

Deposition of Copper by the H₂-Assisted Reduction of Cu(tmod)₂ in Supercritical Carbon Dioxide: Kinetics and Reaction Mechanism

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The kinetics and reaction mechanism for copper deposition by the hydrogen-assisted reduction of bis-(2,2,7-trimethyloctane-3,5-dionato)copper(II), [Cu(tmod)₂], in supercritical carbon dioxide was studied using a differential cold wall reactor. At substrate temperatures between 220 and 270 °C, the measured film growth rate ranged between 5 and 35 nm/min. The overall apparent activation energy was 51.9 kJ/mol. Film growth rate exhibited zero-order dependence on the precursor at precursor concentrations between 0.02 and 0.5 wt % Cu (tmod)₂ in CO₂ and a zero-order dependence on hydrogen at hydrogen concentrations greater than 0.06 wt % in CO₂. Zero-order precursor dependence over large concentration ranges promotes exceptional step coverage. At lower concentrations of either reagent a 1/2-order dependence was observed. Film growth rate was negative order with respect to excess quantities of the hydrogenated ligand byproduct, (tmod)H, and film growth could be suppressed completely at (tmod)H concentrations above 1 wt %. With use of the results of the experiments, a heterogeneous reaction mechanism is proposed. Protonation of the adsorbed ligand (tmod) was found to be the rate-determining step. A Langmuir–Hinshelwood rate expression was used to correlate the data with good agreement.

Introduction

Copper has replaced aluminum as the interconnect material of choice in advanced integrated circuits due to its low electrical resistance and superior electromigration resistance. By 2010, the International Technology Roadmap for Semiconductors (ITRS) predicts microprocessors will enter production at the 45 nm technology node.¹ However, defect-free deposition of Cu and other materials within high aspect ratio features at these dimensions poses a formidable challenge.

Supercritical fluid deposition (SFD) is still a relatively new technique; however, it has been recognized as a potential solution for metallization in demanding features.¹ SFD is a hybrid method that combines the advantages of both liquid-phase and gas-phase processes by exploiting the unique properties of supercritical fluids (SCFs) including carbon dioxide.² The density of SCFs can approach those of liquids, enabling dissolution of a number of metal precursors and deposition at relatively high precursor concentrations.^{3–6} Moreover, transport in solution eliminates precursor vapor pressure constraints often encountered in chemical vapor deposition (CVD) processes. Although SFD is a solution-based process, the transport properties of SCF, such as low

viscosity, high diffusivity, and zero surface tension are closer to those of a gas, facilitating rapid mass transfer within confined geometries. Consequently, SFD is especially capable of achieving conformal step coverage and defect-free fill in high aspect ratio features.

To date, a number of metal films, such as Cu, Pt, Pd, Au, Ni, Co, Rh, and Ru, have been deposited from supercritical CO₂ using appropriate precursors and reaction procedures on various substrates including planar or patterned wafers with or without barrier layers.^{7–11} Cu metallization in supercritical CO₂ has received the most attention and studies to determine the efficacy of different precursors,¹¹ the influence of different reducing agents,¹² and conformality of deposition in high aspect ratio features^{10,13} have been carried out.

While the utility of SFD process has been well-demonstrated, the kinetics and reaction mechanism of the process have not previously been investigated. Knowledge of the reaction mechanism, and especially a rate expression to correlate film growth rate to system variables, is important for system design and optimization. In a recent conference proceeding, we reported the influence of temperature and precursor concentration on copper deposition by hydrogen-assisted reduction of (2,2,7-trimethyloctane-3,5-dionato)-

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copper(II) in supercritical CO₂¹⁴ onto CVD TiN-coated Si substrates. Our preliminary data indicated a zero-order dependence on precursor concentration for SFD deposition at 250 °C with precursor loadings between 0.016 wt % and 0.38 wt %. This zero-order concentration dependence suggests two possible rate-determining steps: surface reaction or byproduct desorption. Zero-order kinetics also favors good step coverage, as the deposition rate can be kept constant even as the precursor concentration profile evolves along the high aspect ratio features.

Here, we extend the study to a broader precursor concentration range and deposition temperatures. We also examine the influence of hydrogen concentration and byproduct concentration on the film growth rate. The ultimate goal of the study is to further understand the reaction chemistry, to propose elementary reaction steps for SFD, to identify the rate-determining step, and to develop a proper rate expression to represent the experiment results.

