cross-linking technique is more appealing.

We have recently become aware that research workers in another group have carried out studies parallel to our own and have come to similar conclusions.[14]

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Laser-Induced Deposition of Copper from (Triethylphosphine)cyclopentadienylcopper(I)

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Laser-induced deposition of metals from organometallics is of interest for numerous electronics applications, including repair of open lines and direct patterning of metal lines for chip and package customization. Most of the work in this field has relied on readily obtainable alkyl, carbonyl, and acetylacetonate compounds.[1] Many of these compounds do not decompose to leave pure metal, or they do so only at temperatures that are too high to be compatible with advanced substrate materials or structures used in microelectronics. In the case of copper, a metal that is highly desirable for use in packaging metallization, successful deposition is further hampered by the fact that no volatile, stable, halide, carbonyl, or alkyl compounds are known. Successful laser-induced deposition of copper has been demonstrated only from acetylacetonate complexes.[2-4] In this Communication we report the first use of (triethylphosphine)cyclopentadineylcopper(I) for the laser-induced deposition of copper. Since it contains no oxygen, this compound offers a potential advantage over the acetylacetonate compounds in producing high-purity copper films. This complex has also recently been demonstrated as a source of copper in the deposition of copper gallium sulfide.[5]

(Triethylphosphine)cyclopentadienylcopper(I) was prepared according to the procedure of Cotton and Marks.[6] The white crystalline material has a room-temperature vapor pressure of 2 mTorr, sublimes without decomposition at 65 °C, and is stable for a few hours in air. The substrates chosen for preliminary deposition studies were silicon, 2000-Å SiO_2 on silicon, and 5-μm polyimide on silicon. The substrates were degreased prior to use and then loaded into a stainless steel cell fitted with a quartz window. The organometallic was loaded into the cell in a drybox, and the cell was evacuated with either a liquid nitrogen trapped roughing pump or a turbomolecular pump. In cases for which deposition rate data are reported below, the deposition cell was heated at 70 °C to increase the vapor pressure of the compound to $\sim$50 mTorr, thereby increasing deposition rates.

For the photothermal deposition studies, the 514-nm output of a coherent Innova 20 argon ion laser was focused on the substrate through a microscope objective to a spot size of $\sim$10 μm, or with a simple lens to a spot size of $\sim$100 μm. Lines were generated by translating the sample chamber beneath the microscope with computer-controlled x–y tables. Estimates of laser power densities in our current apparatus have only order-of-magnitude accuracy. This severely limits our abilities to calculate surface temperatures from simple theory.

For the excimer-laser-induced deposition, the 248-nm (KrF) output of a Lambda-Physik 203 MSC laser or the 308-nm (XeCl) output of a Lumonics TE-860-4, both operated at 5 Hz, was imaged through a mask onto the substrate. Compositional analyses were carried out by Auger spectroscopy after the sample was exposed to air. Minimum detectable levels of impurities are estimated to be $\sim$1% for carbon, oxygen, and phosphorous. In all cases, the top $\sim$200 Å of the sample was sputtered off by 2-keV argon ion bombardment before compositional analysis was performed.

Photothermal deposition on silicon substrates, using power densities of $\sim 10^4$–10^5 W/cm^2 in a spot size of $\sim$100 μm, produced copper dots that were free of impurities, as determined by Auger spectroscopy. We estimate that the surface temperature of the silicon at the beginning of deposition was 200–300 °C.[7] Similar results were obtained when copper dots and lines were written on polymer substrates. Laser power densities were again in the range of 10^4–10^5 W/cm^2 but in a spot size of $\sim$10 μm. No detectable impurities were found below the top 200 Å of the deposits. As a check for thermal damage to the polymer, copper deposits were etched away and the underlying polymer was examined with an optical microscope. Since polyimide is thermally damaged at temperatures above 400 °C and we were able to deposit copper on this substrate without damaging the polymer, the surface temperature required for decomposition of the copper complex to clean metal on polyimide is less than 400 °C.

