Alcohol-Assisted Deposition of Copper Films from Supercritical Carbon Dioxide

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Device quality Cu films were deposited from solutions of bis(2,2,6,6-tetramethyl-3,5-heptanedionate) copper(II) [$Cu(tmhd)_2$] in supercritical CO_2 ($scCO_2$) using alcohols as reducing agents in a cold wall, high-pressure reactor. At 270 °C and pressures between 200 and 230 bar, deposition of copper by the reduction of $Cu(tmhd)_2$ with ethanol was selective for catalytic surfaces such as Co and Ni over the native oxide of Si wafers or TiN. At 300 °C and above, depositions proceeded readily on all surfaces studied. Secondary ion mass spectroscopy indicated that Cu films are remarkably pure; carbon and oxygen contamination were on the order of 0.1% or less. Resistivities of the films were approximately 2 $\mu\Omega$-cm. Reduction of $Cu(thmd)_2$ with primary alcohols including methanol, 1-propanol, and 1-butanol proceeded readily to yield copper films on Co substrates at 270 °C. Sterically hindered alcohols were less effective at the same conditions. Deposition with 2-butanol required higher alcohol concentrations while attempted depositions with 2-propanol were not successful. Reaction mechanisms consistent with these observations are discussed.

Introduction

Cu is the preferred material for interconnect structures in integrated circuits due to its low resistivity and superior electromigration resistance.[1] As device dimensions recede below 90 nm, techniques that yield high purity, void-free deposits in narrow, high aspect ratio features must be developed. Recently, we reported a new technique called chemical fluid deposition (CFD) that can satisfy these requirements.[2−4] CFD involves the chemical reduction of soluble organometallic compounds in supercritical fluids (SCFs) to yield the corresponding metals.[5] Typically, deposition is initiated upon the addition of H_2. Supercritical CO_2 ($scCO_2$) is an attractive medium for the depositions because it is nonflammable and nontoxic and has convenient critical parameters (T_c = 31 °C, P_c = 73.8 bar).[6] Moreover, CO_2 technology is under development in other applications in the microelectronic industry including photoresist drying,[7] development,[8,9] and stripping.[10−12] Nevertheless, other SCFs can be employed for CFD.[4] In addition to Cu, we have deposited Pt, Pd, Au, Ni, and other metal films using appropriate precursors and reducing agents from CO_2.[3,13−16]

The advantages of CFD over conventional deposition techniques are a consequence of the unique properties of supercritical fluids, which lie intermediate to those of liquids and gases.[6] SCFs, including carbon dioxide, can exhibit densities that approach or exceed those of liquids. Consequently, a number of organometallic compounds exhibit significant solubility in CO_2.[17,18] Precursor transport and reduction in solution in CFD offer significant advantages compared to vapor phase techniques such as chemical vapor deposition (CVD). First, precursor concentrations are several orders of magnitude greater than those used in CVD, which reduces mass transport limitations and promotes step coverage and feature fill. Second, transport in solution eliminates volatility as a precursor design constraint. For example, fluorine contamination resulting from the use of common Cu CVD precusors such as bis(1,1,1,5,5,5-hexafluoroacetylacetonate) copper(II) [$Cu(hfac)_2$] has

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Table 1. Summary of the Chemical Fluid Deposition Experiments Conducted Using $Cu(tmhd)_2$

expt	T/°C	reducing agent	wt % $Cu(tmhd)_2$ in CO_2	x_{ROH} in CO_2	ROH/ $Cu(tmhd)_2$[a]	H_2/ $Cu(tmhd)_2$[b]	P/bar	substrate	thickness Cu/nm	comment
1	270	EtOH	0.38	0.05	126	0	214	Co	265	
								Ni	265	XRD shown in Figure 1
2	270	EtOH	0.39	0.08	229	0	219	Co	400	
								SiO_2	–	no deposit
3	270	EtOH	0.33	0.11	378	0	234	Ni	255	
								TaN	–	no deposit
4	270	EtOH	0.50	0.045	71	0	221	Co	225	SIMS shown in Figure 2
5	300	EtOH	0.44	0.05	122	0	203	TaN	350	SIMS shown in Figure 3
										SEM shown in Figure 5a
6	300	EtOH	0.37	0.05	145	0	180	SiO_2	$\ll$100	Cu (220) oriented
7	300	EtOH	0.33	0.05	147	0	200	TiN	200	
8	300	H_2	0.56	0	0	95	195	TaN	255	SIMS shown in Figure 4
										SEM shown in Figure 5b
9	300	none	0.41	0	0	0	217	Co	–	control expt
								TaN	–	no film deposited
10	270	MeOH	0.41	0.07	167	0	217	Co	260	
11	270	1-PrOH	0.39	0.03	88	0	212	Co	300	XPS shown in Figure 7
12	270	2-PrOH	0.42	0.04	90	0	225	Co	–	scant deposit
13	270	2-PrOH	0.35	0.07	199	0	245	Co	–	scant deposit
14	270	1-BuOH	0.35	0.03	83	0	203	Co	200	
15	270	2-BuOH	0.35	0.03	87	0	210	Co	≤100	Cu + Cu_2O
16	270	2-BuOH	0.35	0.06	161	0	200	Co	260	reddish film
17	260	H_2 + EtOH	0.37	0.013	34	116	200	TaN	≤100	H_2 added at 260 °C
18	260	H_2 + EtOH	0.37	0.011	30	68	219	TaN	145	H_2 added at 60 °C; SIMS shown in Figure 6