Experimental Section

Bis(2,2,7-trimethyloctane-3,5-dionato)copper(II), [Cu(tmod)₂], and 2,2,7-trimethyloctane-3,5-dione, [tmodH], were obtained from Epichem, Inc. (Allentown, PA) and used as received. H₂ (ultra-high-purity grade) and CO₂ (Coleman grade) were obtained from Merriam Graves Corp. (Charlestown, NH).

The deposition reactions were carried out in a high pressure, stainless steel differential cold wall batch reactor.¹⁴ The reactor assembly consists of opposed flanges sealed with a Buna O-ring. A 19 mm diameter by 25.4 mm height aluminum stage heated with three internal cartridge heaters (Omega Engineering Inc.) is secured inside the reactor. Depositions for the kinetic study were carried out in batch mode at low precursor concentration conversion (less than 10% for all cases).

In a typical experiment, a 12 mm × 12 mm CVD TiN-coated Si substrate was mounted on the stage. A known mass of precursor was loaded into the reactor before the reactor was sealed. Low-pressure CO₂ was used to flush the reactor while the reactor wall was heated to 60 °C. Supercritical CO₂ was then loaded into the reactor at a pressure between 100 and 138 bar depending on the deposition temperature. The system was maintained at these conditions for 1 h to ensure that the precursor was completely dissolved in the supercritical solution. Three samples of the reactant solutions were collected using high-pressure sample loop with known volume (Valco Instruments Inc.) to determine precursor concentration. Prior to deposition, a known quantity of hydrogen was loaded into the reactor through a high-pressure manifold. Deposition was then initiated by heating the stage. The deposition temperatures for this study were between 220 °C and 270 °C. The stage reached the set point within 40 s. The overall reaction time was 5 min. After the power to the heater was cut, the stage temperature dropped below 200 °C within 10 s, which virtually stops the copper deposition. Two samples of the fluid phase were collected during stage cooling for analysis. All fluid samples were analyzed by UV-Vis spectrometry to obtain precursor concentration before and after deposition. Complete dissolution of the precursor prior to the deposition was verified by measurements of constant fluid-phase concentration. After the deposition, copious quantities of supercritical CO₂ were used to purge the reactor to remove the remaining precursor and any byproduct. The effluent was passed through an activated carbon bed before venting to the atmosphere.

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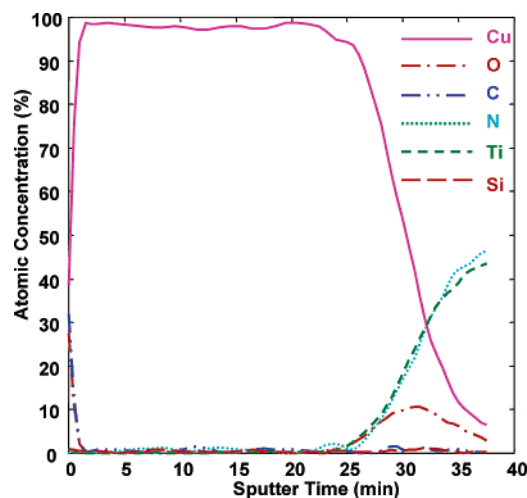
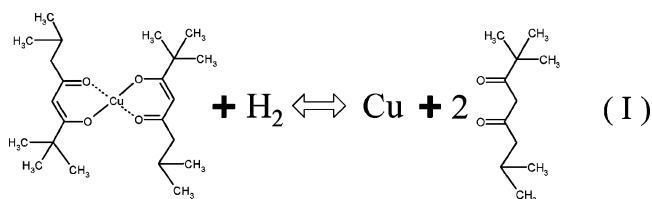


Figure 1. XPS depth profile of a Cu film deposited by the hydrogen-assisted reduction of Cu(tmod)₂ in supercritical carbon dioxide at 250 °C, 207 bar, and reagent concentrations of 0.12 wt % Cu(tmod)₂ and 0.1 wt % H₂.

