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Deposition of Cu films from supercritical fluids using Cu(I) β-diketonate precursors

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Abstract

Cu films were deposited onto planar and etched silicon substrates by the hydrogen-assisted reduction of a series of copper(I)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate)L compounds [Cu(I)(hfac)L] where L is (2-butyne), (1,5-cyclooctadiene), (vinyltrimethylsilane) or (2-methyl-1-hexene-3-yne) in supercritical solvents using a cold wall, high pressure reactor. At substrate temperatures of 225 °C and a pressure of 200 bar, H_2 reduction of Cu(I)(hfac)(2-butyne) in CO_2 yielded high purity films with exceptional step coverage in features as narrow as 100 nm with an aspect ratio of eight. Planar films deposited by H_2 reduction of each of the precursors in supercritical CO_2 and Cu(I)(hfac)(2-butyne) in supercritical C_2F_6 exhibited little carbon or oxygen contamination. Attempts to deposit high purity Cu films by the thermal disproportionation of the Cu(I)(hfac)L precursors in supercritical CO_2 in the absence of H_2 at 225 °C were unsuccessful and yielded highly oxidized Cu films in each case. Thermal disproportionation of Cu(I)(hfac)(2-butyne) in supercritical C_2F_6 also yielded poor quality films, although oxygen contamination was less severe than in CO_2.
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Keywords: Copper metallization; Chemical fluid deposition; Supercritical fluids

1. Introduction

Cu is the preferred conductor for advanced interconnect structures due to its low resistivity and superior electromigration resistance [1]. As device dimensions continue to decrease, deposition methods that provide exceptional step coverage and gap fill in sub-100-nm features while maintaining acceptable purity and resistivity will be required. We recently reported that device-quality copper films meeting these criteria can be deposited onto planar and etched silicon substrates by the reduction of soluble Cu(I) and Cu(II) β-diketonate compounds with H_2 in supercritical carbon dioxide ($scCO_2$) using a process called chemical fluid deposition (CFD). This approach affords exceptional step

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coverage and uniform filling of 100 nm wide × 800 nm deep features [2,3]. In this paper we examine the role of H_2 in depositions from Cu(I) precursors of the type copper(I)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate)L compounds [Cu(I)(hfac)L] where L is (2-butyne), (1,5-cyclooctadiene), (vinyltrimethylsilane) or (2-methyl-1-hexene-3-yne) (Fig. 1). These compounds can yield copper films by chemical vapor deposition (CVD) in the absence of H_2 via a thermal disproportionation reaction [1]. We compare depositions from supercritical fluids with and without H_2 as the reducing agent.

In general, CFD involves the chemical reduction of soluble organometallic compounds in supercritical fluids (SCFs) [4]. The advantages of CFD over conventional deposition techniques are a consequence of the physicochemical properties of SCFs, which lie intermediate to those of liquids and gases. The densities of SCFs can approach or exceed those of liquids. Consequently, many organometallic compounds exhibit significant solubility in $scCO_2$ and other fluids [2,3]. Due to the solubility of the metal precursors, concentrations in CFD are similar to those employed in liquid techniques and several orders of magnitude higher that those used in CVD. Moreover, $scCO_2$ is an excellent solvent for the ligand decomposition products, which facilitates their desorption and therefore reduces film contamination. Although CFD is a solution-based technique, the transport properties of $scCO_2$ (low viscosity and high diffusivity relative to liquids), the absence of surface tension, and its miscibility with gaseous reducing agents such as H_2 mitigate mass transfer limitations and facilitate conformal coverage. Consequently, CFD is especially well-suited for metal deposition in high aspect ratio features.

