to turn green. Over a period of several days, a dark precipitate formed slowly. The material was collected and treated as above.

Another method by which polymeric materials may be chemically oxidized involves exposure to iodine vapor.[40,41] Films of polymers 7 and 8 were cast from THF solution onto a poly(tetrafluoroethylene) sheet. The resultant polymer films were removed and attached to a four-point probe using gold paste. The apparatus and procedure for doping conductive polymers with iodine vapor has been described previously.[42] Exposure to iodine vapor caused the polymers to become dark purple. The conductivity was monitored continuously during this process.

Conductivity Measurements. Conductivity measurements of the pristine polymers were measured on films cast from THF solution. Conductivities of the solution-oxidized polymers were measured for powder samples which were pressed into pellets.[22] The powder samples were placed in a die with a 0.67 cm^2 area bore. A pressure of 5 tons was applied to the die by means of a laboratory press to form the pellets. The resultant pellets usually had poor mechanical properties. As a result, it was difficult to obtain four-point conductivity measurements for many of the samples. Therefore, a two-point method was used when necessary. The two-point conductivity measurements were taken across the pellet while still under pressure. In cases where four-point measurements could be obtained, the conductivities measured by both the two-point and four-point methods were similar (Table IV).

Acknowledgment. The synthetic work described here was conducted at The Pennsylvania State University. The oxidation experiments and conductivity measurements were carried out at Texas A&M University and Colorado State University. We thank the U.S. Army Research Office (H.R.A. and J.A.D.) and the Office of Naval Research and the Air Force Office of Scientific Research (C.R.M. and L.S.V.) for financial support.

Registry No. **3a**, 50966-69-3; **5a**, 141485-35-0; **6a**, 96625-75-1; **8a**, 59311-67-0; **9a**, 60794-90-3; **10**, 141485-33-8; NaOCH$_2$CCHSCHCH, 141485-27-0; [NP(Cl)$_2$]$_3$, 940-71-6; H(OCH$_2$CH$_2$)$_3$Cl, 141485-34-9; Fe(ClO$_4$)$_3$, 13537-24-1; FeCl$_3$, 7705-08-0; I$_2$, 7553-56-2; 1-pyrrolepropionitrile, 43036-06-2; 1-(2-carboxyethyl)pyrrole, 89059-06-3; 3-thiopheneacetonitrile, 13781-53-8; potassium pyrrole, 16199-06-7.

---

(40) Kang, E. T.; Neoh, K. G.; Tan, T. C.; Ong, Y. K. *J. Macromol. Sci. Chem., A* **1987**, *24*, 631.

(41) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

(42) Gibson, H. W.; Pochan, J. M. In *Electrical and Electronic Properties of Polymers: A State-of-the Art Compendium*; Kroschwitz, J. I., Ed.; Wiley: New York, 1988; p 15.

Hot-Wall Chemical Vapor Deposition of Copper from Copper(I) Compounds. 2. Selective, Low-Temperature Deposition of Copper from Copper(I) β-Diketonate Compounds, (β-diketonate)CuL$_n$, via Thermally Induced Disproportionation Reactions

H. K. Shin,[†] K. M. Chi,[†] M. J. Hampden-Smith,*[,†] T. T. Kodas,*[,‡] J. D. Farr,[§] and M. Paffett[§]

Departments of Chemistry and Chemical Engineering, Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, New Mexico 87131, and CLS-1, Los Alamos National Laboratories, Los Alamos, New Mexico 87545

Received November 8, 1991. Revised Manuscript Received March 2, 1992

Chemical vapor deposition of copper using (β-diketonate)Cu(PR$_3$)$_n$ (n = 1 and 2), (β-diketonate)Cu(1,5-COD), and (β-diketonate)Cu(alkyne) (where β-diketonate = hexafluoroacetylacetonate (hfac), trifluoroacetylacetonate (tfac), and acetylacetonate (acac); R = Me and Et; 1,5-COD = 1,5-cyclooctadiene; alkyne = bis(trimethylsilyl)acetylene (BTMSA), trimethylsilylpropyne (TMSP), and 2-butyne) has been studied on Pt, W, Cu, and SiO$_2$ substrates over the temperature range 100–400 °C. Large variations in the selectivity were observed as a function of the nature of the copper ligands, substrate temperature, and nature of the substrate. In the series of compounds (hfac)Cu(PMe$_3$), (hfac)Cu(PMe$_3$)$_2$, (hfac)Cu(PEt$_3$), (hfac)Cu(PEt$_3$)$_2$, (hfac)Cu(1,5-COD), and (hfac)Cu(2-butyne), where the number and nature of the neutral Lewis base ligand was varied, only (hfac)Cu(PMe$_3$) and (hfac)Cu(PEt$_3$) exhibited selective deposition. The lowest temperature at which deposition occurred changed dramatically as a function of the number and nature of Lewis base ligands. Deposition rates as high as 1200 Å/min were observed under unoptimized conditions. The copper films were characterized by Auger electron spectroscopy (AES), which showed pure copper within the detection limits. Resistivities varied from 1.7 to 8 μΩ cm depending on deposition conditions. All of the compounds investigated deposited copper via the thermally induced disproportionation reaction $2(\beta\text{-diketonate})\text{CuL}_n \rightarrow \text{Cu} + \text{Cu}(\beta\text{-diketonate})_2 + 2n\text{L}$. This reaction stoiochiometry was quantified for (hfac)Cu(1,5-COD) and (hfac)Cu(2-butyne) and explains the high purity of the films which results from the absence of thermally induced ligand decomposition.

Introduction

Chemical vapor deposition (CVD) allows formation of thin films of a variety of materials via decomposition of molecular, metal–organic species. The primary advantages of CVD over other methods such as physical vapor deposition (PVD) are that conformal coverage of complex structures and selective deposition are possible.[1] These two aspects are particularly important in electronics applications in which surfaces with complex topographies must be coated. An example is the formation of metal

---

[†] Department of Chemistry.

[‡] Department of Chemical Engineering.

[§] Los Alamos National Laboratories.

* Authors to whom correspondence should be addressed.

(1) Hess, D. W.; Jensen, K. F. *Microelectronics Processing*; American Chemical Society: Washington, DC, 1989.

0897-4756/92/2804-0788$03.00/0

interconnect structures, which consist of a three-dimensional network of metal features.[2]

The metals of primary interest for interconnect structures are W, Al, and Cu. Each has distinct advantages and disadvantages. Selective and blanket deposition of high-purity tungsten using WF_6 has been demonstrated,[3,4] and CVD of Al has been studied extensively.[5-17] However, the resistivities of tungsten and aluminum are too high for many proposed metallization schemes. Thus, CVD of Cu is the subject of much current interest due to its low resistivity (1.67 $\mu\Omega$ cm at 20 °C) relative to other metals (W, 5.65 $\mu\Omega$ cm; Al, 2.65 $\mu\Omega$ cm) and its good resistance to electromigration relative to aluminum.[18]

Several precursors for CVD have been studied, including copper(II) halides,[19] Cu(β-diketonate)$_2$,[20-24] [Cu(O-t-Bu)]$_4$,[25] [(t-BuO)CuL],[26] and (η^5-C_5H_5)CuL.[26,27] All of these compounds possess organic ligands that may undergo thermal decomposition during deposition. This may lead to the possibility of impurity incorporation depending on the specific reaction pathways. Pure copper films can be deposited only under certain conditions such as in the presence of a reducing agent, e.g., H_2. In addition, selective deposition is not always possible, and deposition must often be carried out at relatively high temperatures.

