ROUTES TO HIGH- T_c SUPERCONDUCTING TI-Ba-Ca-Cu-O FILMS USING ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Films of the Ti-Ba-Ca-Cu-O high- T_c superconductor can be prepared by several organometallic chemical vapor deposition routes. Two of these involve Ba-Ca-Cu-O films that are first prepared using the volatile metal-organic precursors Ba(heptafluorodimethyloctanedionate)₂, Ca(dipivaloylmethanate)₂, and Cu(acetylacetonate)₂. Deposition is carried out at a pressure of 5 Torr with argon as the carrier gas and water vapor as the reactant gas. Thallium is next incorporated into these films either by organometallic chemical vapor deposition using Ti(cyclopentadienide) as the source, or by vapor diffusion using bulk Ti-Ba-Ca-Cu-O as the source. Thallium deposition is carried out at atmospheric pressure with an argon carrier and water-saturated oxygen reactant gas, followed by rapid thermal annealing. Both procedures yield films that consist primarily of the $TlBa_2Ca_2Cu_3O_x$ phase, have preferential orientation of the Cu-O planes parallel to the substrate surface, and exhibit onset of superconductivity at ~ 125 K with zero resistance by 100 K.

INTRODUCTION

With the advent of superconducting oxides exhibiting critical temperatures, T_c , in excess of 77 K, intense worldwide interest has been stimulated toward the application of superconductivity to vast new areas of both scientific and technological importance. One area of activity has been the development of processes that produce high-quality thin films of these materials since it is likely that high- T_c superconductors will first have technological impact in this form. To date, efforts have primarily centered on physical vapor deposition (PVD) techniques such as sputtering¹⁻³, thermal⁴ and electron beam evaporation,^{5,6} and laser ablation.⁷ With the development of appropriate molecular precursors, organometallic chemical vapor deposition (OMCVD) would offer an attractive alternative approach with potential advantages of simplified deposition apparatus, high deposition rates, ability to coat complex shapes, compositional control, and excellent film uniformity.

Among the currently known high- T_c superconductors, the Ti-Ba-Ca-Cu-O materials ($Tl_mBa_2Ca_{n-1}Cu_nO_{m+2n+2}$; $m = 1,2$; $n = 1,2,3$) exhibit the greatest multiplicity of phases, high environmental stability, ease of synthesis, and T_c values as high as 122 K.⁸⁻¹² Such valuable characteristics dictate the need for the synthesis of high-quality films of these materials. We report here the preparation of high- T_c Ti-Ba-Ca-Cu-O films by two complementary, OMCVD-based strategies. In the first, thallium is introduced into an OMCVD-derived Ba-Ca-Cu-O film via an OMCVD step using a volatile organothallium complex, while in the second thallium is introduced by a vapor diffusion technique.

RESULTS AND DISCUSSION

The OMCVD process hinges critically on the volatility and gas phase reactivity of the precursor complexes. An attractive strategy for the design of volatile metal complexes is to minimize lattice cohesive energies by encapsulating the metal ion in a sterically saturating, nonpolar environment.

Ligand fluorination is known to further enhance volatility.¹³ In addition, air-stable sources possess the desirable characteristics of being conveniently manipulated and requiring less specialized handling apparatus. As a result, we have chosen as the sources for our initial OMCVD experiments the β -diketonate complexes of Ba, Ca, and Cu and the organothallium complex Tl(cyclopentadienide) ($\text{Tl}(\text{C}_5\text{H}_5)$)¹⁴ which are depicted in Figure 1.

Figure 1. Molecular structures of the sources for OMCVD of Tl-Ba-Ca-Cu-O films.

OMCVD of Ba-Ca-Cu-O films was carried out in a horizontal, cold-wall quartz reactor having individual inlet tubes for the volatile metal-organic sources $\text{Ba}(\text{fod})_2$,¹⁵ $\text{Ca}(\text{dpm})_2$,¹⁶ and $\text{Cu}(\text{acac})_2$,^{15,16} (Figure 1). Deposition was carried out at 5 Torr pressure with an argon carrier gas, source temperatures of 160–210°C, and water as the reactant gas. Films were deposited on single-crystal yttria-stabilized zirconia (YSZ) substrates at 600°C. X-ray photoelectron spectroscopy (XPS) of the as-deposited Ba-Ca-Cu-O films indicates that fluoride (presumably from the decomposition of the fod ligand) and only a small amount of carbon impurities are present. The carbon can be removed by a relatively low temperature (550 °C) anneal, however, the elimination of fluoride required annealing for 2–3 hours at 800°C in flowing water-vapor saturated oxygen. Fluoride is presumably removed from the films as HF .¹⁵ At this point, the black, 10 μm thick films have the approximate stoichiometry BaCaCu_3 as estimated by energy dispersive X-ray analysis.