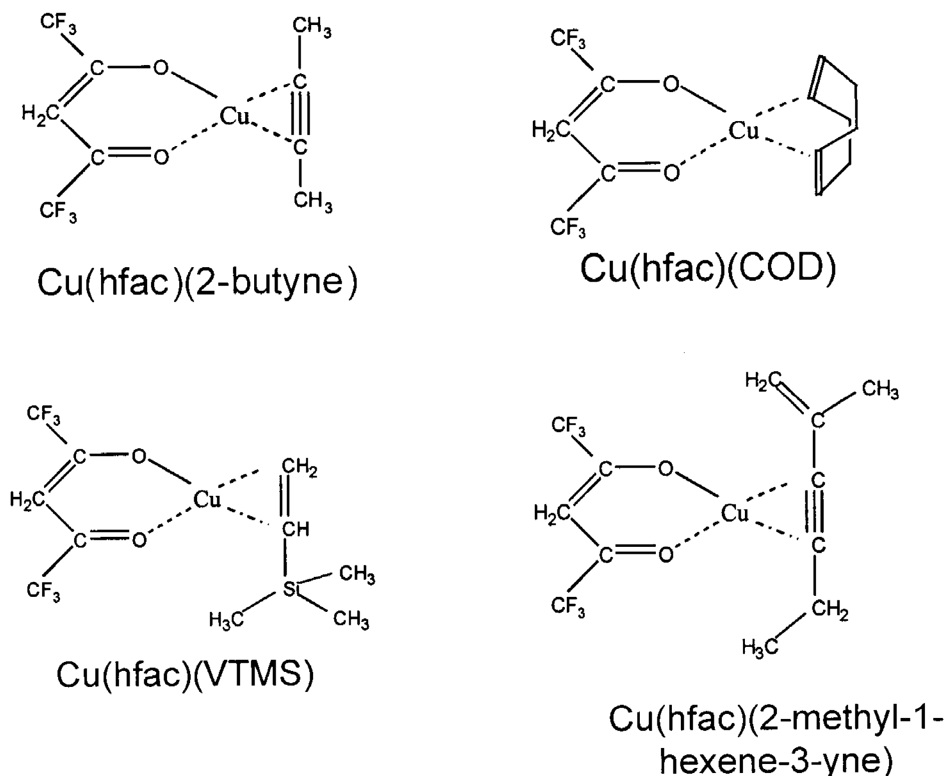


Fig. 1. Cu(I)(hfac)L precursors used in the chemical fluid deposition experiments.

To date we have deposited Cu, Pt, Pd, Au, Ni and other metal films from $scCO_2$ using appropriate precursors [2,3,5–8]. In each case deposition was initiated upon the addition of H_2. $scCO_2$ has been used in most of the experiments because it is widely available, nonflammable, nontoxic, inexpensive and it has convenient critical parameters ($T_C = 30.98$ °C, $P_C = 73.8$ bar) [9]. It is also completely miscible with H_2. While CO_2 is perhaps the best choice for a SCF deposition medium for most applications, other fluids can be used. We provide an example that involves depositions in supercritical hexafluoroethane (scC_2F_6) which also exhibits accessible critical parameters ($T_C = 19.85$ °C, $P_C = 30.6$ bar) [9].

2. Experimental

The precursors Cu(I)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate)(2-butyne) [Cu(I)(hfac)(2-butyne)], Cu(I)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate)(1,5-cyclooctadiene) [Cu(I)(hfac)(COD)] and Cu(I)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate) (vinyltrimethylsilane) [Cu(I)(hfac)(VTMS)] were obtained from Gelest. Cu(I) (1,1,1,5,5,5-hexafluoroacetylacetonate) (2-methyl-1-hexene-3-yne) [Cu(I)(hfac)(2-methyl-1-hexene-3-yne)] was obtained from ADCS. All chemicals were used as obtained without further purification. Carbon dioxide (Coleman grade, 99.99 + % purity), hexafluoroethane (99.95 + % purity) and ultra-high-purity hydrogen (99.999 + %) were obtained from Merrian-Graves and used as received. Test wafers were donated by Novellus Systems.

