Improved electrodeposition process for the preparation of superconducting thallium oxide films


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Abstract

We report on developing a two-layer process to deposit biaxially textured Ti-oxide films by electrodeposition (ED) on Ag-coated, single-crystal substrates. Pole-figure measurements of two-layer, electrodeposited (Tl,Bi)-(Sr,Ba)-Ca-Cu-O (TBSBCCO) films on 300 Å Ag/LaAlO₃ (LAO), with thickness between 1 and 5 μm, clearly show strong biaxial texturing. The omega scan and phi scan of 1.6 μm Tl(Bi)₀.₀₆Sr₁.₆Ba₄.₄Ca₃Cu₄Ag₀.₅Oₓ films indicate the full width at half maximum of only 0.92° and 0.6°, respectively, indicating a very high-quality film prepared by the ED process. Transport measurements for the electrodeposited, thallium-oxide-based superconductor films show values above 10⁶ A/cm² at 77 K in zero field. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thick film; Electrodeposition; Ti-oxides

1. 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 superconducting oxides are excellent candidates because of their high transition temperatures reaching to 127 K and unique features in their growth morphology. Nabatame et al. [1] reported a magnetic field vs. temperature irreversibility line for Ti-1223 that compares favorably at 77 K with the Y-Ba-Cu-O (YBCO) performance. Recent work has also shown that the Ti-1223 compound, with Pb, Bi, and Sr substitution for Tl and Ba, shows improved phase stability and magnetic behavior competitive with the YBCO compound at 77 K [2].

Previously, [3] we reported the transport current of an electrodeposited (Tl,Bi)-(Sr,Ba)-Ca-Cu-O (TBSBCCO) film on 300 Å Ag/LaAlO₃ (LAO) as 24.2 A, which corresponds to 7.84 × 10⁵ A/cm² critical current density using the field criterion of 1
µV/cm. The films as processed had some voids and a thickness of about 0.8 µm. At present, we are trying to prepare thick (> 1 µm) TBSBCCO precursor films with no voids and better uniformity. 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 overall film morphology was poor. A two-layer technique was then tried that used two layers of electrodeposited TBSBCCO films, with an intermediate layer of Ag used to improve the film uniformity. We also observed better film quality by dissolving oxygen in the electrolyte and with excess copper deposited in the precursor film. In this paper, we report the improved transport results obtained from these new techniques for depositing TBSBCCO films.

2. Experimental

The electrodeposited [4,5] precursor films were obtained by coelectrodeposition of the constituent metals using nitrate salts dissolved in dimethyl sulfoxide (DMSO) solvent. The electrodeposition (ED) 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 ED 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 cation ratios of the ED bath were adjusted systematically to obtain (TlBi)$_{1.1}$Sr$_{1.6}$Ba$_{0.4}$Ca$_2$Cu$_4$ precursor compositions. We increased the Cu content in the film from 3 to 4, which helped to obtain good quality films reproducibly. A typical electrolyte bath composition for the TBSBCCO films consisted of 1 g Tl(NO$_3$)$_3$, 1 g Bi(NO$_3$)$_3$·5H$_2$O, 12.6 g Sr(NO$_3$)$_2$, 11.5 g Ba(NO$_3$)$_2$, 6.8 g Ca(NO$_3$)$_2$·4H$_2$O, and 2.3 g Cu(NO$_3$)$_2$·6H$_2$O dissolved in DMSO solvent. The substrates were single-crystal LAO coated with 300 Å Ag. The films were electroplated by using a constant potential of −3 V. All samples were electrodeposited in a "vertical cell", where the electrodes (working, counter, and reference) were sus-

![Fig. 1. Cyclic voltammogram (a) in the absence of oxygen, dashed line; and (b) in presence of oxygen for Ba−Bi−Ca−Cu solution, solid line.](image-url)
pended 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 where the reference electrode was Ag (pseudo-reference) and the counter electrode was Pt gauze. A Princeton Applied Research potentiostat/galvanostat Model 273A with an IBM PC AT computer interface was used for controlling the pulsed-potential electrolysis 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 TBS-BCCO 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 (0.8–1.3 μm) are prepared by ED on Ag/LAO; (c) 300 Å Ag is deposited on ED-TBSBCCO/Ag/LAO; (d) second layer of TBSBCCO is electrodeposited (0.8–1.3 μm) on Ag/ED-TBSBCCO/Ag/LAO and the complete two-layer system is reacted.

The samples were characterized by X-ray diffraction including θ/2θ, pole figures, and phi-scans, resistance vs. temperature (R–T), four-probe transport, magnetization measurements, and scanning electron micrographs (SEM).

