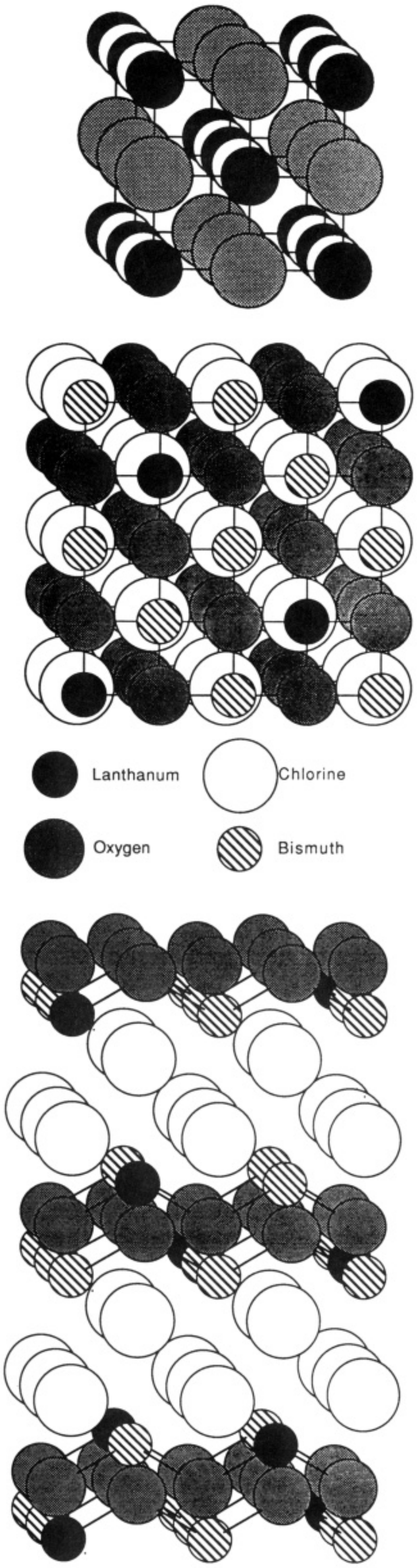

Figure 2. Comparison, roughly to scale, of the size and content of (top) the BiOCl (or LaOCl) structure with (middle and bottom) the $\sqrt{2}.2\sqrt{2}.2$ superlattice of the $Bi_{0.75}La_{0.25}OCl$ structure.

of ammonium chloride. This was subjected to slow evaporation in an alumina crucible, thorough washing to remove excess chloride, compaction into tablets, and then heating for 72 h at 450 °C and 6 h at 900 °C. Phase purity was established by X-ray powder diffractometry. The spatial uniformity and homogeneity of the powdered product were deduced from energy-dispersive X-ray microanalysis carried out using a JEOL-200CX electron microscope on a randomly selected set of 20 microcrystallites. The ratio of the Lα lines of Bi and La was used for this purpose. (Since the Cl K and Bi M lines markedly overlap, it was not possible to probe the spatial uniformity of the anionic content.)

The X-ray diffractogram of the $Bi_{0.75}La_{0.25}OCl$ was the same in appearance as that which we have previously published[8] for both pure BiOCl and $Bi_{0.5}La_{0.5}OCl$. It is not in general feasible, as we have shown elsewhere[9] for other solid solutions containing bismuth and oxygen, readily to discern, from X-ray diffractograms, evidence of any superlattice ordering. With use of electron diffraction, however, superlattice formation is readily apparent (see Figure 1, which shows typical selected area diffraction patterns down two high-symmetry directions).

