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## **Novel Precursors For Chemical Vapor Deposition of Copper Metal**

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Novel Precursors For Chemical Vapor Deposition of Copper Metal

A Thesis

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## **Abstract**

Copper is beginning to replace aluminum and tungsten as the interconnect material between integrated circuit elements. Chemical vapor deposition (CVD) has the potential to deposit clean films of Cu metal on various substrates. We have been studying compounds of  $\text{Cu}(\text{hfac})_2$  that are precursors for Cu CVD. Adducts with piperidine, pyrrolidine, 2,5-dihydrofuran, pentafluorophenylhydrazine, and allylamine have been prepared. Cu film thicknesses and resistivity are presented and compared to those derived from previously studied alcohol adducts.

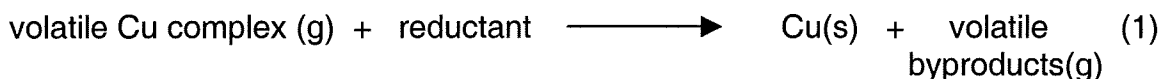
## 1. Introduction

### 1.1 Integrated Circuits

Integrated circuit technology is moving towards increasingly smaller and more densely packed transistors. In the future the current Al and W interconnects will be insufficient. Cu metal, with its lower resistivity than either Al or W, and greater resistance to electromigration than Al, would be a superior replacement<sup>1</sup>.

### 1.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a promising technique for depositing Cu on various substrates because it gives pure and highly conformal films<sup>2</sup>. The CVD process involves heating a volatile metal-organic complex and delivering it via a carrier gas to a heated substrate. Ideally, the complex will adsorb on the surface and decompose to deposit metal and the other byproducts will desorb and be carried away by the carrier gas.



One very well studied precursor for Cu CVD is  $\text{Cu(hfac)}_2$  (see eq. 2). Hydrogen is used as the carrier gas and reducing agent.



The focus of this project is to explore new complexes of the form  $\text{LCu(hfac)}_2$ , where L is some ligand that has the potential to act as the reducing agent, thus making a self-reducing precursor for CVD.

To be useful as a CVD precursor, this compound needs to be volatile so that a substantial amount of it will be delivered to the substrate by the carrier gas. The compound should not decompose with heating or sublimation, i.e., the new ligand should not dissociate from the molecule in the vapor phase. The ligand should act as a reductant to deposit a Cu film, and not contaminate the film.

### 1.3 Alcohol Precursors

Several such self-reducing compounds have already been studied by our group, primarily with  $L=\text{alcohol}$ <sup>3</sup>. The best results were obtained with  $\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$  (see table 1). This adduct, along with several other alcohol complexes, was found to be self-reducing, depositing Cu films in the absence of  $\text{H}_2$  carrier gas. However, many of these alcohol adducts were found to dissociate in the vapor phase, losing the alcohol ligand. Excess alcohol vapor needs to be added to the carrier gas in order for appreciable deposition to occur.

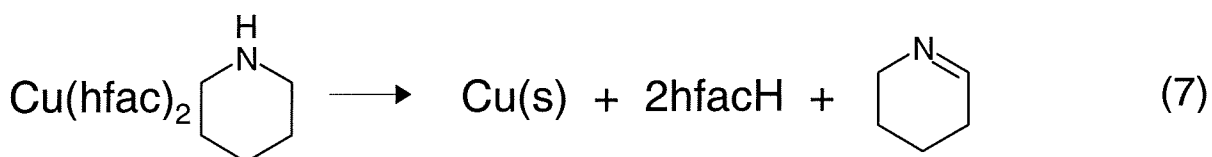
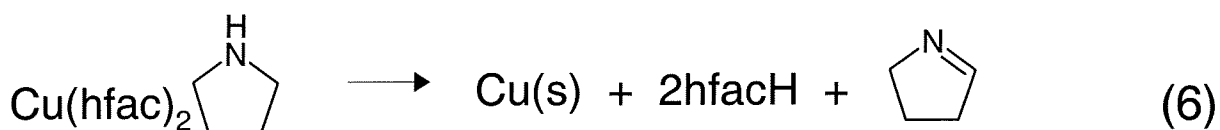
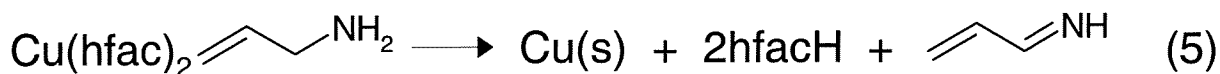
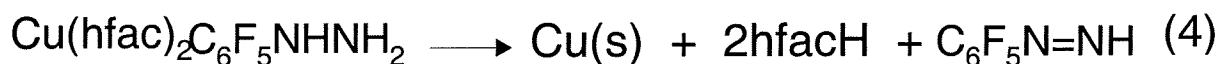
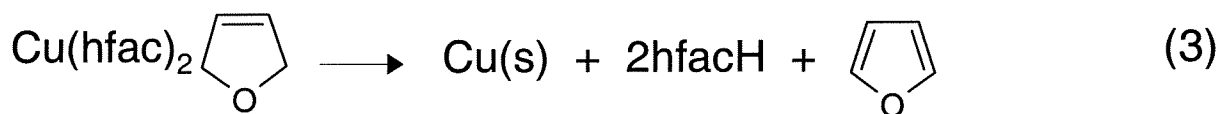
**Table 1: CVD Results for O-adducts of  $\text{Cu}(\text{hfac})_2$ <sup>3</sup>**

