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Carbon Monoxide Promoted Chemical Vapor Deposition of Copper[1]

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Chemical vapor deposition (CVD) using organometallic copper complexes is being extensively pursued for a variety of microelectronic applications.[2] Copper(I) complexes are of particular interest in Cu CVD because they may be easier to reduce than Cu(II) species and because the volatile ligands used in many Cu(I) complexes should be easily removable following copper deposition, leading to improved film purity.[3] Copper(I) complexes such as (hfac)Cu(COD) (HfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, COD = 1,5-cyclooctadiene) have been shown to function as CVD precursors, both by direct reduction (using H_2 as carrier gas/reductant)[4] and by disproportionation to Cu and Cu(II).[5] Herein we report that the temperatures required for evaporation of (hfac)Cu^I(COD) and Cu film formation are approximately 30 °C lower when the carrier gas/reductant is either pure CO or a mixture of CO and H_2 (1:1 v/v, "syngas"). Spectroscopic and chemical evidence indicates that the enhanced evaporation and deposition are due to the intermediate formation of (hfac)Cu^I(CO). The use of metal carbonyls as CVD precursors has often led to large concentrations of C and O in the deposited films; however, the films we obtain in CO/H_2 show negligible amounts of these impurities.

Doyle and co-workers found that (hfac)Cu(CO) could be prepared in CO-saturated THF solution but was not isolable.[6] The ready decomposition of the complex and the generally high volatility of hfac–Cu species suggested that it could be a good Cu CVD precursor either in solution or if generated in situ by treating (hfac)Cu(COD) with a CO-containing carrier gas.

We obtained Cu films when CVD experiments were carried out in a cool-wall glass reactor[4] using either solid (hfac)Cu(COD) or a THF solution containing (hfac)Cu(CO)[7] as precursor in the presence of CO or CO/H_2. When pure CO was used as the carrier gas, green solid Cu(hfac)$_2$·H_2O[8] deposited downstream from the substrate. This suggests that the deposition is occurring by disproportionation, as has been demonstrated recently with other Cu(I) precursors.[5] Thus, following initial formation of (hfac)Cu(CO) (eq 1), Cu CVD can proceed by disproportionation (eq 2).

$$\text{(hfac)Cu(COD)} + \text{CO} \rightleftharpoons \text{(hfac)Cu(CO)} + \text{COD} \quad (1)$$

$$2\text{(hfac)Cu(CO)} \rightarrow \text{Cu} + \text{Cu(hfac)}_2\text{(g)} + 2\text{CO} \quad (2)$$

Experiments using CO/H_2 as carrier gas, on the other hand, produced Cu but no Cu(hfac)$_2$. This suggests that direct reduction of (hfac)Cu(CO) (reaction 3) can also occur. The deposited films were much purer (as judged by Auger analysis; see Table I) in the presence of CO/H_2.[9]

$$2\text{(hfac)Cu(CO)} + \text{H}_2 \rightarrow 2\text{Cu} + 2\text{hfacH(g)} + 2\text{CO} \quad (3)$$

To study the formation of (hfac)Cu(CO) in this system, we examined the reactivity of (hfac)Cu(COD) with carbon monoxide using $^{13}C\{^1H\}$ NMR (see Table II) and IR spectroscopy. ^{13}C NMR spectra were obtained for a CD_2Cl_2 solution containing (hfac)Cu(COD) treated with enriched ^{13}CO (99%; MSD Isotopes; 1 atm) in a sealed NMR tube. The COD —CH= resonance shifts downfield on treatment with CO, and a new resonance appears at 176.6 ppm. We assign the new resonance to coordinated CO in (hfac)Cu(CO); the chemical shift is similar to those found for other copper(I) carbonyl complexes.[10]

The original (hfac)Cu(COD) spectrum can be restored in these solutions when carbon monoxide is removed from the NMR tube either by passage of N_2 or by evacuation. Thus, the reaction of (hfac)Cu(COD) and CO according to eq 1 is rapid and reversible.[11] Our attempts to slow this exchange process at lower temperatures were only partially successful. Even at 203 K, only slight broadening is observed in the COD ^{13}C resonances, indicating that the exchange process has been slowed but not completely stopped.