All the compounds except [Cu(I)(hfac)(COD)] were handled in a glove box. Depositions were carried out on (100) Si test wafers either directly on the native oxide or on a 300 Å TiN barrier layer. Prior to the deposition, the wafers were sonicated in toluene and acetone and dried in a convection oven. Deposition experiments were conducted using an 80-ml stainless-steel high-pressure cold-wall reactor described previously [2,3]. The cold wall reactor is a dual-flange, high-pressure vessel with an internal resistively heated stage. The reactor is lined with PTFE. The temperature of the walls (60 °C) and the stage (225 °C) are controlled independently using PID controllers. In all cases, deposition occurred only on the heated stage. The experiments were conducted in batch mode. For depositions using Cu(I)(hfac)(2-butyne) and Cu(I)(hfac)(COD), which are solids at ambient conditions, the precursor and substrate were loaded into the reactor and the vessel was sealed and purged with N_2. Then the reactor was heated at 60 °C and CO_2 was loaded from a high-pressure syringe pump (ISCO, Model 500D), which was maintained at the same temperature, up to a pressure of 117–124 bar. After precursor dissolution, the pedestal was heated up to 225 °C, while maintaining the walls at 60 °C. Local heating of the CO_2 caused a pressure increase to 180–225 bar. For the H_2 assisted reduction experiments, H_2 was added in excess from a 70-ml manifold via pressure-drop when the temperature of the stage reached 225 °C. The H_2 to precursor molar ratio was between 30 and 40. In every case, the stage was heated for 1.5 h. After the deposition experiments, the effluent was vented through an activated carbon bed. For depositions using Cu(I)(hfac)(VTMS) and Cu(I)(hfac)(2-methyl-1-hexene-3-yne), which are liquids, a 6-port HPLC sample valve (Valco) was used to introduce the precursor to the reactor using sample loops of 0.100 or 0.250 ml filled previously within a glove box. Initial precursor concentrations for the depositions ranged between 0.4 and 1.0 wt.% in CO_2.

For the experiments using scC_2F_6, the fluid was loaded at 60 °C and 52 bar into the reactor. At these conditions, the density of C_2F_6 is 0.448 g cm^{-3} (calculated using the Peng–Robinson equation of state [10]). This value is very close to the density of CO_2 at the loading conditions (0.465 g cm^{-3}

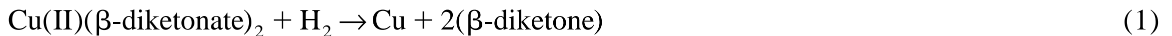
at 60 °C and 124 bar [11]) used in previous depositions. A 30-ml high-pressure manifold was used to transfer the fluid into the cold wall reactor. The amount of C_2F_6 added into the cold wall reactor was measured from weight difference of the manifold. The concentration of Cu(I)(hfac)(2-butyne) in C_2F_6 was between 0.3 and 0.4 wt.%.

Primary characterization of the samples was carried out by X-ray diffraction (XRD) using a Philips X-Pert diffractometer with CuKα radiation. Identification of the films was carried out by comparison of the XRD patterns with the JCPDS database. Selected samples were also studied by secondary ion mass spectroscopy (SIMS) (Accurel). Focused ion beam scanning electron microscopy (FIB-SEM) analysis was carried out by Accurel.

3. Results and discussion

Cu films have been deposited onto Si test wafers via the H_2 assisted reduction of a number of Cu(I) and Cu(II) β-diketonates in $scCO_2$ including Bis(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate) copper (II) [$Cu(hfac)_2$], Bis(2,2,6,6-tetramethyl-2,4-heptanedionate) copper (II) [$Cu(tmhd)_2$], Cu(I)(hfac)(2-butyne) and Cu(I)(hfac)(COD) [2,3]. Here we report new results for depositions from Cu(I)(hfac)(VTMS) and Cu(I)(hfac)(2-methyl-1-hexene-3-yne) in $scCO_2$. In each case reduction was initiated by the addition of H_2 to the solution. At temperatures of 200 °C or less deposition was selective for metal surfaces or catalytic seed layers over the bare Si oxide. At temperatures above 225 °C, Cu deposited directed onto the native oxide of Si or Cu diffusion barrier layers such as TiN. An example of the excellent gap fill obtained using CFD is provided in Fig. 2.