[a] Molar ratio of ROH to $Cu(tmhd)_2$. [b] Molar ratio of H_2 to $Cu(tmhd)_2$.

been implicated in poor film adhesion,[19] but nonfluorinated analogues such as bis(2,2,6,6-tetramethyl-3,5-heptanedionate) copper(II) [$Cu(tmhd)_2$] are not practical alternatives due to low volatility. These considerations are eliminated in CFD. Finally, the use of $scCO_2$ as the reaction medium facilitates desorption of ligand decomposition products, which reduces their incorporation into the metal film and suppresses contamination. While precursor transport and reduction in CFD occur in solution, a supercritical reaction medium exhibits favorable transport properties, which are more akin to those of a gas. These include low viscosity, high diffusivity relative to liquids, and the absence of surface tension. Moreover, the miscibility of CO_2 with reducing agents such as H_2 or alcohols above their respective mixture critical points eliminates interphase mass transfer limitations. This combination of attributes renders CFD especially suitable for metal deposition within restricted geometries.

Previously, we and others reported the deposition of copper onto planar and etched test Si wafers by the H_2-assisted reduction of various Cu(I) and Cu(II) β-diketonates in $scCO_2$.[2–4,20] For Cu(II) β-diketonates, the reaction proceeds according to eq 1 provided that subsequent decomposition of the ligand does not occur. At temperatures of 200 °C or less, deposition using $Cu(hfac)_2$ and $Cu(tmhd)_2$ was selective for metal surfaces or catalytic seed layers over the native Si oxide. At temperatures above 225 °C, however, Cu deposited directly onto the native oxide of Si or Cu diffusion barrier layers such as TiN.

$$Cu(II)(\beta\text{-diketonate})_2 + H_2 \rightarrow Cu + 2(\beta\text{-diketone}) \quad (1)$$

In this paper, we explore the use of alcohols as reducing agents for copper deposition and compare the films produced with those films obtained using H_2. The use of alcohols as reducing agents offers a number of process advantages. For example, since the solid Cu(II)(β-diketonate)$_2$ species are soluble in the alcohols, the use of liquid feed streams for CFD is directly enabled. Moreover, the handling of high-pressure H_2 is eliminated.

Experimental Methods and Materials

Bis(2,2,6,6-tetramethyl-3,5-heptanedionate) copper(II) [$Cu(tmhd)_2$] was obtained from Strem Chemicals. Methanol [MeOH] (+99.9%, Omnisolv, EM Science), ethanol [EtOH] 200 proof (+99.5%, Aldrich), 1-propanol [1-PrOH] (+99.9%, Burdick & Jackson), 2-propanol [2-PrOH] (+99.5%, Mallinckrodt SpectrAR), 1-butanol [1-BuOH] (+99.9%, Mallinckrodt SpectrAR), and 2-butanol [2-BuOH] (+99.5%, Sigma-Aldrich) were used as received. The substrates employed were Si test wafers with and without 300 Å TiN and TaN barrier layers or 100 Å PVD Ni or Co metal surfaces deposited on Ta or TaN barrier layers (donated by Novellus Systems, Inc.). Coleman grade CO_2 (purity +99.99%) and ultrahigh purity H_2 (+99.999%) were supplied by Merrian-Graves.

Table 1 summarizes some of the deposition experiments. Depositions were carried out in an 85 mL stainless steel high-pressure cold-wall reactor described in detail previously.[2–4] Briefly, the cold wall reactor is a dual-flange high-pressure vessel containing a 2-in. diameter electrically heated stage. The inside walls of the reactor are lined with a ceramic. The temperature of the walls and the stage were controlled independently using PID controllers. Typically, the wall temperature was maintained between 60 and 100 °C using heating cartridges, and the aluminum stage was heated to temperatures ranging from 250 to 300 °C. At these conditions, depositions were selective for the heated substrates. Gas-phase nucleation or particle formation was not observed, except as noted in the case of one alcohol/hydrogen co-reduction.