It is clear that, compared with the structure of the pure BiOCl[11] ($a_0 = 38.9$, $c_0 = 73.7$ pm, space group $P4/mmm$), the 3:1 solid solution of Bi^{3+} and La^{3+} yields a new unit cell related to the parent one as shown in Figure 2, the relevant supperlattice factors being $\sqrt{2}$, $2\sqrt{2}$, and 2. On the basis of this idealized superstructure, we have computed, by the multislice method,[9,12] the expected high-resolution microscopic image and compared it with that observed under the appropriate[13,14] electron optical and other conditions. The correspondence is good, and, in particular, the real-space image confirms the reality of the doubling of the *c* axis repeat in the $Bi_{0.75}La_{0.25}OCl$ ordered, solid solution.

We have also examined, by selected area electron diffraction, specimens of the 1:3 and 1:1 solid solution ($Bi_{0.25}La_{0.75}OCl$ and $Bi_{0.5}La_{0.5}OCl$, respectively). No superlattice spots are seen in the former (down the 001 and $1\bar{1}1$ zone axes); and with the latter some incommensurate satellite diffraction spots appear along the $[1\bar{1}2]$ direction.

Careful measurement of the diffraction patterns of the $Bi_{0.75}La_{0.25}OCl$ revealed the presence of a slight lattice distortion away from the idealized orthorhombic state, the γ angle being ca. 91°. Crystals of this composition also show a slight tendency to exhibit twinning. The subtlety of the dependence of catalytic performance on cation ordering in the solid is underlined by this work.

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Low-Temperature Chemical Vapor Deposition of High-Purity Copper from an Organometallic Source

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Thermal chemical vapor deposition (CVD) of copper has been reported from several inorganic sources including

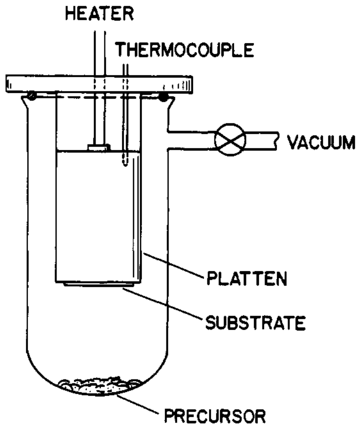

Figure 1. Low-pressure CVD reactor.

copper(II) chloride,[1] copper(II) bis(acetylacetonate),[2] copper(II) bis(hexafluoroacetylacetonate),[3] and copper(I) *tert*-butoxide.[4] We wish to report the deposition of analytically pure copper films by CVD employing organometallic (trialkylphosphine)cyclopentadienylcopper(I) complexes as copper precursors.

Deposition of copper from organometallic sources is made difficult by the instability of organocopper compounds and their tendency to form nonvolatile oligomers and polymers.[5] Binary alkylcopper complexes undergo autocatalytic decomposition to alkanes or alkenes and copper metal at temperatures too low for the compounds to have significant volatility. Binary arylcopper complexes are more stable, but their oligimeric structure lowers their volatility to the point that decomposition occurs before transport.

To overcome these difficulties, we have investigated the thermal decomposition of (trialkylphosphine)cyclopentadienylcopper(I) complexes. The triethylphosphine derivative was first synthesized by Wilkinson and Piper in 1956.[6] A general approach to the synthesis of compounds of the general form $(C_5H_5)CuL$, where L is a two-electron donor ligand, was published by Cotton and Marks in 1970.[7] (Triethylphosphine)cyclopentadienylcopper(I) has previously been used as a copper source for $CuGaS_2$[8] and by us to deposit copper by laser writing of copper lines.[9] We wish to report the first use of (trialkylphosphine)copper complexes to deposit blanket films of copper.

The trimethyl-, triethyl-, and tributylphosphine adducts of cyclopentadienylcopper were chosen because the phosphine ligands are of relatively low molecular weight and impart sufficient stability to allow the complex to transport without decomposition. The triethyl- and tributylphosphine derivatives were prepared by a previously reported method[7] and were sublimed before use. The previously unreported trimethylphosphine derivative was prepared by a modification of the literature procedure (use of diethyl ether rather than alkane solvents). The volatility, decomposition temperatures, and deposition characteristics of all three compounds are similar, so the remainder of this communication will report deposition results obtained by using the triethylphosphine derivative.

