including its inability to chemisorb hydrogen. The decomposition of [$CF_3AuCNMe$] is strongly retarded by free ligand MeNC as shown by by curve (c) in Figure 3. After about 1 h at 250 °C, the isomerization of free MeNC to MeCN was essentially complete as monitored by the FTIR spectra [disappearance of band at 2166 cm^{-1} due to $\nu(C{\equiv}N)$ of free MeNC] and it was at this stage that the rate of decay of [$CF_3AuCNMe$] increased (Figure 3). A similar retardation by free ligand has been observed for the thermolysis of [$PtMe_2(CNMe)_2$] in a closed gas cell[9] and also for the solution phase thermolysis of [MeAuL], where L = PPh_3.[10] The mechanism of decomposition of [RAuL] in the gas cell (R = CF_3, L = MeNC) is therefore likely to be similar to that in solution (R = Me, L = PPh_3),[10] and the proposed mechanism is shown in eqs 3 and 4.

$$[\mathrm{RAuL}] \rightleftharpoons [\mathrm{RAu}] + \mathrm{L} \tag{3}$$

$$[\mathrm{RAu}] + [\mathrm{RAuL}] \rightarrow \mathrm{R{-}R} + 2\mathrm{Au} + \mathrm{L} \tag{4}$$

Present data cannot distinguish between a gas-phase and a surface-mediated, but uncatalyzed, decomposition mechanism. The complex kinetics observed in the gas cell may be due to changes in the concentration of free MeNC as it is formed and then decomposes during the reaction and to a higher activation energy to deposition on glass compared to gold.[11] Clearly the trifluoromethylgold(I) precursor has significant advantages in both ease of handling and in CVD usage compared to the methylgold(I) analog.[2,12]

Acknowledgment. We thank the OCMR, NSERC (Canada), and CEMAID for financial support.

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(10) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* 1973, *61*, 441. A referee notes correctly that our kinetic data are also consistent with the final step 2RAu → R–R + 2Au.

(11) For decomposition of [$CF_3AuCNMe$] in a closed FTIR cell, the steady-state concentration of MeNC is too low to measure. Hence, when CVD is carried out in the presence of free MeNC, essentially all of the FTIR signal of $\nu(N{\equiv}C)$ is attributed to free MeNC. Under normal CVD conditions, the MeNC formed during thermolysis is pumped away from the hot zone and it can then be trapped as major product and identified.[8]

(12) The complex [CF_3AuPMe_3][6] can also give CVD of gold but it requires a higher temperature and gives less pure gold films [CVD temp 340 °C; XPS analysis of film: Au, 86; C, 13; F, 1%; volatile products: C_2F_6 and PMe_3 only] than [$CF_3AuCNMe$].

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c-Axis Oriented Orthorhombic $YBa_2Cu_3O_{7-\delta}$ on Silver from Organic Solvent Solutions of Metal Iodides

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It has been known for some time that highly oriented or single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) formed on substrates such as single-crystal strontium titanate generally show a much higher critical current density (J_c) than bulk samples.[1] Usually these thin films of YBCO are produced by high-energy vapor processes such as sputtering,[2] laser ablation,[3] and molecular beam epitaxy.[4] Hamdi et al.[5] have reported growth of YBCO on $SrTiO_3$ single crystals from solutions of yttrium, barium, and copper neodecanoates. Single-crystal ionic substrates preclude any formation of long lengths of YBCO on flexible substrates. This thin-film study was undertaken to find thin-film processes which might yield YBCO in ribbon or wire configurations. Silver would appear to be a good choice for such a substrate.

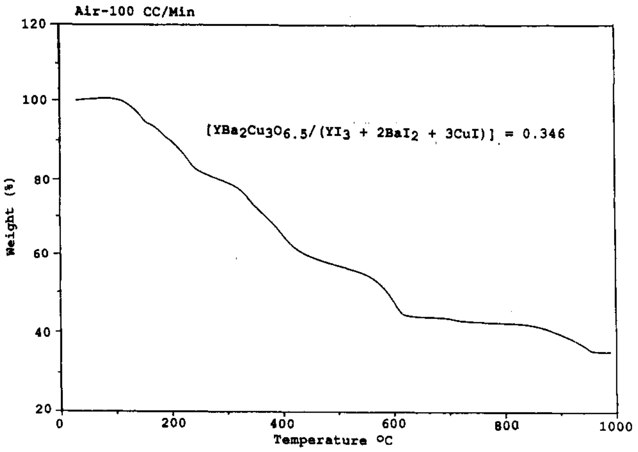

Figure 1. TGA of a metal iodide solid heated at 10 °C/min.