The deposited copper films were analyzed by several techniques. Film thickness was measured using a surface profiler (Sloan Dektak³ surface profiler). Film growth rate was calculated by dividing the film thickness by the reaction time. Film sheet resistance was measured by using a four-point probe (Jandel Engineering Limited) and calculated using the film thickness information. X-ray photoelectron spectroscopy (XPS) (Quantum 2000 Scanning ESCA Microprobe (Physical Electronics USA)) was used to obtain the film composition at the surface and throughout the bulk film. The instrument used monochromatic Al K α X-ray source (1486.6 eV) and was equipped with an Ar⁺ ion-sputtering gun. The X-ray setting was 15 kV, 25 W with 100 μ m beam size. The takeoff angle was set at 45°. The ion gun sputtering setting was 1 kV, 700 nA, with a 1 mm × 1 mm crater dimension, which resulted in an \sim 4 nm/min sputtering rate for the Cu film. The XPS raw data were analyzed using Multipak (version 6.1A, Physical Electronics USA).

Results and Discussion

The overall Cu deposition chemistry in supercritical CO₂ for the study can be written as



NMR analysis confirmed the presence of the hydrogenated ligand byproduct. No ligand decomposition was detected at the reaction conditions used.

The solubility of Cu(tmod)₂ is as high as 3.5 wt %, measured by using a recirculating equilibrium system, at modest temperature and density (50 °C and 130 bar).⁴ The deposition experiments are conducted well below the expected equilibrium solubility limits.

The deposited films were high-purity copper. Figure 1 shows a typical XPS depth profile of a copper film deposited by a SFD. The analysis indicates that oxygen and carbon contamination is present at the surface only. The surface impurities are most likely due to ambient exposure after

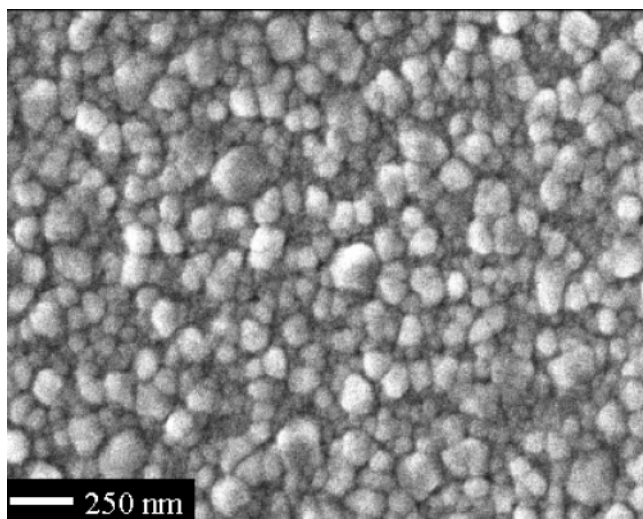


Figure 2. FE-SEM of a copper film deposited by the hydrogen-assisted reduction of $\text{Cu}(\text{tmhd})_2$ in supercritical CO_2 . (Deposition conditions: 250 °C, 207 bar, 0.12 wt % $\text{Cu}(\text{tmhd})_2$, and 0.1 wt % H_2).

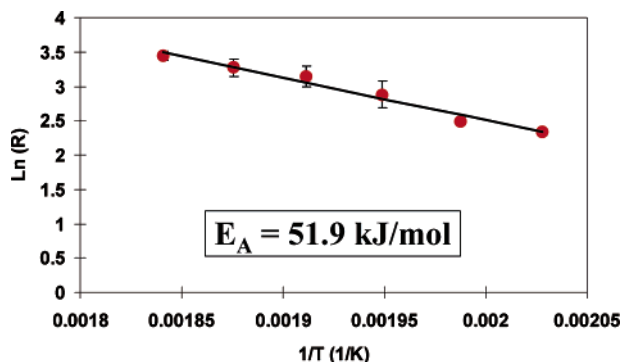


Figure 3. Temperature dependence of copper film growth rate between 220 °C and 270 °C. (Deposition conditions: 207 bar, 0.12 wt % $\text{Cu}(\text{tmhd})_2$ and 0.1 wt % H_2 .)

deposition. The oxygen signal at the Cu/substrate interface is due to the oxides of the barrier layer material (Ti oxides in this case). SEM analysis reveals a well-interconnected, spherical morphology for the Cu film, as shown in Figure 2.

