks further in ultra-large-scale integrated (ULSI) circuits, Cu has replaced Al as the preferred interconnect metal because of its lower resistivity and superior electromigration (EM) resistance.[1,2] However, it is difficult to etch Cu into fine patterns due to lacking appropriate dry etch chemistry. Therefore, Cu interconnects are fabricated by a dual-damascene process, which consists of sputtering for seed layer formation followed by Cu electroplating into trenches and vias.[3] When the feature size scales down to below 45 nm, however, alternative seed layer deposition methods are requisite, because sputtering is essentially a line-of-sight technique, which cannot provide continuous and conformal deposition within high-aspect-ratio features.[4]

Supercritical fluid deposition (SCFD) is a hybrid approach that combines the advantages of CVD and liquid-phase deposition while minimizing their disadvantages. It usually involves a chemical reaction of soluble organometallic compounds in supercritical carbon dioxide ($scCO_2$).[5] The benefit of SCFD over conventional deposition techniques lies in the unique properties of $scCO_2$. Specifically, the liquid-like density of $scCO_2$ enables the dissolution of a number of metal precursors and the deposition at a relatively high precursor concentration.[6,7] And the gas-like transport properties of $scCO_2$, including high diffusivity, low viscosity, and zero surface tension, promote rapid mass transfer within confined geometry, thus SCFD can provide the conformal step coverage and superior gap-filling ability.[8] Although a number of metal films have been prepared using SCFD, including Cu, Ni, Au, Ag, Pt, Pd, Ru, Co, and alloys,[5,7,9–14] the deposition of a thin and smooth Cu seed layer was seldom reported in terms of their surface quality control.

In this paper, we apply SCFD to the deposition of a Cu seed layer by using bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) [$Cu(tmhd)_2$] as a precursor and H_2 as a reducing agent in $scCO_2$. Effects of temperature, precursor concentration, and H_2 concentration on film deposition and the surface roughness are investigated.

2. Experiment

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) copper [$Cu(tmhd)_2$] was obtained from Alfa Aesar. High purity CO_2 (+99.999%) and H_2 (+99.999%) were used in the experiments. An Si wafer with a surface layer of 100-nm Ru was employed as the substrate, since Ru is a promising diffusion barrier for advanced Cu interconnects.[15]

All deposition reactions are carried out in a hot-wall batch system. Figure 1 shows a schematic diagram of the SCFD apparatus used in this research. It consists of a high-pressure syringe pump, a 10-ml stainless-steel reactor and a resistively heated heater. In a typical experiment, a substrate was loaded together with a known mass of Cu precursor, and the reactor was sealed and preheated to 50 °C. Then, H_2 at a predetermined pressure was introduced through a manual pressure

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regulator. The amount of H_2 added was calculated according to the reactor volume and the pressure. Subsequently, CO_2 was pressurized to 11 MPa using the high-pressure syringe pump, and the reactor was then heated to a specific temperature between 170 °C–200 °C for 60 min. The concentration of $Cu(tmhd)_2$ in $scCO_2$ was varied between 0.001 mol/L–0.005 mol/L. The mole ratio of H_2 to precursor over 100 was used for the deposition, and H_2 concentration in $scCO_2$ was 0.19 mol/L–0.75 mol/L. After experiments, the heater was turned off and $scCO_2$ was flushed through the reactor to eliminate ligand decomposition products and residual precursor.

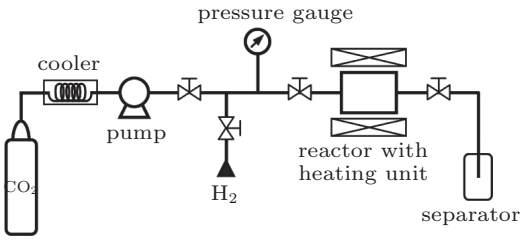


Fig. 1. Schematic diagram of the hot-wall batch reactor for supercritical fluid deposition.