Greuter et al.[6] reported orienting YBCO powder on silver foil by coating a suspension of oxides centrifugally (or by dip coating) to yield microcrystalline *c*-axis oriented textured material. A film of a thickness of the order of 1 μm was achieved after firing at 930 °C. Thus, an investigation of the *c*-axis orientation of YBCO from the solution processing of iodide precursors[7,8] on silver began.

Iodide precursors were expected to offer an advantage over other metalloorganic or solution process routes, as the latter often require temperatures in excess of 850 °C to remove residual carbon in order to produce high-purity YBCO. The metals density of the iodide film is larger than a metalloorganic precursor moiety which should expedite the contraction to an oxide superconductor.[8] Figure 1, the TGA of a 1:2:3 molar mixture of YI_3:BaI_2:CuI, clearly shows that oxidation to YBCO occurs at temperatures well below the melting point of silver (935 °C in oxygen). XRD analysis confirmed the presence of YBCO.[9]

Attempts to produce thin films of the order of 1 μm thickness, necessary for adequate conductivities, were undertaken by both spin and flow coating the precursor onto silver foil substrates. Solution coating via either flow coating or spin coating requires a high concentration of precursors or an increased viscosity to obtain adequate coverage of deposited material with one coating cycle.

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Early attempts to spin coat with the iodide precursors dissolved in acetonitrile (1.8% w/v in ACN) were plagued with film thickness and fractional coverage deficiencies unless multiple spin cycles were employed.[8] Multiple thermal oxidation cycles proved undesirable, giving less pure YBCO with greater fractions of discontinuous coverage. An alternate strategy arriving at micron films involved spreading calculated volumes of precursor (a few microliters) by flow coating on 0.1-mm-thick silver substrates (~1 cm^2 area). These films proved to be handicapped with uniformity problems. Cursory examination of the films in an optical microscope revealed that uniformity was not good. The smallest volumes spread (orders of a few microliters) produced films of YBCO with a variation from a few tenths to several microns thick. This observation is based on the depth of focus at the highest magnification (1000×) of an optical microscope. This "mountain and valley" terrain gave XRD patterns suggesting orientation along the orthorhombic *c*-axis [noticeable increase in the (00*n*) XRD reflections]. It was also evident that the thinnest films gave patterns noticeably weaker, casting doubt on the relative *c*-axis orientation and/or the purity of the YBCO. The X-ray powder pattern intensity is in some measure proportional to the surface area covered, as well as the thickness of the film. A further complication to be reckoned with is the fact that a stoichiometric "iodide film" is volumetrically reduced by a little over 70% upon oxidation to YBCO. It was felt that more uniform and fuller coverage could be reached by centrifugation (spin coating).

Spin coating from solutions of low viscosity (e.g., the acetonitrile solvated iodide precursor) resulted in residuals almost too thin to measure. Multiple spin coats baked from 200 to 400 °C leads to the loss of CuI (see below) and the formation of $Ba_5(IO_6)_2$ on a $SrTiO_3$ substrate as demonstrated by XRD analysis.[8] $Ba_5(IO_6)_2$ is not entirely unexpected in light of its formation in oxygen from to 200 to 400 °C and oxidation to BaO at temperatures well above 900 °C reported by Frit et al.[10] Thus, a measurable film derived with a single spin is desirable. A solution in which a viscosity increase is attained without polymer modifiers is an advantage, as it avoids greater volumetric reduction upon oxidation due to disappearing additives. Experimental efforts turned to dissolving the iodides at molar levels as a stoichiometric "1–2–3" precursor.

