Chem. Mater. **1991**, *3*, 995–997

# Chemical Vapor Deposition of Copper from (Hexafluoroacetylacetonato)(alkyne)copper(I) Complexes via Disproportionation

A. Jain,† K.-M. Chi,‡ T. T. Kodas,*,†
M. J. Hampden-Smith,*,‡ J. D. Farr,§ and
M. F. Paffett§

*Chemical Engineering Department and*
*Department of Chemistry, University of New Mexico*
*Albuquerque, New Mexico 87131 and*
*CLS-1, Los Alamos National Laboratories*
*Los Alamos, New Mexico 87545*

*Received July 22, 1991*
*Revised Manuscript Received September 13, 1991*

Chemical vapor deposition (CVD) of copper films has been attracting attention recently because copper has a relatively low resistivity and has potential applications as an interconnect metal in microelectronic devices.[1,2] Copper CVD has been reported using copper(II) bis(hexafluoroacetylacetonate) [$\mathrm{Cu(hfac)_2}$][3-7] with Ar and $H_2$ carrier gases, resulting in varying levels of film purity. Recently, copper(I) β-diketonate compounds such as (β-diketonate)CuL, where L = trimethylphosphine ($\mathrm{PMe_3}$),[8-12] vinyltrimethylsilane (VTMS),[13] and 1,5-cyclooctadiene (1,5-COD)[14,15] have been shown to deposit pure copper films by CVD without the use of carrier gas via a thermally induced disproportionation reaction:

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

This reaction has recently been quantified for (hfac)Cu(1,5-COD), where hfac = hexafluoroacetylacetonate.[15] Selective deposition of copper onto Pt, Cu, and W substrates in the presence of $SiO_2$ was observed for (hfac)$\mathrm{CuPMe_3}$ at substrate temperatures of 150–350 °C, but selectivity was lost above 150 °C for (tfac)$\mathrm{CuPMe_3}$, where tfac = trifluoroacetylacetonate.[8,9,12] In contrast, selective deposition was not observed for (hfac)Cu(1,5-COD) under similar conditions.[15]

To understand the factors that affect all aspects of copper deposition (i.e., selectivity, morphology, purity, resistivity, and mechanism) from copper(I) β-diketonate compounds, we have prepared several alkyne adducts. These species are suitable for copper CVD,[12] and the ligands can be subtly substituted to modify the thermally induced disproportionation reaction. We report here a preliminary study of the deposition characteristics including measurement of the activation energy for CVD of copper from (hfac)Cu(2-butyne) where deposition rates of nearly 1 μm/min were achieved at 200 °C, one of the highest deposition rates reported for copper CVD.

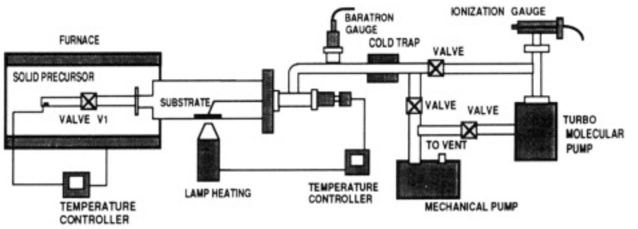

**Figure** 1. Lamp-heated warm-wall turbomolecular-pumped CVD reactor.

**Table I. Deposition Rate Data of (hfac)Cu(I)(2-butyne) Compound at Precursor Partial Pressure of 50 mTorr**

| temp, °C | deposition rate, Å/min | film thickness, μm | av size of surface grain struct, μm | av resistivity, μΩ cm |
|---|---|---|---|---|
| 210 | 9,000 | 9.0 | 2.0 | 2.0 |
| 200 | 9,000 | 9.0 | 2.0 | 2.1 |
| 190 | 5,100 | 5.0 | 1.5 | 2.3 |
| 180 | 2,900 | 2.9 | 0.5 | 2.4 |
| 170 | 1,650 | 1.7 | 0.4 | 2.1 |
| 160 | 900 | 0.9 | 0.3 | 2.7 |
| 150 | 480 | 0.5 | 0.2 | 5.1 |