A. Temperature Dependence. The temperature dependence of the film growth rate is shown in Figure 3. The minimum deposition temperature for copper film growth was about 200 °C. Film growth rates were measured at temperatures between 220 °C and 270 °C using 10 °C increments. The apparent activation energy of the overall reaction was found to be 51.9 kJ/mol. By comparison, the activation energy for metal organic chemical vapor deposition (MOCVD) using copper(II) hexafluoroacetylacetonate, $\text{Cu}(\text{hfac})_2$, has been reported to be $\sim 75\text{--}80$ kJ/mol.^{15,16} In those studies, the surface reaction was assumed to be the rate-limiting step. The activation energy calculated from data reported for MOCVD using bis(2,2,6,6-tetramethyl-3,5-heptadionato)copper(II), $\text{Cu}(\text{tmhd})_2$, was ~ 60 kJ/mol.¹⁷ Son et al. reported an activation energy of 62.8 kJ/mol for copper deposition

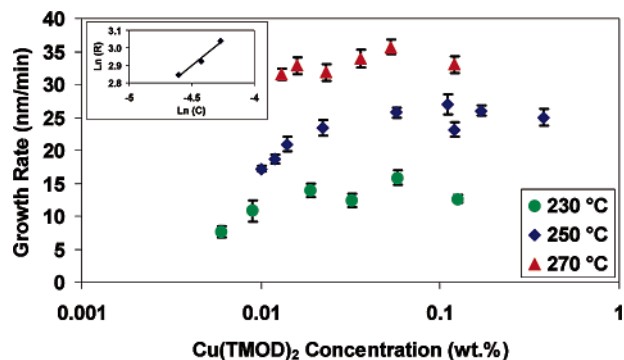


Figure 4. Film growth rate dependence on precursor concentration at 230 °C, 250 °C, and 270 °C. (Deposition conditions: 207 bar and 0.1 wt % H_2 .) The inset shows the precursor dependence at low precursor concentration and 250 °C in a log–log plot. The slope of the line is $\sim 1/2$.

from hexafluoroacetylacetonatecopper(I) allyltrimethylsilane, (hfac)Cu(ATMS), in a reaction rate-limited regime.¹⁸ Apparently, the activation energy of SFD process is slightly less than other MOCVD processes. However, this lower activation energy does not necessarily imply a different rate-determining step. We will come back to this point later.

B. Precursor Concentration Dependence. Precursor concentration dependence of the film growth rate was studied at three different temperatures, 230 °C, 250 °C, and 270 °C with excess hydrogen loading. The precursor concentration varied from 0.006 wt % to 0.38 wt %. The results are shown in Figure 4. Film growth rates at 270 °C were as high as 35 nm/min. The growth rate remained constant at each of the temperatures over a broad range of precursor concentration. Zero-order dependence suggests two possible rate-determining steps: surface reaction or byproduct desorption. This zero-order kinetics at high concentration also suggests an explanation for conformal step coverage of high aspect ratio features in SFD. In SFD, Cu films can be deposited at high precursor concentration while maintaining zero-order kinetics and, consequently, the deposition rate along the feature walls can be kept constant even if the precursor concentration decreases appreciably with depth.

When the precursor concentration is very low, typically less than ~ 0.02 wt %, film growth rate begins to exhibit a power-law type dependence on the precursor concentration. The inset in Figure 4 is a plot of the logarithm of film growth rate vs the logarithm of precursor concentration at 250 °C in the low-concentration regime. The data fall on a straight line, with a slope of $1/2$.

C. H_2 Concentration Dependence. The dependence of film growth rate on hydrogen concentration was studied at 250 °C and 207 bar using a 0.12 wt % $\text{Cu}(\text{tmhd})_2$ loading. Hydrogen was introduced into the cold wall reactor by a high-pressure manifold with a known volume. The pressures of the manifold before and after hydrogen loading were recorded. The amount of hydrogen added into the reactor was then calculated based on the volume and pressure information. Thermophysical properties of hydrogen were obtained from the National Institute of Standards and Technology database. Figure 5 shows the effect of hydrogen

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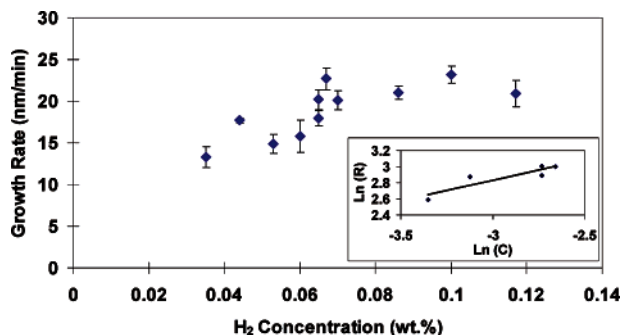


Figure 5. Film growth rate dependence on hydrogen concentration. (Deposition conditions: 250 °C, 207 bar, and 0.12 wt % $\text{Cu}(\text{tmod})_2$). The inset plot shows the H_2 concentration dependence at low hydrogen concentration in a log–log plot. The slope of the line is $1/2$.