To make resistivity measurements, we wrote copper lines on silicon substrates overcoated with 2000 Å of silicon dioxide and containing gold contact pads. Figure 1 shows scanning electron microscope (SEM) pictures of copper lines deposited on Si–SiO_2 by laser-induced thermal decomposition. The polycrystalline, granular morphology is typical of laser chemical vapor deposition (CVD) grown material, with the line shape, growth rate, and morphology being very sensitive to power density and scan rate.[3,4,8] The line in Figure 1a was drawn with a laser power density of $\sim 5 \times 10^5$ W/cm^2 in a spot size of $\sim$10 μm scanned at

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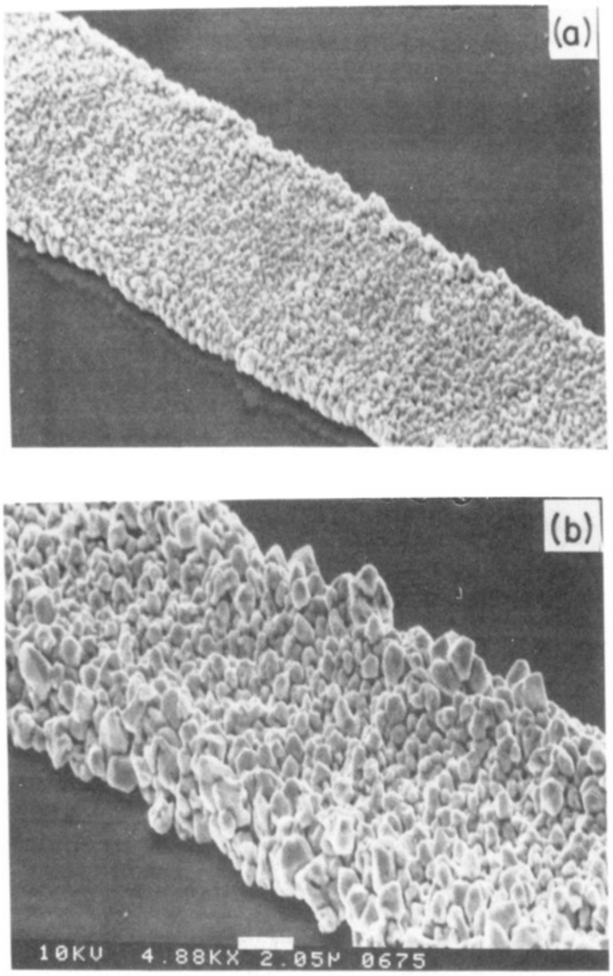

Figure 1. Copper lines deposited on 2000-Å SiO_2 on Si by photothermal CVD. The 514-nm laser light is focused to 5×10^5 W/cm^2 (8-μm fwhm) and scanned at 0.5 μm/s. Part a shows a 0.7 μm high by 10 μm wide line made by one scan. The line in part b was made by a double scan under the same conditions and is 2.5 μm high by 16 μm wide. The grain size increases from ~500 Å for part a to ~1 μm for the larger grains in part b.

0.5 μm/s. Figure 1b results from a double scan under the same conditions. The small, closely packed nodules seen in the single scan are contrasted with the loosely packed, 0.5–1.0-μm size particles seen in the double scan. The average growth rate increases from 400 Å/s in the first scan to 1000 Å/s in the second scan. The as-deposited resistivity, including contact resistance between the copper lines and the contact pads, of the double scanned lines is ~4 times the bulk, which was slightly better than the value for the single scans. Auger analysis shows no phosphorous or oxygen impurities but does show significant levels of carbon (~10%). Metal purity on the SiO_2-coated substrates did not change appreciably as the laser power was increased from near threshold (~10^5 W/cm^2) to power densities above ~10^6 W/cm^2 where significant volcano shapes appear.[9]