All experiments were conducted in batch mode. The solid precursor and substrate(s) were loaded into the reactor, and the vessel was sealed and purged with N_2. The reactor was then heated to 60 °C, and CO_2 was loaded from a high-pressure ISCO Inc. model 500D syringe pump at 60 °C at a pressure between 110 and 120 bar. The concentration of $Cu(tmhd)_2$ in

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CO_2 was between 0.3 and 0.6 wt %, which is below its solubility limits.[2] After allowing 30 min for dissolution of the precursor, a known volume of alcohol was added to the reactor using a 6-port HPLC sample valve (Valco, Inc.) by flushing CO_2 through the sample loop (0.5 or 2 mL) at a pressure of ca. 130 bar. Quantities greater than 2 mL were introduced via multiple additions. For EtOH, concentrations of up to 0.11 mole fraction in CO_2 were studied. For the experiments with MeOH, 1-PrOH, 2-PrOH, 1-BuOH, and 2-BuOH, the mole fraction of the alcohol in CO_2 was between 0.03 and 0.07. At the concentrations and conditions used in the experiments (60 °C and 110−130 bar), CO_2 and each of the alcohols are in a single phase above the mixture critical point.[21−23] Immediately after adding the alcohol, the pedestal was heated to a specific temperature between 200 and 300 °C for 15−20 min while maintaining the walls at a lower temperature. Final pressures in the reactor for each experiment are given in Table 1. After the deposition experiments, the effluent was vented through an activated carbon bed. In selected cases, the reaction byproducts were collected for subsequent analysis by venting through a bubbler containing $CDCl_3$ located upstream of the carbon bed. During sample collection, the bubbler was immersed in an ice bath to improve the trapping efficiency for volatile species.

For reductions using both EtOH and H_2, two variations of a similar procedure were used. In the first, H_2 was added to the reactor containing a solution of $Cu(tmhd)_2$ and EtOH in CO_2 after the pedestal reached a temperature of 250−260 °C. In the second, H_2 was added into the reactor containing a solution of $Cu(tmhd)_2$ in pure CO_2 at 60 °C ($Cu(tmhd)_2$ is not reduced by H_2 at these conditions). EtOH was then added to the reactor, and the pedestal was heated to 250−260 °C. The concentration of EtOH in the EtOH/H_2 reductions was considerably lower than those for the reductions using only EtOH. In both cases, H_2 was added in excess from a high-pressure 70 mL manifold.

Samples were characterized by X-ray diffraction (XRD) using a Philips X-PERT diffractometer with a Cu Kα radiation. Selected samples were also studied by secondary ion mass spectroscopy (SIMS) (Accurel, Inc.). Field emission scanning electron microscopy (SEM) was carried out in a JEOL JSM 6320 FXV instrument. X-ray photoelectron spectroscopy (XPS) was carried out using a Quantum 2000 spectrometer (Physical Electronics) with an Al Kα source at 1486.6 eV. Atmospheric contaminants were removed from the sample by Ar^+ sputtering (3 keV). NMR spectra were recorded using a DPX300 Bruker instrument. Resistivities of the samples were measured using a four-point probe (Jandel). The thickness of the films was estimated from the weight gain of the samples after deposition assuming formation of pure copper. In selected cases, the thickness of the film was confirmed using a Dektak[3] profilometer (Veeco instruments, Inc.). Effluent analysis was also conducted with a gas-chromatograph (GC) HP 6890 series equipped with a 60/80 Carboxen 1000 column for separation of permanent gases and light hydrocarbons.

Results and Discussion

Reductions of $Cu(tmhd)_2$ in $scCO_2$ using EtOH as the reducing agent yield Cu metal films at temperatures slightly higher than those employed for H_2 reductions (Table 1). At 270 °C, Cu deposited selectively on Co and Ni PVD surfaces versus the native SiO_2, TiN, and TaN barrier layers (experiments 1−4). In comparison, depositions on Co and Ni PVD surfaces using hydrogen proceed efficiently at 175 °C. A minimum amount of EtOH, far in excess of stoichiometric requirements, was necessary for the reaction to proceed readily. For example, with a 0.4 wt % (0.0004 mol fraction) solution of $Cu(tmhd)_2$ in CO_2, a mole fraction of EtOH in CO_2 of approximately 0.05 or more was required to deposit copper on the metal surfaces. If reduction proceeds by EtOH oxidation (see below), the quantity of alcohol required represents more than a 100-fold molar excess relative to the copper precursor in most of the experiments. Figure 1 shows the XRD of a Cu film deposited from ethanol-assisted CFD of $Cu(tmhd)_2$ on a Ni PVD surface at 270 °C (experiment 1). Only reflections due to Cu apart from those of Si were identified. Reflections due to the thin Ni PVD film are not apparent in the XRD due to the very small thickness (100 Å) of this layer.