Cu deposition from Cu(II)(β-diketonate)$_2$ precursors requires the addition of H_2 as reducing agent



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

By contrast, deposition from precursors of the type Cu(I)(β-diketonate)L_n by CVD can proceed by an alternative mechanism, thermal disproportionation, in the absence of H_2 [1]

$$2\text{Cu(I)}(\beta\text{-diketonate})\text{L}_n \rightarrow \text{Cu} + \text{Cu(II)}(\beta\text{-diketonate})_2 + 2\ n\text{L} \quad (2)$$

Since both Cu and Cu(II)(β-diketonate)$_2$ are products of the disproportionation, the maximum Cu yield of this reaction is 50%. The addition of H_2 resolves this issue, because the Cu(II)(β-diketonate)$_2$ generated in reaction (2) can further react according to (1). We examine the utility of thermal disproportionation for Cu deposition via CFD in the absence H_2 and compare these results to H_2 assisted reductions.

Each attempt to prepare Cu films by thermal disproportionation of Cu(I)(hfac)(2-butyne)/CO_2 solutions on a TiN wafer at 225 °C in the absence of H_2 yielded dark films of poor quality. XRD of the film revealed the presence Cu_2O. The same result was obtained on a bare Si wafer. However, when H_2 was added to the system, a bright, reflective copper film was obtained. XRD confirmed the presence of pure Cu (Fig. 3). Peaks at 2Θ values of ~33 and ~69 correspond to the (200) and (400) planes of Si.

SIMS analysis of the film deposited using Cu(I)(hfac)(2-butyne) in the presence of H_2 showed fluorine contamination in the order of 2 at.% whereas carbon and oxygen concentrations were <0.5 at.%. (Fig. 4). In contrast, SIMS data of the film deposited without H_2 revealed very high oxygen

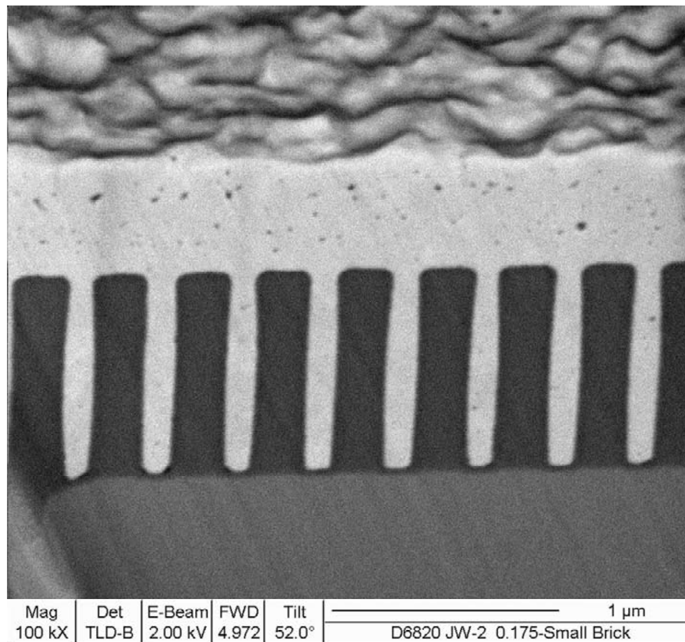


Fig. 2. FIB-SEM of a Cu film deposited from H_2 reduction of a 0.8 wt.% Cu(I)(hfac)(2-butyne) solution in CO_2 at 225 °C and 207 bar.