For the thallium introduction into the $\text{BaCaCu}_3\text{O}_x$ films via OMCVD, volatile $\text{Tl}(\text{C}_5\text{H}_5)$ was employed. Deposition was carried out at atmospheric pressure with an argon carrier gas and water-saturated oxygen as the reactant gas. The source temperatures employed were between 50 and 80°C with a $\text{BaCaCu}_3\text{O}_x$ substrate temperature of 300°C. The as-deposited films were amorphous by X-ray diffraction (XRD) and XPS indicated only a small, predominantly hydrocarbon-type carbon impurity. In order to produce the superconducting phase, a short (1–2 min.) post-deposition anneal at 860°C was required. Due to the high vapor pressure of thallium and its oxides, annealing was best carried out under a thallium-rich atmosphere. Such an environment was provided by annealing the films in a covered crucible containing a small amount of bulk Tl superconductor (a source of volatile Tl_2O and Tl_2O_3).^{3,5,6,17,18} The annealed films display XRD patterns ($\text{Cu K}\alpha$) (Figure 2(a)) that indicate they consist predominantly of the $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ phase.^{1–5,14} The enhanced intensities of the (00l) reflections indicate that the crystallite c -axes are preferentially oriented perpendicular to, and therefore the Cu-O planes parallel to, the substrate surface. Four-probe resistivity (ρ) measurements were performed with instrumentation described previously using 25 μm gold wire contacts attached with gold paste.¹⁹ As can be seen in Figure 3, the transition to the superconducting state begins at ~ 120 K with zero

resistance achieved by 100 K. The metallic character ($dp/dt < 0$) of the transport at temperatures above 120 K is typical of high-quality, high- T_c films.

Figure 2. X-ray diffraction pattern of (a) a Ti-Ba-Ca-Cu-O film on YSZ prepared by OMCVD and (b) a Ti-Ba-Ca-Cu-O film on YSZ prepared by OMCVD of a Ba-Ca-Cu-O film followed by vapor diffusion of Ti.

Figure 3. Charge transport characteristics of the Ti-Ba-Ca-Cu-O film shown in Fig. 2(a). Variable temperature resistivity is indicated by *. Thermoelectric power indicated by o (relative to the Au electrodes).

The thermoelectric power, relative to the gold contacts, was measured by a slow ac technique (10^{-2} Hz) with thermal gradients of 0.5-1 K in a conventional type of apparatus.²⁰ Figure 3 shows the results of these measurements which display a sharp transition to zero over the same temperature range as the resistivity; properties expected for a high-quality superconducting film. The magnitude of the thermoelectric power as well as the temperature dependence of the in the normal region is typical of bulk high- T_c superconducting materials.²¹

For thallium introduction via a vapor diffusion approach, the annealed $\text{BaCaCu}_3\text{O}_x$ films were heated under air in a closed crucible containing a small amount of Ti-Ba-Ca-Cu-O superconductor for 3 min at 880°C and cooled slowly to room temperature. XRD patterns for these films (Fig. 2(b)) are similar to those obtained by the OMCVD process, consisting of predominantly c -axes oriented crystallites of the $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ phase. The resistivity characteristics of these films are

similar to those depicted in Figure 3 with a superconducting transition which begins at ~ 120 K with $p=0$ at 101 K.

These results show that high- T_c superconducting Tl-Ba-Ca-Cu-O films with excellent electrical properties can be synthesized either by a purely OMCVD approach using volatile molecular precursors or by an OMCVD approach in which one of the components (Tl) is introduced by vapor diffusion. Presently we are examining the simultaneous deposition of all four molecular components along with the relationship between film composition/properties and deposition/processing parameters.

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