Solution FT-IR spectra recorded while bubbling CO or CO/H_2 into a CH_2Cl_2 solution containing (hfac)Cu(COD) reveal a new band at 2130 cm^{-1}. We assign this band to ν_{CO} in (hfac)Cu(CO).[12] This frequency is similar to those

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(1) Reported in part at the Seventh Conference on Advanced Metallization for ULSI Applications, Murray Hill, NJ, Oct 1991.

(2) (a) Gross, M. E. *J. Electrochem. Soc.* **1991**, *138*, 2422. (b) Yablonovitch, E. *Science* **1989**, *246*, 347.

(3) For early reports of CVD using Cu(I) precursors, see: Jeffries, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8. Dupuy, C. G.; Beach, D. B.; Hurst, J. E., Jr.; Jasinski, J. M. *Chem. Mater.* **1989**, *1*, 16.

(4) Kumar, R.; Fronczek, F. R.; Maverick, A. W.; Lai, W. G.; Griffin, G. L. *Chem. Mater.* **1992**, *4*, 577.

(5) Jain, A.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. *J. Mater. Res.* **1992**, *7*, 261. Reynolds, S. K.; Smart, C. J.; Baran, E. F.; Baum, T. H.; Larson, C. E.; Brock, P. J. *Appl. Phys. Lett.* **1991**, *59*, 2332.

(6) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Organometallics* **1985**, *4*, 830. Our attempts to isolate this complex (e.g., by removal of solvent) also failed, giving green Cu(hfac)$_2$·H_2O and a copper mirror in the reaction flask.

(7) These experiments were performed with solutions of (hfac)Cu(CO) in THF, prepared according to the method of Doyle and co-workers;[6] the carrier gas was bubbled through the THF solution and then into our standard CVD apparatus.

(8) Although the Cu^{II}(hfac)$_2$ product should be produced in its anhydrous form, this purple material has been shown to react rapidly even with traces of water adsorbed on the inner surfaces of CVD apparatus (Norman, J. A. T., personal communication). For a discussion of the Cu^{II}(hfac)$_2$–H_2O system, see: Funck, L. L.; Ortolano, T. R. *Inorg. Chem.* **1968**, *7*, 567.

(9) Addition of CO to the carrier gas had no effect on Cu CVD using Cu^{II}(hfac)$_2$ as precursor under similar conditions.

(10) $[Cu(CO)(OC(CH_3)_3)]_4$, 173 ppm: Geerts, R. L.; Huffman, J. C.; Folting, K.; Lemmen, T.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 3503. Compare uncomplexed CO (dissolved in CD_3COCD_3), 184.3 ppm: Heaton, B. T.; Jonas, J.; Eguchi, T.; Hoffmann, G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 331.

(11) In principle, CO and COD could coordinate simultaneously to Cu. However, since (hfac)Cu(COD) is known to be primarily in the η^2 form (see ref 4; also: Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Duesler, E.; Kodas, T. T. *Polyhedron* **1991**, *10*, 2293), we believe a four-coordinate (hfac)Cu(CO)(η^2-COD) complex is unlikely.

(12) Passing CO into more concentrated solutions of (hfac)Cu^I(COD) leads to IR absorptions at 2020 and 1995 cm^{-1} (in addition to the 2130-cm^{-1} band). These may be due to a binuclear complex with bridging carbonyl ligands, such as [(hfac)Cu^I]$_2$(μ-CO)$_2$, or a mononuclear complex in which the hfac ligand is C bound, such as $(CF_3CO)_2CHCu(CO)_2$. Both of these species would be expected to show two ν_{CO}, at lower energy than (hfac)Cu^I(CO). However, we have not been able to isolate this product for full characterization.

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Table I. Influence of CO on CVD Conditions and Cu Film Properties[a]

		temp/°C			Auger analysis/%[b]		
precursor	carrier gas	source	substrate	$\rho/\mu\Omega$ cm	Cu	C	O
(hfac)Cu(COD)[c]	H_2	70	200–205	3.6 ± 1.5	96	2	2
(hfac)Cu(COD)	CO	30–35	170–175		81	7	12
(hfac)Cu(CO) (in THF)	CO	30–35	170–175	>9	84	13	3
(hfac)Cu(COD)	CO/H_2[d]	30–35	170–175	3.6 ± 0.8	98	1	1

[a] Deposition on borosilicate glass disk in cool wall reactor[4] under standard conditions: carrier gas flow rate 80–100 mL min^{-1} at 1 atm; deposition rate 0.7–0.8 μm h^{-1}. [b] ±1%; after Ar sputtering to remove surface impurities. F was below detection limit (1%) in all films. [c] Data from ref 4. [d] 1:1 v/v.