The lack of phosphorus in the film indicates that triethylphosphine is not the source of the carbon contamination in films grown on Si–SiO_2 substrates. Previous studies of the growth of InP from triethylphosphine showed that the onset of thermal cracking of triethylphosphine is in excess of 650 °C.[10] Although there is little information in the literature on the pyrolysis of late transition metal–cyclopentadiene complexes, a mass spectroscopic study of the pyrolysis of nickelocene on the walls of an oven showed that the only hydrocarbon products were cyclopentadienyl radical and 9,10-dihydrofulvalene, even at temperatures above 900 °C.[11] This indicates that the C_5H_5 ring is unlikely to fragment under the conditions of thermal film growth in our experiment. A study of (pentamethylcyclopentadienyl)carbonylcopper(II),[12] a compound structurally related to the film precursor of this investigation, identified decamethyl-9,10-dihydrofulvalene as the hydrocarbon product of thermal decomposition in solution at room temperature, indicating that a low-temperature pathway may exist for the elimination of the cyclopentadienyl fragments by dimerization to form a dihydrofulvalene. A reasonable conclusion regarding the incorporation of carbon in the films grown on Si–SiO_2 is that the higher laser-power density required to achieve nucleation and deposition results in higher growth temperatures, which in turn no longer allows the clean elimination of the cyclopentadiene moiety due to a change in the mechanism of cyclopentadiene loss. Further mechanistic studies are required to establish whether the cyclopentadiene fragments dimerize to a dihydrofulvalene or are eliminated as cyclopentadienyl radicals, but it would appear that lower deposition temperatures result in higher purity films in the case of this precursor.

To explore the possibility of large area deposition, we deposited patterned copper lines on Si wafers by mask projection techniques using an excimer laser operating at 248 nm. The copper complex shows strong electronic absorption at this wavelength,[13] so the deposition mechanism may have both photochemical and photothermal components. Typical conditions were 500 pulses at 5 Hz with a power density of ~150 mJ/cm^2. These conditions produced deposits ~1500 Å high, composed of uniformly distributed 500–1000-Å particles (Figure 2a). The mask consisted of 65-μm lines and spaces, and the deposits showed resolved features with ~100-μm dimensions. Unlike results reported for excimer laser deposition of copper from the acetylacetonate complex,[14] the thickness of the copper deposit from the 248-nm excimer light did not appear to be self-limiting. Features 2 μm high were produced with 2500 laser pulses (Figure 2b). The thin deposits were shiny and copper colored, but as the thickness increased with prolonged exposure to the laser, the material became noticeably roughened and darker. As shown in Figure 2b, the morphology of the 2-μm feature is dominated by 5000-Å particles, which are slightly fused together. The deposit shows surface roughness of several thousand angstroms. The fusing together of the grains could be indicative of high peak temperatures and slight flowing during the intense excimer laser pulse. This structure is to be contrasted with the open stacked structure of the thermally deposited material in Figure 1b. Auger depth profiles indicate that the deposit is a uniform, roughly equal mixture of copper and carbon, with no detectable phosphorous. A plausible explanation for the observed metal quality is clean liberation of the phosphine ligand but either entrapment or laser fragmentation of the cyclopentadienyl ligand. Triethylphosphine does not absorb 248-nm light (λ_{max} = 210 nm),[15] but the cyclo-

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pentadienyl moiety does absorb[16] and therefore may undergo fragmentation at this wavelength. It was not determined whether the carbon impurities are in the form of incorporated amorphous carbon or intact cyclopentadiene rings.