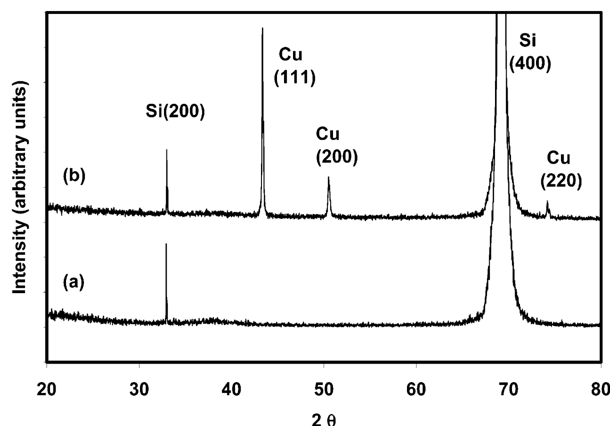

Figure 1. XRD of a Ni PVD wafer (a) before deposition and (b) after deposition of Cu by ethanol-assited CFD using a 0.38 wt % solution of $Cu(tmhd)_2$ in CO_2 at 260 °C.

The influence of EtOH concentration on the deposition was studied by increasing the concentration of ethanol up to mole fractions in CO_2 of 0.11 at 270 °C (experiments 2 and 3). At these EtOH concentrations, Cu did not deposit on SiO_2, although it deposited readily on Co and Ni. A light deposition on a TaN wafer was also observed. Additional experiments were conducted at elevated deposition temperatures up to 300 °C, while keeping the EtOH mole fraction nearly constant at 0.05. At 300 °C, highly reflective Cu films were deposited on TaN and TiN wafers (experiment 5 and 7). At the same conditions, deposition of copper on a SiO_2 substrate yielded a very thin dark-reddish film (<100 nm) that was identified by XRD as metallic Cu (experiment 6). At each temperature, films deposited using EtOH on the substrates other than SiO_2 were bright, reflective, and homogeneous. Control experiments using solutions of $Cu(tmhd)_2$ in CO_2 without adding ethanol or other reducing agent (experiment 9) confirmed that copper is not deposited on Co or TaN surfaces by thermal decomposition of $Cu(tmhd)_2$ in neat CO_2, even at 300 °C. Thus, EtOH must play a role in the reduction mechanism.

SIMS data for a copper film deposited at 270 °C on a Co substrate from a solution of $Cu(tmhd)_2$ in CO_2 using EtOH as the reducing agent are shown in Figure 2 (experiment 4). Oxygen concentration in the bulk of the sample is lower than 0.3 at. %, and carbon contamination is nearly 1 order of magnitude lower than oxygen.

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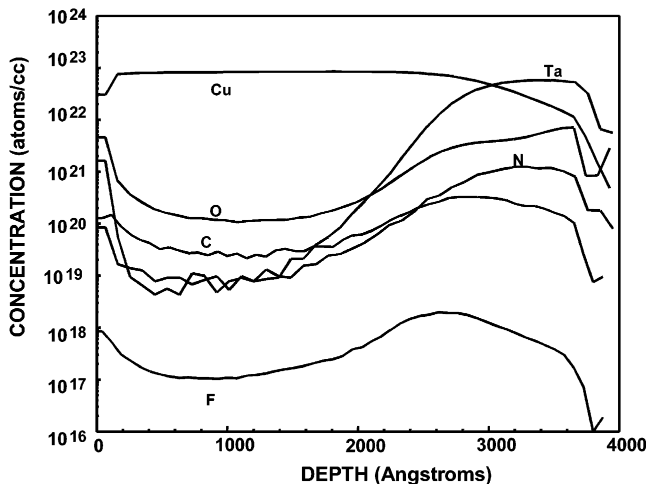

Figure 2. SIMS data for a copper film deposited by ethanol-assisted chemical fluid deposition using a 0.50 wt % solution of $Cu(tmhd)_2$ in CO_2 at 270 °C on a Co/Ta substrate.