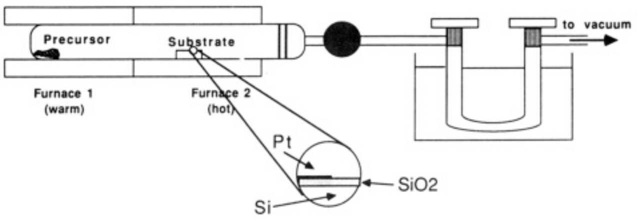

Figure 1. Schematic of hot-wall reactor.

The goals of the work described here are to explore alternative approaches for copper CVD. This may allow deposition of copper films with lower impurity levels, low resistivities, and better film morphologies and at lower temperatures than can currently be achieved. Furthermore, with suitable molecular design, the mechanisms of selective deposition onto different substrates may be explored and understood. This is a crucial step that must be accomplished before acceptance of selective copper CVD processes.

A series of metal–organic copper(I) compounds, (β-diketonate)CuL$_n$ (L = Lewis base, n = 1 or 2), have recently been identified that fulfill these goals by being capable of systematic substitution of β-diketonate and L to tailor volatility and reactivity.[29-40] These precursors can deposit copper via thermally induced disproportionation reactions (eq 1). Ligand decomposition is not required since

$$(\beta\text{-diketonate})\mathrm{Cu^IL}_n \rightarrow \mathrm{Cu^0} + \mathrm{Cu^{II}}(\beta\text{-diketonate})_2 + 2n\mathrm{L} \quad (1)$$

thermally induced disproportionation occurs at temperatures at which the volatile Lewis base and the copper(II) product are transported out of the reactor intact.[28]

Here we describe studies of hot-wall CVD of copper from (β-diketonate)CuL$_n$, where β-diketonate = hexafluoroacetylacetonate (hfac), trifluoroacetylacetonate (tfac), and acetylacetonate (acac) and where L = trimethylphosphine (PMe$_3$) and triethylphosphine (PEt$_3$) (n = 1 and 2), L = 1,5-cyclooctadiene (1,5-COD), and L = alkyne = bis(trimethylsilyl)acetylene (BTMSA), trimethylsilylpropyne (TMSP), and 2-butyne). This series of compounds allows examination of decomposition temperatures, selectivity, and film purity as a function of the nature of the β-diketonate and Lewis base, L. Preliminary reports of some

---

(2) White, L. S.; Blumenthal, R.; McAdams, H. *Conference Proceedings*, VLSI VI; **1991**, 3.

(3) Green, M. L.; Levy, R. A.; Nuzzo, R. G.; Coleman, E. *Thin Solid Films*, **1984**, *114*, 367.

(4) See, e.g.: *Advanced Metallization for ULSI Applications*; Rana, V. S., Joshi, R. V., Eds.; Materials Research Society: Pittsburgh, 1991.

(5) Cheung, K. P.; Case, C. J.; Liu, R.; Schutz, R. J.; Wagner, Kwakman, L. F. Tz.; Huibergtse, D.; Piekaar, H. W.; Granneman, E. H. A. *Proc. 7th IEEE VLSI Multilevel Interconnect Conference*, 1990.

(6) Kwakman, L. F. Tz.; Huibergtse, D.; Piekaar, H. W.; Granneman, E. H. A.; Cheung, K. P. Case, C. J.; Liu, R.; Schutz, R. J. Wagner, R. S. *Proc. 7th IEEE VLSI Multilevel Interconnect Conference*, 1990.

(7) Tsubouchi, K.; Masu, N.; Shigeeda, N.; Matano, T.; Hiura, Y.; Mikoshiba, N. *Appl. Phys. Lett.* **1990**, *57*, 1221.

(8) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634.

(9) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Sci. Technol. A* **1988**, *6*, 1920.

(10) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *Mater. Res. Soc. Proc.* **1988**, *101*, 177.

(11) Bent, B. E.; Dubois, L. H.; Nuzzo, R. G. *Mater. Res. Soc. Proc.* **1989**, *131*, 327.

(12) Dubois, L. H.; Zegarski, B. R.; Gross, M. E.; Nuzzo, R. G. *Surf. Sci.* **1991**, *1*, 1.

(13) Gladfelter, W. L.; Boyd, D. C., Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339.

(14) Gross, M. E.; Cheung, K. P.; Fleming, C. G.; Kovalchick, J.; Heimbrook, L. A.; *J. Vac. Sci. Technol. A* **1991**, *9*, 57.

(15) Gross, M. E.; Fleming, C. G.; Cheung, K. P.; Heimbrook, L. A. *J. Appl. Phys.* **1991**, *69*, 2589.

(16) Beach, D. B.; Blum, S. E.; LeGoues, F. K. *J. Sci. Technol. A* **1989**, *7*, 3117.

(17) Dubois, L. H.; Zegarski, B. R.; Kao, C.-T.; Nuzzo, R. G. *Surf. Sci.* **1990**, *7*, 236.

(18) Murarka, S. P.; Peckerar, M. C. *Electronic Materials*; Academic Press: Boston, 1989.

(19) Kuznetov, G. D.; Badad-Zakhryapin, A. A.; Giod, F. *Protect. Met.* **1972**, *8*, 565. Gillardeau, J.; Hasson, R.; Oudar, J. *J. Cryst. Growth* **1968**, *2*, 149.

(20) Temple, D.; Reisman, A. *J. Electrochem. Soc.* **1989**, *136*, 3525.

(21) Van Herment, R. L.; Spendlove, L. B.; Sievers, R. E. *J. Electrochem. Soc.* **1965**, *112* (2), 1123.

(22) Arita, Y., *Mat. Res. Soc. Proc., VLSI V* **1990**, 335.

(23) Kaloyeros, A. E.; Feng, A.; Garhart, J.; Brooks, K. C.; Gosh, S. K.; Saxena, A. N.; Leuthers, F. *J. Electron. Mater.* **1990**, *19*, 271.

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

(25) Jefferies, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8.

(26) Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M. F.; Farr, J. D.; Shin, H. K. *Chem. Mater.* **1990**, *2*, 636.

(27) Beach, D. B.; LeGoues, F. K.; Hu, C. K. *Chem. Mater.* **1990**, *2*, 216.

(28) Shin, H. K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Polyhedron* **1991**, *6*, 645.

(29) Shin, H. K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424.

(30) Cohen, S. L.; Liehr, M.; Kasi, S. *Mechanism of Copper Chemical Vapor Deposition from the 1,5-cycloctadiene Copper(I) hexfluoroacetylacetonate Precursor*; 4th Chemical Congress of North America, August 25–30, New York, 1991; Absract COLL 26.

(31) Cohen, S. L.; Liehr, M.; Kasi, S. *Appl. Phys. Lett.*, in press.

(32) Reynolds, S. K.; Smart, C. J.; Baran, E. F.; Baum, T. H.; Larson, C. E.; Brock, P. J. *Organic Ligand Stabilized Copper(I) Hexafluoroacetylacetonato complexes for Copper CVD*; 4th Chemical Congress of North America, August 25–30, New York, 1991; Absract COLL 29.