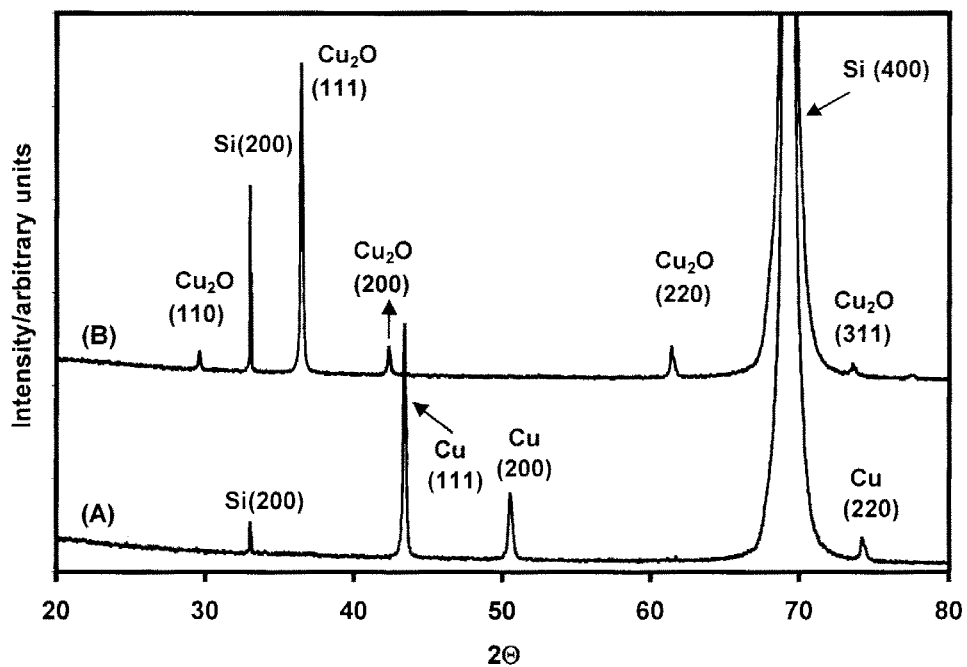


Fig. 3. XRD pattern of films deposited from Cu(I)(hfac)(2-butyne)/CO_2 solutions at 225 °C: (A) with H_2 and (B) without H_2.

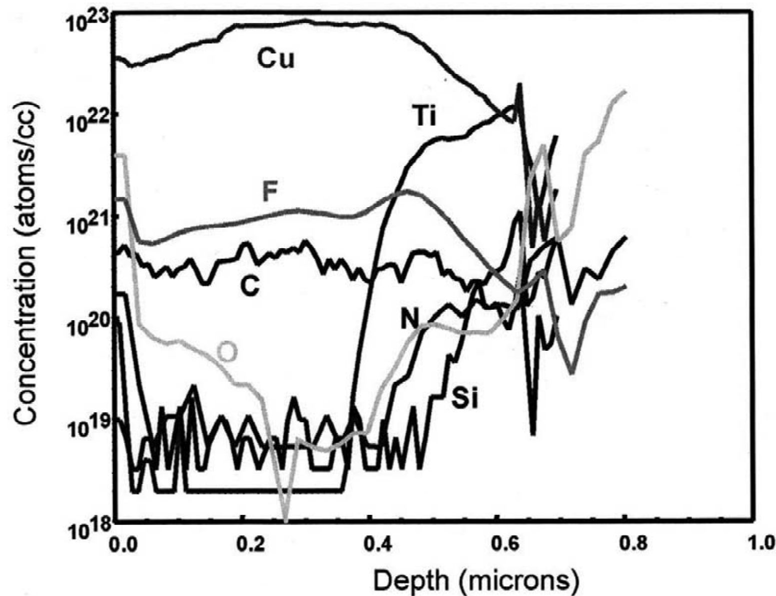


Fig. 4. SIMS analysis of a Cu film deposited from H_2 reduction of a 0.6 wt.% Cu(I)(hfac)(2-butyne) solution in CO_2 at 225 °C and 214 bar.

content. Fluorine contamination was between 6 and 8 at.% and much higher than in the films deposited with H_2. Carbon contamination of the film was <0.5 at.%.