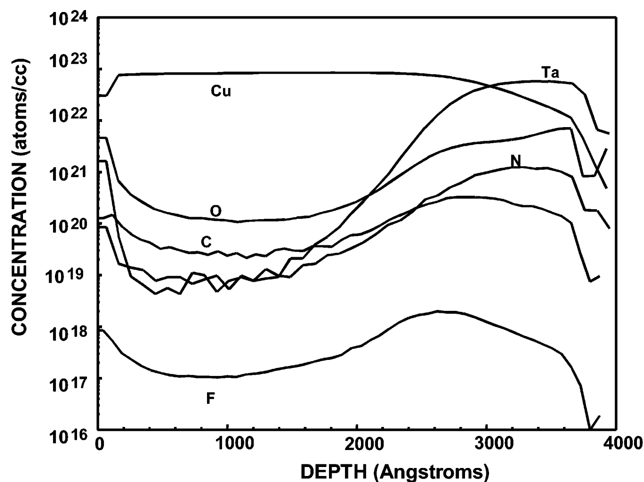

Figure 3. SIMS data for a copper film deposited by ethanol-assisted chemical fluid deposition using a 0.44 wt % solution of $Cu(tmhd)_2$ in CO_2 at 300 °C on a TaN substrate.

SIMS data for Cu films deposited at 300 °C on TaN wafers from solutions of $Cu(tmhd)_2$ in CO_2 using either EtOH or H_2 are shown in Figures 3 and 4, respectively (experiments 5 and 8). SIMS analysis revealed that oxygen and carbon concentrations in the samples deposited at 300 °C using EtOH are on the order of 0.1% or less. At the same temperature, the film deposited using H_2 showed oxygen and carbon concentrations an order of magnitude lower. Comparison of Figures 2 and 3 shows that the purity of the samples deposited using EtOH at 270 and 300 °C is very similar. Although at 300 °C the oxygen and carbon content of the sample deposited with H_2 (Figure 4) seems to be slightly lower than in the alcohol-assisted experiment (Figure 3), either route yields remarkably pure films in comparison to films produced by CVD or electrochemical depositions. Even for the samples deposited via CFD using ethanol, the level of carbon contamination does not appear to have an appreciable effect on the resistivity of the films. In fact, the resistivity of the CFD films deposited at temperatures between 260 and 300 °C using $Cu(tmhd)_2$ and ethanol are very similar to those of the films deposited using H_2 ($\sim$2.0 $\mu\Omega$-cm), which easily meets the integration requirements specified by

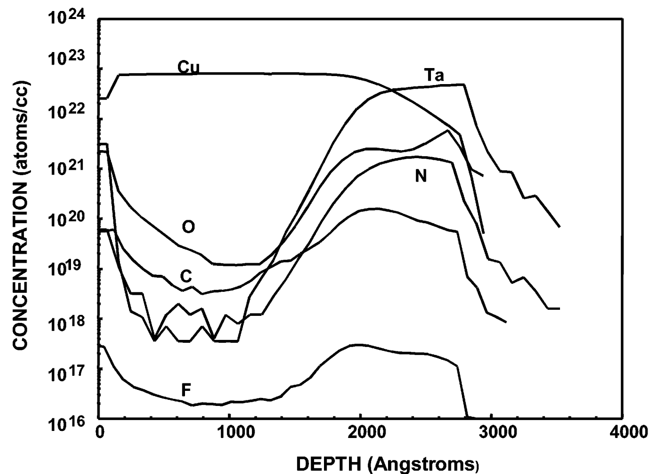

Figure 4. SIMS data for a copper film deposited by H_2-assisted chemical fluid deposition using a 0.56 wt % solution of $Cu(tmhd)_2$ in CO_2 at 300 °C on a TaN substrate.

the Semiconductor Industry Association for interconnect structures.[24] Consequently, EtOH is an effective reducing agent for producing device-quality films.

The morphologies of the films deposited using H_2 and EtOH are similar. Figure 5 shows SEM images of samples deposited at 300 °C on TaN wafers using (a) EtOH (experiment 5) and (b) H_2 (experiment 8) as reducing agents. In both cases, the films are composed of large facetted grains. The large grain size may be a result of the high deposition temperature, which effectively provides in situ annealing. With the exception of the thin film deposited on SiO_2 at 300 °C, which is oriented the (220) direction, none of the films showed preferential orientation.

A few experiments were also carried out using both EtOH and H_2 to deposit Cu on TaN wafers at 260 °C. In these cases, the amount of alcohol used was much lower than in the ethanol-assisted experiments. The quality of the films varied depending on the conditions and sequence of EtOH and H_2 addition. Thick and comparatively rough films were obtained when H_2 was added to the reactor at 60 °C (experiment 18). Figure 6 shows SIMS analysis of a Cu film deposited at 260 °C on a TaN wafer from a solution of $Cu(tmhd)_2$ in CO_2/H_2 adding EtOH (experiment 18). Data show oxygen and carbon contents of the samples as low as 0.8 and 0.1 atomic %, respectively. These values are slightly higher than those of the film deposited by ethanol-assisted CFD of $Cu(tmhd)_2$ at 270 °C on cobalt (shown in Figure 2), but still remarkably low. When H_2 was introduced to the reactor containing CO_2, the precursor, and alcohol, after the pedestal was preheated to 260 °C (experiment 17), the deposited films were comparatively thinner. This could be due to a decrease in stability of $Cu(tmhd)_2$ in the alcohol/CO_2 solution (see below) resulting in gas-phase nucleation upon H_2 addition. Gas-phase nucleation is not observed when H_2 alone is used as a reducing agent at equivalent conditions. A reduction of the deposition temperature for copper CVD using hydrogen in the presence of alcohols has been previously reported. For example, Cho et al.[25] found a significant reduction in the processing temperature and a marked