The (hfac)copper(I) alkyne complexes (where alkyne = (trimethylsilyl)acetylene, diphenylacetylene, 2-butyne, and 2-pentyne) were prepared by the reaction of Na(hfac) with a mixture of CuCl and the corresponding alkyne in pentane solution and are described in detail elsewhere.[16] These derivatives are generally pale yellow, low-melting, volatile solids and were purified by sublimation at 40 °C and $10^{-2}$ Torr. Preliminary CVD experiments were carried out in a hot-wall reactor (previously described)[8-12] under conditions of high precursor conversion.[17] The compounds (hfac)Cu(2-butyne) and (hfac)Cu((trimethylsilyl)acetylene) deposited pure copper within the detection limits of Auger electron spectroscopy (AES) over the temperature range 120–200°C with quantitative disproportionation according to eq 1.[18]

To obtain quantitative kinetic data, CVD experiments were carried out using a lamp-heated, warm-wall, turbomolecular-pumped CVD reactor (Figure 1). The reactant (approximately 500 mg) was loaded into the source chamber in a nitrogen atmosphere drybox. This chamber was attached to the main reactor with valve V1 closed, and the reactor chamber was pumped down to a base pressure of

---

† Chemical Engineering Department, University of New Mexico.
‡ Department of Chemistry, University of New Mexico.
§ Los Alamos National Laboratories.
* Authors to whom correspondence should be addressed.

(1) Murarka, S.; Peckerar, M. C. *Electronic Materials Science and Technology*; Academic Press: New York, 1989.

(2) Pai, P. L.; Ting, C. H. *6th Int. IEEE VLSI Multilevel Interconnect Conf.* **1989**, *1*, 258.

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

(4) Temple, D.; Reisman, A. *J. Electrochem. Soc.* **1989**, *136* (11), 3525.

(5) Temple, D.; Reisman, A. *Technical Report, Microelectronic Center of North Carolina* **1988**, no. 4.

(6) Arita, Y. *Mater. Res. Soc. Symp. Proc. VLSI V (MRS)* **1990**, 335.

(7) Kaloyeros, A. E.; Feng, A.; Garhart, J.; Brooks, K. C.; Ghosh, S. K.; Saxena, A. N.; Luethrs, F. *J. Electronic Mater.* **1990**, *19* (3), 271.

(8) Shin, H.-K.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. F. *Mater. Res. Soc. Symp. Proc*: Spring 1990 MRS Meeting, Symposium J., in press.

(9) Shin, H.-K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr J. D.; Paffett, M. F. *Mater. Res. Soc. Symp. Proc*: Fall 1990 MRS Meeting, Symposium E **1991**, *204*, 421.

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

(11) Shin, H.-K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Duessler, E. N. *Inorg. Chem.*, in press.

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

(13) Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Roberts, D. A.; Hochberg, A. K. *J. Phys. (Paris)*, in press.

(14) Shin, H.-K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Duessler, E. N. *Polyhedron*, in press.

(15) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Kodas, T. T.; Farr J. D.; Paffett, M. F. *J. Mater. Res.*, in press.

(16) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Kodas, T. T.; Duessler, E. N. *Inorg. Chem.*, in press.

(17) The nonselective behavior of (hfac)Cu(2-butyne) led to copper deposition on the substrate as well as the Pyrex reactor walls in the hot-wall CVD reactor resulting in high precursor conversion. Because of the high conversion, volatile byproducts in addition to the precursor partial pressure contribute significantly to the total pressure and information about kinetics cannot be obtained under these conditions. However, high precursor conversion is necessary for quantitative byproducts analysis.

(18) To investigate the disporportionation reaction, hot-wall CVD of (hfac)Cu(2-butyne) compound was carried out in a specially designed reactor. The precursor temperature was maintained at 65 °C and reactor temperature at 200 °C. The only products observed were Cu, $\mathrm{Cu(hfac)_2}$, and 2-butyne. The mass of each component was within 6% of the calculated value which probably represents the error of the experimental procedure.

