

Metal-organic chemical vapor deposition/open flow thallium annealing route to epitaxial $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ thin films

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Phase-pure epitaxial $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ thin films have been grown on single crystal (110) LaAlO_3 substrates using an improved metal-organic chemical vapor deposition process. First, Ba-Ca-Cu- O_x precursor films are grown on LaAlO_3 (110) substrates using $\text{Ba}(\text{hfa})_2$ -tet, $\text{Ca}(\text{hfa})_2$ -tet, and $\text{Cu}(\text{hfa})_2$ (hfa=hexafluoroacetylacetonate; tet=tetraglyme) as volatile metalorganic precursors. Thallium is then incorporated into the films during a post-anneal in the presence of a Ti_2O_3 , BaO, CaO, CuO powder mixture at 820 °C for 12 h in a flowing 10% O_2/Ar atmosphere. The films have a transport-measured $T_c=115$ K and $J_c=1.5\times 10^5$ A/cm² (80 K), while magnetic hysteresis measurements yield $J_c=6\times 10^5$ A/cm² (77 K). Preliminary surface resistance measurements give $R_s=0.35$ m Ω at 5 K, 10 GHz.

$\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Ti-2223) is the highest T_c phase ($T_c=125$ K) of the environmentally robust and structurally diverse class of thallium-based superconductors (TBCCO).¹ In thin film form, members of this family exhibit excellent current-carrying properties,² while the low attainable surface resistances are compatible with a range of microwave device technologies (e.g., passive filters).³ To date, high-quality TBCCO films have largely been grown by physical vapor deposition (PVD) techniques such as laser ablation,⁴ sputtering,⁵ spray pyrolysis,⁶ and electron beam evaporation,⁷ while metalorganic chemical vapor deposition (MOCVD) techniques have received less attention.⁸⁻¹¹ MOCVD processes offer the attraction of simplicity of apparatus, independence from line-of-site deposition, ability to coat large areas and complex shapes, high throughput, and film growth under highly oxidizing conditions.

We report here an MOCVD process for phase-pure, epitaxial Ti-2223 films that employs fluorinated β -diketonate metal-organic precursors and a flowing gas thallium annealing process. The films are characterized by a variety of microstructural and charge transport techniques.

The vast majority of TBCCO film growth procedures reported to date employ initial growth of a Ba-Ca-Cu- O_x (BCCO) precursor films that is subsequently thallinated at high temperature (frequently in sealed quartz tubes). In the present procedure, BCCO films were grown by MOCVD using the reactor design shown in Fig. 1. The volatile metalorganic precursors are transported from Pyrex reservoirs immersed in constant temperature baths. Argon is used as a carrier gas, with flow maintained by mass flow controllers. The precursor gases are mixed at a common manifold, and the oxidizing gas is introduced immediately upstream of the reaction chamber entrance. To produce a laminar flow, an expansion adapter as well as a quartz laminar flow chamber

are placed inside the main reaction chamber. The high aspect ratio (3:1) of the cross section in the quartz laminar flow chamber reduces the turbulent flow induced by the thermal buoyancy effects of the heated substrate.¹² The substrate susceptor, made of silicon carbide-coated graphite, is angled at 9° to help maintain a uniform diffusion boundary. The substrate susceptor is heated by a water-cooled ir lamp, and all precursor delivery lines are resistively heated to 150 °C. This reactor design affords uniform deposition rates and uniform film elemental composition ($\pm 1\%$) over a 25 cm² area.

In the present study, $\text{Ba}(\text{hfa})_2$ -tet, $\text{Ca}(\text{hfa})_2$ -tet, and $\text{Cu}(\text{hfa})_2$ (hfa=hexafluoroacetylacetonate, tet=tetraglyme) were used as volatile metal sources due to their superior volatility and thermal stability. For BCCO precursor film growth, cleaned (sonicated in methanol), single-crystal LaAlO_3 (110) substrates were employed. During MOCVD growth, the Ar carrier flow rate for each source was 50–100 sccm and the Ba, Ca, and Cu precursor temperatures were 115, 86, and 34 °C, respectively. The oxidizing gas was $\text{H}_2\text{O}(25\text{ °C})$ -saturated O_2 flowing at 100 sccm. The addition of water in this step appears to increase the oxidation rate

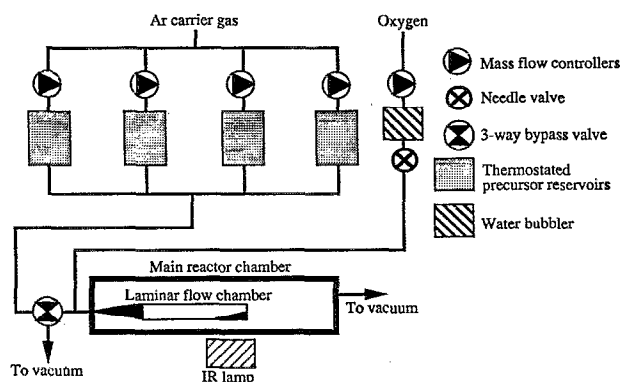


FIG. 1. Schematic of the MOCVD reactor used in the growth of Ba-Ca-Cu- O_x precursor thin films.