(24) The International Technology Roadmap for Semiconductors, ITRS, 2001, http://public.itrs.net/.

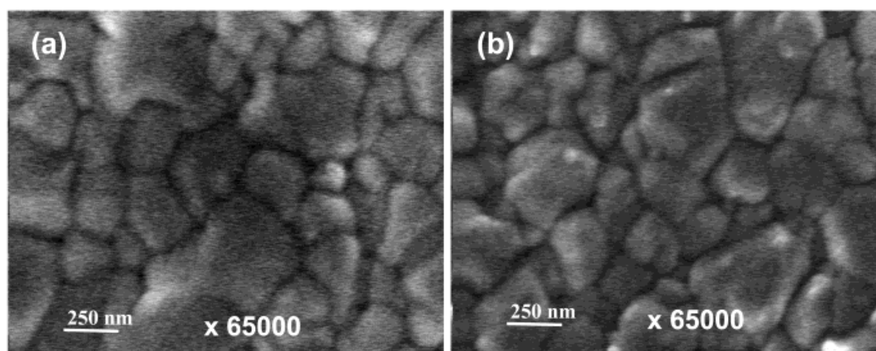

Figure 5. SEM images of copper films deposited onto TaN substrates by chemical fluid deposition using solutions of $Cu(tmhd)_2$ in CO_2 at 300 °C reduced with (a) ethanol and (b) H_2.

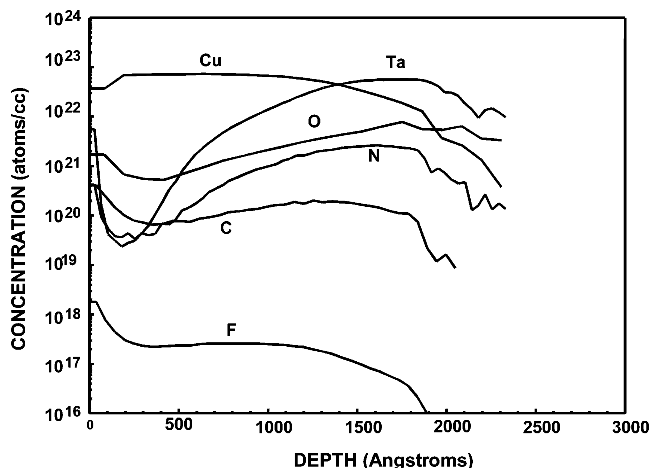

Figure 6. SIMS data for a copper film deposited by chemical fluid deposition by addition of H_2 and EtOH to a 0.37 wt % solution of $Cu(tmhd)_2$ in CO_2 at 260 °C on a TaN substrate.

improvement in the growth rate and quality of copper when 2-propanol, methanol or isobutanol were used as co-reactants with $Cu(hfac)_2$ and H_2.

The precise pathway for the EtOH-assisted reductions of $Cu(tmhd)_2$ is not known, but our experiments indicate that the oxidation of EtOH is involved. The reaction byproducts of the ethanol-assisted CFD of $Cu(tmhd)_2$ at 270 °C on Co and at 300 °C on TiN substrates were trapped in $CDCl_3$ and examined by NMR. Apart from a very large concentration of ethanol present in the effluent, ^1H NMR showed the distinctive presence of small quantities of acetaldehyde (9.71 ppm (quadruplet); 2.15 ppm (singlet)). The analysis also revealed the presence of the hydrogenated ligand, 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) (5.67 ppm). The other expected resonance of the Htmhd ligand (at 1.10 ppm) is obscured by the EtOH reasonances. Other minor peaks were observed but not identified. GC analysis of the effluent revealed the presence of a trace amount of H_2.

