CHEMISTRY of MATERIALS

VOLUME 7, NUMBER 12 DECEMBER 1995

© Copyright 1995 by the American Chemical Society

Communications

Use of Single-Source, Mixed-Metal Precursors for Chemical Vapor Deposition of Cu–Sn Alloys

Pascal Doppelt[†] and Thomas H. Baum*

IBM Almaden Research Center, 650 Harry Road
San Jose, California 95120-6099

Received February 21, 1995
Revised Manuscript Received September 26, 1995

Low-resistivity metals in tandem with low dielectric constant materials are required for future integrated circuit (IC) metallization to decrease RC time delays and increase processing speeds. Low-resistivity metals, such as copper, make this goal readily accessible.[1,2] Several IC manufacturers and academic groups are exploring copper CVD as a method for future interconnection.[3–7] Typically, CVD processes utilize vinyltrimethylsilane (VTMS) copper(I) hfac,[5] which is a thermally labile, commercial material.

In our search for novel CVD copper precursors,[3] we synthesized several new mixed-metal precursors for copper alloy CVD. Vinyltrialkyltin species were used as the Lewis base, to stabilize the reactive copper(I) β-diketonate moiety (Figure 1). These previously unknown complexes are similar to other Lewis base copper(I) hfac analogues. Chemical substitution of the alkyl groups on the Sn(IV) center enables the physical properties of the precursor to be modified. Thus, chemical control of the precursor's volatility and thermal stability may be realized via structure–property relationships. Simultaneously, we have demonstrated the utility of these complexes for the CVD of Cu–Sn alloys, which can be used to provide copper films with improved thermal, electrical and mechanical properties.[8] Copper alloys (i.e., Cu/Mg) may be required to enhance the electromigration resistance of the copper interconnects.[9]

As previously reported for copper CVD, thermal disproportionation of two Cu(I) β-diketonates produces pure copper, as shown in eq 1. When L is an alkene,

$$2\mathrm{LCu(I)}(\beta\text{-diketonate}) \rightarrow \mathrm{Cu(0)} + \mathrm{Cu(II)}(\beta\text{-diketonate})_2 + 2\mathrm{L} \quad (1)$$

diene, or alkyne, very pure copper films are deposited.[3] For the vinyltrialkyltin ligand, thermal decomposition is known to occur near 200 °C.[10] Thermal decomposition of the copper–tin complexes in this temperature regime will induce both disproportionation of two Cu(hfac) species and decomposition of the tin-containing Lewis base ligand. Thus, we expect both tin and copper to be deposited simultaneously from a single-source, Sn–Cu precursor. The deposition of copper–tin films is observed and is strongly substrate-temperature dependent, as expected from the previous discussion.

[†] Present address: ESPCI (CNRS, URA 429), 10 rue Vauquelin, 75231 Paris Cedex 05, France.

* To whom correspondence should be addressed. Present address: Advanced Technology Material, Inc., 7 Commerce Street, Danbury, CT 06810.

(1) Pai, P. L.; Ting, C. H. *IEEE Electron Dev. Lett.* **1989**, *10*, 423–425.

(2) Small, M. B.; Pearson, D. *J. IBM J. Res. Dev.* **1990**, *34*, 858–867.

(3) Doppelt, P.; Baum, T. H. *MRS Bull.* **1994**, *19* (8), 41–48.

(4) (a) Jain, A.; Farkas, J.; Kodas, T. T.; Chi, K. M.; Hampden-Smith, M. J. *Appl. Phys. Lett.* **1992**, *61*, 2662–2664. (b) Jain, A.; Chi, K. M.; Kodas, T. T.; Hampden-Smith, M. J. *J. Electrochem. Soc.* **1993**, *140*, 1434–1439. (c) Jain, A.; Kodas, T. T.; Jairath, R.; Hampden-Smith, M. J. *J. Vac. Sci. Technol.* **1993**, *B11*, 2107–2213.

(5) Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Roberts, D. A.; Hochberg, A. K. *J. Phys. (Paris)* **1991**, *4*, C2-271–278. Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Roberts, D. A.; Hochberg, A. K.; Dubois, L. H. *Mater. Sci. Eng.* **1993**, *B17*, 87–92.

(6) Gelatos, A. V.; Marsh, R.; Kottke, M.; Mogab, C. J. *Appl. Phys. Lett.* **1993**, *61*, 2842–2844.

(7) Stumm, T. H.; van der Bergh, H. *Mater. Sci. Eng.* **1994**, *B23*, 48–53.

(8) Lee, Y. W.; Ling, F. W.; Shapiro, S. U.S. Patent 4,492,602, 1985.