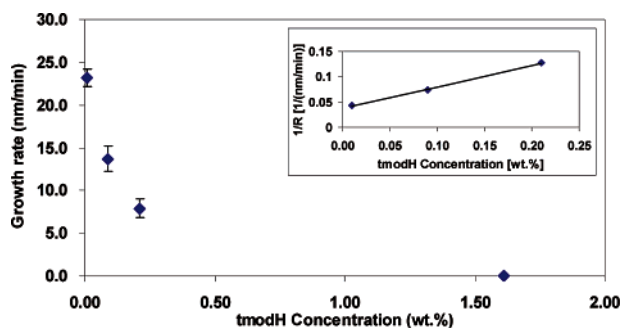


Figure 6. Film growth rate dependence on tmodH concentration. (Deposition conditions: 250 °C, 207 bar, 0.12 wt % $\text{Cu}(\text{tmod})_2$, and 0.1 wt % H_2 .) The inset is the plot of the inverse of film growth rate vs the tmodH concentration.

concentration on the film growth rate. The results indicate that hydrogen concentration affects the film growth rate in a similar manner as that of precursor concentration. When the hydrogen concentration was high, film growth rate remained at a constant value. When the H_2 concentration was below 0.07 wt %, growth rate exhibited a $1/2$ -order dependence on H_2 concentration (inset of Figure 5).

D. Byproduct Concentration Dependence. The concentration dependence of film growth rate for the reaction product tmodH was also studied. Experiments were carried out with 0.12 wt % $\text{Cu}(\text{tmod})_2$ and 0.1 wt % H_2 loading at

250 °C and 207 bar (Figure 6). The data indicate that film growth rate exhibits a negative-order dependence on tmodH concentration. At elevated tmodH concentrations film growth can be arrested completely. This negative-order dependence suggests that the surface reaction is the rate-determining step in hydrogen reduction of $\text{Cu}(\text{tmod})_2$ in supercritical CO_2 . The inverse growth rate is plotted against the tmodH concentration in the figure inset and the data fall on a straight line, which is consistent with single-site adsorption.

Mechanism and Modeling

Supercritical fluid deposition is a fundamentally new approach for metallization. The deposition process occurs on a solid surface, similar to heterogeneous catalysis and most CVD mechanisms. As shown in Figure 7, the reaction pathway of hydrogen-assisted metallization in supercritical CO_2 is assumed to go through the following steps: first, precursor and hydrogen diffuse to the substrate and adsorb onto the surface; then adjacent reactants undergo a surface reaction to liberate copper and hydrogenated ligands; finally, hydrogenated ligands desorb from the surface and diffuse into supercritical solution, leaving pure metal on the substrate surface forming conformal metal layers. This pathway is similar to that of a typical CVD process.^{19,20} As a starting point it is reasonable to assume that the SFD process has similar reaction mechanism as the CVD processes.

Mechanistic studies for metal-organic chemical vapor deposition (MOCVD) have been carried out for decades. In 1965, Van Hemert et al. studied the hydrogen-assisted CVD of Cu from $\text{Cu}(\text{hfac})_2$, and bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II), $\text{Cu}(\text{tfac})_2$, in a hot-wall, Pyrex tube reactor with two temperature-controlled zones, vaporization zone, and reduction zone.²¹ β -Diketonates, H(hfac) and H(tfac), were obtained from the reactions, respectively. The authors reported that the deposition temperature and concentration of the metal chelate affected film growth rate. However, no activation energy or detailed mechanism was discussed. Cohen et al. investigated mechanisms of copper CVD on silver from 1,5-cyclooctadiene-Cu(I)-hexafluoroacetylaceto-