Similar results to those obtained from Cu(I)(hfac)(2-butyne)/CO_2 solutions at 225 °C were obtained when Cu(I)(hfac)(COD), Cu(I)(hfac)(VTMS) and Cu(I)(hfac)(2-methyl-1-hexene-3-yne) were used. In every case, highly reflective Cu films were obtained from the H_2 assisted reduction of the precursors. When no H_2 was added to the system, very thin green-blue colored films were obtained. XRD of the films deposited in absence of H_2 showed weak peaks due to Cu_2O apart from those due to the Si substrate (Fig. 5). In all cases deposition efficiency under the conditions studied in the absence of H_2 was very low and very thin and poor quality films were deposited. SIMS analysis of films deposited in the presence of H_2 using Cu(I)(hfac)(COD) and Cu(I)(hfac)(VTMS) showed low carbon and fluorine contamination (<0.2 and <1 at.%, respectively) in the bulk of the film. Oxygen content varied between 1 and 2.5 at.%. When no H_2 was used in the deposition, films showed a very high oxygen content. This result is consistent with the appearance of Cu_2O in the XRD analysis. The carbon and fluorine contamination of the film was <0.1 and <1 at.%, respectively.

Deposition experiments using Cu(I)(hfac)(2-butyne) were also conducted in scC_2F_6. Significant deposition occurred on bare Si wafers but not on TiN wafers. Although most of the experiments were conducted at 225 °C, the temperature dependence of the thermal disproportionation reaction in scC_2F_6 was studied. H_2 assisted reduction in scC_2F_6 at 225 °C yielded a reflective copper colored film (Cu by XRD). The film, however, adhered poorly to the substrate and delaminated spontaneously. In contrast, at the same temperature in absence of H_2, inhomogeneous dark brown-reddish films were deposited. Fig. 6 shows XRD of films obtained in C_2F_6 with and without H_2. When reaction was conducted adding H_2, only strong and well-defined Cu reflections were observed apart from those due to Si. When the deposition was carried out without H_2, both Cu and Cu_2O phases were identified in the