(33) Reynolds, S. K.; Smart, C. J.; Baran, E. F.; Baum, T. H.; Larson, C. E.; Brock, P. J. *Appl. Phys. Lett.* **1991**, *59*, 2332.

(34) Kumar, R.; Maverick, A. W.; Fronczek, F. R.; Lai, G.; Griffin, G. L. *Precursors for Chemical Vapor Deposition of Copper*; 200th American Chemical Society Meeting, Atlanta, April 1991; Abstract INOR 256.

(35) Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Roberts, D. A.; Hochberg, A. K. New OMCVD Precursors for Selective Copper Metallization. *J. Phys.* **1991**, *4*, C2–271.

(36) Shin, H. K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M. F.; Farr, J. D. *Angew. Chem. Adv. Mater.* **1991**, *3*, 246.

(37) Jain, A.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M. F.; Farr, J. D. *Chem. Mater.* **1991**, *3*, 995.

(38) Chi, K. M.; Shin, H. K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Polyhedron* **1991**, *10*, 2293.

(39) Chi, K. M.; Shin, H. K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1991**, *30*, 4293.

(40) Jain, A.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M. F.; Farr, J. D. *J. Mater. Res.* **1992**, *7*, 261.

aspects of this work have been communicated.[36-38]

Experimental Section

General Procedures. All manipulations were carried out either under an atmosphere of dry nitrogen or under reduced pressure, as previously described.[29] Molecular precursors of the general formula (β-diketonate)Cu(PMe$_3$) (where β-diketonate = acac, tfac, and hfac) were prepared by both metalation and metathesis reactions, as described elsewhere.[28,29] Cu(hfac)$_2$ was purchased from Alfa Chemical Co. and was sublimed before use. The compounds (β-diketonate)Cu(PMe$_3$)$_2$,[29] (β-diketonate)Cu(1,5-COD),[38] and (β-diketonate)Cu(alkyne)[39] (where alkyne = bis(trimethylsilyl)acetylene, diphenylacetylene, and 2-butyne) have been independently synthesized and characterized. These species were purified by sublimation before CVD experiments.

Configuration of CVD Reactor and Experimental Procedure. CVD experiments were carried out in a hot-wall reactor fitted with a liquid nitrogen U-trap to allow examination of the product distribution. The appratus consisted of the following (Figure 1): (i) precursor evaporation, furnace 1, where the precursor was sublimed at a controlled temperature into the hot reactor; (ii) reactor, furnace 2, where deposition was carried out on substrates oriented horizontally; (iii) cold region, where unreacted precursor and less volatile reaction byproducts condensed on the cold walls between the deposition zone and a cold trap; (iv) U-trap, where volatile and condensible reaction byproducts were trapped at liquid nitrogen temperature. The reactor and evaporator were a single unit that consisted of a single Pyrex tube and had dimensions of 25-mm i.d. and 550-mm length. The system was evacuated with an oil diffusion pump that provided base pressures of 10^{-5} Torr. The precursor was heated independently from the substrate by a separate furnace to control the evaporation rate. Precursor evaporation temperatures were measured by a thermocouple in contact with the container used to hold the precursor. The substrates consisted of silicon wafers coated with 2000 Å of thermally grown SiO$_2$, which had been partially covered with Pt or W by contact masking and electron beam evaporation of the metal. The substrates were typically 1 cm × 1 cm. Substrates were degreased according to the following procedure: The silicon wafers were washed with 1,1,2-trichloro-1,2,2-trifluoroethane and than heated to 140 °C for 10 min in air. They were than cooled under vacuum (1 mTorr) and subsequently handled under a dry nitrogen atmosphere. The substrate temperature was measured by a thermocouple placed against the reactor wall below the substrate position in the deposition zone. In control experiments, the temperature difference between the reactor and the substrate was measured under the same conditions as deposition of films by placing an additional thermocouple inside the heated deposition zone. The average temperature difference measured was less than 5 °C. The substrate temperatures and base pressures were monitored continuously during each experiment.

For each experiment, the reactor was loaded with a substrate and precursor and assembled in a nitrogen atmosphere drybox because some of the copper(I) compounds are air sensitive. Approximately 0.3–0.5 g of precursor was used for each experiment. A single substrate was used for each deposition and was located in the middle of the reactor in most cases. The assembled reactor was connected to the U-trap, which itself was attached to the pumping system. The precursor was cooled to dry ice temperature (−78 °C), while the system was evacuated. At the same time, the deposition zone was preheated for 30 min to achieve a constant temperature. The cooled precursor was then quickly warmed to 45 °C to allow transfer of the precursor into the deposition zone. Deposition was continued until all of the precursor had evaporated. No carrier gas was used. Deposition was carried out over a temperature range of 75–400 °C at 25 or 50 °C intervals, with at least three experiments at each temperature. Deposition times ranged from 30 to 360 min. The reactor pressure was on the order of 10^{-2} Torr, which ensured that only surface chemical reactions would occur.

Reaction byproducts were collected from both the cold walls of the deposition chamber and the liquid nitrogen cold trap (−196 °C). These condensible reaction byproducts were separated and analyzed by elemental analysis, NMR, and mass spectroscopy and compared to authentic samples to examine reaction product distributions. Deposited copper films were cooled to room temperature before they were exposed to air to reduce oxidation. The film purity was examined by Auger electron spectroscopy (AES). Film morphology was examined by scanning electron microscopy (SEM). Film thicknesses were measured with a Tencor stylus profilometer and SEM, and resistivities were measured using a four-point probe. Measurements were taken at several positions and then averaged to obtain resistivities.

Results and Discussion

Physical and Chemical Properties of the Precursors. The synthesis and characterization of the compounds (β-diketonate)CuL$_n$ (where L = PMe$_3$, PEt$_3$, n = 1 and n = 2;[28,29] L = 1,5-COD[38] and alkyne,[39] and β-diketonate = hfac, tfac, and acac) have been reported elsewhere. Their relevant physical and chemical properties are summarized briefly here.

The species (hfac)CuPMe$_3$ and (tfac)CuPMe$_3$ are monomeric in benzene solution as determined by cryoscopic molecular weight measurement. Single-crystal X-ray diffraction studies revealed that representative examples of (hfac)CuL (where L = PMe$_3$,[28,29] 1,5-COD,[38] diphenylacetylene,[39] and 2-butyne[41]) are monomeric in the solid state. All these species are sufficiently volatile that they can be sublimed, in vacuo, between room temperature and 60 °C. Although the degree of aggregation has not been determined in the gas phase, these species are probably monomeric since they are monomeric in the liquid and solid phases.

The vapor pressures of (hfac)CuPMe$_3$[29] and (hfac)Cu(1,5-COD)[33] have been measured as a function of temperature.[22] Compared to the literature data for Cu(hfac)$_2$ (e.g., ~250 mTorr at 60 °C),[42] (hfac)CuPMe$_3$ (100 mTorr at 60 °C) and (hfac)Cu(1,5-COD) (56 mTorr at 62 °C) have lower vapor pressures.