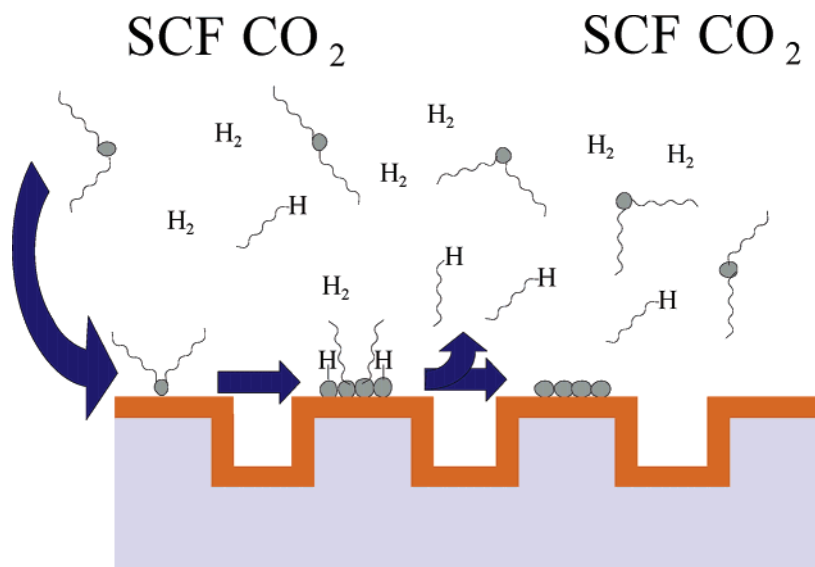


Figure 7. Schematic of the reaction mechanism for H_2 -assisted metallization in supercritical carbon dioxide.

nate, (COD)Cu(hfac) and Cu(hfac)₂, by using XPS and high-resolution electron energy loss spectroscopy (HREELS).²² The study showed that both precursors adsorbed on the Ag surface to yield Cu(I)-hfac as the intermediate. No evidence of COD ligand was found on the surface after (COD)Cu(hfac) adsorption. However, for Cu(hfac)₂ adsorption, the second hfac ligand was found to be directly bound to the Ag surface and removed by reaction with adsorbed H as a proton source to form volatile H(hfac). The authors concluded that ligand protonation is the rate-limiting step in Cu CVD from Cu(hfac)₂. Donnelly et al. studied the adsorption of Cu(hfac)₂ and hexafluoroacetylacetonate Cu(I) vinyltrimethylsilane, Cu(hfac)(vtms), on an air-exposed TiN surface (TiN(O)) by XPS and temperature-programmed desorption mass spectrometry using an ultrahigh vacuum system.²³ They found that the surface was covered by a stable monolayer of Cu^(I)(hfac) for both precursor systems. The Cu(hfac)₂-exposed TiN surface contained additional organic species, which could be the second hfac ligand or the fragments of it. The reduction of Cu^(II) to Cu^(I) occurred upon adsorption of Cu(hfac)₂ on the TiN(O) surface. The possible involvement of the second hfac ligand in the surface-mediated reduction could explain the observed ligand fragmentation. Chae et al. also studied Cu CVD from (hfac)-Cu(vtms) on a TiN surface in a hot-wall tubular reactor.²⁴ They found that the weak Cu-(vtms) bond was cleaved by heating in the gas phase. The actual metal precursor involved in the surface reaction is the intermediate Cu(hfac). Girolami et al. studied the adsorption of Cu(hfac)₂ and Cu(hfac)(vtms) on Cu(111) and Cu(100) single-crystal substrates in ultrahigh vacuum and found the only species on the surface is hfac ligand at 300 K and this surface-adsorbed hfac ligand remains stable until ~375 K, when fragmentation started to take place.²⁵

Using a cold-wall, vertical flow bell-jar reactor, Kim et al. studied copper deposition by the hydrogen reduction of Cu(hfac)₂ and proposed a mechanism for the process.¹⁵ The proposed mechanism involved surface adsorption of precursor and hydrogen, surface reaction, and desorption of byproduct. Protonation of the surface-adsorbed ligand was identified as the rate-determining step. Finally, they correlated the film growth rate to a 1/2-order dependence on both the precursor and the hydrogen concentrations. However, the authors did not include the ligand byproducts concentration dependence in the final rate expression. Inhibition from the reaction byproduct was reported by Awaya et al.²⁶ for Cu CVD via hydrogen reduction of Cu(hfac)₂. Moreover, their study revealed a negative influence on film morphology upon addition of H(hfac), probably due to metal etching. Borgharkar

et al. also proposed a reaction mechanism for hydrogen reduction of Cu(hfac)₂.²⁷ The proposed mechanism led to a Langmuir-Hinshelwood-type rate expression in which the authors proposed a first-order dependence on Cu(hfac)₂ and H(hfac) and a 1/2-order dependence on H₂. The rate-limiting step was assumed to be the surface reaction between the adsorbed H atom and hfac ligand, which had dissociated from Cu(hfac)₂.