(9) Murarka, S. P.; Gutman, R. J.; Kalayeros, A. E.; Lanford, W. A. *Thin Solid Films* **1993**, *236*, 257.

(10) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515–517.

0897-4756/95/2807-2217$09.00/0

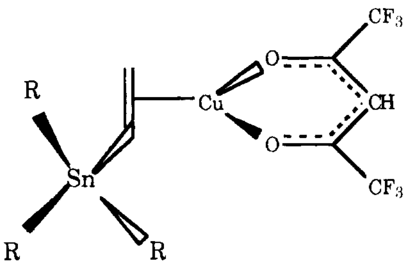

Figure 1. Proposed chemical structure for the vinyltrialkyltin copper(I)(hfac) complexes reported in this work. Complexes with R = CH_3(VTMT), C_2H_5 (VTET), and n-C_4H_9 (VTBT) were synthesized and each is a liquid at room temperature.

The synthesis of several vinyltrialkyltin(IV) ligands was accomplished by extensions of the literature methods.[11] Reaction of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfac) with Cu_2O in the presence of the vinyltrialkyltin reagent leads to the formation of a vinyltrialkyltin(IV) copper(I)hfac complexes. These materials were characterized by NMR (^{1}H and ^{13}C), IR, and elemental analyses. Thus far, vinyltrimethyltin (VTMT), vinyltriethyltin (VTET), and vinyltributyltin (VTBT) copper (hfac) analogues were synthesized, and the proposed structure is shown in Figure 1. Isolation of pure, yellow, liquid Sn−Cu complexes was accomplished via column chromatography and solvent distillation. Stabilization in the mixed Sn−Cu complexes is similar to that reported for VTMS Cu(hfac), namely, positive inductive polarization[12] and back-electron donation from the vinyl group to the Sn center ($\pi \rightarrow$ Sn). Comparison of the NMR spectral shifts in the "free" vinyltin(IV) ligand with that bound to the copper(I) species displays discrete chemical shift ($\Delta\delta$) changes.[13] As previously reported for other LCu(hfac) species, shielding of the vinyl protons ($\Delta\delta = -0.92$ ppm) is indicative of an increased electron density at the vinyl group. Chemical shift changes ($\Delta\delta$) are also observed for the vinyl carbons using ^{13}C NMR spectroscopy. For VTBT Cu(hfac), the vinyl carbons are shielded ($\Delta\delta \cong -40$ ppm) upon Cu(I) hfac complexation, analogous to that observed in VTMS Cu(hfac).[5] Each copper−tin complex displays similar ^{1}H and ^{13}C spectral shifts ($\Delta\delta$) by NMR. Further, the mixed-metal complexes display good thermal stability in solution; disproportionation to copper metal and $Cu(hfac)_2$ appears to be slow relative to other Lewis base Cu(I) hfac complexes.[3−7] Spectroscopic studies (UV−vis) to quantitate the thermal decomposition and disproportionation of the Cu−Sn complexes are underway, but outside the scope of this communication.

Preliminary deposition of copper tin films was carried out in a warm-walled belljar reactor using (VTMT)Cu(hfac) and (VTET)Cu(hfac). Depositions were performed on quartz wafers coated with Cr (200 Å)/Au (1500 Å). The reactor pressure was maintained between 5 and 8 Torr, while the substrate temperature was varied (Table 1). Under these reactor conditions, copper−tin films were grown at an average rate of 50 nm/min. The Sn content in the films ranged from 0 to 2 at. % as determined by XPS, after sputtering the environmentally exposed surface. The identity of the carrier gas (He or 4% H_2 in N_2) influences the composition and purity of the deposited films. The use of H_2/N_2 during film growth appears to result in higher Sn content, but this also requires further detailed study. Postdeposition annealing was observed to alter the deposited film purity, as shown in Tables 1 and 2. This may be a result of secondary decomposition of adsorbed tin-containing ligands. The highest purity copper−tin film was deposited at 180 °C after annealing to 250 °C in 0.3 Torr vacuum (sample 2). The resistivity was measured to be $\approx 3.0\ \mu\Omega$ cm. At higher substrate temperatures, a larger amount of carbon is observed from both precursors, regardless of carrier gas or use of postannealing treatments. Since the complete elimination of C and O contaminants is required for microelectronic device applications, chemical modifications to the precursor molecular structure may be required. For example, CF_3 substitution of the Sn center will provide Cu−Sn complexes with higher volatilities. Hydride substitution of the Sn center may provide carbon-free Cu−Sn films, provided premature reduction of the copper(I) center does not occur. Simultaneously, the volatility of the