The surface morphology of the deposited film was investigated by field emission scanning electron microscopy (FE-SEM, FEI, Quanta FEG 450) and atomic force microscopy (AFM, Shimadzu, SPM-9500J3). X-ray photoelectron spectroscopy (XPS, ULVAC-PHI 5000C) with an Mg Ka source (1253.6 eV) was employed to analyze the chemical composition and stoichiometry of the film. Atmospheric contaminants were removed from the sample by Ar^+ sputtering at 2 keV for 30 s before the XPS measurement.

3. Results and discussion

The effect of temperature on Cu deposition was first investigated. $Cu(tmhd)_2$ of 0.002 mol/L and H_2 reducing agent of 0.75 mol/L were utilized for the deposition. Figure 2 shows the surface morphologies of the films deposited at different temperatures between 170 °C–200 °C. When a Cu precursor was introduced with H_2 reducing agent, a rough surface with isolated islands on the Ru substrate was obtained after maintaining the temperature at 170 °C as shown in Fig. 2(a). After deposition under 180 °C, a partially-coalesced film was formed ((Fig. 2(b)). When the temperature was increased to 190 °C, a 20-nm thick film composed of well-defined grains was observed as shown in Fig. 2(c). Further increasing the temperature led to a film with larger grains and a rougher surface (see Fig. 2(d)).

The morphology evolution observed from the SEM examination demonstrates the nucleation and growth process of Cu films in $scCO_2$. Specifically, Cu started to nucleate on the Ru surface at 170 °C, but the resulting Cu clusters could not grow and coalesced at such a low temperature. And thus some isolated islands were obtained. Momose *et al.*[16] studied the nucleation and growth of Cu on a Ru surface by *in-situ* monitoring surface reflectivity, and found that the Cu nucleation temperature from $Cu(tmhd)_2$ was around 180 °C, which is higher than our results. A possible reason is that the high H_2 concentration in the current research, which is twice higher than that in Ref. [16], lowered the formation temperature of the initial Cu nuclei. With the increase of the deposition temperature, Cu nuclei grew gradually and touched each other to form a partially-connected film on the Ru substrate. When the temperature was further enhanced to 190 °C, Cu nuclei grew promptly and fully coalesced to a continuous film.

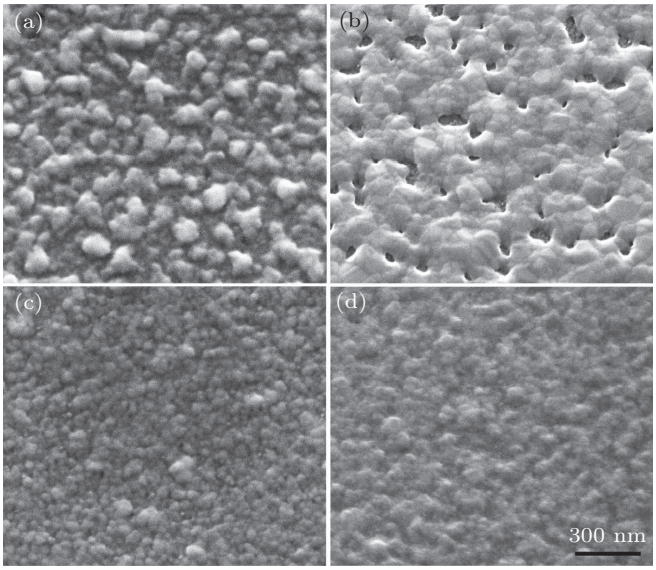


Fig. 2. SEM images of the Cu films deposited from 0.002 mol/L $Cu(tmhd)_2$ and 0.75 mol/L H_2 at temperatures: (a) 170 °C; (b) 180 °C; (c) 190 °C; (d) 200 °C. Scale bar: 300 nm.