The dehydrogentation of alcohols over copper is well documented.[26–32] Iwasa and Takezawa[29] studied the dehydrogenation of ethanol to acetaldehyde over copper based catalysts. Other reaction byproducts such as ethyl acetate, acetic acid, and C_4-species (butyraldehyde, 1-butanol, and methylethyl ketone) were also identified. Byproduct composition was greatly influenced by the support. Basic supports such as silica favor dehydrogenation versus dehydration reactions. Selectivity of the reaction also depends on the ensemble size of the supported metal.[28,30] Studies on the dehydrogenation reaction of methanol, 2-propanol, and 2-butanol have been also reported.[27,31,32] Other supported metals such as Co and Ni are also active for the catalytic dehydrogenation of alcohols, although with higher activation energies.[26]

Alcohols have been previously used in copper CVD to enhance the deposition rate.[1] This enhancement is partly due to improved delivery. The high solubility of Cu(II)(β-diketonate)$_2$ in alcohols has been used in CVD to develop a simple liquid delivery system which provides highly accurate, reproducible, and controllable flow.[33–36] Furthermore, many Cu(II)(β-diketonate)$_2$ species such as $Cu(hfac)_2$ coordinate reversibly to alcohols and form adducts.[37,38] Some of these adducts have higher vapor pressures and lower melting points than the corresponding Cu(II)(β-diketonate)$_2$,[39,40] rendering them better precursors for CVD. Apart from the improved transport, alcohols, introduced in the system as solvents or additives, or coordinated to the precursor in an adduct, can act as reducing agents. This role has been proposed in both photochemical[41] and thermal

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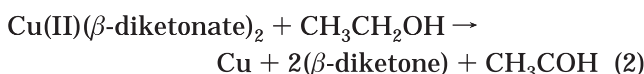
activated copper CVD.[40,42] Houle et al.[41] showed that carbon contamination in films grown by photolitic decomposition of $Cu(hfac)_2$ using ultraviolet light was greatly reduced when the corresponding ethanolate was used. They proposed a radical mechanism in which the alcohol provided a hydrogen radical for combination with hexafluoroacetylacetonyl radical. More recently, Maverick et al.[40] reported the thermal CVD of copper from the self-reduction of adducts of $Cu(hfac)_2$ with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. Deposition of Cu occurred as a result of the reduction of the metal center by the alcohols, which were oxidized to the corresponding carbonyl compounds. In other CVD experiments, however, alcohols have been used along with other reducing agents such as H_2.[25,42] The role of the alcohol in this case seems to be catalytic.[42] An enhanced nucleation rate of copper and reduced substrate temperature required to deposit copper have been reported.[25]

The effect of alcohols on the decomposition of several organometallic compounds under supercritical conditions has been also studied. Mhamdi et al.[43] showed that the decomposition temperature of $Cu(hfac)_2$ in $scCO_2$ was reduced 70 °C in $scCO_2$/EtOH solution (from 230 °C in $scCO_2$ to 160 °C in $scCO_2$/EtOH at $x_{EtOH} = 0.15-0.25$). More recently, Cansell's group exploited the use of $scCO_2$/EtOH mixtures ($x_{EtOH} = 0.2$) as a reaction medium to decompose $Cu(hfac)_2{\cdot}H_2O$ and produce submicron metal particles.[44-47] In none of these cases, however, has the role of the alcohol in the deposition mechanism been firmly established.

Our results indicate that alcohols assist the reduction of $Cu(tmhd)_2$ during CFD, which is in line with previous CVD experiments.[25,42] Formally, the overall reaction of $Cu(II)(\beta\text{-diketonate})_2$ with EtOH may proceed through eq 2.



$$Cu(II)(\beta\text{-diketonate})_2 + CH_3CH_2OH \rightarrow Cu + 2(\beta\text{-diketone}) + CH_3COH \quad (2)$$

Again, the particular details of the surface reaction are unknown. One possibility is that the alcohol oxidizes to the aldehyde on the surface to produce hydrogen[26,28-30] which is then used to reduce $Cu(tmhd)_2$ according to eq 1. Another possibility involves the formation of the adduct of ethanol and $Cu(tmhd)_2$ as a reaction intermediate that could self-reduce to deposit copper. Although no such species has been detected in this work, there is strong evidence of coordination of ethanol to other $Cu(II)(\beta\text{-diketonate})_2$ species in the literature.[37,38]

Finally, deposition experiments were carried out using a series of alcohols (MeOH, 1-PrOH, 2-PrOH, 1-BuOH, and 2-BuOH) at equivalent deposition conditions, precursor concentrations, and alcohol loadings

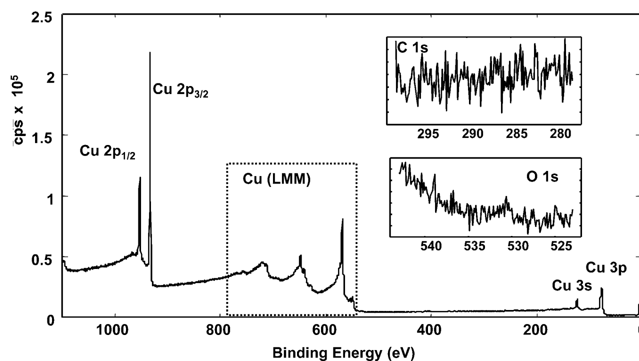


Figure 7. XPS survey analysis of a copper film deposited onto a Co/Ta substrate by alcohol-assisted chemical fluid deposition of a 0.39 wt % solution of $Cu(tmhd)_2$ in CO_2 at 270 °C using 1-PrOH as the reducing agent (93.90 eV pass energy). Multiplex spectra for C and O are shown as insets (29.35 eV pass energy).