It is known that YI_3 and BaI_2 are quite soluble in ethanol.[11] CuI is fairly soluble in acetonitrile [2.8% (w/v)], but that solvent is further limited by the low solubility of BaI_2 and YI_3. CuI is somewhat soluble in dimethylformamide, but little more than its solubility in acetonitrile. As Munaka and Endicott[12] suggest, the presence of iodide anion tends to form complexes according to

$$CuI + nI^- = [CuI_{n+1}]^{n-} \qquad n = 2\text{–}4$$

Although NH_4I is only slightly soluble in acetonitrile, it is soluble to the extent of 30–35% (w/v) in dimethylformamide (DMF). Thus, the use of dimethylformamide as a solvent would increase both the solubility of the metal iodides and the solution viscosity significantly. It turns out that a solvent combination of anhydrous DMF and ethanol with NH_4I as a complexing agent gives solutions approaching 35% (w/v) in metal iodides (about 0.6 M in CuI).[8] This solution concentration in metals is somewhat less than reported for the trifluoroacetate precursor (~2 M in copper trifluoroacetate).[13,14] However, the metals density of the trifluoroacetate thin film is about 10 times smaller than that of the iodide precursor film due anion radius differences.[8] The 35% solutions in turn yield about 12% metal oxide (w/v) of the original solution. The iodides in DMF/ethanol solution provide an excellent candidate for thin films and fibers without further modification of the solution. Thus, this complex solution was studied in the process sequences described below. It was found that a 30% solids iodide precursor in DMF/ethanol spun at 2000–3000 rpm gave a fired film of 1–2 μm (by optical microscopy, 1000×, depth of focus) with excellent coverage. Spin coating with these solutions was generally expedited in a drybox under a heat lamp during the spin cycle to remove the last traces of DMF and to prevent water from condensing in the film. The presence of water leads to substoichiometric metal hydroxides (especially copper) moieties which are volatile and deleterious to the YBCO stoichiometry.

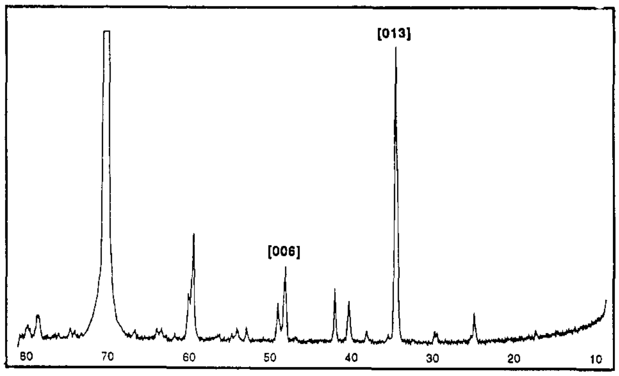

Figure 2. XRD of YBCO powder.

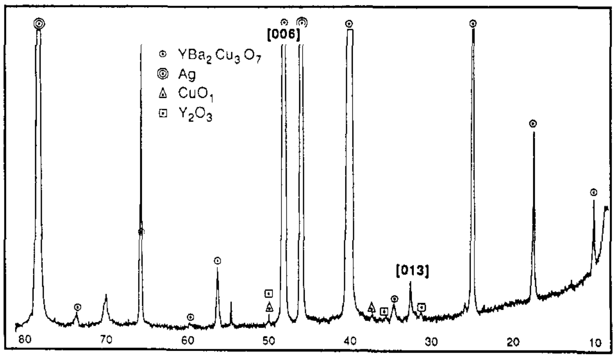

Figure 3. XRD of YBCO oriented at 900 °C on silver foil.

High relative intensities of the (00*n*) crystal planes or reflections are indicative of a high *c*-axis orientation.[6] As a figure of merit to indicate the degree of orientation, the ratio of the X-ray intensities of the (013) to the (006) axes' reflections [Miller indices for reflections from Cu Kα radiation at 2θ = 32.8° and 46.5°, respectively] were measured and reported here. This ratio for a normal *powder* pattern is 4.5.[9] Greuter et al.[6] measured about 0.02 for their films with the highest orientation. The axial intensity ratio [(013)/(006)] achieved from iodides in DMF/ethanol was as low as 0.01, approaching 500 times the normal powder ratio, when the solid-state reaction temperature was 900 °C for an hour in oxygen from spin cast films. Figures 2 and 3 show the XRDs of normal YBCO (*a bulk*