Precursor	Carrier gas	Thickness (nm)	Resistivity ( $\mu\Omega \cdot \text{cm}$ )
$\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$	$\text{N}_2$	none	
$\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$	$\text{H}_2$	$280 \pm 70$	$2.8 \pm 0.4$
$\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$	$\text{N}_2 + i\text{-PrOH(g)}$	$1300 \pm 300$	$2.9 \pm 1.2$
$\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$	$\text{H}_2 + i\text{-PrOH(g)}$	$460 \pm 140$	$2.0 \pm 0.9$
$\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$	$\text{N}_2$	none	
$\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$	$\text{H}_2$	$560 \pm 80$	$3.3 \pm 0.7$

Standard conditions: 1 atm, 1hr, evaporation temperature 80 °C, substrate borosilicate glass, substrate temperature 200 °C;  $\text{Cu}(\text{hfac})_2 \cdot i\text{-PrOH}$ : carrier gas 175 mL/min,  $\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$ : carrier gas 400 mL/min.

### 1.4 Amine Precursors

Amine adducts were considered in this project for several reasons. Because of their greater basicity, amines are expected to bind more strongly to Cu than alcohols and water, and thus be less likely to dissociate in the vapor phase. Amines that could act as reducing agents were selected. There is not much in the literature regarding the enthalpies of dehydrogenation for various amines (presumably because their oxidized counterparts are unstable and difficult to isolate). However, the  $\Delta H$  for dehydrogenation of pyrrolidine to 1-pyrroline was estimated by Wiberg and co-workers<sup>4</sup> to be 67 kJ/mol. Though this is endothermic, the overall reaction (eq. 7) is exothermic when the dehydrogenation of pyrrolidine is subtracted from eq. 2 ( $\Delta H = -83$  kJ/mol<sup>5</sup>). In this project, we studied precursors made from five new neutral ligands that might act as reducing agents as shown below: 2,5-dihydrofuran (eq. 3), pentafluorophenylhydrazine (eq. 4), and allylamine (eq. 5), piperidine (eq. 6), and pyrrolidine (eq. 7). Dihydrofuran was chosen as the oxygen analog of 3-pyrroline, which was attempted but turned out to be too difficult to synthesize.



Several attempts were made to synthesize adducts of other hydrazine derivatives.  $\text{Cu}(\text{hfac})_2 \cdot 2\text{hydrazine}$  had been previously reported<sup>6</sup>. We had found this adduct could be used as a CVD precursor<sup>3</sup>. We attempted to make adducts with 1,2-dimethylhydrazine and 1,2-diethylhydrazine. These hydrazine derivatives are safer than hydrazine, and they are still excellent reducing agents. The enthalpy of dehydrogenation of 1,2-dimethylhydrazine has been estimated to be  $-60 \text{ kJ/mol}$ .<sup>3</sup> In both cases we were unsuccessful in isolating a product. Our attempts at synthesizing the hydroxylamine adduct were also unsuccessful.

## 2. Experimental

All of the syntheses were done under inert atmosphere in an Ar-filled glove box. The precursors were made from commercially available ligands. Anhydrous  $\text{Cu}(\text{hfac})_2$ , a blue-gray powder, was prepared by dehydrating commercially available  $\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$  in a desiccator at reduced pressure, over  $\text{P}_2\text{O}_5$ .

### 2.1 Synthesis of $\text{Cu}(\text{hfac})_2 \cdot \text{dihydrofuran}$

$\text{Cu}(\text{hfac})_2$  (1.0 g, 2.2 mmole) was dissolved in methylene chloride and 2,5-dihydrofuran (0.18 mL, 2.4 mmole) was added. The solution was allowed to stir overnight, and then the solvent was evaporated leaving a teal colored solid with a melting point of  $80\text{-}81^\circ\text{C}$ . Calculated C 30.17%, H 1.47%. Found C 30.65%, H 1.47%.