Figure 3 shows the high-resolution XPS spectra of the film deposited at 190 °C after 30 s etching with Ar^+. The Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks at 952.7 eV and 932.9 eV, as well as the binding energy difference between these two peaks, 19.8 eV, indicates that the film is composed of metallic Cu (Fig. 3(a)). After removing atmospheric contaminants on the film surface, oxygen impurity less than 0.6 at% was detected in the film (Fig. 3(b)), and the level of carbon in the bulk of the sample was below the instrument detection limit (see Fig. 3(c)). No signal from the Ru substrate was detected, suggesting that a continuous Cu film covered the Ru surface. XPS analysis on the film deposited at 200 °C suggests a discontinuous Cu film, since the Ru signal was detected from the as-deposited film (not shown). This is attributed to the hot-walled SCFD reactor used in our experiments, so a higher fraction of Cu precursor was consumed by depositing on the reactor walls at a higher temperature than 190 °C. A similar phenomenon has also been reported for Ag deposition by SCFD in Ref. [10].

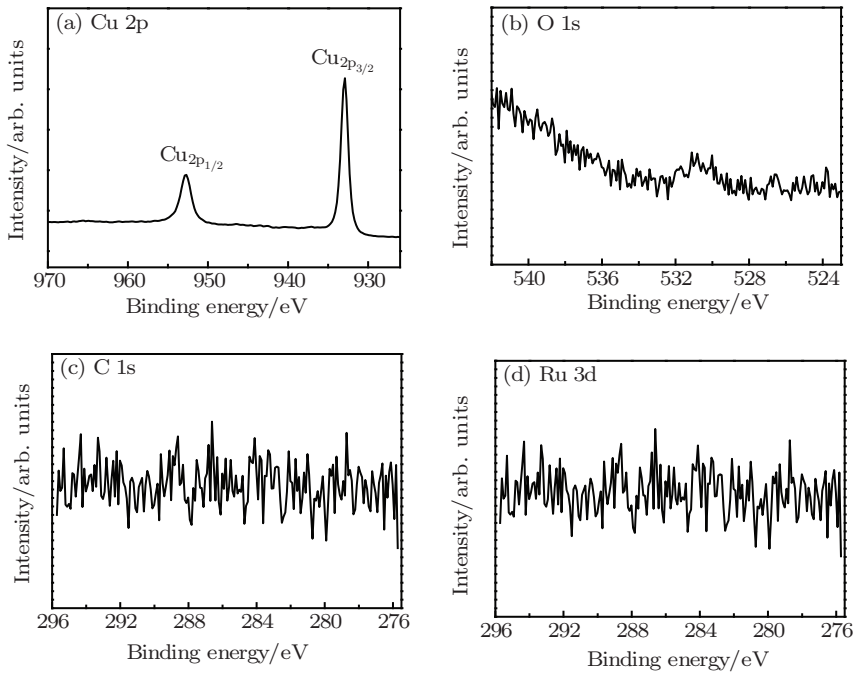


Fig. 3. High-resolution XPS spectra of (a) Cu 2p, (b) O 1s, (c) C 1s, and (d) Ru 3d for the Cu film deposited by 0.75 mol/L H_2 reduction of 0.002 mol/L $Cu(tmhd)_2$ at 190 °C.

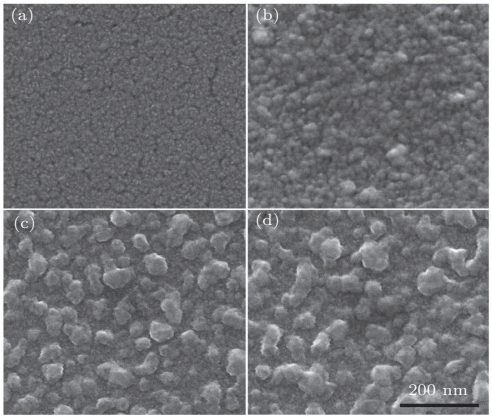


Fig. 4. SEM images of the Cu films deposited at 190 °C from 0.75 mol/L H_2 and at 190 °C and precursor concentrations: (a) 0.001 mol/L; (b) 0.002 mol/L; (c) 0.003 mol/L; (d) 0.005 mol/L. Scale bar: 200 nm.