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and to assist in the removal of fluorides derived from the thermolysis of the fluorinated ligands. The substrate temperature in the present work was 730 °C and the total system pressure was 5.0 Torr (0.3 Torr background pressure) during film growth. The mass-transport limited deposition rate was 0.6 μm/h and film growth was generally 0.75 h in duration.

Inductively coupled plasma atomic emission spectrometry was used to determine the metal stoichiometries of the BCCO precursor films. X-ray diffraction data (Ni-filtered Cu Kα radiation) from the as-deposited films show qualitatively small amounts of crystalline BaF₂, Ba₂CuO, and CaO. Previous studies with fluorinated precursors indicated that a post-anneal of the BCCO films in water-saturated O₂ (720 °C for 8 h) is necessary to remove fluoride¹³ and allow the formation of the superconducting phase. The present, higher deposition temperature of 730 °C in combination with H₂O, eliminates the need for a separate H₂O/O₂ annealing step. As assessed by x-ray diffraction, residual traces of crystalline BaF₂ are readily removed during the subsequent thallination anneal (*vide infra*), presumably as volatile TlF.

To form the superconducting phase, Tl₂O is introduced into the BCCO precursor film from a Tl₂O₃:BaO:CaO:CuO (1:2:2:3) pellet during a high temperature anneal. About 0.8 g of the TBCCO powder is pressed into a 1-cm-diam pellet and placed in a small gold crucible. The BCCO film is placed over the pellet, face down, with gold foil used as a spacer to prevent direct film-pellet contact. The crucible is then tightly wrapped with gold foil and a flowing 10% O₂ in Ar gas mixture (100 sccm) is used to purge the crucible and furnace before annealing is initiated. A 10% O₂ mixture is used since reduced O₂ pressures (in sealed quartz tube annealing schemes) are known from PVD studies¹⁴ to reduce the temperature for Tl-2223 formation and to improve film surface morphology. A rapid temperature ramp is used to bring the furnace to the setpoint of 820 °C within 15 min. This procedure has distinct advantages over sealed-tube thallination methodologies in terms of efficiency and amenability to scale-up.

For the highest *T_c* films, 2.0:2.2:2.7 Ba:Ca:Cu precursor films were annealed as described above for 12 h at 820 °C. A θ - 2θ x-ray diffraction scan [Fig. 2(a)] shows essentially phase-pure Tl-2223. Only the (00*l*) peaks are observed, indicating that the film is highly *c*-axis oriented. The θ -rocking curve (a further measure of *c*-axis orientation) exhibits a full width at half-maximum of 0.8° [Fig. 2(b)] which is comparable to values for typical PVD-derived films. Such linewidths can be attributed to randomly dispersed intergrowths of less ordered TBCCO layers in Tl-2223 domains, thus reducing the *c*-axis coherence length.¹⁵ An in-plane ϕ scan [Fig. 2(c)] shows the relative orientation of the crystallite *a*, *b* axes within the film plane. Reflections appear every 90° as expected for an epitaxial, tetragonal TBCCO film. Figure 3 shows a cross-sectional high resolution transmission electron microscopic (TEM) image of an MOCVD derived Tl-2223 film (001) which evidences epitaxial growth and an abrupt TBCCO/LaAlO₃ interface. The TEM studies also show trace intergrowths of *c*-axis-oriented layers of Tl-2212 and Tl-2201 phases within the Tl-2223 structure, although they are not detected by x-ray diffraction. Similar intergrowths have

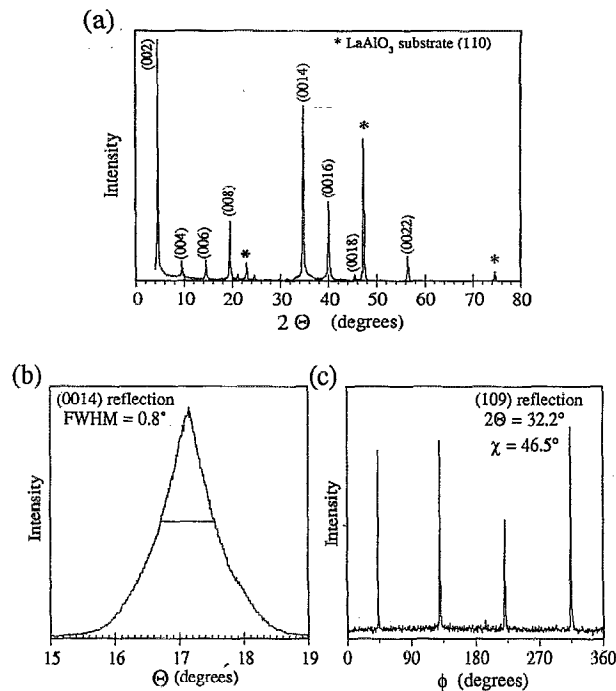


FIG. 2. (a) θ - 2θ x-ray diffraction pattern of an MOCVD-derived Tl-2223 thin film grown on (110)LaAlO₃. (b) θ -rocking curve of the (0014) reflection of an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO₃. (c) ϕ scan of the (109) reflection of an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO₃.