0897-4756/91/2803-0995$02.50/0 © 1991 American Chemical Society

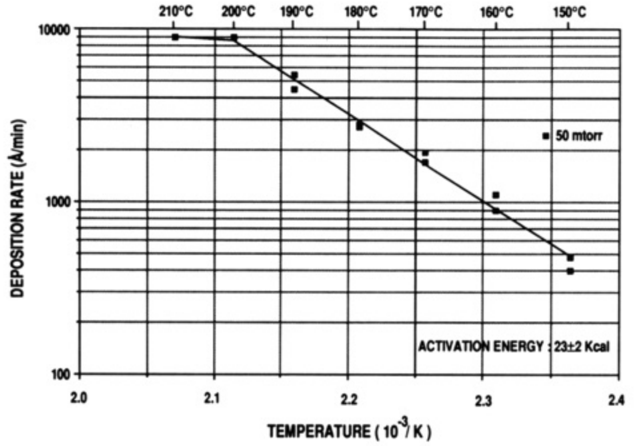

**Figure 2.** Deposition rate of (hfac)Cu(2-butyne) precursor as a function of deposition temperature at a precursor partial pressure of 50 mTorr.

$2 \times 10^{-5}$ Torr. The source chamber was cooled to −78 °C using dry ice and evacuated through V1. The precursor was then heated to 65 °C in a cylindrical furnace with V1 closed and the substrate heated to the desired temperature until thermal equilibrium was established. Valve V1 was then opened to start the deposition experiment. The substrate was heated from the back side by a lamp with a beam diameter of 1.5 cm, while the walls of the quartz reactor were kept warm to prevent condensation of the precursor. This closely approximated a differential reactor where deposition occurred only on the substrate. As a result, the overall conversion of the precursor was kept low (<2% as calculated from substrate weight increase) and the pressure measured by the Baratron was approximately equal to the partial pressure of the precursor. The precursor partial pressure was kept constant by adjusting the pumping speed. The temperature was measured by a thermocouple touching the front side of the substrate.

Copper was deposited on a 1000-Å blanket CVD tungsten layer over a silicon substrate (surface area of approximately 1.0 $cm^2$). The film thickness was calculated from the increase in weight of the substrate. Table I shows the average surface grain structure, film thickness, deposition rates, and resistivity of the films deposited over the temperature range 150–210 °C at 50 mTorr. Each experiment was repeated at least twice in the linear portion of the graph. The minimum temperature was limited to 150 °C because deposition rates lower then approximately 400 Å/min could not be measured accurately due to the small increase in weight of the substrate. A deposition rate of 9000 Å/min was observed at 200 °C. Above this temperature deposition became feed-rate-limited[19] (see Figure 2). In the feed-rate-limited regime, the deposition rate became insensitive to substrate temperature and precursor pressure because the feed rate of molecules to the reactor chamber was lower than the rate at which they could be consumed at a particular temperature if the surface reaction were to limit the deposition rate. The deposition rate instead depended on sublimation temperature in this regime since it controlled the mass flow rate of precursor to the reaction chamber. This situation is frequently encountered for solid precursors which cannot be transported to the reactor at sufficiently high mass flow rates. At such high deposition rates, thick copper lines can be deposited by CVD in a reasonable amount of time.