---

(11) **Caution**: Tin-containing compounds can be toxic and should be handled accordingly. All of the starting materials were commercially available and used as received, except for VTMT and VTET, which were synthesized using the reported procedures.[10] Infrared spectra were obtained using an IBM instrument IR44 single beam spectrometer. The spectra were obtained by evaporating a pentane solution of the complex onto NaCl slides or neat between two NaCl slides. ^{1}H and ^{13}C NMR spectra were carried out on a Bruker Instrument 250 MHz spectrometer. **Syntheses of the complexes**: The general reaction was carried out under a steady flow of nitrogen. Although the complexes are slightly O_2 sensitive, it is not necessary to purge the solution prior to the synthesis. A three-neck round-bottom flask was charged with 5.5 g (38 mmol) of Cu_2O (Aldrich) and 50 mL of spectroscopic grade methylene chloride. 1,1,1,5,5,5-Hexafluoroacetylacetone (10.7 g, 51 mmol, Aldrich) was added dropwise to the magnetically stirred solution which contained 9.7 g (51 mmol) of VTMT, 11.9 g (50 mmol) of VTET, or 16 g (50 mmol) of VTBT. The reaction was stirred during the addition and for 30 min after the addition was completed. The initially clear solution containing the suspended brick-red cuprous oxide becomes yellow-green as the reaction proceeds. Excess cuprous oxide was filtered off and the methylene chloride solution was purified by flash chromatography using a 1.3 in. (diameter) by 5 in. (height) neutral alumina (Aldrich) column under nitrogen. After chromatography and solvent distillation, 18 g of yellow liquid (VTMT)Cu(hfac) was obtained (75−85% yield). The complexes are sensitive to oxygen exposure and thermally decompose at temperatures above 165 °C. **(VTMT)Cu(hfac)**: IR (neat) 2985(m), 2922(m), 1639(s), 1604(m), 1555(m), 1529(m), 1479(s), 1347(w), 1324(m), 1258(s), 1203(s), 1147(s), 952(w), 800(m), 773(m), 744(w), 722(w), 673(m), 629(w), 588(m), 532(m), 516(w) cm^{-1}. ^{1}H NMR ($CDCl_3$, T = 298 K) 0.26 (s, 9H, satellites ^3J(H−^{117}Sn and H−^{119}Sn 52.5 and 55.2 Hz), 4.70 (m, 1H), 5.15 (m, 2H). ^{13}C NMR 178.1 (q, 35 Hz, CO), 117.7 (q, 286 Hz, $C\mathrm{F_3}$), 99.7 (s, $\mathrm{CH_2{=}}C\mathrm{{-}Sn}$, satellites: ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 380 Hz), 94.3 (s, $C\mathrm{H_2{=}CH}$), 89.7 (s, CH), −4.3 (s, $C\mathrm{H_3}$ satellites: ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 346 and 362 Hz). Anal. Calcd for $C_{10}H_{13}O_2$CuSn: C, 26.03, H, 2.62, F, 24.70. Cu, 13.77, Sn, 25.72. Found: C, 25.96, H, 2.78, F, 25.29, Cu 13.54, Sn, 22.11. **(VTET)Cu(hfac)**: IR (neat) 2949(m), 2911(m), 2871(m), 1639(s), 1603(m), 1555(m), 1529(m), 1495(m), 1473(s), 1424(w), 1347(w), 1322(m), 1256(s), 1202(s), 1149(m), 1102(w), 948(w), 811(m), 801(m), 673(s), 588(m), 505(w) cm^{-1}. ^{1}H NMR ($CDCl_3$, T = 298 K) 1.0 (m, 9H), 1.23 (m, 6H), 4.94 (m, 1H), 5.15 (ppm (m, 2H), 6.12 (s, 1H). ^{13}C NMR 178.1 (q, 34 Hz, CO), 117.7 (q, 286 Hz, $C\mathrm{F_3}$), 100.0 (s, $\mathrm{CH_2{=}}C\mathrm{{-}Sn}$, satellites ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn 274 Hz) 96.9 (s, $C\mathrm{H_2{=}CH}$, 89.9 (s, CH), 10.7 (s, $C\mathrm{H_3}$, satellites ^3J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn 25 Hz), 1.52 ppm (s, $C\mathrm{H_2}$, satellites: ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 238 and 353 Hz). **(VTBT)Cu(hfac)**: IR (neat) 2960(m), 2927(m), 2874(w), 2854(w), 1639(s), 1601(w), 1555(w), 1529(w), 1493(w), 1472(s), 1321(w), 1256(s), 1208(s), 1150(s), 1102(m), 1074(w), 801(m), 673(m), 587(m), 504(w), 493(w) cm^{-1}. ^{1}H NMR ($CDCl_3$, T = 298 K) 0.9 (m, 9H), 1.5 (m, 18H), 4.9 (m, 1H), 5.3 ppm (m, 2H). ^{13}C NMR 178.0 (q, 35 Hz, CO), 117.7 (q, 286 Hz, $C\mathrm{F_3}$), 105.6 (s, $C\mathrm{H_2{=}C}$, satellites ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 268 Hz), 101.3 (s, $\mathrm{CH_2{=}}C\mathrm{H}$, 89.8 (s, CH), 29.0 (s, $C\mathrm{H_3{-}CH_2}$, satellites ^4J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 21.4 Hz), 27.3 (s, $\mathrm{CH_3{-}}C\mathrm{H_2{-}CH_2}$, satellites ^3J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 63.5 Hz), 13.6 (s, $\mathrm{CH_3}$), 10.2 (s, $C\mathrm{H_2{-}Sn}$, satellites ^2J(^{13}C−^{117}Sn and ^{13}C−^{119}Sn) 230 and 245 Hz).