been recently reported in PVD-derived films.^{15,16}

Transport measurements provide further indications of film quality. The resistivity versus temperature behavior of an MOCVD-derived Tl-2223 film [Fig. 4(a)] indicates *T_c* = 115 K, the highest recorded to date for an MOCVD-derived HTS film. Several films were patterned using standard photolithography and ethylenediamine tetraacetic acid etching¹⁷ to define an 80-μm-wide microbridge. Critical current density (*J_c*) results from dc and pulsed transport mea-

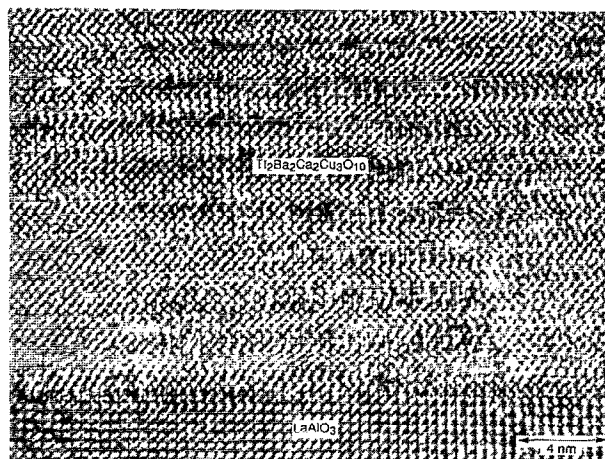


FIG. 3. Cross-sectional high resolution transmission electron micrograph of the interface between an MOCVD-derived (001) Tl-2223 thin film and (110) LaAlO₃ substrate.

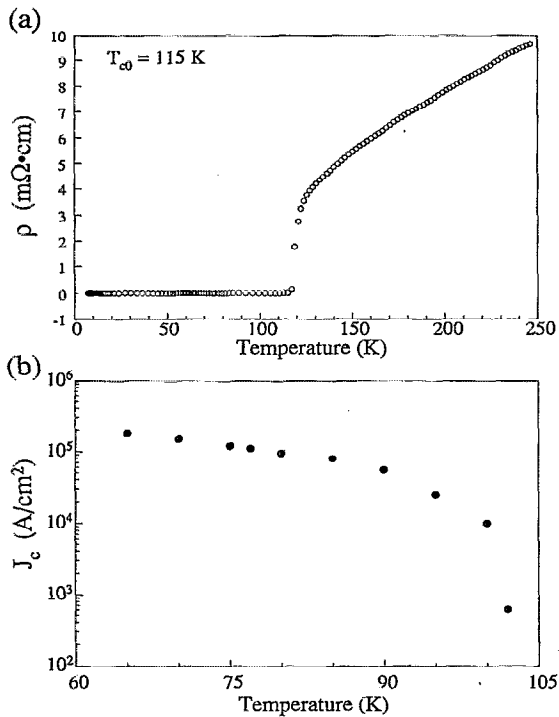


FIG. 4. (a) Variable temperature resistivity vs temperature data for an MOCVD-derived TI-2223 thin film grown on (110) LaAlO₃. (b) Transport-measured critical current vs temperature for an MOCVD-derived TI-2223 thin film grown on (110) LaAlO₃.

measurements appear in Fig. 4(b). At 77 K (0 T), $J_c = 1.5 \times 10^5$ A/cm², as defined by a 10 μ V/cm offset criterion. Bean model¹⁸ calculations using a SQUID susceptometer data yield $J_c = 4 \times 10^6$ A/cm² at 5 K (0 T) and 6×10^5 A/cm² at 77 K (0 T). The 77 K J_c values obtained from transport and magnetic measurements agree reasonably well, suggesting that intragrain coupling does not adversely affect the transport capacity. These transport properties are comparable to those of the highest quality PVD-derived films.¹⁹ Preliminary surface resistance measurements on a film containing admixed TI-2212 phase (as judged by x-ray diffraction), performed in a parallel plate resonator against a YBCO standard, yield $R_s = 0.35$ m Ω at 5 K, 10 GHz, approaching the lowest values reported for PVD-derived films.²⁰

In summary, high-quality TI-2223 thin films have been grown in an improved two-step MOCVD process. Ba-Ca-Cu-O_x precursor films are grown via MOCVD using fluorinated β -diketonate polyether metal-organic precursors and an improved reactor design. The superconducting phase

is then formed during a subsequent flowing gas post-anneal in the presence of a TI-Ba-Ca-Cu oxide mixture. These films show epitaxial growth, good transport properties, and low surface resistance at 10 GHz. Further research is in progress to understand processing/microstructure/charge transport relationships of TI-2223 and other TBCCO phases.

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- ²⁰W. L. Holstein, L. A. Parisi, C. Wilker, and R. B. Flippen, *IEEE Trans. Appl. Superconductivity* **3**, 1197 (1993); $R_s = 0.024$ m Ω (4.2 K, 10 GHz) for TI-2212 films; R_s values are typically $\sim 10 \times$ higher for TI-2223 films [W. L. Holstein (private communication)].