Table II. $^{13}C\{^1H\}$ NMR Data for Cu(I) Complexes with CO[a]

sample	Cu—CO	CH_2	—CH═	CF_3 (^1J(C–F))	CF_3CO (^2J(C–F))	$CH(CO)_2$
COD		28.4	129.0			
(hfac)Cu(COD)		28.6	114.1	118.6 (287)	177.8 (33)	89.0
(hfac)Cu(COD) + CO	176.6	28.6	115.9	117.9 (287)	177.8 (33)	88.8
(hfac)Cu(COD) + CO[b]	171.4	28.0	115.1	117.0 (287)	176.0 (33)	88.2

[a] In CD_2Cl_2 (50.29 MHz; Bruker AM-200); chemical shifts δ/ppm vs TMS; coupling constants/Hz in parentheses. [b] At 203 K (100.58 MHz; Bruker AM-400); Cu—CO and —CH═ resonances noticeably broadened.

observed for several other Cu(I) carbonyl complexes with poor donor ligands.[13]

The above data show that CO is able to displace COD from (hfac)Cu(COD) in solution. We believe that this ligand-substitution process also occurs under CVD conditions. In order to test this hypothesis, we measured the rate of (hfac)Cu(COD) evaporation gravimetrically under N_2, H_2, CO, and CO/H_2 carrier gas (80–100 mL min^{-1}) at 38 ± 3 °C. The evaporation rates under CO (6 ± 1 mg h^{-1}) and CO/H_2 (4 ± 1 mg h^{-1}) are significantly larger than that under H_2 or N_2 (1.0 ± 0.7 mg h^{-1}). These results suggest that solid (hfac)Cu(COD) also reacts with CO, producing gaseous (hfac)Cu(CO).

We attempted to confirm this substitution directly using gas-phase FT-IR spectroscopy. CO was passed over solid (hfac)Cu(COD) and then into a cell (10-cm path length), or the solid precursor was placed directly in the cell in the presence of CO. These samples showed no absorbance changes in the 1900–2200-cm^{-1} region compared to pure CO. Unfortunately, these experiments are not conclusive, because of the intense background absorption due to free CO in the 2050–2140-cm^{-1} region (P branch). Thus, CO increases the rate at which (hfac)Cu(COD) evaporates, presumably by producing (hfac)Cu(CO) and increasing the concentration of Cu species in the gas phase; this explains our lower evaporation temperature in CVD. However, we could not confirm the formation of gaseous (hfac)Cu(CO) directly.

A common problem associated with the use of metal carbonyls as CVD precursors is high levels of carbon and oxygen contamination in the deposited films. This problem is especially severe in CVD of Fischer–Tropsch-active metals such as Ni and Pt.[14] Although we find similar results when using pure CO as carrier gas,[15] deposition under CO/H_2 yields much purer films. This could be due to a change of reaction mechanism, bypassing the steps that lead to C and O impurities, or to continuous reduction of the impurities by H_2.[16,17]

Gross[2a] has reported a comparison of $[Cu\text{-}OC(CH_3)_3]_4$ and its CO adduct, $[(CO)Cu\text{-}OC(CH_3)_3]_4$, as Cu CVD precursors. In this case, the CO complex is also more volatile, leading to deposition at lower temperatures. However, neither of these species is as volatile as (hfac)-Cu^I(COD). Our work also shows that even if the CO complex is not isolable, addition of CO to the carrier gas, by forming an intermediate carbonyl complex, can lead to evaporation and deposition under milder conditions.

Recent mechanistic studies suggest that Cu CVD using $Cu^{II}(hfac)_2$ and (hfac)Cu^I(COD) as precursors occurs by similar mechanisms. With $Cu^{II}(hfac)_2$,[18,19] deposition is believed to occur via adsorbed hfac (which can also be viewed as a Cu^I–hfac moiety as part of the Cu surface), and the rate-limiting step is believed to be combination of these species with adsorbed H atoms to produce hfacH, which then desorbs. Copper(I) precursors (hfac)CuL produce similar intermediates, at least under UHV conditions, because the neutral ligand L (e.g., COD) is lost immediately following adsorption.[20] If the two mechanisms are similar, they might be expected to occur with similar rates and temperature dependences. For this reason, we were surprised to discover the lower deposition temperature in the presence of CO.

