Solid State Photochemistry of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ in Thin Films: The Photochemical Formation of High-Quality Films of Copper and Copper(I) Oxide. Demonstration of a Novel Lithographic Technique for the Patterning of Copper

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In this communication we report the first utilization of amorphous films of metal−organic molecules for the direct lithographic patterning of metallic copper. Light is used in this process to selectively activate molecules, initiating the conversion to metallic copper in the illuminated regions. The use of light allows us to produce, in a kinetic fashion, different materials *via* the illumination of precursor molecules under controlled conditions. This kinetic control of solid state synthesis of materials opens up numerous possibilities for new preparations of materials.

Films of materials have applications in the semiconductor industry.[1−5] Of particular interest is the patterning of thin films of copper[5] and copper(I) oxide.[6] Copper(I) oxide has received interest due to its use as a high band gap (2 eV) semiconductor and its use in photovoltaic cells.[6] Copper metal is particularly attractive for ULSI applications.[7−10] In spite of its high conductivity, several materials issues remain, including fabrication (deposition), diffusion, and etching.[5,11,12] Current methods to deposit copper include the use of molecular precursors in chemical vapor deposition processes.[5,13,14] This approach has been used with the assistance of lasers to decompose the precursors to copper metal, most likely in a photon-energized thermal process resulting in high surface temperatures.[1a,b,15] The use of a true photochemical process will allow low deposition temperatures and thus the possibility for the formation of multilayer VLSI devices. Here we describe the deposition of copper and Cu_2O on Si(111) substrates using a photochemical process incorporating a facile decomposition of the ligand, resulting in volatile organic fragments which are easily lost from the film.

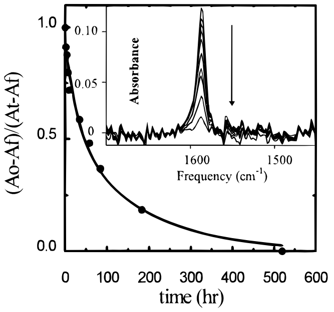

Figure 1. Plot of intensity of the 1587 cm^{-1} band of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ vs irradiation time. Insert: FTIR spectral changes accompanied by the photolysis of an 800 nm thick film of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ on Si(111).

The film deposition method pursued in our laboratory utilizes amorphous films of metal−organic compounds. Photolysis of these films results in the ejection of the ligands, leaving the metal on the surface.[16−21] It is necessary to have a nonvolatile photoactive precursor that forms a high-quality amorphous film on a suitable substrate. The bimetallic $Cu_2(OH_2)_2(O_2CR)_4$ (R = $(CH_2)_4CH_3$) compound[22,23] is utilized in this study. The analogous $Cu_2(OH_2)_2(O_2CCH_3)_4$ compound photoreacts in solution according to eq 1.[23−25] However, this compound forms a

$$Cu_2(O_2CMe)_4 \xrightarrow{h\nu} 2Cu + 4CO_2 + 4Me^{\bullet} \qquad (1)$$

powder upon spin coating. The hexanoic acid derivative was chosen for the solid state photochemistry because the long carbon chains lower the intermolecular interactions. This allows the formation of high-quality thin (50−1000 nm) films upon spin coating from hot toluene onto a suitable substrate. The films appear amorphous under an optical microscope up to 1000× magnification.

The photodeposition of Cu^0 or Cu_2O, depending on conditions (*vide infra*), is achieved by UV irradiation of the amorphous film. The infrared spectrum of the compound on Si(111) was used to monitor the photoreaction (Figure 1, insert). The band due to the carboxylate (at 1587 cm^{-1}) decreases in intensity with photolysis.

The product of photolysis of a film under high vacuum (10^{-6} Torr) was analyzed by Auger spectroscopy. Upon sputtering with Ar^+ for 1 min, to clean the surface, the film contained only Cu (76 ± 12%) and C (24 ± 4%). The surface produced by reaction under roughing pump vacuum (0.5 Torr) is Cu_2O as detected by Auger spectroscopy. The film contained only Cu (64 ± 10%) and O (36 ± 6%) after sputtering with Ar^+ for 5 min. The formation of Cu_2O is attributed to the oxidation of the photoproduced copper by O_2 present in the sample container and upon handling the film in air after deposition.[26] Films irradiated under a flow of H_2 (approximately 3 mL/min) showed the highest purity of photochemically produced copper; Auger analysis showed Cu (86 ± 13%), O (4 ± 1%), and C (10 ± 2%) after sputtering with Ar^+ for 30 s. The carbon in the films is probably due to contamination rather than problems inherent

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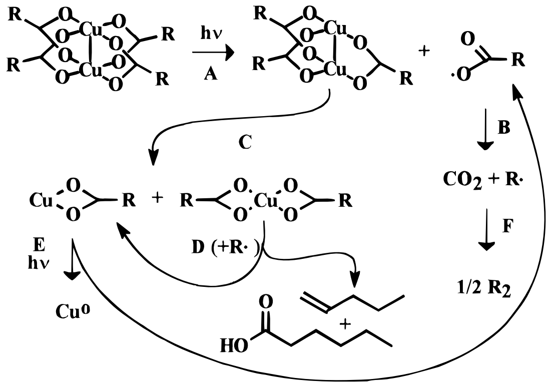
Scheme 1. Mechanism of the Photodeposition of Copper by Photolysis of Thin Films of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$[a]



[a] Note that the aqua ligands are omitted for clarity.

in the photochemistry. Annealing the films under H_2 at 200 °C produced pure copper metal as shown by Auger spectroscopy.