### 2.2 Synthesis of $\text{Cu}(\text{hfac})_2 \cdot \text{piperidine}$

$\text{Cu}(\text{hfac})_2$  (2.6 g, 5.4 mmole) was dissolved in methylene chloride and piperidine (0.5 mL, 5.4 mmole) was added. The solution was allowed to stir for three days, and then the solvent was evaporated leaving a turquoise colored solid with a melting point of  $82\text{-}83^\circ\text{C}$ . The structure of this complex was determined by single crystal X-ray diffraction (see Fig. 1).



### 2.3 Synthesis of $\text{Cu}(\text{hfac})_2 \cdot 2\text{allylamine}$

$\text{Cu}(\text{hfac})_2$  (1.0 g, 2.2 mmole) was dissolved in methylene chloride and allylamine (0.4 mL, 5.0 mmole) was added. The solution was allowed to stir for two hours and then the solvent was evaporated leaving a lime green solid with a melting point of 128-130 °C. The structure of this complex was determined by single crystal X-ray diffraction (see Fig. 2).

### 2.4 Synthesis of $\text{Cu}(\text{hfac})_2 \cdot \text{pentafluorophenylhydrazine}$

Pentafluorophenylhydrazine (0.25g, 1.2 mmole) was dissolved in methylene chloride.  $\text{Cu}(\text{hfac})_2$  (0.5g, 1.1 mmole) was added and the solution was stirred for 2.5 hours. The solvent was then evaporated to leave an olive green solid with a brown ring of decomposed material marking the original solvent level in the flask. Only the green material was collected. The compound does not melt but decomposes to a black liquid at 92-93 °C, with some gas evolution.

### 2.5 CVD Experiments

The compounds were heated at reduced pressure to evaluate their sublimation properties. Melting points of sublimed materials were taken to confirm that the compounds sublimed intact. CVD experiments were performed in a CVD apparatus (see fig. 3) using  $\text{H}_2$  and  $\text{N}_2$  as carrier gases at a flow rate of 400 mL/min. The precursors were heated at a range of temperatures, within ca. 20 °C of their melting points for evaporation. Borosilicate glass substrates were maintained at 230-240 °C for deposition.

### 2.6 Film Quality Analysis

All films were evaluated for film thickness and film resistivity. However, not all films were coherent enough to yield data. SEM photographs were supplied by Dr. Gregory Griffin, LSU Department of Chemical Engineering. Film thickness was measured using a stylus profilometer (Tencor Alpha-Step 200), and resistivity using a four-point probe (Veeco FPP-100). Calculated resistivities were multiplied by a correction factor of 1.44, to compensate for instrument error.