Hot-Wall Reactor Results. (*a*) *General Observations.* All CVD experiments were carried out in the hot-wall reactor (Figure 1). This reactor configuration allowed high precursor conversion, when desired, to facilitate byproduct distribution analysis. Measurements of deposition rates and activation parameters using a warm-wall turbomolecular pumped reactor with a lamp-heated substrate under surface reaction-limited conditions with low precursor conversion are reported elsewhere.[37,40,43] In the hot-wall system, the precursor temperature could be controlled, but the rate of precursor evaporation was not due to variations in precursor surface area with time. As a result, deposition rates were not optimized and were not necessarily reproducible. However, when the precursor was more finely divided by grinding it in a mortar and pestle, the deposition rate increased. For example, CVD of (hfac)CuPMe$_3$ at 400 °C, where the (hfac)CuPMe$_3$ was crushed, provided deposition rates of 1000–1200 Å/min. These values are significantly higher than in comparable experiments where the precursor was not crushed (350 Å/min).

CVD of copper from (β-diketonate)Cu(L)$_n$ compounds was carried out under conditions noted in Tables I–III. The compounds (acac)Cu(1,5-COD) and (tfac)Cu(1,5-COD) were too thermally unstable for CVD experiments under similar conditions.[38]

Similar deposition rates and purity and identical selectivity were observed in both an oil-diffusion pumped system with a base pressure of 10^{-5} Torr and a mechani-

---

[41] Baum, T. H.; Larson, C. E. *Chem. Mater.*, in press.

[42] Wolf, W. R.; Sievers, R. E.; Brown, G. H. *Inorg. Chem.* **1972**, *11*, 1995.

[43] Shin, H. K.; Chi, K. M.; Jain, A.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M. F.; Farr, J. D. *SPIE Conf. Proc., Metalization: Performance and Reliability Issues for VLSI and ULSI*; San Jose, CA, 1991, Vol. 1596, 23.

Table I. Deposition Data for (hfac)CuPMe$_3$ on Pt Substrates

temp, °C	film thickness, μm	grain size, μm	resistivity, μΩ cm	deposition rate, Å/min	adhesion (Scotch tape)	selectivity (Pt/SiO$_2$)
150	0.1–0.6	0.2	3.2–6.0	20–50	good	yes
200	0.3–0.5	0.3	2.1–2.5	20–60	good	yes
250	1.2–2.1	0.6	1.7–2.6	70–210	good	yes
300	1.2–1.8	1.0	4.0–4.1	70–210	peel off	yes
350	1.0–2.2	1.5	5.2–5.3	150–170	peel off	no
400	3.0–5.8	2.0	3.5–4.4	1000–1200	peel off	no

Table II. Deposition Data for (tfac)CuPMe$_3$ on Platinum Substrates

temp, °C	film thickness, μm	grain size, μm	resistivity, μΩ cm	deposition rate, Å/min	adhesion (Scotch tape)	selectivity (Pt/SiO$_2$)
80	0.4–0.8	0.4	5.0–9.0	20–30	good	yes
100	1.3–1.8	0.7	2.6–3.0	90–100	good	yes
150	0.6–1.0	<0.1	1.7–2.2	70–100	good	no
200	0.5–1.1	0.3	2.2–2.6	20–60	good	no
250	0.4–3.2	0.4	20–>100	20–50	peel off	no
300	0.8–1.0	0.6	10–>100	40–60	peel off	no
350	0.7–1.0	0.7	>100	30–70	peel off	no
400	0.8–0.9	0.8	>100	40–60	peel off	no

Table III. Deposition Data for (hfac)Cu(COD) on Pt Substrates

temp, °C	film thickness, μm	grain size, μm	resistivity, μΩ cm	deposition rate, Å/min	adhesion (Scotch tape)	selectivity (PtSiO$_2$)
120	0.56	0.6	2.2	62	good	no
150	0.63	0.9	1.7	63	good	no
180	1.13	1.3	1.8	87	good	no
200	1.66	1.6	1.9	125	good	no
250	1.69	1.9	1.8	169	good	no

cally pumped system with a base pressure of 10^{-2} Torr. The selectivity reported here was also reproduced in the warm-wall reactor described elsewhere.[37] Films produced at a single temperature from the same precursor were smooth, rough, columnar, equiaxed, or needles, depending on the surface cleaning, reactant partial pressure, precursor purity, and other conditions.

(*b*) *Film Purity.* Film purity was examined by Auger electron spectroscopy (AES). AES could be deposited at reactor temperatures above 150 °C for (hfac)CuPMe$_3$, above 80 °C for (tfac)CuPMe$_3$, and as low as 40 °C for (acac)CuPMe$_3$. AES showed that the films deposited over the temperature range 150–400 °C using (hfac)CuPMe$_3$ contained no detectable C, F, O, or P impurities. A typical AES spectrum and depth profile for films derived from (hfac)CuPMe$_3$ are shown in Figure 2. AES results for (tfac)CuPMe$_3$ showed carbon contamination for films deposited at 80 and 100 °C but showed high-purity copper at 150 °C and higher. The film deposited from (acac)CuPMe$_3$ at 200 °C did not contain impurities above the levels detectable by AES.

CVD from (hfac)Cu(PR$_3$)$_2$ where R = Me or Et was carried out in the temperature range 100–400 °C but did not result in significant deposition below 300 °C. Films deposited over the region 300–400 °C contained no impurities within the limits of AES.

Films deposited from (hfac)Cu(1,5-COD) and (hfac)Cu(2-butyne) over the reactor temperature range 120–250 °C showed no detectable impurities by AES. However, the (hfac)Cu(alkyne) compounds, where alkyne = bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, did not deposit below 200 °C and between 200 and 250 °C gave discontinuous deposits.

In comparison, films deposited from other copper(I) compounds, such as CpCuL,[26,27] *t*-BuOCuL,[26] and [Cu(O-*t*-Bu)]$_4$,[25] in the absence of a reducing agent (e.g., H$_2$) over the same temperature ranges generally showed evidence of impurity incorporation by AES. The deposition of copper films from Cu^{II}(hfac)$_2$ in the absence of H$_2$ has been studied over a variety of substrate temperatures.[20] No deposition was observed below 310 °C. Films deposited at 340 and 390 °C were pure copper as determined by XPS. Above this temperature significant contamination was observed to the extent of 25% Cu, 65% C, and 10%

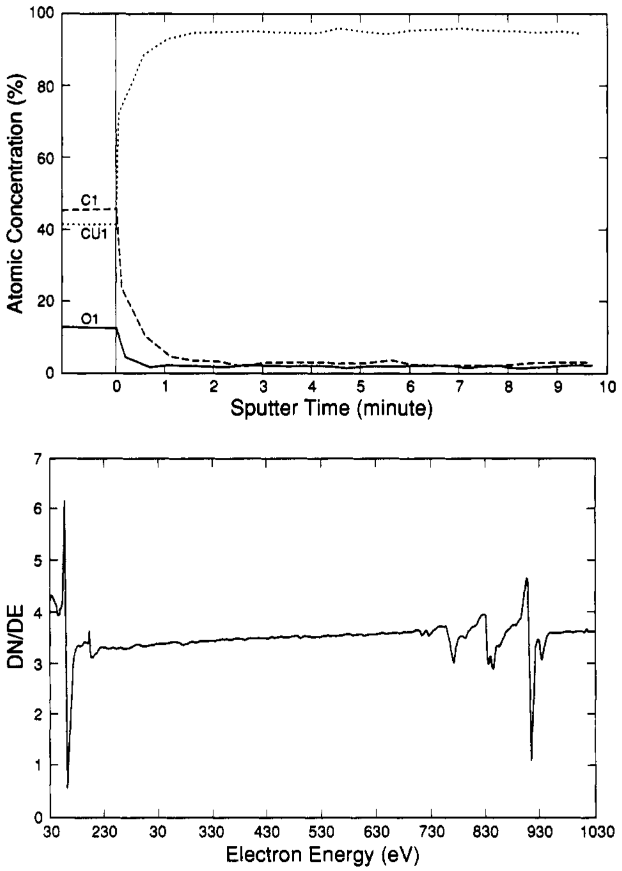

Figure 2. Auger electron spectroscopy depth profile (top) and spectrum (bottom) for film deposited using (hfac)CuPMe$_3$.