(experiments 10–16). Copper films deposited readily on Co wafers at 270 °C by CFD via $Cu(tmhd)_2$ in $scCO_2$ using MeOH, 1-PrOH, and 1-BuOH as reducing agents (experiments 10, 11, and 14); however, Cu did not deposit readily when 2-PrOH or 2-BuOH was used at the same conditions (experiments 12 and 15). In experiment 15 using 2-BuOH, a very thin film composed of a mixture of Cu and Cu_2O was obtained. For the 2-PrOH and 2-BuOH experiments, the concentration of alcohol was increased further up to 4 mL (experiments 13 and 16). No films could be deposited with 2-PrOH (experiment 13); however, at this higher alcohol concentration, highly reddish and reflective copper films were deposited using 2-BuOH (experiment 16). At the conditions at which copper deposited on Co, thin inhomogeneous copper films were deposited on TaN with all of the alcohols studied except MeOH. Slight differences in the selectivity toward the metal in the copper deposition were observed for the different alcohols.

Figure 7 shows an XPS survey analysis at 45° takeoff angle of a Cu film deposited from alcohol-assisted CFD of $Cu(tmhd)_2$ on a Co wafer at 270 °C using 1-PrOH. After 1 min of Ar^+ sputtering to remove atmospheric contaminants, levels of carbon and oxygen in the film are below the instrument detection limit (showed as an inset).

The different efficiencies of the alcohols for $Cu(tmhd)_2$ reduction cannot be explained by the alcohols' susceptibility to oxidation alone. Maverick et al.[40] compared the heats of dehydrogenation, bond dissociation energies, and acidity constants of different alcohols, including those used in our experiments. In the gas phase, oxidation of 2-PrOH to acetone is less endothermic than the oxidation of MeOH, EtOH, and 1-PrOH to the corresponding aldehydes, and therefore, it is thermodynamically favored. They speculate that the cleavage of the C–H bond at the α carbon atom is the rate-determining step. The C–H bond dissociation energies and gas-phase acidity constants suggest that 2-PrOH is most susceptible to oxidation. However, our data show that the alcohol-assisted CFD of $Cu(tmhd)_2$ in $scCO_2$ using 2-PrOH at the studied temperatures and concentrations does not yield copper films. This seems to indicate that steric considerations for the interaction of the alcohol with the surface and/or with the precursor may be important. The same argument applies whether

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the alcohol and $Cu(tmhd)_2$ adsorb to the surface and then react, or the alcoholate $Cu(tmhd)_2 \cdot ROH$ is the species that adsorbs onto the surface and self-reduces. For 2-PrOH, the interaction with the metal center is sterically hindered due to the bulky *tert*-butyl groups of the ligand, and therefore, reduction may not be efficient at these conditions. A similar line of reasoning can be employed for 2-BuOH. However, in this case when the amount of alcohol added into the system is increased, highly reflective copper films were deposited. The heat of oxidation of 2-BuOH is very similar to 2-PrOH,[48] but in the gas phase, 2-BuOH appears to be more acidic[49] as a consequence of the larger induced polarization of the longer alkyl chain. This could explain the difference between the sterically hindered alcohols. It is possible that 2-PrOH could serve as a reducing agent for other β-diketonate compounds with less severe steric constraints.

(48) Calculated using heats of formation taken from the compilation of data given by NIST (http://webbook.nist.gov/).

(49) Gas-phase acidity defined as ΔG for $ROH(g) \Rightarrow RO^-(g) + H^+(g)$ taken from the compilation of data given by NIST (http://webbook.nist.gov/).

Conclusions

Device quality Cu films were deposited by chemical fluid deposition (CFD) via $Cu(tmhd)_2$ solutions in $scCO_2$ using alcohols as reducing agents. At 270 °C and pressures between 200 and 230 bar, the depositions were selective for Co and Ni PVD surfaces over the native oxide of Si and TiN. At 300 °C and above, copper deposited readily on all the surfaces studied. Secondary alcohols were less effective than primary alcohol under the same conditions.

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