After determining the desired temperature for Cu deposition, the effect of the precursor concentration was subsequently investigated. Five different concentrations of $Cu(tmhd)_2$ were explored, 0.001 mol/L–0.005 mol/L, while other experimental parameters were kept constant. Figure 4 shows the SEM images of the Cu films deposited from $Cu(tmhd)_2$ of various concentrations. When the precursor concentration was 0.001 mol/L, no obvious deposition was found on the Ru surface (Fig. 4(a)), while a dense and continuous Cu film was deposited when 0.002 mol/L Cu precursor was loaded (see Fig. 4(b)). With $Cu(tmhd)_2$ concentration increasing to above 0.003 mol/L, the Cu films became bumpy with some large grains protruding from their surface (Figs. 4(c) and 4(d)). AFM analysis was also employed to evaluate the surface quality of the Cu film. Table 1 lists root-mean-square (RMS) roughness results of the Cu films deposited from different concentrations of $Cu(tmhd)_2$. Obviously, the RMS roughness increases with the Cu precursor content increasing, which is consistent with the SEM observation. 0.002 mol/L was an appropriate concentration for continuous and smooth Cu films. A similar effect of precursor concentration was also reported in the H_2-assisted deposition of Pd film in $scCO_2$. Blackburn *et al.*[17] found that Pd film quality was degraded when the precursor concentration exceeded 1 wt%, because an excess amount of precursor leads to the nucleation and deposition of Pd particulates, similar to the gas-phase reaction in a typical CVD process.

Table 1. Dependence of surface roughness on Cu precursor concentration.

$Cu(tmhd)_2$ concentration/(mol/L)	RMS roughness/nm
0.001	2.8
0.002	6.1
0.003	14.4
0.004	11.1
0.005	11.7

Considering that the reducing agent concentration in $scCO_2$ may influence Cu deposition and film quality, different H_2 concentration levels between 0.19 mol/L–0.75 mol/L were studied. A $Cu(tmhd)_2$ concentration of 0.002 mol/L and deposition temperature of 190 °C were utilized. Figure 5 shows the AFM images of the Cu films deposited from various H_2 concentrations. For H_2 content lower than 0.56 mol/L, the surface roughness of the Cu film increased with the H_2 concentration

increasing. Further enhancing H_2 content in $scCO_2$, the Cu films gradually became smoother and reduced RMS roughness. It was inferred that a higher temperature was necessary to achieve nucleation and growth of Cu when using low H_2 concentration in $scCO_2$. Therefore, when the H_2 concentration was lower than 0.56 mol/L, only some Cu nuclei were formed on the Ru surface instead of continuous films. And the higher the H_2 concentration used, the higher the nucleation density achieved. So the RMS roughness increased with H_2 content increasing. Above 0.56 mol/L, Cu nuclei experienced growth upon keeping temperature at 190 °C, so the film surface gradually became flat with the H_2 concentration increasing, when the Cu grains touched and started to coalesce together. Finally, a smooth Cu film of 20 nm in thickness with RMS roughness around 6.1 nm was deposited at an H_2 concentration of 0.75 mol/L. XPS analysis confirmed the discontinuous Cu deposition in the cases of 0.37-mol/L and 0.67-mol/L H_2 concentration. Dependence of the nucleation temperature on the H_2 concentration was also reported in the literature. Momose *et al.*[16] found that the nucleation temperature of Cu increased from 180 °C to 215 °C as the H_2 concentration decreased, which accords well with our results.