Table IV. Selectivity as a Function of Precursor Composition Substrate and Temperature[a]

precursor	selectivity	temp range, °C	ref
(hfac)Cu(PMe$_3$)	Pt, W, Cu vs SiO$_2$	150–300	36, this work
(tfac)Cu(PMe$_3$)	Pt, W, Cu vs SiO$_2$	100–150	this work
(acac)Cu(PMe$_3$)	Pt, W, Cu vs SiO$_2$	<80	this work
(hfac)Cu(1,5-COD)	none for Pt, W, Cu vs SiO$_2$	120–250	this work
(hfac)Cu(1,5-COD)	certain degree of selectivity for Ta, Cu, Ag, Au and Cr vs SiO$_2$ and Si$_3$N$_4$	<200	33
(hfac)Cu(VTMS)	W vs SiO$_2$	120–420	35
	TiN vs SiO$_2$	150–180	35
	PtSi vs SiO$_2$	150–200	35
(hfac)Cu(VTMS)	none for W vs SiO$_2$	120–250	43
(hfac)Cu(BTMS)	none for Pt, W, Cu vs SiO$_2$	120–250	37
(hfac)Cu(2-butyne)	none for Pt, W, Cu vs SiO$_2$	120–250	37, this work
(hfac)Cu(2-butyne)	Co, Mo vs SiO$_2$ and polyimide	120–250	41
(hfac)Cu(2-pentyne)	none for Pt, W, Cu vs SiO$_2$	120–250	37

[a] See references for details of deposition conditions and reactor configurations.

O at 430 °C and 100% C at 500 and 650 °C. Addition of hydrogen gas during deposition significantly increased the purity of the films deposited from Cu(hfac)$_2$.[22–24] The purity of the copper films deposited from all the (β-diketonate)CuL$_n$ precursors described here appears to be consistently higher than that deposited from other copper containing metal organic compounds in the absence of a reducing agent. Also, copper deposition from (β-diketonate)CuL precursors was generally observed at lower temperatures than with copper(II) bis(β-diketonate) complexes.

(c) *Resistivity, Morphology, Deposition Rate, and Selectivity.* Deposition data are summarized in Tables I–III for (hfac)Cu(PMe$_3$), (tfac)Cu(PMe$_3$), and (hfac)Cu(1,5-COD) respectively. Selectivity data are summarized in Table IV.

(i) *(hfac)CuPMe$_3$.* Copper films were deposited from (hfac)CuPMe$_3$ at reactor temperatures as low as 150 °C. Lower temperatures gave no deposition. Deposition rates ranged from 20 to over 1000 Å/min. Resistivity values ranging from near bulk (1.7 μΩ cm) at 250 °C to as high as 6.0 μΩ cm at 350 °C (Table I). One possible cause of the high resistivities was contamination. However, AES analysis showed high-purity copper for all films. SEM revealed that the surface morphology of thicker films (which were produced at higher temperatures) consisted of large grains that were poorly connected (Figure 3b) compared to the films deposited at lower temperatures. Thus the high resistivities of the thicker films were probably due to poor film morphology. We have not yet examined the relative importance of substrate temperature and film thickness in determining film morphology.

Adhesion was generally poor at and above 250 °C, and films deposited on Pt and W substrates could be peeled off with adhesive tape. Adhesion of films deposited below 250 °C was excellent. Adhesion on SiO$_2$ was poor for all temperatures where films could be deposited.

Selective deposition onto platinum seed layers was possible for temperatures of 150–300 °C. Selectivity was lost above 300 °C where some copper nuclei were observed by SEM on the SiO$_2$. Selective deposition onto 1000-Å W was also possible below 300 °C. Deposition times were 40–90 min, and film thicknesses were 0.3–1.5 μm. Resistivities were 2.7–8.9 μΩ cm. Deposition rates were 30–360 Å/min. In general, the trends in selectivity were similar to those for deposition onto Pt. Selectivity was not lost for the thicker films as is often the case for W CVD on SiO$_2$ using WF$_6$.[44] No deposition was observed on the clean, silica reactor walls at or below 250 °C. Selective deposition was also observed for deposition onto substrates partially coated with copper.

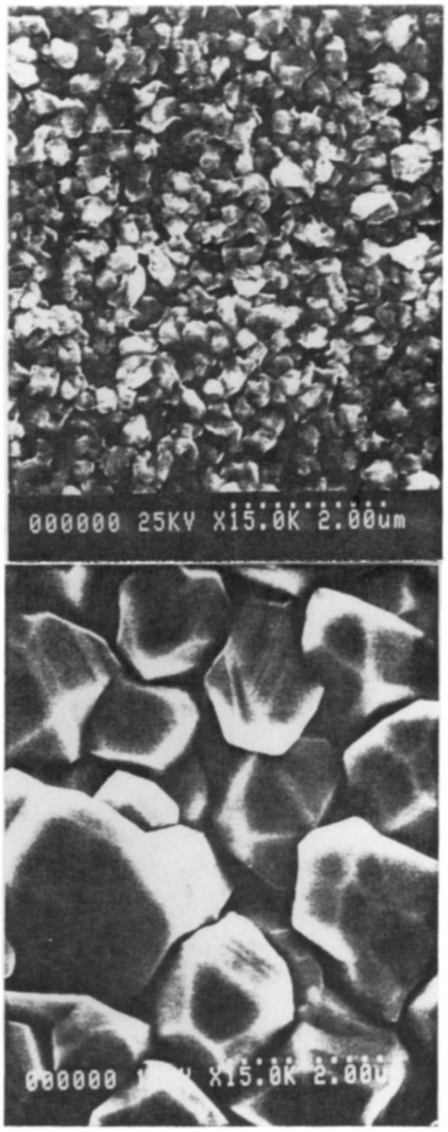

Figure 3. (a, top) Scanning electron micrograph of small-grained film deposited at 200 °C from (hfac)CuPMe$_3$. (b, bottom) SEM of large-grained film deposited at 400 °C from (hfac)CuPMe$_3$.