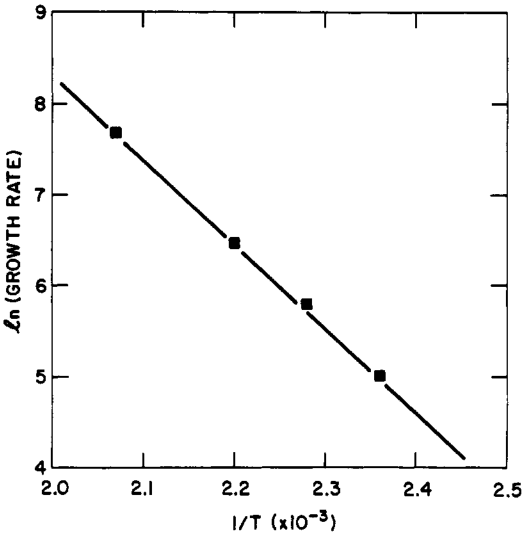

Figure 2. Arrhenius plot of copper growth from (triethylphosphine)cyclopentadienylcopper(I).

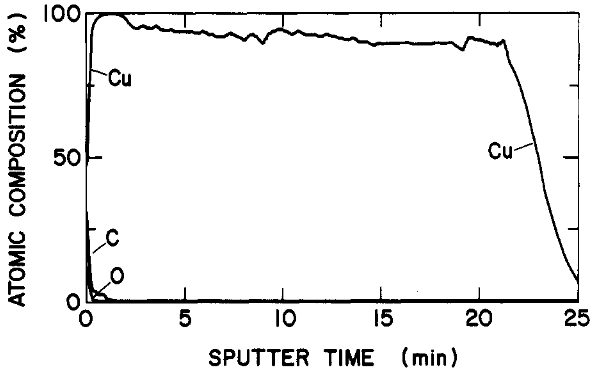

Figure 3. Auger argon-ion sputter profile of a CVD copper film.

Depositions were carried out in the apparatus depicted in Figure 1. This reactor is basically a vacuum sublimer with the coldfinger replaced by a 2.5-cm resistively heated platten thermostated at between 150 and 220 °C. The platten was fabricated from a copper block, and the exterior vacuum vessel was made from stainless steel (top) and glass (outer jar). In a typical experiment, the reactor was charged with 200 mg of the copper complex (all of these complexes are unaffected by brief exposure to the atmosphere), the reactor was evacuated with a trapped diffusion pumped vacuum system, the platten was heated to the desired temperature, and the exterior of the reactor was warmed to 70 °C to initiate deposition. Deposition continued until all of the complex had transported, typically 15 to 20 min. Unreacted complex condensed in the lines between the reactor and the pump, while more volatile products were trapped in a liquid nitrogen trap for subsequent analysis.

While it was possible to grow copper films on all substrates above 200 °C, the decomposition of all of the phosphine complexes appears to show some selectivity in that it was not possible to obtain continuous growth on Si or SiO_2 substrates below 200 °C, while deposition on Cr/Cu-seeded (500 Å each layer, sputtered) Si wafers occurred at temperatures as low as 130 °C. (Since the substrates were exposed to air before deposition, the Cu

