

The Chemical Vapor Deposition of Copper, Copper(I) Oxide, and Silver from Metal-Organic Precursors

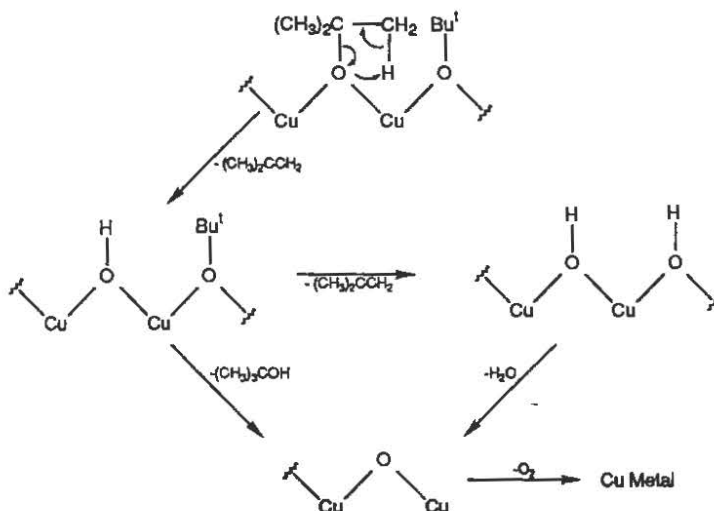
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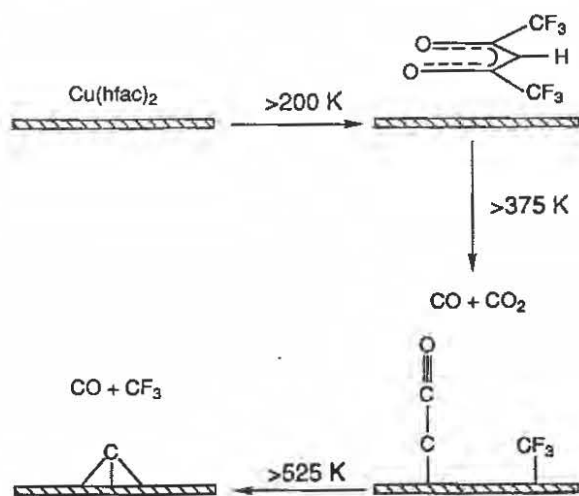
The metal-organic chemical vapor deposition (MOCVD) of thin films of copper metal [1-11] and high- T_C superconductors [12-16] is of current interest because of the many potential electronics applications of these materials. We are interested in developing and studying copper compounds used as precursors for the deposition of copper containing phases.

MOCVD from the tetrameric precursor copper(I) *tert*-butoxide, $[\text{Cu}(\text{O}-t\text{-Bu})]_4$, results in the deposition of pure copper(I) oxide whiskers at 510 K and of copper metal films with ~2% oxygen contamination at 670 K [17-19]. Quantitative analyses of the gaseous byproducts generated during the deposition, electron energy loss spectroscopy, and temperature programmed desorption experiments indicate that copper(I) oxide is formed by elimination of *iso*-butylene from surface-bound *tert*-butoxide groups to yield copper hydroxide intermediates which subsequently engage in proton transfer processes to produce *tert*-butanol and water and that copper metal is formed by deoxygenation of the initially deposited copper(I) oxide phase.



The reaction of $[\text{Cu}(\text{OMe})_2]_n$ with a fluorinated alcohol in the presence of an amine has afforded a series of new copper(II) alkoxide compounds: $\text{Cu}(\text{hfip})_2(\text{tmed})$, **1**, $\text{Cu}(\text{hfip})_2(\text{teed})$, **2**, $\text{Cu}(\text{hfip})_2(\text{bipy})$, **3**, $\text{Cu}(\text{hfip})_2(\text{py})_2$, **4**, $\text{Cu}(\text{hftb})_2(\text{tmed})$, **5**, $\text{Cu}(\text{hftb})_2(\text{bipy})$, **6**, and $\text{Cu}(\text{hftb})_2(\text{py})_2$, **7**, where hfip = hexafluoro-*iso*-propoxy, hftb = hexafluoro-*tert*-butoxy, tmed = *N,N,N',N'*-tetramethylethylenediamine, teed = *N,N,N',N'*-tetraethylethylenediamine, bipy = bipyridine, and py = pyridine [20]. Compounds **4** and **7** can also be prepared by the reaction of CuBr_2 with $\text{Na}(\text{hfip})$ or $\text{Na}(\text{hftb})$ and py. Crystallographic analyses of **1** and **5** reveal that both compounds are monomeric and assume tetrahedrally-distorted square-planar geometries. The dihedral angles between the CuN_2 and CuO_2 planes are 16.1° for **1** and 40.6° for **5**. EPR and UV-vis spectroscopy indicate that the degree of distortion from square planar geometry increases in the order $3 < 1 < 2 < 6 < 4 < 5 < 7$. The increase in the degree of distortion is attributed to the larger steric demand of the larger ligands. Compounds **1**, **2**, **3**, **5**, and **6** are volatile and thus are potential MOCVD precursors. Sublimation of **2** and passage of the resulting vapor over silicon substrates at 570 K results in the deposition of copper metal.

Copper β -diketonate complexes have typically been employed as MOCVD precursors in the preparation of copper containing materials [1-16]. Accordingly, the surface chemistry of the copper β -diketonate complexes $\text{Cu}(\text{hfac})(\text{vtms})$ and $\text{Cu}(\text{hfac})_2$, where hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate and vtms = vinyltrimethylsilane, was examined under ultrahigh vacuum conditions on copper single crystals with temperature programmed desorption studies, electron energy loss spectroscopy, infrared spectroscopy, and Auger spectroscopy [19]. Above 200 K, the ligands migrate from the adsorbed copper precursor to give hfac ligands on the surface oriented such that the plane of the hfac ligand is essentially parallel with the surface. The ligands remain unchanged until ~ 375 K at which temperature the ligands begin to fragment to give principally, CO, CO_2 , and trifluoromethyl and ketenylidene surface species. At ~ 525 K, the trifluoromethyl groups desorb and ketenylidene groups decompose leaving a carbon residue on the surface.



Silver has been shown to be an attractive dopant in high- T_c superconductors [21-23]. We are investigating compounds that may prove useful in the MOCVD of silver doped high- T_c superconductors. Silver films have been prepared by MOCVD from $[\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{Ag}]_4$ at 550 K; these films contain small amounts ($<1\%$) of fluorine and oxygen and no carbon. The principal organic compounds formed are *trans*- $\text{CF}_3\text{CF}=\text{CH}(\text{CF}_3)$ (50%) and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ (40%). It is argued that $\text{CF}_3\text{C}\equiv\text{CCF}_3$ is produced by elimination of silver(I) fluoride from $[\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{Ag}]_4$, silver(I) fluoride then loses fluorine to form silver metal, the fluorine reacts to form hydrogen fluoride, and lastly hydrogen fluoride reacts with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ to form *trans*- $\text{CF}_3\text{CF}=\text{CH}(\text{CF}_3)$. The crystal structure of $[\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{Ag}]_4$ was determined and reveals a tetrameric structure consisting of a square plane of silver atoms with a perfluorobutenyl ligand bridging each edge.

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