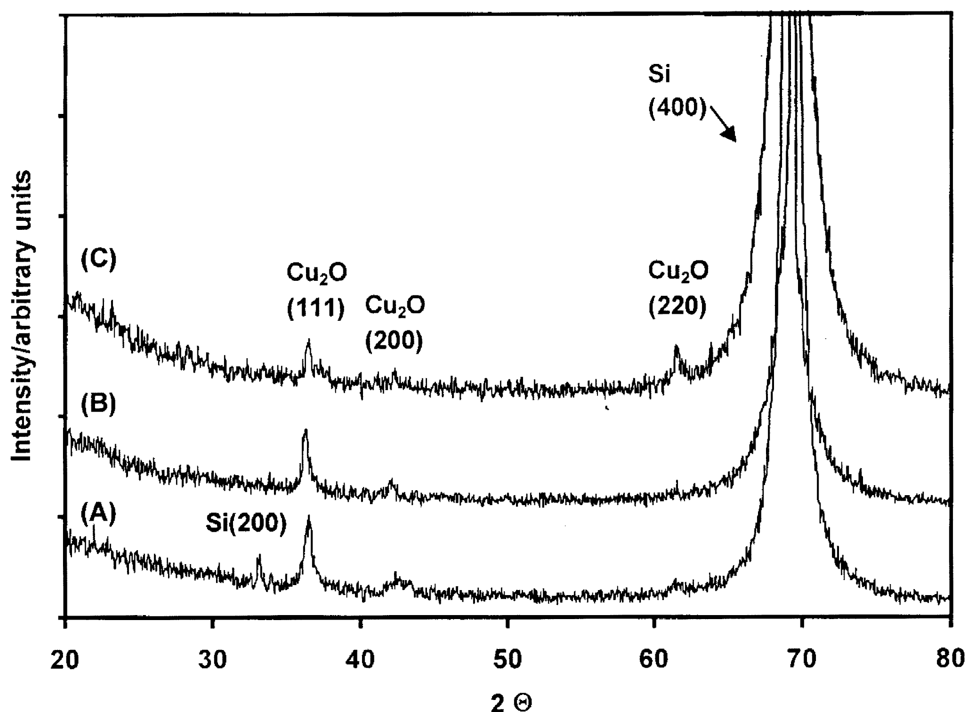


Fig. 5. XRD pattern of films deposited using Cu(I)(hfac)L/CO_2 solution without H_2 at 225 °C: (A) L=(VTMS), (B) L=(COD), (C) L=(2-methyl-1-hexene-3-yne).

XRD. The relative amount of Cu_2O to Cu increased with the deposition temperature. In the absence of H_2, formation of Cu_3Si on bare Si substrates was also observed.

The deposition of copper oxide phases by CVD has been previously reported [12]. CuO and Cu_2O can be deposited from bis(acetylacetonate) copper (II) [$Cu(acac)_2$] using oxidants such as O_2 and N_2O in the carrier gas [12–14]. However, there are also a number of examples in which formation of copper oxide phases from metal organic CVD [15] and plasma enhanced CVD [16,17] of Cu(II) β-diketonates in Ar atmosphere has been observed. The authors suggest that the decomposition of the precursor produces reactive species that oxidize Cu during deposition. Although Cu has been also deposited via thermal decomposition of $Cu(hfac)_2$ in Ar [18], the addition of H_2 facilitates deposition of high purity Cu films. The role of H_2 is twofold. It reacts with the ligand to form neutral organic compounds that desorb readily from the film surface and at the same time it suppresses the formation of copper oxides.

We have found similar results for chemical fluid deposition using Cu(I)(β-diketonate)L_n compounds. Our results show the need to add H_2 or another reducing agent to the SCF solution in order to deposit high purity copper films. The thermal decomposition of the ligand in absence of H_2 and the presence of trace impurities in the supercritical fluid seem to be responsible of the oxidation of the film. For the different Cu(I)(hfac)L compounds studied, Hhfac fragmentation may produce species that can then oxidize Cu to Cu_2O or simply react with Cu(I) to form Cu_2O.

These results are also consistent with an early attempt to deposit Cu on Si from $Cu(hfac)_2 \cdot H_2O$ in C_2F_6 solutions by Louchev et al. via thermal decomposition at very high deposition temperatures