The samples were evaluated for their superconducting properties by R–T measurements and four-probe transport (critical current) measurements in He vapor. Four Ag contacts were made on the sample by evaporating Ag in a vacuum. Ag wires were soldered to the Ag contacts using In solder. The samples were inserted slowly into the pre-cooled chamber of the squid-magnet which is capable of producing maximum fields of 5.5 T. The criterion for the critical current density measurements was 1 μV/cm electric field. The magnetic field was applied parallel to the c-plane (H || c).

3. Results and discussion

3.1. Electrochemistry

To determine the effect of dissolved oxygen on deposition potential, a cyclic voltammogram experiment was performed on a solution mixture containing Bi(NO₃)₃·5H₂O, Ba(NO₃)₂, Ca(NO₃)₂·4H₂O, and Cu(NO₃)₂·6H₂O dissolved in DMSO solvent with and without bubbled oxygen. The reduction peaks of the corresponding Bi, Ba, Ca, and Cu were shifted toward the more favorable positive direction in the presence of oxygen (Fig.1). The deposited materials were more stable in the presence of oxygen and were not stripped significantly from the electrode surface during the positive-direction scan. This behavior is most likely due to the deposition of
BiBaCaCu-oxide precursor, as described by the following reaction

\[ M^{n+} + n/2O_2 + ne^- \rightarrow MO, \quad E_0 < E_0(\text{Std}). \quad (1) \]

The morphology for the electrodeposited materials is a very important step of the electrogrowth because it influences directly the structure of the annealed film and, therefore, its properties. In the ED process, the adatoms or adions incorporate in the...
The resistive transition curve of an annealed ED-TBSBCCO/Ag/ED-TBSBCCO/Ag/LAO film.

With time, as the film thickness increases, the deposition continues either by the buildup on previously deposited material (old nucleation centers) or the formation and growth of new ones. These two processes are in competition and can be influenced by different factors. High-surface diffusion rates, a low population of adatoms, and low overpotentials enhance the buildup of old nucleation centers; conversely, low surface diffusion rates, a high population of adatoms, and high overpotentials on the surface enhance the creation of new nucleation centers. In our deposition process, when we tried to increase the film thickness by increasing the deposition time, the film thickness did in fact increase with longer deposition time; however, the film morphology was poor because of the buildup on the old nucleation centers. The two-layer technique, where a...
new Ag layer was deposited in-between, helped to fill up the voids by creating new nucleation centers, which improved the film morphology.

The Nernst equation \( E = E^0 + RT/nF \ln[a/\Gamma] \) describes how the equilibrium potential depends on the ionic activity. The Nernst equation teaches us that changing ionic activity concentration can change the equilibrium drop for a given metal and solvent system. In our ED process, we have used this concept for the deposition of multicomponent systems. We have adjusted the individual salt concentrations to deposit desired precursor films.

3.2. Annealing of electrodeposited precursor and results

An electrodeposited 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 (Fig. 2a). The pole-figure measurements of the (103) HKL peak shows biaxial texture (Fig. 2b). The omega scan (Fig. 3b) and phi scan (Fig. 3c) indicate the full width at half maximum (FWHM) of only 0.92° and 0.6°, respectively, which indicate a very high quality film. The SEM analyses of the presently annealed two-layer film show dense and melted plate-like structure development without any voids (Fig. 4b), compared with the previous single-layer annealed film with voids (Fig. 4a). The thickness of the annealed two-layer film varied from 0.8 to 2.6 μm. The superconductive transition temperature of this film, determined resistively, is about 110 K (Fig. 5). Fig. 6 shows the critical current density vs. magnetic field values at 77 K of 0.8, 1.6 and 2.6 μm thick films. At 77 K and no magnetic field, the critical current density value of a two-layer, 0.8 μm thick film is \( 1.1 \times 10^6 \) A/cm² (Fig. 6) 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 × 0.8 μm). The two-layer, 2.6 μm thick (width = 3.2 mm) TBSBCCO film prepared by the ED process showed critical current \( (I_c) \) of 28.24 A at 77 K (normalized \( I_c = 88.25 \) A for 1 cm wide samples). The critical current density values vs. magnetic field measured at 40, 64 and 77 K temperatures for two-layer 1.6 and 2.6 μm thick films are shown in Fig. 7 and Fig. 8, respectively. These values for current density for ED Tl-1223 films are the highest ever reported for a processing technique that does not involve a vapor transport method such as pulsed-laser deposition, sputtering, or e-beam. These latter methods have demonstrated typical current densities for Tl-1223 epitaxial films on single-crystal substrates (LAO, YSZ, etc.) of around \( 10^6 \) A/cm² at 77 K in zero field, which represents the highest value that is also obtained by ED-TBSBCCO film.

4. Conclusions

Cathodically, electrodeposited superconducting oxide precursor films can be rapidly synthesized with controlled stoichiometry. Upon thalliation, they produced high-quality material with promising critical current densities. ED processing of Tl-oxide superconductors deserves more attention and represents a strong viable candidate for the production of HTS tape operating at temperatures near 77 K.

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References