(12) Bock, H.; Seidl, H. *J. Chem. Soc. B* **1968**, 1158.

(13) Baum, T. H.; Larson, C. E.; May, G. *J. Organomet. Chem.* **1992**, *425*, 189–200. Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *43*, C7. Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 135. Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.

Table 1. Precursor and Reactor Conditions Used To Deposit the Copper–Tin Films[a]

LCu(hfac)	sample no.	T_{bubbler} (°C)	flow (sccm)/gas	T_{sub} (°C)	postanneal	Sn/Cu ratio (%)
L = VTMT	1	40	30/He	180	none	0.2
	2	40	30/He	180	30 m at 250 °C	0.6
	3	40	30/H_2 in N_2	180	30 m at 250 °C	1.6
	4	40	30/H_2 in N_2	200	30 m at 250 °C	1.7
L = VTET	5	50	60/He	200	none	0.8
	6	50	60/He	220	none	1.0
	7	50	60/He	240	none	0

[a] Precursor and reaction conditions used to deposit the copper–tin films. The deposited films were annealed in situ using 250 °C and 0.3 Torr vacuum. The copper–tin ratio was calculated from the XPS analyses (see Table 2).

Table 2. Atomic Purities of the Deposited Films Determined by XPS Analysis after Argon Sputtering to an Estimated Depth between 200 and 300 Å[a,b]

LCu(hfac)	sample no.	Cu (at. %)	Sn (at. %)	C (at. %)	O (at. %)	F (at. %)
L = VTMT	1	91.2	0.2	4.0	4.0	ND
	2	99.4	0.6	ND	ND	ND
	3	91.0	1.5	1.9	3.9	1.8
	4	88.8	1.5	5.8	1.8	2.0
L = VTET	5	87.1	0.7	7.8	4.5	ND
	6	71.8	0.7	21.7	3.7	1.9
	7	85.7	ND	14.2	ND	ND

[a] The precursor structure, substrate temperature, carrier gas identity and postdeposition annealing are all important variables toward the deposited film purity. At 180 °C, a clean copper–tin alloy film was deposited from VTMT Cu(hfac). At higher substrate temperatures, carbon contamination increases for each precursor examined, regardless of carrier gas identity and postannealing treatments. [b] Atomic purities of the deposited films determined by XPS analysis after argon sputtering to an estimated depth between 200 and 300 Å. ND = not detected (below the detection limit for that element).

mixed-metal complexes should be increased.

As demonstrated in this preliminary study, a single-source, mixed-metal precursor may be used to deposit doped metal films and thereby alter the film's mechanical, thermal, or electrical properties. Small quantities of tin metal are known to alter the physical properties of copper metal, specifically resistivity and tensile strength. For example, a 1.3% Sn–98.7% Cu alloy (No. C50500) has a resistivity of 3.59 $\mu\Omega$ cm at 20 °C, and the tensile strength is dramatically improved.[14] Furthermore, metal alloys are known to enhance the electromigration resistance of circuits under electrical stressing (i.e., high current densities) and provide improved thermal stability at elevated temperatures. However, the level of doping must be minimized to provide electrical resistivities below the values obtained for Al/Cu films or the motivation for shifting toward copper interconnects will be lost. Toward this end, a wide range of tin–copper precursors can be synthesized and used to chemically deposit copper–tin alloys.

Acknowledgment. We are grateful to the CNRS (France) and to the DRET (DGA, France Contract 93-1197) for partial financial support. The authors gratefully thank Ms. D. Miller and Ms. E. Sigari (IBM) for the XPS measurements.

CM950085G

---

(14) Bardes, P. *Metal Handbook*, **2**, Amer. Soc. Metals, 1979, 353–354.