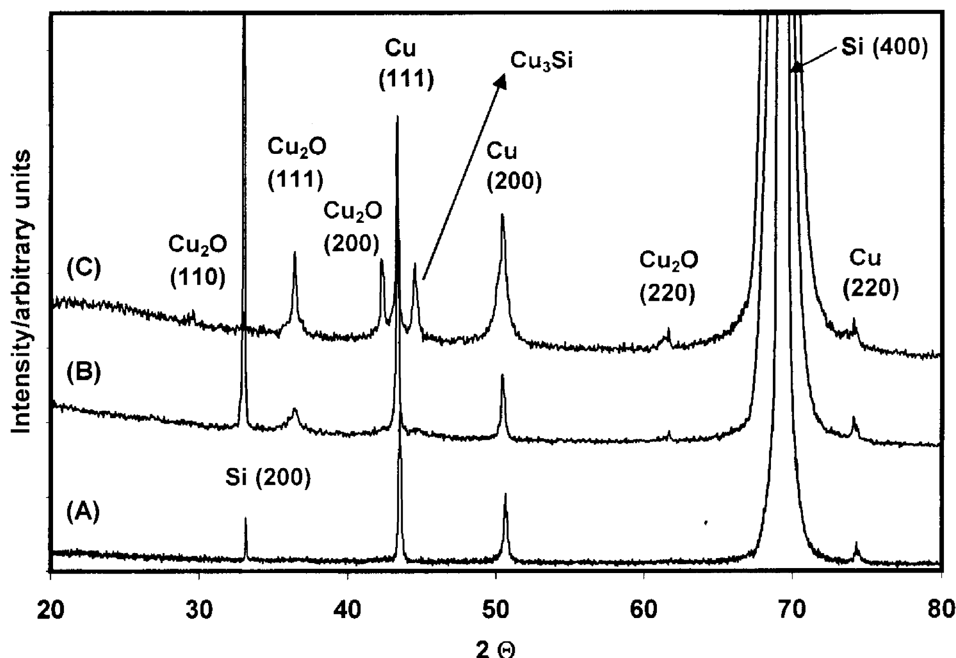


Fig. 6. XRD pattern of films deposited using Cu(I)(hfac)(2-butyne)/C_2F_6 solution: (A) at 225 °C with H_2, (B) at 225 °C without H_2, (C) at 250 °C without H_2.

(600–800 °C) [19]. Using Auger electron spectroscopy, the authors detected a very high oxygen content in the films and attributed oxide formation to the presence of H_2O in the complex and decomposition of the ligand during deposition.

The experiments conducted in scC_2F_6 show that our technique is not limited to $scCO_2$ as reaction medium. We have deposited highly reflective Cu films from the H_2 reduction of Cu(hfac)(2-butyne) in scC_2F_6. Cu can also be deposited from the thermal decomposition of Cu(hfac)(2-butyne) in scC_2F_6 solutions without adding H_2 (Fig. 6) although the films contained some Cu_2O. When the deposition temperature was increased to 250 °C, the relative amount of Cu_2O to Cu increased. Decomposition of the ligand at higher temperatures is more extensive and produces more Cu_2O. Nevertheless the films deposited in the absence of H_2 were not reflective and exhibited much higher resistivities than those deposited in the presence of H_2, which suggest a higher level of contamination throughout the film.

4. Conclusion

We have deposited device-quality Cu films onto planar and etched silicon substrates from the H_2 assisted reduction of soluble Cu(I)(hfac)L precursors in supercritical fluids using the chemical fluid deposition (CFD) technique. The experiments were performed in a cold wall, high pressure reactor from solutions of Cu(I)(hfac)L compounds where L is (2-butyne), (COD), (VTMS) or (2-methyl-1-hexene-3-yne) in $scCO_2$ and Cu(I)(hfac)(2-butyne) in scC_2F_6. At temperatures above 225 °C, high purity Cu can be deposited directly onto the native oxide of Si or Cu diffussion barrier layers such as

TiN. Films deposited by H_2 reduction of each of the precursors exhibited little carbon or oxygen contamination. The experiments conducted in scC_2F_6 show that our technique is not limited to $scCO_2$ as reaction medium.

We have also examined the utility of thermal disproportionation for Cu deposition via CFD in the absence H_2 and compared these results to the H_2 assisted reductions. Attempts to deposit high purity Cu films by the thermal disproportionation of the Cu(I)(hfac)L precursors in $scCO_2$ in the absence of H_2 at 225 °C were unsuccessful and yielded highly oxidized Cu films in each case. Films deposited from the thermal decomposition of Cu(hfac)(2-butyne) in scC_2F_6 rendered films composed of mixtures of Cu and Cu_2O.

These results indicate a need to add H_2 or other reducing agent to the SCF solution in order to deposit high purity copper films. The thermal decomposition of the ligand in absence of H_2 and the presence of trace impurities in the supercritical fluid are likely responsible for the oxidation of the film. Some supercritical fluids could also participate directly in the oxidation process.

Acknowledgements

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