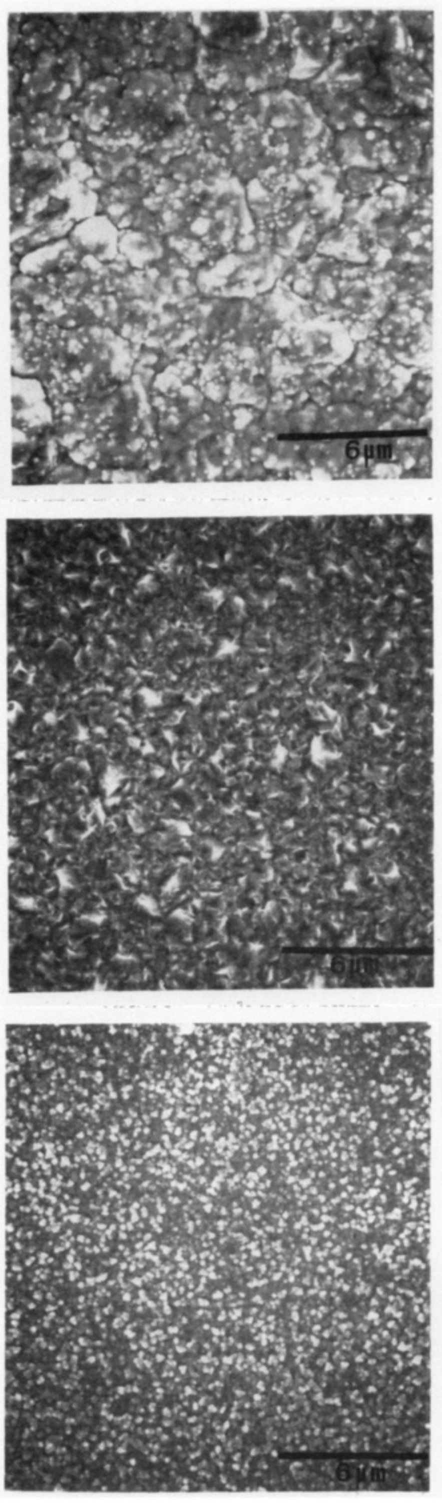

**Figure 3.** Scanning electron micrographs of copper film deposited at a precursor partial pressure of 50 mTorr for temperatures 200 °C (left), 170 °C (middle), and 150 °C (right) showing increase in grain structure with temperature.

An activation energy of 23 (2) kcal/mol at 50 mTorr for CVD of copper from (hfac)Cu(2-butyne) was calculated from the linear portion of the plot of log of deposition rate versus $T^{-1}$ (Figure 2). This value is probably in the range consistent with a rate-limiting copper-hfac ligand bond cleavage reaction.[20] The (hfac)Cu(2-butyne) compound did not show complete selectivity for deposition onto the

---

[19] The feed-rate-limited condition differs from the diffusion-rate limitation which occurs due to formation of a concentration boundary layer over the substrate for near atmospheric pressure deposition conditions. At low pressures a concentration boundary layer is not formed and there is no diffusion limitation.

[20] Girolami, G. S.; Dubois, L. H. *4th Chemical Congress Of North America*; New York, Aug 1991; Abstract COLL 25.

metal surface; deposition was seen on the glass wall directly under the lamp beam. However, an induction period for deposition on the glass wall was observed which increased with decreasing substrate temperature.

Figure 3 shows typical films deposited at a precursor partial pressure of 50 mTorr. The surface morphology showed differences in grain structure as a function of temperature. Films deposited at 200 °C (Figure 3, left) had an average surface grain structure of approximately 2.0 $\mu$m with well-connected grain boundaries. Despite the large grain structures (>1 $\mu$m), the films were specular, which suggested that they were smooth. Such films with large grain structures can exhibit high electromigration resistance.[21] This is an important reliability issue for devices operating at high frequency and high current density.[22] The high density and purity of the films were reflected in the near bulk resistivity (2.0–2.1 $\mu\Omega$ cm) obtained for films deposited above 170 °C. However, higher resistivities were measured for films deposited below 170 °C (Table I) where the morphology changed from well-connected grains to near spherical grains ($\sim$0.2 $\mu$m) which were connected at only a few points (Figure 3, right). Because all of the films deposited in the cold-wall reactor were high-purity copper as determined by AES, this demonstrates the impact of film morphology on the electrical characteristics of the deposited films.

In summary, hot-wall CVD from (hfac)copper(I) alkyne compounds produces pure copper films via disproportionation over the temperature range 150–250 °C. In a cold-wall differential reactor, high deposition rates of up to approximately 1 $\mu$m/min were achieved, but above 200 °C the deposition rate did not increase with temperature and was feed-rate-limited under the conditions employed. The activation energy for CVD of copper from (hfac)Cu(2-butyne) was 23 (2) kcal/mol. The film morphology had a direct impact on the resistivity of the films. Dense well-connected grains were obtained for temperatures above 170 °C, with grain structure increasing with temperature. Further experiments are underway to determine the effect of precursor partial pressure on the deposition rate and to understand the chemical significance of the activation energy.

**Acknowledgment**. We thank NSF (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 PYI program CTS-9058538. We also thank Shirley Weaver for obtaining the SEM data.

**Supplementary Material Available:** SEM and AES data of copper films deposited from (hfa)Cu(2-butyne) (11 pages). Ordering information is given on any current masthead.

---

[21] Kwok T. *Proc. IEEE VLSI Multilevel Interconnect Conf.*; Santa Clara, CA; June 1987; p 456.

[22] White, L. S. *Workshop on Tungsten and other Advanced Metals for VLSI application VII*; Oct 1990; p 3.

