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Superconducting Thallium Oxide and Mercury Oxide Films

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Superconducting Thallium Oxide and Mercury Oxide Films

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ABSTRACT

Previously we reported on a two-layer electrodeposition process of thallium oxide superconductors that showed transport critical current density above 10^6 A/cm^2 at 77 K in zero field. In this article, we report our effort to convert an electrodeposited thick film of $(Tl,Bi,Pb)_2(Sr,Ba)_2Ca_1Cu_2O_x$ to $(Hg,Bi,Pb)_2(Sr,Ba)_2Ca_1Cu_2O_x$ by the cation-exchange process. We are also reporting magneto-optical imaging data on Tl oxide superconductor films, which are compared with YBCO. Magneto-optical imaging provides insight into the nature of current flow in the Tl oxide superconductor, and thus, will help us to improve the critical current density in bulk high-temperature superconductor wire or tape.

INTRODUCTION

The primary technical challenge that must be satisfied to permit high-temperature superconductor (HTS) wire or tape in superconducting magnets or power-related applications is the successful demonstration of a low-cost, high-field, high-current-carrying wire or tape with acceptable mechanical properties. The thallium-based and mercury-based superconducting oxides are excellent candidates because of their high transition temperature reaching to 130 K and unique features in their growth morphology. Recently, Wu et al. developed a cation-exchange technique where a Tl oxide superconductor was converted to a Hg oxide superconductor [1]. In this process, Hg replaced Tl by reacting a Tl oxide superconductor ($TlBa_2CaCu_2O_x$) in the presence of Hg vapor. We attempted to perform similar experiments using electrodeposited thick films of $(Tl,Bi,Pb)(Sr,Ba)_2CaCu_2O_x$.

In general, the electrodeposition of superconductor tapes for conductor applications has considerable practical potential, particularly in the fabrication of large non-planar devices. Electrodeposition is a potentially low-cost, non-vacuum process that has the ability to easily deposit superconductor precursor films or tapes at thicknesses up to 15 μm. Electrodeposited films of all the oxide superconductors have been demonstrated, with the Tl system emerging as most promising [2-4].

In this paper we also report recent studies on the magneto-optical imaging (MOI) of Tl oxide superconductors. In low-T_c superconductors [5,6], critical current density (J_c) is almost entirely determined by the pinning of vortices at microstructural defects or precipitate in the material (flux pinning). In HTS, the J_c measured by transport over macroscopic lengths is determined not only by intragrain flux pinning at microstructural defects, but also, by grain-boundary misalignment that influences the connectivity of the superconducting filaments.

Some defects in HTS such as cracks and large second-phase particles, act as permanent barriers to current flow, whereas others (e.g., high-angle grain boundaries) exhibit a weak coupling effect that markedly degrades the transport in moderate magnetic fields. This spatially variable electromagnetic coupling produces percolative current flow, meaning that not all of the cross section is useful for carrying transport current. This so-called granular behavior [7] has been visualized by magneto-optical imaging (MOI) in YBCO superconductors. The MOI of Tl oxide superconductor on rolling-assisted biaxially textured substrate (RABiTS) Ni suggest that the Ni grain boundaries may in fact be less of a problem for Tl-oxide superconductor than for YBCO.

EXPERIMENTAL DETAILS

The electrodeposited [4] precursor films were obtained by coelectrodeposition of the constituent metals using nitrate salts dissolved in dimethyl sulfoxide (DMSO) solvent. The electrodeposition was performed in a closed-cell configuration at 24°C in the presence of dissolved oxygen (oxygen gas was bubbled in the solution during the deposition). A number of electrodeposition runs were performed with different electrolyte compositions, and the precursor films were analyzed by inductively coupled plasma (ICP) spectrometry to establish the stoichiometric ratios of the deposited elements. The films were electroplated by using a constant potential of -3 V. All samples were electrodeposited in a "vertical cell," in which the electrodes (working, counter, and reference) were suspended vertically from the top of the cell. All chemicals were of Analar or Puratronic-grade purity and were used as received. A conventional three-electrode cell was employed, in which the reference electrode was Ag (pseudo-reference) and the counter electrode was a Pt gauze. A Princeton Applied Research potentiostat/galvanostat Model 273A with an IBM PC AT computer interface was used to control the potential of electrodeposition and to monitor the current and voltage profiles. At first, we tried to increase the film thickness by increasing the deposition time. The film thickness did in fact increase with longer deposition time, but the film morphology was poor. A two-layer technique was then tried that used two layers of TBSBCCO films, with an intermediate layer of Ag to improve the film uniformity. The deposition process is as follows: (a) single-crystal substrates are coated with 300-Å Ag; (b) TBSBCCO films (0.8 to 1.3 μm) are prepared by electrodeposition (ED) on Ag/LAO; (c) 300-Å Ag is deposited on ED-TBSBCCO/Ag/LAO; (d) second layer of TBSBCCO is electrodeposited (0.8 to 1.3 μm) on Ag/ED-TBSBCCO/Ag/LAO; and the complete two-layer system is reacted.