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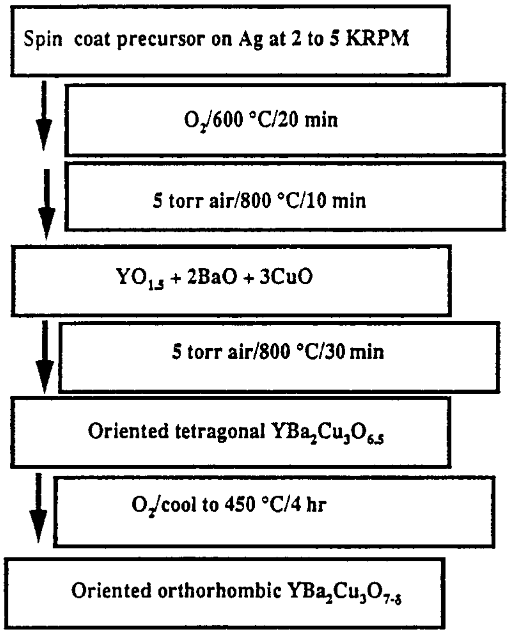

Figure 4. Typical process for producing thin film oriented YBCO from an iodide precursor.

powder) and oriented YBCO (*a thin film on silver foil*) derived from the iodide precursor as described above.

Though films of lower quality are produced, the respective axial intensity ratios for volumes of 5–50 μL flow coated over 1 cm^2 were 0.2–3.2, demonstrating a trend of decreasing orientation with increasing thickness indicated by the Greuter report.[6] This gradation also occurs by changing the spin-coating speed. Thus, on increasing the spin coater speed from 2750 to 5000 rpm the axial intensity ratio decreased (relative *c*-axis orientation increased) from 0.8 to 0.5 after reaction at 750 °C. The maximum oxidation temperature (orientation temperature) effects the intensity ratio dramatically. Ratios from slightly less than 1 at 750 °C to around 0.01 at 900 °C were observed.

As suggested by Lay[15] and others[16,17] YBCO of high purity can be produced in ambients with a low oxygen pressure from CuO, Y_2O_3, and $BaCO_3$ at solid-state reaction temperatures as low as 750 °C in order to avoid oxygen stoichiometries above 7.0. With the iodide precursors it was an advantage to operate at a pressure of 5 Torr of dry air at the solid-state reaction temperature for this reason and in order to remove the $Ba_5(IO_6)_2$ formed during earlier oxidation in high oxygen ambients as suggested by Frit.[10] Losses due to the formation of volatile copper compounds (CuI, CuOH, etc.) were reduced by a high heating rate (20–30 °C/min) in oxygen above the temperature of oxidation of CuI (300–500 °C). Apparently the oxidation rate of CuI is much faster than its sublimation rate. The sublimation rate of CuI is generally less than that of soluble metalloorganic copper compounds.[8] A typical process, shown in Figure 4, included heating the green film in about 20 min to 600 °C in oxygen, then heating to the solid-state reaction temperature, and holding there for about 1 h in 5 Torr of air. Subsequent slow cooling in oxygen to about 450 °C and holding produced the highly *c*-axis oriented orthorhombic YBCO (see Figure 3).

Preliminary conductivity measurements at Oak Ridge National Laboratory with a four-point probe technique revealed the *bulk* YBCO reached "zero resistivity" at 92 K for pelleted samples derived from thermally evaporated solutions of the iodide precursor which were subsequently oxidized as in Figure 4.[8] The best thin films showed a conductivity inflection at 90 K but reached "zero resistivity" at about 30 K. Connectivity needs to be improved. The foil substrates are not very planar in relation to micron-thick films, leading to poorer conductivities than reported from other spin-coated films on lapped strontium titanate.[13,14] A possible solution would be an evaporated silver film on a lapped substrate (e.g., semiconductor silicon).

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Registry No. YI_3, 13470-38-7; BaI_2, 13718-50-8; CuI_2, 7681-65-4; silver, 7440-22-4.

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