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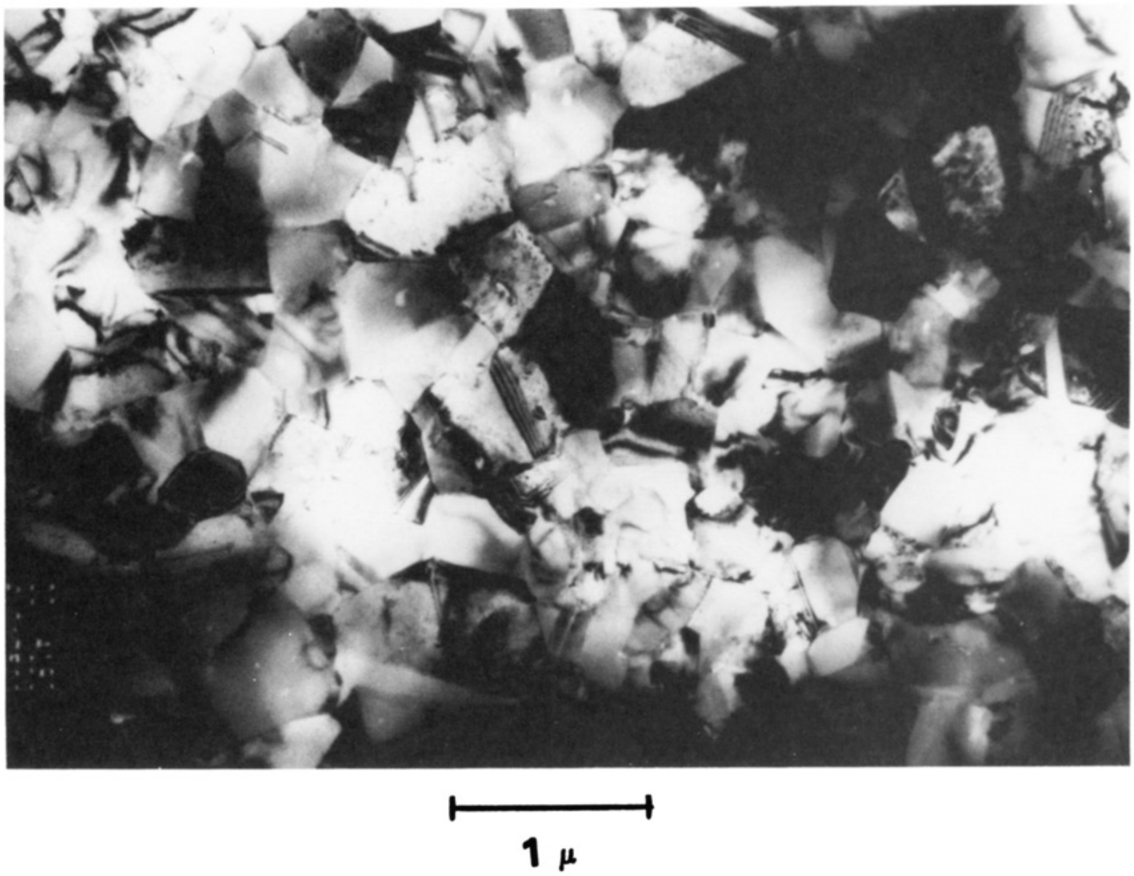

Figure 4. Plan view TEM of a CVD copper film.

surface was undoubtedly oxidized.) Above 200 °C, it is reasonable to assume that either the activation barrier to surface reaction is overcome or homogeneous decomposition just above the wafer causes a copper seed layer to be deposited.

Because the pressure in the deposition system could not be readily measured or controlled, the film growth rate as a function of temperature could only be estimated. Still, the growth rate on a Cr/Cu-seeded Si substrate as a function of temperature for constant run time and reactor wall temperature does yield a straight Arrhenius plot (Figure 2) for four temperatures in the range 150–210 °C, with an activation energy of 18 kcal/mol. The growth rate at 210 °C was 2200 Å/min, while the deposition rate at 150 °C was 150 Å/min. These results should be regarded as preliminary, because without proper control of the reactor pressure and the precursor flow rate, the relative contribution of gas and surface processes to the measured film growth rate could vary with pressure and flow.