The superconducting Tl-2212 films studied by MOI were prepared by a dc-magnetron sputtering process on textured Ni substrates [8,9]. The sputtering was carried out using a pair of faced Tl-2212 targets in a gaseous mixture of 80% Ar and 20% O_2. The as-deposited precursor films were amorphous with a composition of Tl:Ba:Ca:Cu=2:2:1:2. The precursor films were placed in an Al_2O_3 crucible together with a reacted Tl-Ba-Ca-Cu-O pellet and annealed at a temperature of about 760°C for 6 hours in pure argon of 1 atm pressure to obtain superconducting Tl-2212 film.

RESULTS AND DISCUSSION

An electrodeposited $(TlBi)_1(SrBa)_2Ca_2Cu_{3.5}O_x$ {TBSBCCO} precursor film on 300-Å Ag/LAO, annealed in air at 870°C in the presence of a TBSBCCO pellet, shows Tl-1223 phase development [4]. The pole-figure measurement of the (103) HKL peak shows biaxial texture.

The omega scan and phi scans indicate the full width at half maximum (FWHM) of only 0.92° and 0.6°, respectively, which indicate a very high-quality film.

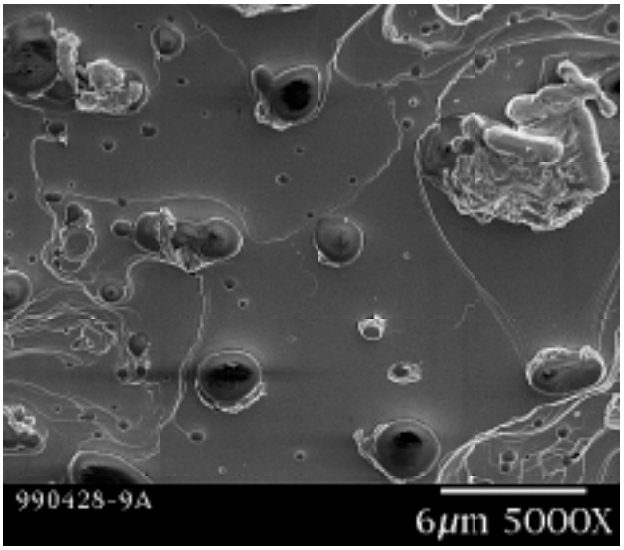


Figure 1. The SEM of a two-layer annealed ED-TBSBCCO/Ag/ED-TBSBCCO/Ag/LAO film.

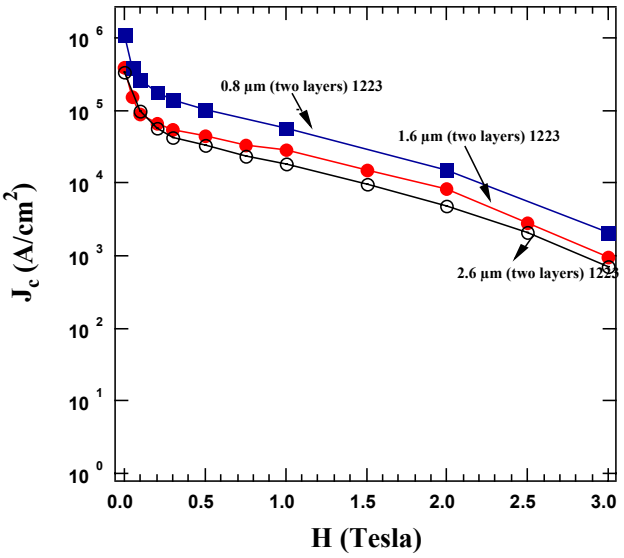


Figure 2. The magnetic field dependencies of transport J_c at 77 K (H // c) for two-layer 0.8, 1.6, and 2.6 μm ED-TBSBCCO/Ag/ED-TBSBCCO/Ag/LAO film.