These selectivity trends are particularly interesting in light of the observation that Cu(β-diketonate)$_2$ compounds appear to show selectivity for deposition onto SiO$_2$ in the presence of Si in the absence of a carrier gas.[20]

(ii) *(tfac)CuPMe$_3$.* Films were deposited at temperatures from 80 to 400 °C with deposition times of 70–660 min. Feature sizes on the film surfaces ranged from 0.3 to 0.8 μm. Resistivities for continuous films were as low as 1.7 μΩ cm. Above 200 °C, extensive deposition occurred on the reactor walls leading to discontinuous films on the

---

[44] Singer, P. *Semiconduct. Int.* **1991**, *March*, p 46.

substrate surface and high resistivities. Selective deposition onto Pt and W was observed at and below 100 °C. This is in contrast to the results with (hfac)CuPMe$_3$ that gave selective deposition below 300 °C. Deposition rates were 10–100 Å/min, lower than for (hfac)CuPMe$_3$ under similar conditions. This was probably due primarily to the lower volatility of the (tfac)CuPMe$_3$. Poor adhesion was observed above 250 °C. In general, (tfac)CuPMe$_3$ is not as attractive as (hfac)CuPMe$_3$ as a precursor for Cu CVD. This is due to the lower volatility, smaller range of temperatures for selective deposition, and poorer thermal stability. It is also noteworthy that above 300 °C noticeably thicker, more continuous copper films were deposited onto SiO$_2$ than platinum as determined by SEM and resistivity measurements. This was probably due to formation and decomposition of Cu(tfac)$_2$ which tends to deposit copper on SiO$_2$ above 300 °C.

(*iii*) *(acac)CuPMe$_3$*. CVD using (acac)CuPMe$_3$ films was carried out at temperatures up to 200 °C, but substantial precursor decomposition was observed at the reactor inlet before the high-temperature region. Less decomposition was observed when the reactor temperature was maintained at or below 80 °C in this reactor geometry. Films were deposited at 40 and 80 °C with deposition times of 300–600 min. Even at the relatively low sublimation temperature of 40 °C, significant decomposition of the precursor was observed in the precursor chamber. Film thicknesses were 0.1–0.2 μm, and the films were shiny. Resistivities of the films at 80 °C were 5.0 $\mu\Omega$ cm because of the poor connectivity between grains on the surface. The deposition rate was less than 100 Å/min because of the low substrate temperature. Excellent adhesion was observed.

Although (acac)CuPMe$_3$ is a poor precursor for Cu CVD, there are several reasons to examine its behavior. The most critical reason was to determine whether selective deposition could be achieved. Selective deposition could be obtained onto Pt at both 40 and 80 °C. This suggested that changing from the tfac to the acac ligand was not enough to eliminate selectivity. This is useful information since changing from the hfac to the tfac ligand resulted in a drop from 350 to 150 °C for the temperature below which selective deposition could be obtained onto Pt and W.

(*iv*) *(hfac)Cu(PR$_3$)$_2$*. CVD of (hfac)Cu(PR$_3$)$_2$, where R = Me and Et, was also carried out on Pt/SiO$_2$ substrates. These precursors could be heated to 100 °C due to their higher thermal stability compared to the corresponding monophosphine compounds. No deposition onto Pt, SiO$_2$, or the reactor walls was observed for either compound below 300 °C. Above 300 °C deposition was observed onto both Pt and SiO$_2$. An AES of a film deposited from (hfac)Cu(PEt$_3$)$_2$ onto SiO$_2$ at 400 °C showed pure copper.

(*v*) *(hfac)Cu(1,5-COD)*. CVD of copper from (hfac)Cu-(1,5-COD) was carried out over the temperature range 120–250 °C with total pressure 100 mTorr and with a precursor temperature of 70–75 °C. Resistivities were 1.8–2.2 $\mu\Omega$ cm. Deposition rates were 60–170 Å/min. AES spectra and depth profiles showed no contamination. No selectivity was observed at any temperature; copper was deposited on Pt, SiO$_2$, and the reactor walls. The morphology and grain sizes of the films deposited on both Pt and SiO$_2$ at a given temperature were similar.

(*vi*) *(hfac)Cu(alkyne)*. Copper was deposited on Pt, SiO$_2$, and the reactor walls over the temperature range 120–250 °C using (hfac)Cu(2-butyne). The films were pure as determined by AES, and low resistivity values were observed. However, (hfac)Cu(BTMSA) and (hfac)Cu(TMSP) did not deposit copper below 200 °C. At substrate temperatures of 200 and 250 °C, only isolated nuclei were observed on both Pt and SiO$_2$.

(*vii*) *Cu(β-diketonate)$_2$*. For the purpose of comparison, CVD of Cu(hfac)$_2$ and Cu(tfac)$_2$ was carried out under conditions similar to those used for the (β-diketonate)copper(I) species and in the same reactor. It has been reported that Cu(hfac)$_2$ deposits copper selectively on SiO$_2$ in the presence of Si in the absence of hydrogen carrier gas.[20] Here, we were primarily interested in investigating whether any selectivity for either Pt or SiO$_2$ was observed. CVD of Cu(hfac)$_2$ and Cu(tfac)$_2$ was carried out over the temperature range 250–400 °C. Consistent with the literature data, the onset of thermal decomposition was near 330 °C for both compounds. In each case, deposition was observed between 330 and 400 °C on both the reactor walls and on the SiO$_2$ portion of the substrate but not on the Pt-coated area. Another notable feature was the low deposition rate relative to the copper(I) precursors under similar conditions. Since the properties of the films deposited as a function of temperature from these compounds have been described previously, the characteristics of these films were not investigated further.

V. Reaction Byproduct Analysis. Reaction byproduct distributions were examined by characterizing the product species condensed on the cold walls of the reactor (see Figure 1) or collected in the cold trap. Species that condensed on the cool reactor walls before entering the coldtrap were collected by removing the reactor to a nitrogen atmosphere glovebox.

(*i*) *(β-diketonate)Cu(PMe$_3$)*. The products from CVD using (hfac)CuPMe$_3$ were mainly Cu(hfac)$_2$ and (hfac)Cu(PMe$_3$)$_2$ and trace amounts of hfacH. At lower temperatures (150 °C), very little Cu(hfac)$_2$ was observed, consistent with the small degree of reaction of the precursor. The compound (hfac)Cu(PMe$_3$)$_2$ was also observed and was probably formed by reaction of (hfac)CuPMe$_3$ with PMe$_3$ in the precursor holder or in the reactor. The compound (hfac)Cu(PMe$_3$)$_2$ is an orange solid that can be distinguished from (hfac)CuPMe$_3$ by its ^{1}H, ^{13}C and ^{31}P NMR spectral data. No PMe$_3$ was observed in the liquid nitrogen trap at any temperature. As the reactor temperature was increased (200–250 °C), several trends were observed. The amount of (hfac)Cu(PMe$_3$)$_2$ formed increased relative to the amount of unreacted (hfac)CuPMe$_3$. At the highest temperatures (350–400 °C), only (hfac)Cu(PMe$_3$)$_2$ and Cu(hfac)$_2$ were observed. This was probably due to formation of increased amounts of PMe$_3$ at higher temperatures. The amount of Cu(hfac)$_2$ increased as the temperature was raised, again consistent with an increased reactant conversion.