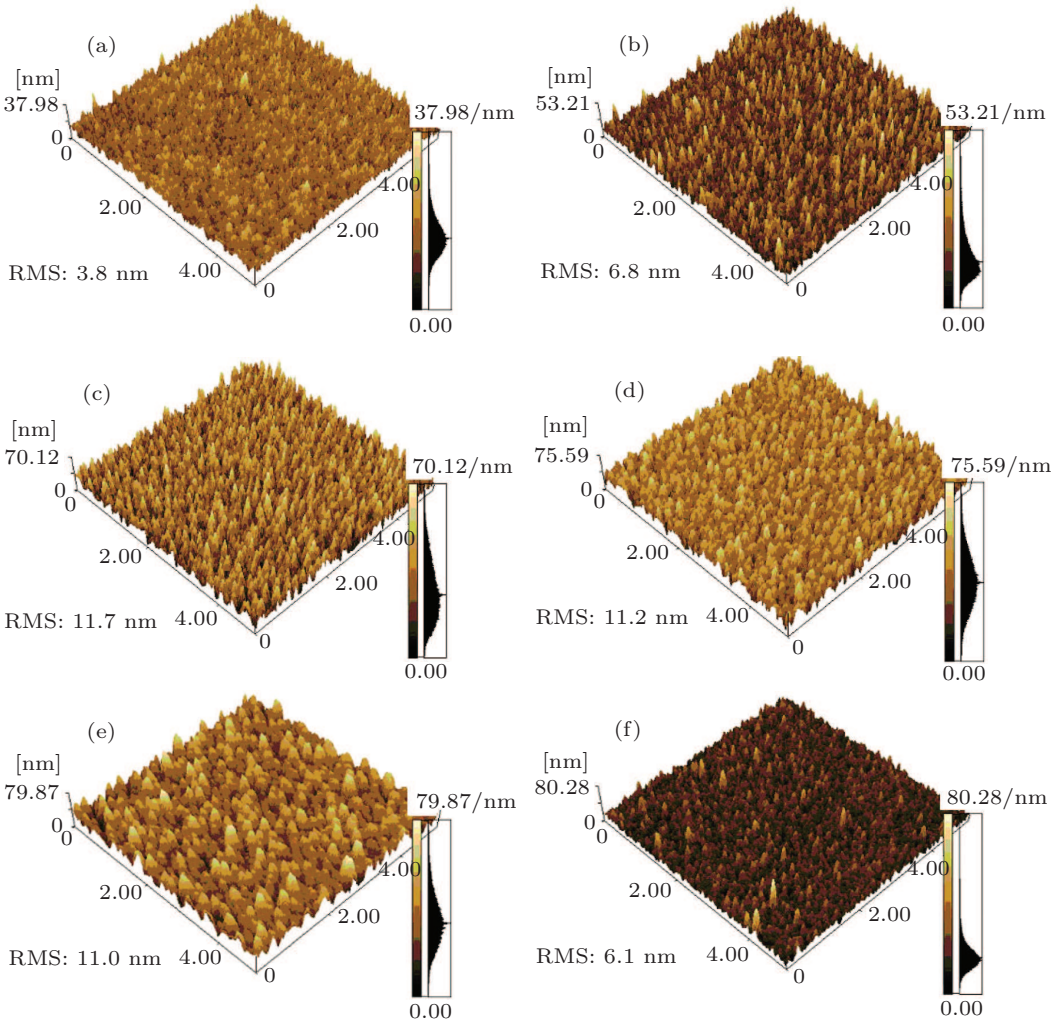


Fig. 5. (color online) AFM images of the Cu films deposited from 0.002 mol/L $Cu(tmhd)_2$ at 190 °C and H_2 concentrations: (a) 0.19 mol/L; (b) 0. 38 mol/L; (c) 0.56 mol/L; (d) 0.67 mol/L; (e) 0.71 mol/L; (f) 0.75 mol/L.

4. Conclusions

In this paper, the SCFD technique is employed to prepare thin and smooth Cu seed layer films. The effects of deposition temperature, precursor, and H_2 concentrations are investigated to optimize Cu deposition. Deposition at a temperature below 180 °C does not yield a continuous film, and continuous metallic Cu films are deposited on the Ru substrates at 190 °C when a 0.002 mol/L Cu precursor was introduced with 0.75 mol/L H_2. A Cu precursor concentration higher than 0.002 mol/L has negative effects on the surface qualities of Cu films. The surface roughness of the Cu film shows an improving tendency as the H_2 concentration increases to a value above 0.56 mol/L. Finally, a smooth Cu film of 20 nm in thickness with an RMS

roughness around 6.1 nm is deposited at an H_2 concentration of 0.75 mol/L, a $Cu(tmhd)_2$ concentration of 0.002 mol/L, and 190 °C, which may be used as a seed layer in advanced Cu interconnects.

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