As an explanation for the lower deposition temperature in the presence of CO, we considered the possibility that nucleation is promoted by CO. (Different nucleation rates on glass or oxidized Si surfaces might be expected for different L, since the initial reaction of (hfac)Cu(COD) with oxide surfaces appears to involve loss of *hfac* rather than L.[20]) However, two additional experiments strongly suggest that nucleation rates are not a factor. First, we found that when the substrate is at 200 °C (so that

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(13) (a) Cu(CO)Cl, 2127 cm^{-1}: Håkansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241. (b) $[Cu(CO)(\mu\text{-}O_3SR)]_n$, 2113–2130 cm^{-1}: Doyle, G.; Eriksen, K. A.; Van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892. (c) CO on Cu_2O, 2110–2136 cm^{-1}: Roberts, D. L.; Griffin, G. L. *J. Catal.* **1988**, *110*, 117. Most other Cu(I) carbonyl complexes, which contain amine or other more strongly donating ligands, show ν_{CO} in the 2060–2110-cm^{-1} range: Villacorta, G. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 3672. Casella, L.; Gullotti, M.; Pallanza, G.; Rigoni, L. *J. Am. Chem. Soc.* **1988**, *110*, 4221. Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325.

(14) Zinn, A.; Niemer, B.; Kaesz, H. D. *Adv. Mater.* **1992**, *4*, 375.

(15) The absence of F impurities, even when the C and O levels are high, indicates strongly that the carbon impurities derive from CO rather than from hfac.

(16) Cohen, S. L.; Liehr, M.; Kasi, S. *Appl. Phys. Lett.* **1992**, *60*, 1585.

(17) For an example of H_2 reduction of ligands coordinated to copper, see: Pasquali, M.; Leoni, P.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1982**, *21*, 4324.

(18) Cohen S. L.; Liehr, M.; Kasi, S. *Appl. Phys. Lett.* **1992**, *50*, 60. Dubois, L. H.; Jeffries, P. M.; Girolami, G. S. In: *Advanced Metallization for ULSI Applications*; Rana, V. V. S., Joshi, R. V., Ohdomari, I., Eds.; Materials Research Society: Pittsburgh, PA, 1992; p 375.

(19) Lai, W. G.; Xie, Y.; Griffin, G. L. *J. Electrochem. Soc.* **1991**, *138*, 3499.

(20) Cohen, S. L.; Liehr, M.; Kasi, S. *J. Vac. Sci. Technol. A* **1992**, *10*, 863.

deposition occurs with both carrier gases), there is no induction period with either carrier gas, and the deposition rate is greater with CO/H_2. (The deposition rate could be higher because the gas-phase precursor concentration is higher in the presence of CO, as discussed above.) In a second experiment, we prepared a thin film (ca. 0.2 μm) of Cu by deposition at 200 °C under H_2 and then placed this film in the apparatus again at 175 °C under H_2. (We expected that, if the limiting step under H_2 were nucleation, deposition would continue on the Cu surface even at 175 °C under H_2.) No further deposition was observed.

Alternatively, the neutral ligand L may affect the steady-state deposition rate more directly. At first, this appears to conflict with the surface studies,[20] which have concluded that L is lost immediately following adsorption on metal surfaces. However, our conditions (ca. $^1/_2$ atm of CO) are very different from those of UHV experiments; the higher concentrations of L in our experiments may prevent complete dissociation of L, or lead to a significant concentration of adsorbed CO throughout deposition. Also, recent temperature-programmed desorption studies of Dubois and Zegarski[21] indicate significant differences in Cu–L bond strengths for different L. A more complete answer to this mechanistic puzzle will require detailed kinetic studies under CVD conditions; these are now in progress.

To summarize, in contrast to the detrimental effects on CVD frequently exhibited by carbon monoxide, we find that CO *enhances* deposition of pure Cu films from copper(I) precursors. We are now studying the effects of CO addition on selectivity of deposition and film quality and deposition rates as a function of total pressure and CO/H_2 ratio.

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(21) Dubois, L. H.; Zegarski, B. R. *J. Electrochem. Soc.* **1992**, *139*, 3295.