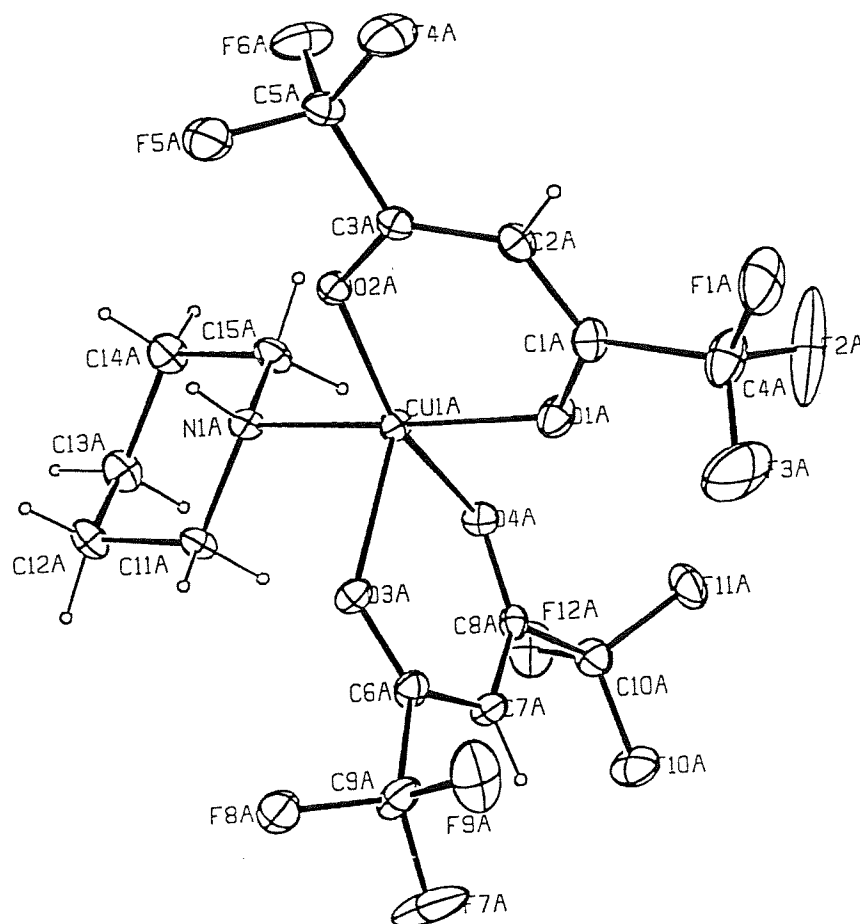


Figure 1. Cu(hfac)<sub>2</sub>·piperidine

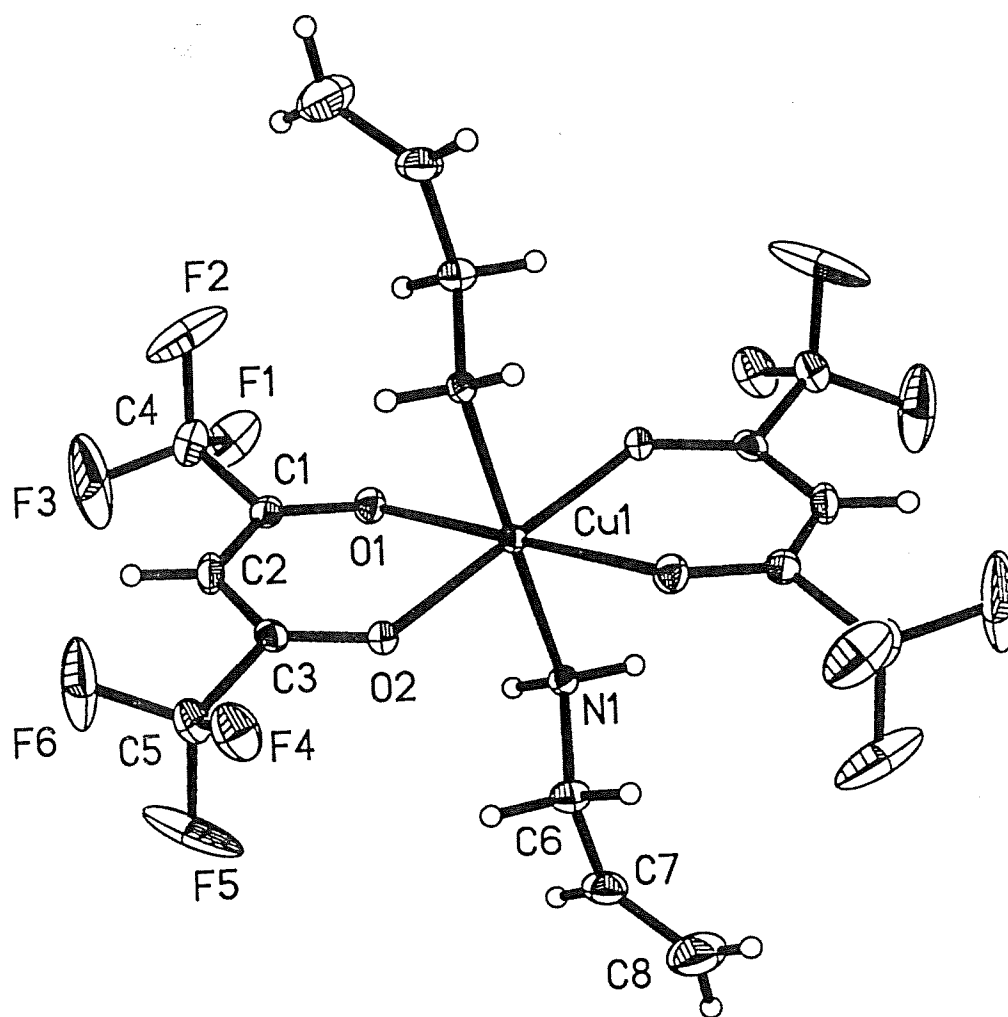


Figure 2.  $\text{Cu}(\text{hfac})_2 \cdot 2\text{allylamine}$

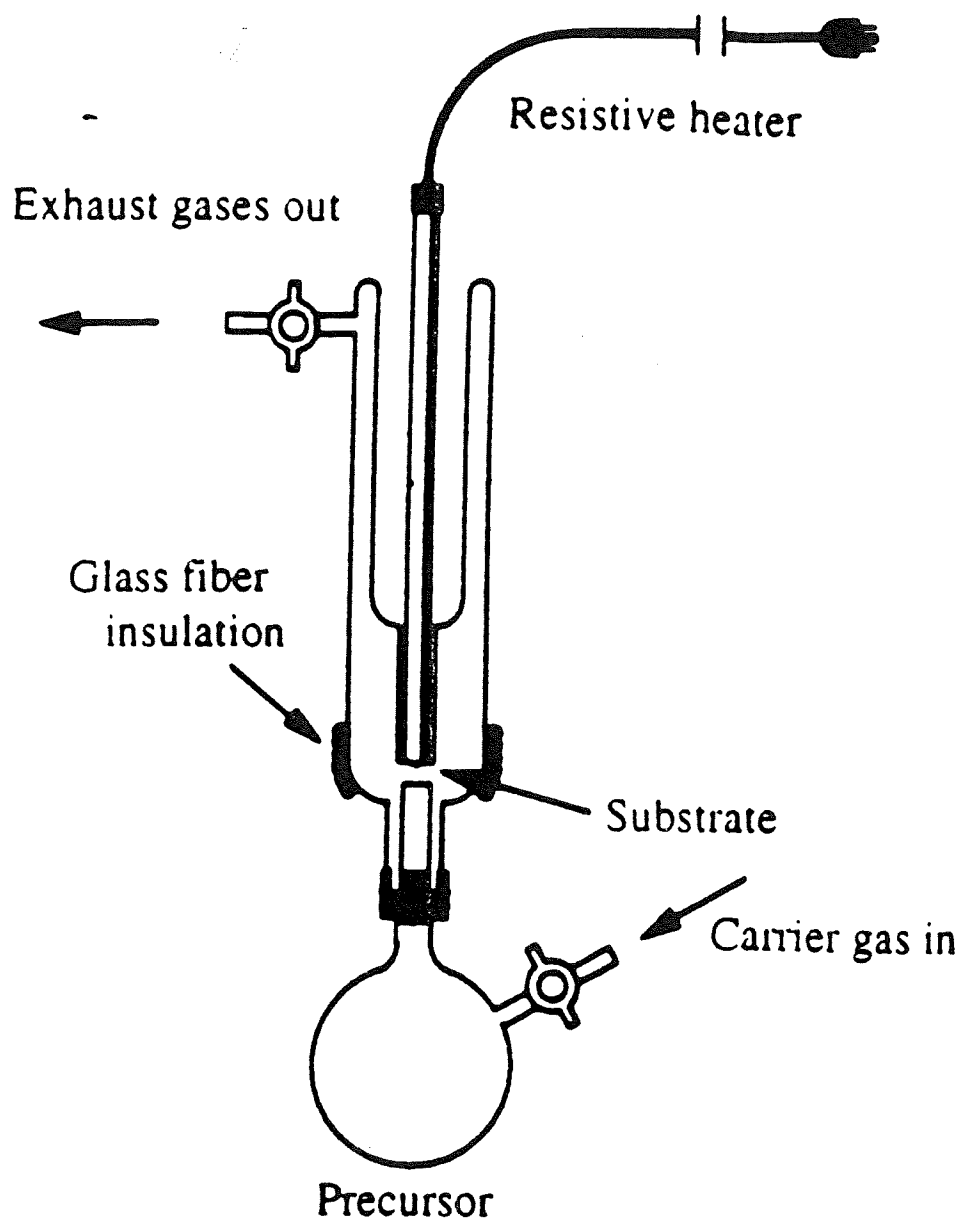


Figure 3. Schematic of CVD apparatus

### 3. Results

Film thicknesses and resistivities for the five precursors are summarized in table 2.

**Table 2: CVD Results for New Precursors**

Precursor	Thickness (nm)	Resistivity ( $\mu\Omega\cdot\text{cm}$ )	Deposition Rate (nm/min)
$\text{Cu}(\text{hfac})_2\cdot 2,5\text{-dihydrofuran}$	$920 \pm 70$	$2.6 \pm 0.6$	$15 \pm 1$
$\text{Cu}(\text{hfac})_2\cdot \text{C}_6\text{F}_5\text{NHNH}_2$	NA	NA	NA
$\text{Cu}(\text{hfac})_2\cdot 2\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$	$1000 \pm 300$	$2.6 \pm 0.9$	$20 \pm 7$
$\text{Cu}(\text{hfac})_2\cdot \text{piperidine}$	$280 \pm 70$	$4.8 \pm 0.3$	$5 \pm 1$
$\text{Cu}(\text{hfac})_2\cdot \text{pyrrolidine}$	$500 \pm 200$	$3.5 \pm 0.7$	$8 \pm 3$

Standard conditions: Carrier gas  $\text{H}_2$ , flow rate 400 mL/min, 1 atm, 50-60 minutes, evaporation temperature near mp of precursor, substrate borosilicate glass, substrate temperature 225-240 °C.