These results are consistent with a mechanism in which deposition takes place by thermally induced disproportionation to produce Cu and Cu(hfac)$_2$ according to eq 2 (L = PMe$_3$):

$$2(\mathrm{hfac})\mathrm{CuL} \rightarrow \mathrm{Cu} + \mathrm{Cu(hfac)_2} + 2\mathrm{L} \qquad (2)$$

The liberated phosphine reacts with (hfac)CuPMe$_3$ according to eq 3:

$$(\mathrm{hfac})\mathrm{CuPMe_3} + \mathrm{PMe_3} \rightarrow (\mathrm{hfac})\mathrm{Cu(PMe_3)_2} \qquad (3)$$

This is consistent with solution experiments where (hfac)Cu(PMe$_3$)$_2$ was formed from the reaction of (hfac)CuPMe$_3$ with 1 equiv of PMe$_3$.[29] Occasionally, a white solid was observed in the cold region of the reactor which was identified as the salt [hfac]$^-$[Cu(PMe$_3$)$_4$]$^+$ by comparison to spectroscopic data of an independently prepared authentic sample. This species can be prepared quantitatively from the reaction of (β-diketonate)Cu(PMe$_3$)

compounds with an excess of PMe_3 according to eq 4.[45]

$$(\beta\text{-diketonate})Cu(PMe_3) + \text{excess } PMe_3 \rightarrow [\beta\text{-diketonate}]^-[Cu(PMe_3)_4]^+ \quad (4)$$

The results of (tfac)$CuPMe_3$ were qualitatively similar to those for (hfac)$CuPMe_3$. At 80 and 100 °C, very small amounts Cu(tfac)$_2$ were detected. Small amounts of tfacH were also observed along with the reactant and (tfac)Cu(PMe_3)$_2$. As the temperature was increased, the relative amounts of Cu(tfac)$_2$ and (tfac)Cu(PMe_3)$_2$ increased. At the highest temperatures, all the reactant was consumed.

Similar reaction byproducts were observed when a sample of (acac)Cu(PMe_3) was heated in a closed vessel. Thus, the byproduct distribution for decomposition of (hfac)$CuPMe_3$, (tfac)$CuPMe_3$ and (acac)Cu(PMe_3) are comparable.

(ii) (hfac)Cu(PR$_3$)$_2$. CVD of (hfac)Cu(PMe_3)$_2$ provided only low deposition rates and small quantities of reaction products. The major product isolated was unreacted starting material together with a small amount of $[hfac]^-[Cu(PMe_3)_4]^+$. No copper(II) species were observed. It is possible that in this case deposition occurred via thermal decomposition of the ligands. Alternatively, disproportionation occurred, but the copper(II) species formed thermally decomposed as previously observed since the substrate temperature was >300 °C. For (hfac)Cu(PEt_3)$_2$ no copper(II) reaction byproducts were observed probably because of the high reactor temperature. In this case, salt formation was not observed, consistent with solution experiments were PEt_3 does not react further with (hfac)Cu(PEt_3)$_2$.[45]

(iii) (hfac)CuL, L = 1,5-COD, 2-butyne. Over the temperature range 120–250 °C, CVD of (hfac)CuL, L = 1,5-COD, 2-butyne, resulted in the disproportionation reaction of eq 2. The copper(II) product was isolated as large dark green crystals on the cold reactor walls and the free ligands, 1,5-COD or 2-butyne, were isolated from the liquid nitrogen trap. No evidence for isomerization of L was observed, in contrast to the thermal decomposition of other metal (1,5-COD) complexes.[46] This reaction is virtually quantitative under CVD conditions by mass balance and no evidence for formation of hfac thermal decomposition products was observed. This observation is reasonable since the reactor temperature was lower than the thermal decomposition temperature of Cu(hfac)$_2$.

Selectivity Loss. Selective deposition of copper is a complex process that can depend on the nature of the precursor and the surface, reactor type (hot-wall, cold-wall, plasma, etc.) and operating conditions (temperature, pressure, etc.), surface preparation procedure, deposition time, and other factors. Thus, results from one system cannot always be used in another system unless care is taken to reproduce the conditions. For this reason, precautions were taken to keep as many conditions constant as possible when examining selectivity. Substrate cleaning was always carried out in the same manner and the same substrates were always used. Reactor type and operating conditions were kept constant. The precursors was synthesized and purified in the same manner.

Table IV summarizes the selectivity data reported here together with literature data. The origin of selectivity for deposition of copper onto different surfaces is not clear. It is likely that quantitative data to address this point will only come from studies conducted in differential reactors where the precursor partial pressure can be controlled and from ultrahigh-vacuum (UHV) experiments. Experiments under UHV conditions have shown that disproportionation cannot be observed due to low surface coverages.[47] However, different modes of adsorption can be observed on different substrates which may lead to useful information.[48]

A number of qualitative conclusions can be drawn from the data presented here.

(1) Selective deposition of copper from (hfac)Cu(PMe_3) onto Pt in the presence of SiO_2 occurs below 300 °C but is lost above 300 °C. Above ~300 °C separate experiments indicate that Cu(hfac)$_2$ selectively deposits on SiO_2 in the presence of Pt. Therefore, one explanation for the loss of selectivity above 300 °C during deposition from (hfac)Cu(PMe_3) is copper deposition onto SiO_2 from the Cu(hfac)$_2$ liberated in the disproportionation reaction of eq 2.

(2) The selectivity for deposition onto Pt in the presence of SiO_2 is lost at a lower temperature for (tfac)Cu(PMe_3) than for (hfac)Cu(PMe_3). Thus, selectivity is influenced by the nature of the β-diketonate ligand substituent in the absence of other changes to the deposition conditions or the copper coordination sphere. However, the mechanism of selectivity loss for (tfac)Cu(PMe_3) is unlikely to be due to deposition of copper from Cu(tfac)$_2$ evolved during disproportionation because in control experiments, Cu(tfac)$_2$ does not significantly thermally decompose below 330 °C. This suggests that the mode of precursor adsorption may determine selectivity.

(3) Changing the Lewis base (L) from PMe_3 to 1,5-COD or alkyne in (hfac)CuL results in loss of selectivity. Thus, selectivity is influenced by the nature of the Lewis base ligand in the absence of other changes to the deposition conditions or the copper coordination sphere. These results are in contrast to the results reported for another olefin complex (hfac)Cu(VTMS), where VTMS = vinyltrimethylsilane where selective deposition was reported on a variety of substrates (Table IV).[35] These observations demonstrate either that selectivity can be achieved by subtle changes in the Lewis base ligand or that the tungsten/SiO_2 surfaces were significantly different.

Conclusions

These experiments demonstrate that compounds of the general formula (hfac)CuL, where L = PMe_3, 1,5-COD, and 2-butyne, are suitable precursors for the CVD of high-purity copper films. On the basis of the analysis of the byproduct distribution, the primary reaction pathway appears to involve thermally induced disproportionation. The derivatives (tfac)CuL and (acac)CuL are less suitable due to their lower volatility and lower thermal decomposition temperature. The minimum deposition temperature for (β-diketonate)$CuPMe_3$, which decreases in the order hfac > tfac > acac, is consistent with the expected order of the β-diketonate-Cu bond strengths.

Selective deposition onto metallic substrates (Pt, Cu, W) as a function of temperature, Lewis base, and β-diketonate ligands has been demonstrated. As the substrate temperature is raised, selectivity for Pt over SiO_2 is lost for (β-diketonate)$CuPMe_3$ compounds in the following order of increasing threshold: acac < tfac < hfac. Selective deposition onto Pt in the presence of SiO_2 was observed

---

[45] Shin, H. K.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *J. Chem. Soc., Dalton Trans.*, in press.