The SEM analyses (Fig.1) of the presently annealed two-layer film show dense and melted plate-like structure development without any voids. The thickness of the annealed two-layer film varied from 0.8 to 2.6 μm. The superconductive transition temperature of the films, determined resistively, is about 110 K. Figure 2 shows the critical current density versus magnetic field values at 77 K of 0.8-μm, 1.6-μm, and 2.6-μm two-layer films. At 77 K and no magnetic field, the critical current-density value of a two-layer, 0.8-μm-thick film is 1.1 x 10^6 A/cm^2 (Fig.2)

using the field criterion of 1 μV/cm. The critical current density of the film is calculated using the full cross-section of the sample (3.7 mm x 0.8 μm). The two-layer, 2.6-μm-thick (width = 3.2 mm) TBSBCCO film prepared by the electrodeposition process showed critical current (I_c) of 28.24 A at 77 K (normalized I_c = 88.25 A for 1-cm-wide samples).

We were not very successful of forming the 1223-TBSBCCO phase on Ag, Ag/Pd (10% Pd), and also on textured Ni. The Tl-2212 or Tl-1212 phase mostly formed on these metal substrates. The Tl-2212 or 1212 phases lack good magnetic-field-dependent properties. A recent study by Wu et al. [1] showed that cation exchange of Tl by Hg took place for both Tl-2212 and Tl-1212 phases. The quality of the sample made in the cation-exchange process is superior to Hg-1212 synthesized directly by the conventional sealed-tube annealing process. Cation-exchanged Hg-1212 showed critical current densities nearly an order of magnitude higher than the best value reported on conventionally processed Hg-1212 thin films [10]. The sputtered deposition process limited the thickness of the Tl oxide films to only about 300 nm. We attempted to convert the thick electrodeposited Tl-2212 film (Pb,Bi,Sr doped) into Hg-1212 by the cation-exchange process. Figures 3a and 3b show the X-ray diffraction analysis of the Tl-2212 and partially cation-exchanged Hg-1212 films. It seems that some cation-exchange reaction took place, but we need to further optimize the processing conditions to obtain fully converted Hg-1212 films.