---

# Contact Electrification: Ion Transfer to Metals and Polymers

A. F. Diaz,* D. Wollmann, and D. Dreblow

*IBM Almaden Research Center K93/803*
*650 Harry Road, San Jose, California 95120*

*Received September 17, 1991*

The contact and separation of two different surfaces cause them to charge with the opposite sign. Because it is a surface phenomenon, changes in the composition of either surface affect both the sign and magnitude of the charge. The charging mechanism with polymers has been attributed to the transfer of ions[1-4] and electrons.[5-7] Thus, salts or ionomers[2-7] are often added to polymers to control the charge. In particular, ionomers are useful for studying the charging mechanism because one of the ions is covalently bonded to the polymer, while the accompanying counterion can be mobile. Therefore, an ionomer and a molecular salt with the same ions will charge differently in an ion-transfer process but will charge similarly for an electron-transfer process because the structural difference due to binding to the polymer has a marginal effect on the ionization potentials and electron affinities.

Contact electrification studies with ionomers have been carried out using a metal (conductive)[5-7] or a polymer (insulative)[3,4] as the second surface. Methyltriarylphosphonium arylsulfonate salts were employed where, in one case, the phosphonium cation was attached covalently to the ionomer chain while in the other, the arylsulfonate anion was attached.[5-7] Powders containing either ionomer charged positive against a metal surface (independent of ion mobility) and the charge increased with the ion content in the blend. A correlation was found between the charge, the HOMO levels, and the redox potentials for a series of substituted arylsulfonate ions. Thus, electron transfer was proposed as the mechanism for charging. Electron transfer has also been proposed for the development of charge with substituted polystyrenes,[8] salicylaldehyde anils,[8] and polymer-bound triphenylphosphines[9] when contacted with metal particles. The proposal is again based on correlations between the charging behavior and the calculated $\pi$ energy levels for the aromatic structures[8] and work functions.[9]

The case for ion transfer has been strengthened by two separate studies. In one, a blend of a styrene–butyl methacrylate copolymer and an ionomer containing poly(styrene-*co*-*N*-methyl-4-vinylpyridinium toluenesulfonate) ([P]-PyMe$^+$OTs$^-$) was contacted with another polymer (insulative).[3,4] The ionomer-blended powder developed a positive charge, and the charge again increased with the ionomer content. Furthermore, the OTs$^-$ was observed by XPS on the surface of the second polymer after contact and removal of the powder. This evidence supports the ion-transfer mechanism (OTs$^-$ transfer). In the charging experiments between cetylpyridinium bromide blended with polystyrene and indium,[10] the polymer acquired a positive charge. Both ions were detected by SIMS on the negatively charged indium surface after contact; however, the Br$^-$ was in large excess of the cation. Again, the direct observation of the transferred ion on the contacted surface is strong evidence for ion transfer. Since the conductivity

---

[1] Birkett, K. L.; Gregory, P. *Dyes Pigm.* **1986**, *7*, 341.

[2] Macholdt, H.-T.; Sieber, A. *Dyes Pigm.* **1988**, *9*, 119.

[3] Diaz, A. F.; Fenzel-Alexander, D.; Miller, D. C.; Wollmann, D.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1990**, *28*, 75.

[4] (a) Diaz, A. F.; Fenzel-Alexander, D.; Miller, D. C.; Wollmann, D.; Eisenberg, A. 5th International Congress on Non-Impact Printing Technologies, San Diego, CA, 1989. (b) Diaz, A. F.; Fenzel-Alexander, D.; Miller, D. C.; Wollmann, D.; Eisenberg, A. 63rd Colloid and Surface Science Symposium, ACS, Seattle, WA, 1989.

[5] Anderson, J. H.; Bugner, D. E. 4th International Congress on Non-Impact Printing Technologies, New Orleans, LA, 1988; p 79.

[6] Bugner, D. E.; Anderson, J. H. ACS National Meeting, Los Angeles, CA; *Polym. Prepr.* **1988**, *29*, 463.

[7] Anderson, J. H.; Bugner, D. E.; DeMejo, L. P.; Sutton, R. C.; Wilson, J. C.; U.S. Patent 4,837,392, June 6, 1989.

[8] Gibson, H. W. *J. Am. Chem. Soc.* **1975**, *97*, 3832.

[9] Nanya, T.; Tsubuko, K. Japan Hardcopy '88; Soc. Electrophotography Japan, 1988; p 9.

[10] Mizes, H. A.; Conwell, E. M.; Salamida, D. P. *Appl. Phys. Lett.* **1990**, *56*, 1597.

0897-4756/91/2803-0997$02.50/0