### 3.1 Cu(hfac)<sub>2</sub>•2,5-dihydrofuran

This compound melts at 82-83 °C. It was found to sublime intact. However, upon standing in air, water gradually displaces some of the dihydrofuran ligands. As the complex reacts with water, it becomes markedly lighter in color, and its melting point rises approximately 10 degrees. The original color and melting point can be restored by placing the material under reduced pressure for several minutes. This adduct deposited copper with CVD using H<sub>2</sub> as a carrier gas. Experiments under N<sub>2</sub> failed to produce a copper film even at substrate temperatures of 270 °C, although a faint yellow tint was observed on the substrate at these highest temperatures. Thus, this compound is not a self-reducing precursor; however, its deposition performance under H<sub>2</sub> is quite good.

### 3.2 Cu(hfac)<sub>2</sub>•C<sub>6</sub>F<sub>5</sub>NHNH<sub>2</sub>

This compound decomposes at 92-93 °C to deposit copper metal and liberate gas. This is definitely a self-reducing complex. However, it is not a good precursor for CVD because it fails to sublime appreciably. CVD experiments under N<sub>2</sub> did not yield any deposition.

### 3.3 Cu(hfac)<sub>2</sub>•2CH<sub>2</sub>=CHCH<sub>2</sub>NH<sub>2</sub>

This compound melts at 127-130 °C. It is very volatile above 125 °C and sublimes intact. It does not deposit significantly under N<sub>2</sub> but produces a substantial copper film with H<sub>2</sub> carrier gas. A SEM photograph showed a typical particle size of ca 1.4 μm. (see Fig. 4)

### 3.4 Cu(hfac)<sub>2</sub>•piperidine

This compound melts at 82-83 °C. It is volatile and sublimes intact. This complex also did not deposit Cu under N<sub>2</sub> CVD. The results under H<sub>2</sub> CVD were the worst of the precursors studied.

### 3.5 Cu(hfac)<sub>2</sub>•pyrrolidine

The pyrrolidine adduct was synthesized according to the method of Bufaroosha<sup>7</sup> and several CVD experiments were performed. This was the only compound found to act as a self-reducing precursor. Cu films were observed with CVD using N<sub>2</sub> as a carrier gas, although most were too thin to measure. The only film suitable for analysis was 1000 ± 400 nm thick and had a resistivity of 200 ± 100 Ωcm. Gaseous products from the N<sub>2</sub> CVD were trapped. GC/MS of these showed a band not seen in the H<sub>2</sub> CVD products, containing fragments of masses corresponding to the 1-pyrroline monomer and its dimer. 1-pyrroline rapidly trimerizes<sup>4</sup>. Nomura and coworkers have noted that MS conditions readily fragment this trimer.<sup>8</sup> Thus, Cu CVD occurs with this precursor according to eq. 6 (pg. 3).

### 3.5 Other Precursors

We attempted to synthesize adducts of 1,2-dimethylhydrazine and 1,2-diethylhydrazine. In each case we were unsuccessful in isolating a product. These hydrazine derivatives were purchased as hydrochloride or dihydrochloride salts. In order to generate the free amine, a strong base such as hydroxide or methoxide was used. However, in each case the reactants decomposed presumably because the base attacked the hfac<sup>-</sup> ligand. Finally, pentafluorophenylhydrazine was chosen because it could be obtained as the free hydrazine, and its adduct was readily synthesized. As expected, this hydrazine derivative is a self-reducing complex, but the complex is not sufficiently volatile to be a good CVD precursor.

We also attempted to make the hydroxylamine adduct, and again encountered the same problems with the use of strong bases to deprotonate NH<sub>2</sub>OH•HCl. On one such attempt, a greenish solid was collected. Attempts to purify it by sublimation were made, but this gave a dark blue crystalline sublimate which proved to be anhydrous Cu(hfac)<sub>2</sub>.