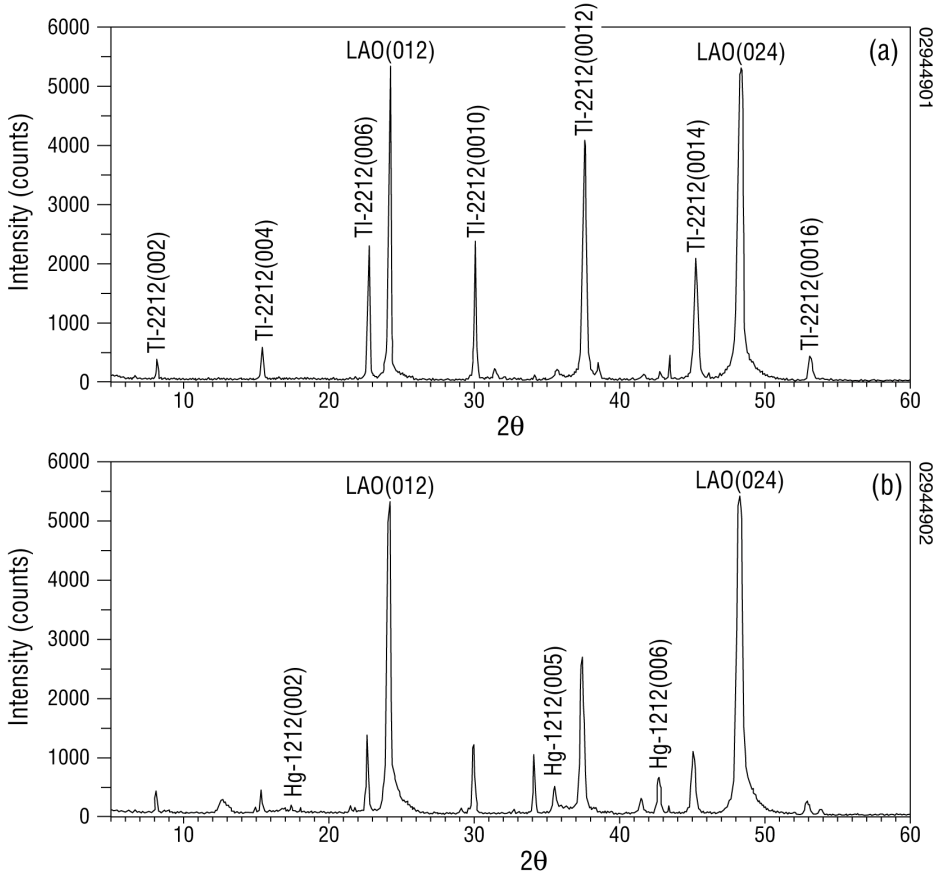
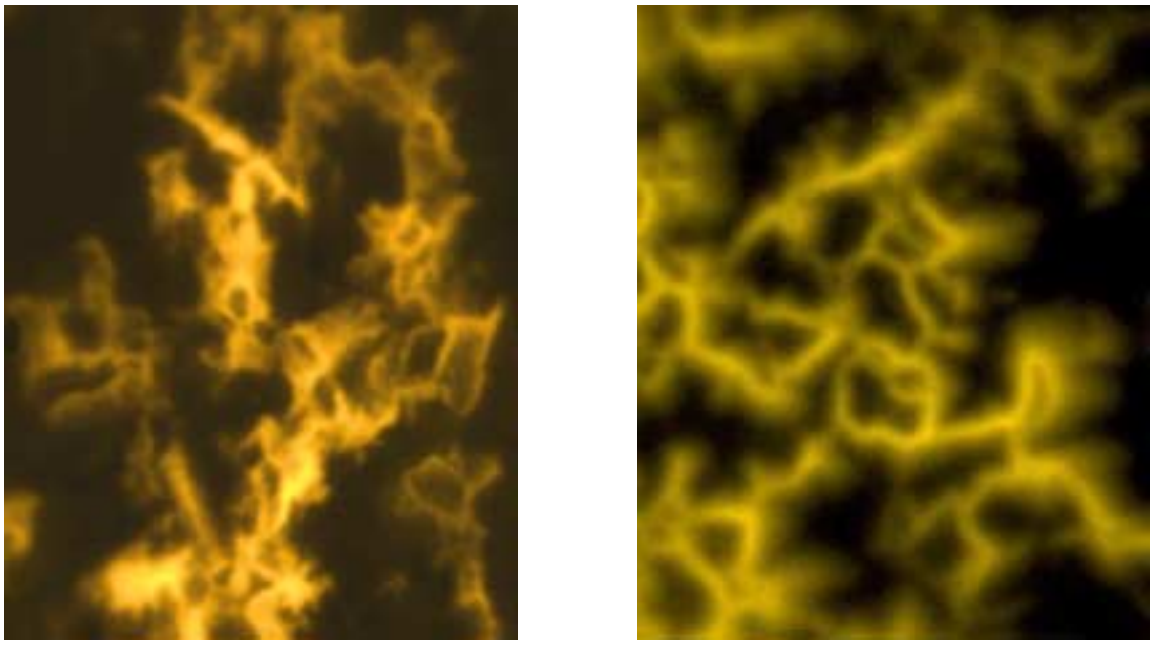


Figure 3. X-ray diffraction analysis of (a) electrodeposited Tl-2212 and (b) the films after processing in Hg vapor (cation exchanged).

The MOI data were collected from sputtered Tl-2212 films on textured Ni substrates. The MOI image of a Tl-2212 film is compared in Fig. 4 with PLD YBCO deposited on RABiTS Ni. The MOI image of Tl-2212 (Fig. 4a) shows no indication of grain-boundary replication of the Ni substrate for the Tl oxide superconductor. These MOI images suggest that the Ni grain boundary may in fact be less of a problem for the Tl oxide superconductor than for YBCO. This suggested behavior is a direct result of the unique microstructural morphology for Tl oxide films. Even though high epitaxy can be observed following the partial-melt processing for Tl oxide films, the substrate features (i.e., grain boundaries) are not observed. Therefore, grain-boundary misalignment problems in the substrates may not be replicated for the Tl oxide superconductors, which may ease the problem for developing long-length conductors. Further studies on Tl oxide films on RABiTS are needed to fully resolve the advantages of the Tl oxide superconductor films.



(a) **(b)**

Figure 4. Magneto-optical imaging of (a) Tl-2212 on RABiTS Ni (460 μm x 350 μm), (b) YBCO on RABiTS Ni (460 μm x 350μm).

CONCLUSIONS

Cathodically electrodeposited Tl-oxide precursor films can be rapidly synthesized with controlled stoichiometry, and upon thallianation, they produce high-quality material with promising critical current density. We demonstrated partial cation-exchange reaction for electrodeposited, doped thick-films. The MOI images revealed that the Tl oxide superconductor

does not copy the substrate's grain boundaries, in contrast to YBCO. This leads us to believe that grain-boundary misalignment in the substrates may not present any problem for the Tl-oxide superconductor films on metallic substrates, which may ease the problem for developing very long-length conductors.

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