In summary, literature studies of copper deposition via hydrogen reduction of bis(β-diketonate)copper(II) suggest that (1) Cu(I)(β-diketonate) and β-diketonate ligands are the surface-adsorbed species, (2) hydrogenated β-diketonate byproducts are formed by ligand protonation from an adjacent surface-adsorbed hydrogen atom, (3) the hydrogenated β-diketonate ligand has a negative effect on the film growth rate, and (4) the surface reaction is most likely the rate-determining step among all elementary steps. These conclusions, even though based on the studies for MOCVD processes, are consistent with our experimental findings for Cu deposition in supercritical CO₂.

For the heterogeneous reaction, a Langmuir-Hinshelwood expression is often used to model the experimental data. On the basis of our results and previous CVD studies, we propose the following reaction steps for copper deposition by hydrogen reduction of Cu(TMODO)₂ in supercritical CO₂:



in which L represents the (tmod) ligand, ⊗ and ⊕ symbolize surface-active sites for chemisorption, and A⊗ and B⊕ are the species chemisorbed on the active sites. Steps 1 and 2 represent the adsorption of precursor and 2-step dissociation of the ligands for copper formation. Step 3 is the adsorption and dissociation of hydrogen onto the surface. Step 4 represents the protonation of ligand from adjacent surface-adsorbed ligand and hydrogen atom to form volatile byproduct. Finally, in step 5, hydrogenated ligand, byproduct, desorbs and diffuses into supercritical CO₂ solution to free the surface-active sites for future reaction. Step 4 is identified as the rate-determining step, while the others are assumed to be in quasi-equilibrium. If we use k_n as the forward reaction constant for step n , K_n as the equilibrium constant of the n th step, and r_n for the reaction rate of step n , the overall reaction rate becomes

$$R = r_1 = r_2 = r_3 = \frac{r_4}{2} = \frac{r_5}{2} = \frac{1}{2}(k_4[\text{L}\otimes][\text{H}\oplus])$$

With the site balance analysis, the concentration of free sites is expressed as

$$[\otimes] = \frac{C_{\text{t}\otimes}}{\left[1 + \sqrt{\frac{K_1}{K_2}}[\text{CuL}_{2(\text{g})}] + \sqrt{K_1 K_2}[\text{CuL}_{2(\text{g})}] + \frac{1}{K_5}[\text{LH}_{(\text{g})}] \right]}$$

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and

$$[\Theta] = \frac{C_{t\Theta}}{1 + \sqrt{K_3}[\text{H}_{2(g)}]}$$

in which $C_{t\Theta}$ and $C_{t\otimes}$ are the total active sites for different adsorbed species, assumed to be constants for our case.

From steps 1, 2, and 3, the concentrations of chemisorbed ligand and hydrogen can be expressed as

$$[\text{L}\otimes] = \frac{C_{t\otimes} \sqrt{K_1 K_2} [\text{CuL}_{2(g)}]}{1 + \sqrt{\frac{K_1}{K_2}} [\text{CuL}_{2(g)}] + \sqrt{K_1 K_2} [\text{CuL}_{2(g)}] + \frac{1}{K_5} [\text{LH}_{(g)}]}$$

and

$$[\text{H}\Theta] = \frac{C_{t\Theta} \sqrt{K_3} [\text{H}_{2(g)}]}{1 + \sqrt{K_3} [\text{H}_{2(g)}]}$$

Therefore, the final overall rate expression is

$$R = \frac{C_{t\otimes} C_{t\Theta} k_4 \sqrt{K_1 K_2} K_3^{1/2} [\text{CuL}_{2(g)}]^{1/2} [\text{H}_{2(g)}]^{1/2}}{2 \cdot \left[1 + \left(\sqrt{\frac{K_1}{K_2}} + \sqrt{K_1 K_2} \right) [\text{CuL}_{2(g)}]^{1/2} + \frac{1}{K_5} [\text{LH}_{(g)}] \right] \cdot \left[1 + \sqrt{K_3} [\text{H}_{2(g)}]^{1/2} \right]}$$

The rate expression contains a $1/2$ -order dependence on Cu(tmod)₂ and H₂ concentration in both numerator and denominator, and a 1st-order dependence on the byproduct, (tmod)H, concentration in the denominator only.