The structure of this anhydrous Cu(hfac)<sub>2</sub> was determined by X-ray diffraction; see Fig. 5. The most unusual feature of this structure is an unusually

short nonbonded distance between the Cu and a F on a  $\text{CF}_3$  group of an adjacent molecule (Cu-F 2.710(1) Å). This distance is indicative of the high affinity of the Cu atom in  $\text{Cu}(\text{hfac})_2$  for even very weak bases.



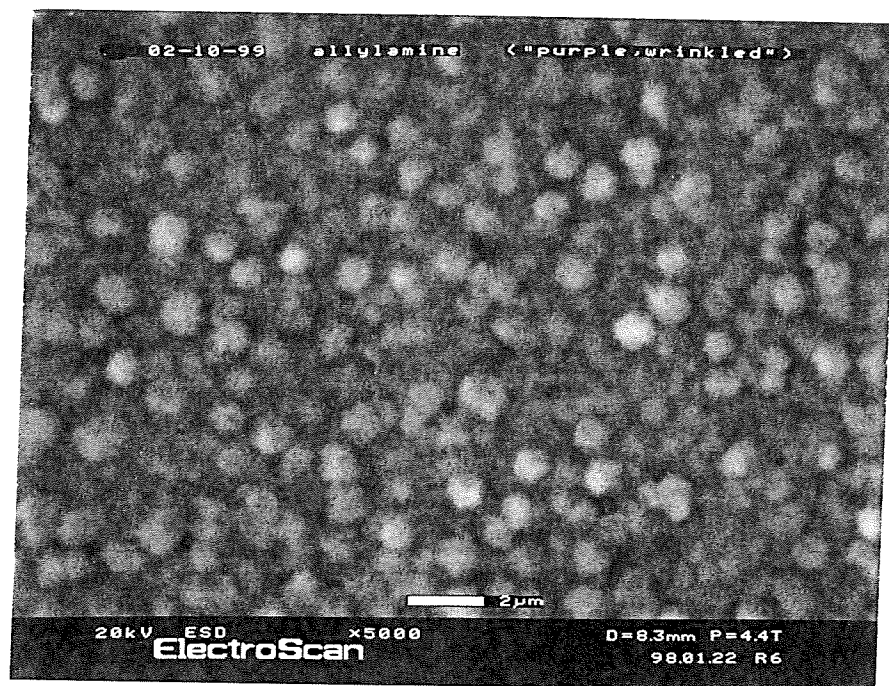


Figure 4. SEM photograph of Cu film from  $\text{Cu}(\text{hfac})_2 \cdot 2\text{allylamine}$  CVD