Copper films were characterized by Auger spectroscopy, electrical resistivity measurements, and transmission electron microscopy (TEM). Figure 3 shows an argon-ion-sputtered Auger depth profile of a 1.5-μm film deposited at 190 °C on Cr/Cu-seeded Si substrate. Only surface contamination of C and O are observable, and these impurities fall to the level of detection (1%) within the first approximately 100 Å. No phosphorus was detected in any of the films. The resistivity of six films of between 0.3- and 4.4-μm thickness was measured with a four-point resistivity tester. The average resistivity of these films was 2.05 ± 0.05 μΩ cm, a value only slightly higher than bulk copper (1.7 μΩ cm). Figure 4 shows a plan view TEM of a film deposited at 165 °C. Tightly packed grains of 0.6-μm average size are obtained, and the grain boundaries are free of precipitates. The grain size distribution is very similar to sputtered films deposited at 300–400 °C.

Table I. Decomposition Temperatures of C_5H_5Cu–Ligand Compounds

ligand	dec temp, °C	ligand	dec temp, °C
$P(C_6H_5)_3$	130	$CNCH_3$	25 (rapid)
$P(C_4H_9)_3$, $P(C_2H_5)_3$	100–120	CO	−20
$P(OCH_3)_3$	25 (slow)		

As mentioned earlier, the volatile decomposition products were trapped for analysis. The trapped material from the decomposition of $Cu(C_5H_5)P(C_2H_5)_3$ was fractionated on a standard high-vacuum line to yield triethylphosphine and a less volatile hydrocarbon. This hydrocarbon spontaneously polymerized on warming to room temperature. In one experiment, deposition was carried out in a system equipped with a quadrupole mass spectrometer residual gas analyzer. After correction for the reactor background and unreacted source material, the mass spectrum of the product gases consisted of peaks assignable to triethylphosphine and a hydrocarbon with a base peak at m/e = 65 ($C_5H_5^+$) and a cluster of peaks at m/e = 126–131. We believe the m/e = 130 peak to be the molecular ion of a $C_{10}H_{10}$ hydrocarbon compound. (The M + 1 peak at m/e = 131 was 10% of the m/e = 130 peak.) This result suggests that the organic molecule produced in this reaction was a fulvalene, possibly 9,10-dihydrofulvalene (the unrearranged product of the reaction of two cyclopentadiene radicals). This molecule has previously been reported as a product of the thermolysis of nickelocene (dicyclopentadienylnickel(II))[10] and is also reported to undergo Diels–Alder polymerization at room temperature. Further support for the proposal that the organic product

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in this copper CVD reaction is 9,10-dihydrofulvalene comes from work on the related compound (pentamethylcyclopentadienyl)carbonylcopper(I), which decomposes to give decamethyl-9,10-dihydrofulvalene.[11]

From the data presented by Cotton and Marks[7] in their study of (C_5H_5)CuL complexes, Table I was constructed. The order of stability appears to correlate strongly with the σ-donor abilities of the two-electron-donor ligand.[12] This implies that the rate-limiting step in the decomposition of all of these compounds is the dissociation of the two-electron-donor ligand, followed by the rapid decomposition of the 16-electron C_5H_5Cu fragment. This stability trend, the apparent low activation energy for film growth, and the evidence that dihydrofulvalene is the organic product of decomposition strongly suggest that the mechanism for the decomposition of the (alkylphosphine)cyclopentadienylcopper complexes of our CVD study is the surface adsorption and dissociation of the molecules to give free alkylphosphine and unstable adsorbed cyclopentadienyl copper. This is followed by coupling of the organic radical fragments which then desorb, leaving a pure copper film.