The physical properties of the films change upon UV irradiation. Under hydrogen or high vacuum the film thickness changes from 800 to 68 nm. The resistivity of the photoproduced Cu^0 film is 1×10^5 $\mu\Omega$ cm. Annealing the film under H_2 lowered this resistivity to 1.5 $\mu\Omega$ cm (bulk value is 1.67 $\mu\Omega$ cm[27]) and the thickness to 50 nm. The resistivity of the photoproduced Cu_2O film is 2×10^{16} $\mu\Omega$ cm, near the literature value of 1.8×10^{17} $\mu\Omega$ cm.[6] After reduction of the Cu_2O to Cu^0 the film thickness drops from 500 to 50 nm and the resistivity drops to 2.1 $\mu\Omega$ cm. The morphology of all films was excellent with no grains, islands, or other features observed by optical microscopy. All films adhere to silicon oxide and silicon substrates as demonstrated by the "Scotch tape test".[28]

The reaction quantum yield at 313 nm was measured. The decay of absorbance data is best fitted by a double exponential function (Figure 1). This is due to the overlap between the absorbance of the starting material and that of an intermediate, indicating that the deposition proceeds by two sequential photochemical processes. The photodeposition is efficient, with a quantum yield of 0.012[29] for a film 800 nm thick and 0.074 for a film 400 nm thick. The thickness dependence is presumably due in part to self-quenching.

As stated above, the inorganic product of the photochemical reaction in the film is copper metal. The organic products were CO_2, 1-pentene, hexanoic acid, and decane, as detected by mass spectral analysis. A mechanism consistent with all these observations and the known[24,25,30] chemistry of copper carboxylates is outlined in Scheme 1.

Upon UV photolysis, LMCT generates $Cu^{II/I}(O_2CR)_3$ and a carboxy radical (Scheme 1, step A).[23−25,30] Carboxy radicals decarboxylate, forming CO_2 and an alkyl radical (step B).[30,31] The primary photoproduct, $Cu^{II/I}(O_2CR)_3$, undergoes fragmentation to form the known $Cu^{II}(O_2CR)_2$ and $Cu^{I}(O_2CR)$ carboxylates[30] (step C). The production of 1-pentene and hexanoic acid indicates the formation of the monomeric $Cu^{II}(O_2CR)_2$ species and reaction D in Scheme 1. Kochi *et al.* reported that monomeric $Cu^{II}(O_2CR)_2$ species can react with radicals to form the alkene and a carboxylic acid.[30,32] The $Cu^{I}(O_2CR)$ undergoes a LMCT induced photoreaction resulting in copper(0) and a carboxy radical (step E). The carboxy radical decarboxylates, forming CO_2 and a pentyl radical (step B). The decane results from the radical coupling of two pentyl radicals (step F).

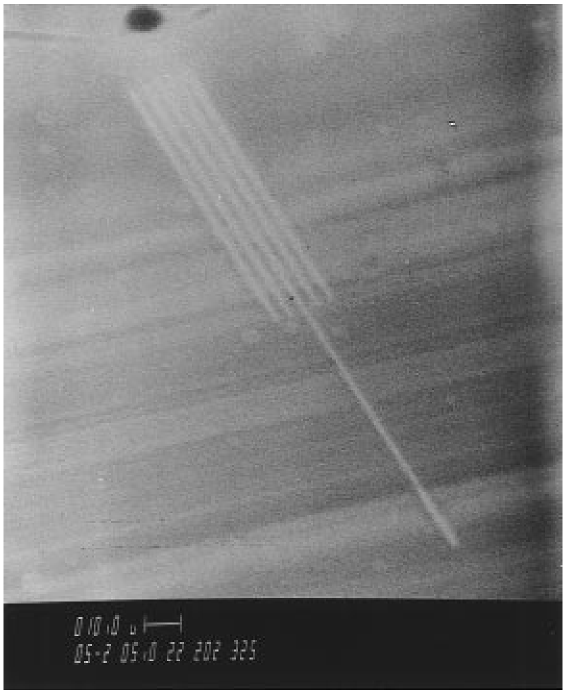


Figure 2. Scanning electron micrograph of a photogenerated lithographic pattern of Cu^0.

To demonstrate the utility of this process for the lithographic deposition of copper, a 200 nm thick film of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ was exposed to UV photolysis under a test mask and rinsed with methanol. Figure 2 shows the scanning electron micrograph of a test pattern. The resolution of 1 μm wide lines was possible.

In summary, the photodeposition of thin films of Cu^0 and Cu_2O from amorphous thin films of $Cu_2(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ has been demonstrated. The lithography of 1×100 μm lines of copper on silicon substrates shows that this technique is compatible with standard technology and offers several significant advantages: (1) the products can be controlled by conditions, (2) a simplified lithographic process is used, (3) deposition is done under mild conditions, and (4) the films demonstrate good adhesion to the substrates. Additionally, the demonstration of solid state bimolecular radical chemistry not only underscores the diversity of chemistry possible in this medium but opens up the possibility of designing a radical chain process to enhance the photosensitivity.

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Supporting Information Available: Experimental details (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[32] Radical disproportionation is ruled out as the source of 1-pentene because no pentane (the expected sister product) was detected in the mass spectrum.