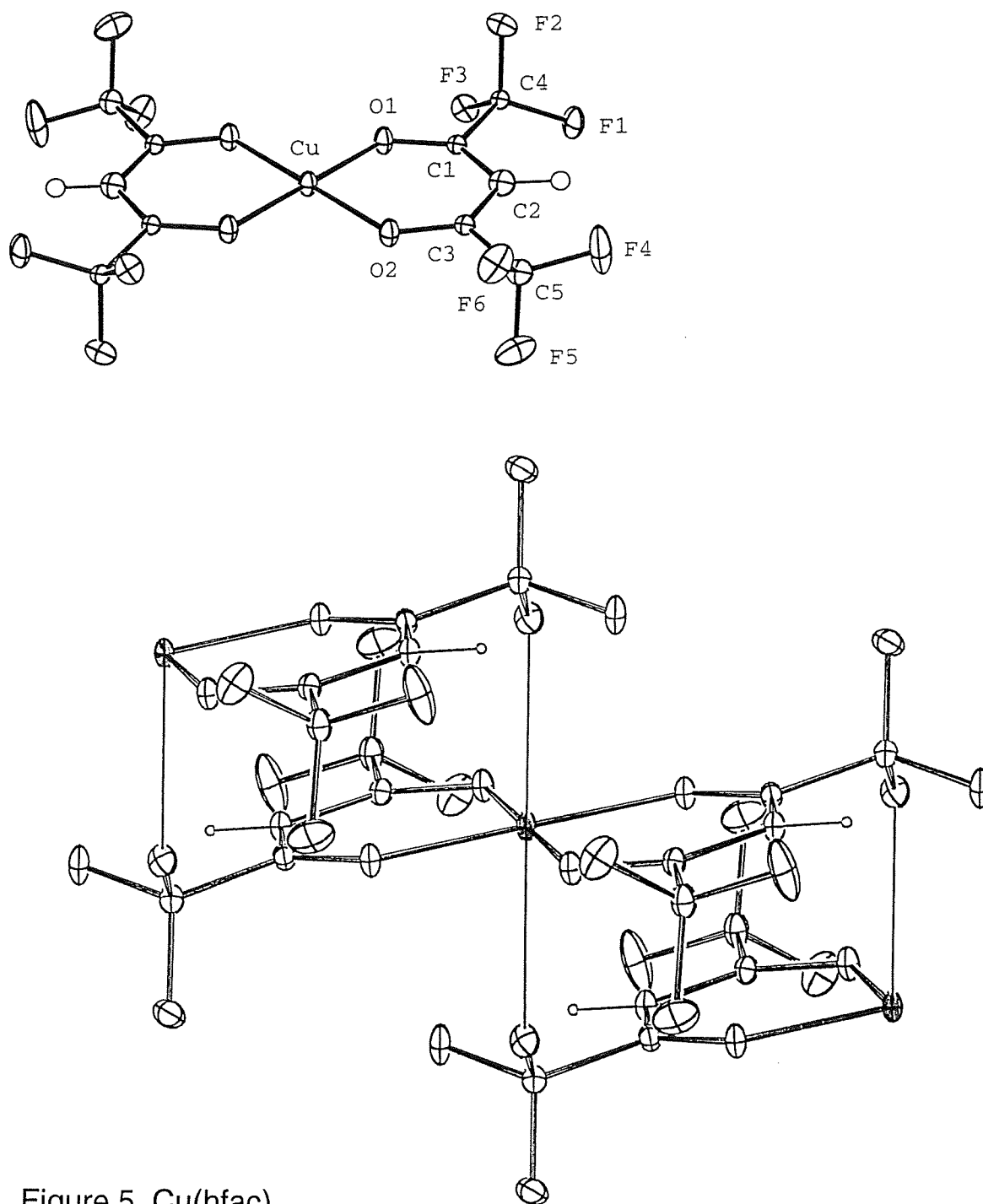


Figure 5.  $\text{Cu}(\text{hfac})_2$

#### 4. Conclusions and Future Work

Unlike the ROH adducts, all of the ligands studied were found to remain bound to Cu in the vapor phase.  $\text{Cu}(\text{hfac})_2 \cdot 2\text{allylamine}$  and  $\text{Cu}(\text{hfac})_2 \cdot \text{dihydrofuran}$  gave results comparable to or better than the alcohol adducts in terms of film thicknesses and resistivities under  $\text{H}_2$  CVD. Although neither of these ligands appears to make a precursor that is self-reducing, the high volatility of the allyamine adduct makes it worthy of further investigation. The pyrrolidine adduct was the only compound that appeared to be self-reducing. However, CVD reaction conditions need to be optimized. In addition the extraordinarily high resistivity observed for the film deposited with  $\text{Cu}(\text{hfac})_2 \cdot \text{pyrrolidine}$  under  $\text{N}_2$  indicates very poor film quality. This may be due to contamination of the film by pyrrolidine or its decomposition product.

The most promising combinations discussed here are  $\text{Cu}(\text{hfac})_2 \cdot 2\text{allylamine}$  for CVD under  $\text{H}_2$ , and  $\text{Cu}(\text{hfac})_2 \cdot \text{pyrrolidine}$  for CVD under  $\text{N}_2$ .

## References

- 1) Kodas, T and Hampden-Smith, M eds. *The Chemistry of Metal CVD*. New York: VCH Publishers Inc. **1994**, chapter 4.
- 2) Gelatos, A.V., Jain, A., Marsh, R., Mogab, C.J. "Chemical Vapor Deposition of Copper for Advanced On-Chip Interconnects", *Materials Res. Soc. Bulletin*, August 1994, 49-54.
- 3) Maverick, A.W, James, A.M., Fan, H., Isovitsch, R.A., Stewart, M.P., Azene, E., Cygan, Z.C. "New Routes Toward Chemical and Photochemical Vapor Deposition of Copper Metal". (*ACS Symp. Ser.*, in press)
- 4) Wiberg, K.B., Nakaji, D.Y., Morgan, L.M. *J. Am. Chem. Soc.* **1993**, 115, 3527-3532.
- 5) Riberio da Silva, M., Ferrao, M.L. *J. Chem. Thermodynamics* **1988**, 20, 359-361.
- 6) Bublik, Zh. N., Volkov, S.V., Mazurenko, E. A., *Russ. J. Inorg. Chem.* **1984**, 29, 73-76.
- 7) Bufaroosha, M. and Maverick, A.W. Unpublished Work
- 8) Nomura, Y., Ogawa, K., Takeuchi, Y., Tomoda, S. *Chem. Letters* **1977**, 693-696.

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