The modest spatial resolution achieved in the projection experiments suggests that a surface process, either photodissociation of an adlayer of precursor or localized heating of the surface, is involved in the excimer laser deposition. To attempt to differentiate the photochemical from the photothermal aspects of the mechanism, we repeated the excimer laser deposition experiment with a XeCl excimer laser operating at 308 nm. At this wavelength bulk copper and silicon still absorb strongly, but direct absorption by the copper precursor is reduced by an order of magnitude.[13] Films with a limiting thickness of ~1000 Å were grown on silicon and on 2000-Å SiO_2 on silicon with a power density of 200 mJ/cm^2. The composition of the copper films as determined by Auger spectroscopy was ~65% carbon and ~35% copper with no detectable phosphorus. There were indications, again by optical microscopy of the underlying substrate, that deposition occurred with 308-nm irradiation only after an initial damaging of the Si or SiO_2 surface. In contrast, the 248-nm excimer laser irradiation produced deposits without apparent damage to the substrate surface. While the results do not clearly establish any one mechanism, the differences in growth characteristics and material composition suggest that processes in addition to heating of the substrate occur in the 248-nm laser-induced deposition.

In summary both visible and UV laser-induced deposition of copper from (triethylphosphine)cyclopentadienylcopper(I) have been explored. The results of the photothermal deposition experiments suggest that this molecule is a useful precursor for laser direct writing of copper, because reasonably pure copper deposits can be produced under mild conditions on several technologically important substrate materials. This result is surprising, because the molecule is chemically more complex than simple metal halides or carbonyls. It does suggest that chemical mechanisms exist for the facile elimination of ligands such as organophosphines and aryl groups from the film growth surface and that, therefore, the presence of these relatively "complicated" ligands in a deposition precursor does not necessarily preclude the deposition of clean metals. The nature and generality of these mechanisms with respect to the ligands and the metal remain to be elucidated. Pulsed ultraviolet laser-induced deposition results in films that are heavily contaminated with carbon but contain no detectable phosphorous.

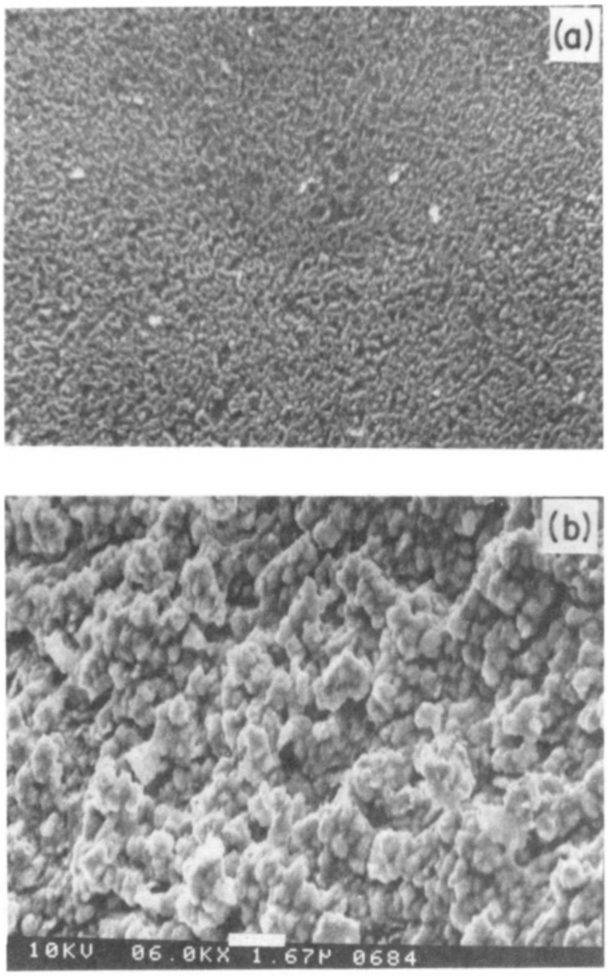

Figure 2. Material deposited by krypton fluoride (248 nm) excimer laser irradiation. The substrate is silicon. The deposit in part a was produced by 500 laser pulses at a repetition rate of 5 Hz with a power density of 150 mJ/cm^2. The 2-μm feature in part b was produced with 2500 laser pulses. Auger analysis indicates a mixture of 50% copper and 50% carbon but no detectable phosphorus. The ~5000-Å particles in part b are slightly fused together, and the surface morphology is noticeably more textured than the continuous wave thermal decomposition with the Argon ion laser (Figure 1).

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