[46] Wark, T. A.; Gulliver, E. A.; Hampden-Smith, M. J.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4360.

[47] Dubois, L. H.; Jeffries, P. M.; Girolami, G. S. In *Advanced Metallization for ULSI Applications*; Rana, V. S., Joshi, R. V., Eds.; Materials Research Society: Pittsburgh, 1991.

[48] Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; *Chem. Mater.*, in press.

for (hfac)CuL, L = PMe$_3$, PEt$_3$ but not for L = 1,5-COD and 2-butyne. These observations indicate that the β-diketonate ligand and Lewis base ligands play a crucial role in determining the deposition selectivity. It is noteworthy that some degree of selectivity has recently been reported (under different conditions) for (hfac)Cu(1,5-COD) below 200 °C for Ta, Cu, Ag, Au, and Cr versus SiO$_2$ and Si$_3$N$_4$.[33]

On the basis of the trends observed for the (β-diketonate)CuPMe$_3$ series, it is tempting to speculate that the cleavage of the β-diketonate ligand is involved in the rate-determining step of the reaction. However, differences in the adsorption/desorption behavior of the reactants and products are likely to be important also and are currently under investigation.[47,48]

Acknowledgment. M.J.H.-S. and T.T.K. thank NSF (No. CHE-9107035) for partially funding this work. M. J.H.-S. thanks the NSF chemical instrumentation program for purchase of a low-field NMR spectrometer, and T.T.K. acknowledges support from the NSF Presidential Young Investigator program (No. CTS-9058538).

Registry No. (hfac)Cu(PMe$_3$), 135707-05-0; (tfac)Cu(PMe$_3$), 135707-06-1; (acac)Cu(PMe$_3$), 135707-07-2; Cu, 7440-50-8; W, 7440-33-7; SiO$_2$, 7631-86-9; Pt, 7440-06-4.

Synthesis and Electrochemistry of Conductive Copolymeric Porphyrins

Judith R. Fish,[†] Eugeniusz Kubaszewski,[†] Alexander Peat,[†] Tadeusz Malinski,*[,†]
Jozef Kaczor,[‡] Piotr Kus,[‡] and Leszek Czuchajowski*[,‡]

Department of Chemistry, Oakland University, Rochester, Michigan 48309-4401, and
Department of Chemistry, University of Idaho, Moscow, Idaho 83843

Received November 18, 1991. Revised Manuscript Received April 9, 1992

This work focuses on electrochemical synthesis and characterization of conductive porphyrinic polymeric and copolymeric materials and their application for electrocatalytic oxidation of methanol and hydrazine and reduction of oxygen directly to water. Conductive polymeric and copolymeric films have been obtained by oxidative electropolymerization of several free-base and metalated porphyrins (*N,N'*-bis[5-*p*-phenylene-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrin]-1,10-phenanthroline-4,7-diamide, H$_2$-(1,10-phen)(TMHPP)$_2$; 5-*p*-(pyrrol-1-yl)phenylene-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrin, H$_2$(p-pyr)TMHPP; *meso*-tris(3-methoxy-4-hydroxyphenyl)(*p*-aminophenyl)porphyrin, H$_2$(p-NH$_2$)TMHPP) and their respective analogues that contain *p*-tolyl substituents (TTPP) instead of 3-methoxy-4-hydroxyphenyl. Metaloporphyrins with zinc(II) and cobalt(II) have been studied. Studies present evidence to show that the copolymeric new materials can have significantly altered electrocatalytic properties. Copolymers of Zn(1,10-phen) (TMHPP)$_2$ and Zn(*p*-NH$_2$)TTPP show significant enhancement of catalytic process over their constituents. This was especially true for electrocatalytic oxidation of hydrazine and reduction of oxygen directly to water. Electrocatalytic reduction of oxygen directly to water was enhanced for all copolymers studied. The current density (0.8–1.1 mA/cm^2) for methanol (5%) oxidation on polymeric and copolymeric porphyrins is 5–7 times higher than that observed on a platinum electrode.

Introduction

Porphyrins containing diethylamino,[1,2] [2.2]paracyclophanyl,[2-5] or 3-methoxy-4-hydroxyphenyl[6,7] meso substituents form conductive polymeric films that show good catalytic properties for a number of reactions on electrodes. The role played by the quinonoid system of bonds formed in the intermediates was ascribed as a key factor involved in the polymerization process.[3-5,7,8] We have synthesized some new porphyrin free bases and their metalo derivatives which can be electrochemically polymerized and studied their catalytic properties. Structures and abbreviations of the free bases are shown in Figure 1.

One set of new porphyrins contains 1,10-phenanthroline as an azaheteroaromatic meso substituent with 3-methoxy-4-hydroxyphenyl groups as the remaining substituents. The 1,10-phenanthroline is attached to the porphine by carboxamide-*p*-phenylene bridges at the 4 and 7 positions of the phenanthroline. This linkage forms a diporphine species in which the phenanthroline acts as a "spacer" between the two porphyrin rings. A second set of compounds contains a *p*-(pyrrol-1-yl)phenyl and, a third, *p*-aminophenyl, replacing one of the 3-methoxy-4-hydroxyphenyl substituents. These later compounds are monoporphyrinic. Also, an analogue of each compound has been synthesized with *p*-tolyl substituents instead of the 3-methoxy-4-hydroxyphenyls. Eventually, these analogues will allow polymerization in the absence of the quinone producing 3-methoxy-4-hydroxy substituents to be investigated.

This article reports our investigations of conductive film formation both from the new species and from combinations of these newly synthesized components. The cata-

---

[†] Oakland University.

[‡] University of Idaho.

(1) Malinski, T.; Bennett, J. E. In *Redox Chemistry and Interfacial Behavior of Biological Molecules*; Dryhurst, G., Niki, K., Eds.; Plenum Press: New York, 1988; p 87.

(2) Bennett, J. E.; Malinski, T. *Chem. Mater.* **1991**, *3*, 490.

(3) Bennett, J. E.; Wheeler, D. E.; Czuchajowski, L.; Malinski, T. *J. Chem. Soc., Chem. Commun.* **1989**, 723.

(4) Czuchajowski, L.; Bennett, J. E.; Goszczynski, S.; Wheeler, D. E.; Wisor, A. K.; Malinski, T. *J. Am. Chem. Soc.* **1989**, *111*, 607.

(5) Czuchajowski, L.; Goszczynski, S.; Wheeler, D. E.; Wisor, A. K.; Malinski, T. *J. Heterocycl. Chem.* **1988**, *25*, 1825.

(6) Malinski, T.; Ciszewski, A.; Fish, J. R.; Czuchajowski, L. *Anal. Chem.* **1990**, *621*, 909.

(7) Malinski, T.; Ciszewski, A.; Bennett, J. E.; Czuchajowski, L. *Proceedings of the Symposium on Nickel Hydroxide Electrodes*; Electrochemical Society: Pennington, NJ, 1990; Vol. 177, p 90.

(8) Malinski, T.; Ciszewski, A.; Bennett, J. E.; Fish, J. R.; Czuchajowski, L. *J. Electrochem. Soc.* **1991**, *138*, 2010.

0897-4756/92/2804-0795$03.00/0 © 1992 American Chemical Society