The model was compared with experiment data, as shown in Figure 8, Figure 9, and Figure 10. As shown in the plots, the model predicts the effects of precursor concentration and byproduct concentration very well. The discrepancy in predicting the hydrogen concentration effect may be explained as follows: Hydrogen plays two roles during the deposition process. First, it is the reducing agent for metallization. Second, as reported previously, excess H₂ is necessary to reduce copper oxides^{11,28} formed by in situ reaction of Cu with adventitious oxidizing agents in compressed CO₂. Even though the exact amount of hydrogen consumed in the reduction of Cu oxides is uncertain, the trends in the data and the model are consistent. Accounting for the H₂ consumed by oxide reduction would shift the data to the left, in closer agreement with the model prediction.

Conclusion

The kinetics of metal deposition in supercritical carbon dioxide are reported for the first time. For copper deposition by hydrogen reduction of Cu(tmod)₂, the overall apparent activation energy of the process is 51.9 kJ/mol. The growth rate is well-represented by a Langmuir–Hinshelwood-type rate expression with precursor concentration, hydrogen concentration, and byproduct concentration as the variables. The film growth rate follows zero-order kinetics for both

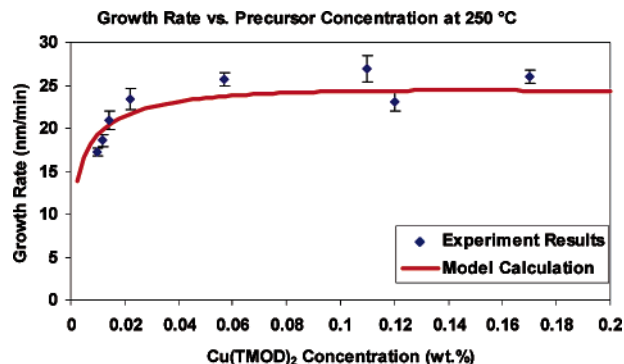


Figure 8. Comparison between model calculation and experimental results for Cu(tmod)₂ concentration dependence of the film growth rate at 250 °C.

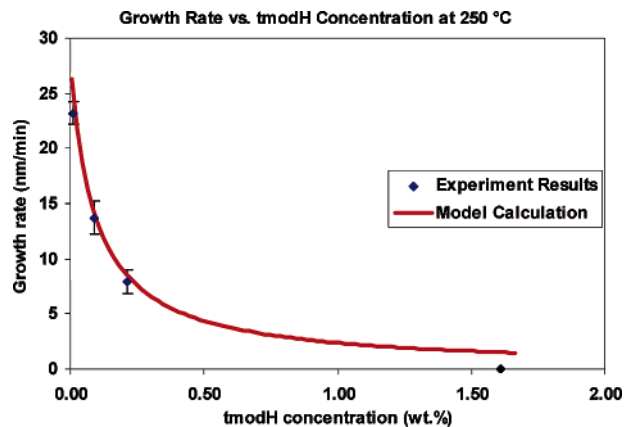


Figure 9. Comparison between model calculation and experimental results for tmodH concentration dependence of the film growth rate at 250 °C.

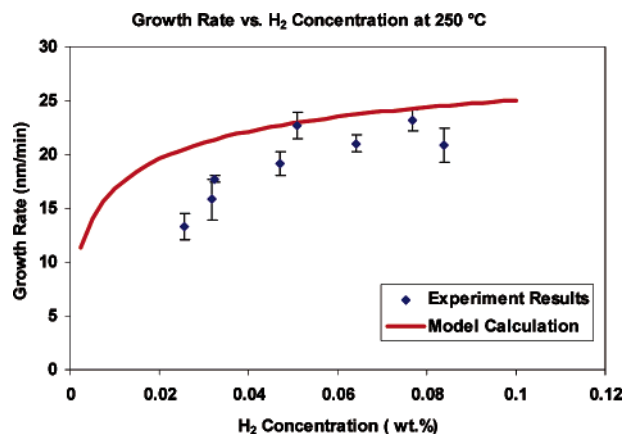


Figure 10. Comparison between model calculations and experimental results for H₂ concentration dependence of the growth rate at 250 °C.

precursor concentration and hydrogen concentration over most condition studies. When concentrations of the precursor or H₂ become very low, a $1/2$ -order dependence was observed. Product concentration exhibits a negative-order dependence on the film growth rate. The rate-determining step appears to be the surface reaction between adsorbed hydrogen atom and adsorbed (tmod) ligand dissociated from surface-adsorbed precursor.

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