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Hydrothermal Synthesis of Sodium Tungstates

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The tungsten trioxides and their alkali-metal-intercalated products $M_xWO_{3+\delta}$ have attracted considerable attention over the years because of the variety of crystalline structures they can take up and their electrochemical and electronic properties, which make them attractive as active electrodes in electrochromic displays and as catalysts.[1,2] These structure come from joining the corner-shared WO_6 octahedral building blocks in a variety of arrangements. Through recent developments in low-temperature synthesis two metastable forms, a hexagonal[3,4] and a cubic phase,[5-7] of tungsten trioxide have been reported in addition to the well-known ReO_3-related phase. Both phases possess a rigid tungsten-oxygen framework built up of layers containing distorted corner-shared WO_6 octahedra and arranged to form six-membered rings. In hexagonal WO_3, the layers are stacked along [001] axis, giving one-dimensional tunnels. In cubic pyrochlore WO_3, the layers are linked along the [111] direction to form interconnected three-dimensional tunnels. These three tungsten oxides provide an interesting set to study the effect of structure on chemical reactivity and physical properties. In addition, it allows one to determine the impact of the openness of the structure on its behavior. As indicated in Figure 1 the pyrochlore structure has expanded about 26% above that of the simple structure which is itself relatively open, being a distorted perovskite, ABO_3, with all the A sites vacant; WO_3 is not unique in this behavior, TiO_2 showing an even larger number of structures. Here, we report the synthesis and characterization of two novel sodium tungstates with the cubic pyrochlore and a hexagonal structure.

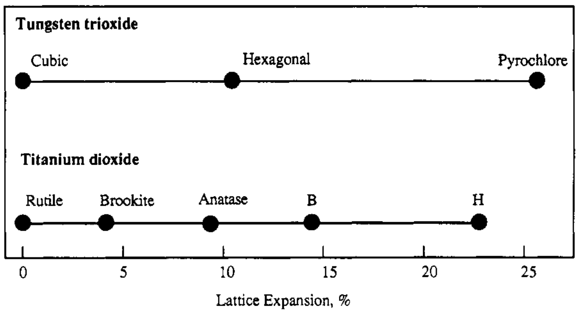

Figure 1. Lattice expansion of different structural forms of WO_3 and TiO_2; data from ref 1.

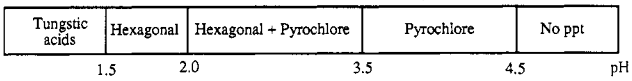

Figure 2. Effect of initial pH on structure formed on acid hydrolysis of sodium tungstate.

Günter et al.[7] recently reported the formation of the pyrochlore WO_3 by a simple hydrothermal acid hydrolysis of sodium tungstate. We followed that technique in this study and found that by careful control of the pH of the solution one could prepare tungsten trioxides in either the hexagonal or pyrochlore structures. In every case we found that these structures contained sodium ions. In a typical experiment, 20 mL of 1 M $Na_2WO_4{\cdot}2H_2O$ solution was acidified at room temperature with the required amounts of 1 M HCl so as to give a pH in the range 4.5–1.5. The solution was sealed in 1-mm wall Pyrex tubes and heated in an oven at 155 °C and autogenous pressures (about 5 atm.) for 3 days. *Care must be taken as these tubes occassionally exploded at this temperature*; thus, we are now using Parr 4745 stainless steel acid digestion bombs. At the lower pH values, prolonged standing of the acidified solution led to precipitation, so the solutions were sealed and heated within an hour of preparation. While pH values above 4.5 did not yield any precipitate after hydrothermal treatment, pH's of less than 1.5 resulted in a mixture of unidentified phases believed to be tungstic acids. After cooling to room temperature, the resulting microcrystalline product was filtered, washed with water, and dried in air; the yield was about 20%.

Powder X-ray diffraction studies of the samples showed that two distinct white phases were formed depending on the initial pH of the acidified solution. For pH's of 3.5–4.5, the patterns could be completely indexed on a cubic pyrochlore-type lattice with $a \sim 10.30$ (2) Å. A hexagonal phase appeared for pH's of less than 2.5 with cell parameters of $a \sim 7.319$ (4) and $c \sim 7.788$ (2) Å; these values are typical of a hexagonal tungsten bronze type phase. No additional lines were found in either set of patterns. For intermediate pH ranges, however, a mixture of cubic and hexagonal phase was obtained. The best yields obtained

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