Fabrication and Characterization of Tl-Ba-Ca-Cu-O Superconducting Films on LaAlO₃ Substrates

P. ARENDT, N. ELLIOTT, R. DYE, K. HUBBARD, M. MALEY, J. MARTIN, Y. COULTER and B. BENNETT
Los Alamos National Laboratory, Los Alamos, NM, 87545

A multi-step process is used to fabricate Tl₂Ba₂Ca₃Cu₄O₈ films on (100) LaAlO₃ substrates. Submicron thick precursor films of Ba-Ca-Cu-O are rf magnetron sputter deposited from a single target. Film stoichiometry is measured by ion beam backscattering spectroscopy. Deficiencies of the alkaline earths that are found in the precursor films are then compensated for by the addition of appropriate CaF₂ and/or BaF₂ films onto the surface of the precursor film. Post deposition annealing of the films is then done in an atmosphere of thallium oxide and oxygen in order to form the superconducting phases. The annealed films are examined using x-ray diffraction (XRD), an ac inductance technique, and critical current in an external magnetic field. XRD shows the c-axis length of the superconducting phase to increase as the overall film stoichiometry approaches 2212. The transition widths measured by inductive coupling weakly correlate with 77 K critical current measurements. Our best critical current results are 1.5*10⁶ amps/cm² for a film measured at 4 K in an 8 T magnetic field (parallel to the films’ c-axis).

Key words: TlBaCaCuO films, superconductivity, LaAlO₃ substrates

INTRODUCTION

Tl-based superconductors have been produced into wire and tape form by loading superconducting power into silver tubes which are then drawn and rolled multiple times. The material is then post sintered at high temperatures to optimize the superconducting properties. The resulting Jc values for these Tl-based tapes have not been as high as for Bi-based superconducting tapes processed by similar techniques. However, Jc values for Tl-based superconducting films on single crystal substrates are comparable to those for the Bi-based films on single crystal substrates.

The Tl-based superconductor-in-silver studies discussed above do not mention if attempts were made to optimize the material properties. This paper investigates how the parameter of film composition influences Jc for a single Tl-based superconducting phase (2212). The substrates used in this study are (100) LaAlO₃ single crystal substrates. This is thought to be an optimum substrate which will have minimal deleterious effects on the film properties. The Jc vs film composition information is expected to be useful in follow up studies on optimizing Tl-based superconducting materials on silver substrates.

EXPERIMENT

Precursor films of Ba-Ca-Cu-O were prepared by a rf magnetron sputtering process previously described. The 600 nm thick films were deposited onto (100) LaAlO₃ substrates. The precursor film stoichiometry was measured by ion beam backscattering spectroscopy using 4 MeV He ions. The precursor films were found to have a composition of Ba₁ₓCa₀₉ₓCu₂₀O₈.

A composition nearer that of the final annealed phase (2212) was thought to be desirable. Attempts to vary the stoichiometry of the precursor films by varying several deposition parameters were unsuccessful. A more direct method for increasing the alkaline earth content of the precursor films was then employed. This consisted of resistively evaporating films of BaF₂ and/or CaF₂ onto the precursor films. The films were then annealed in an atmosphere of thallium oxide and oxygen.

The annealed films were examined by theta two-theta x-ray diffraction (XRD). X-ray pole figure analyses for the (0012) and (105) reflections were done for a full 360° of rotation (φ). Dynamic impedance (DI) vs temperature was also measured. This latter technique is similar to ac susceptibility measurements and has been previously described. Transport Jc was determined by four point resistive measurements using a 0.51 V criterion. The bridge widths were approximately 100 microns. The maximum magnetic field in which the films could be measured is 8 T. Most of the measurements were performed with the magnetic field parallel to the c-axis of the films. The measurements were done at liquid He (4 K), liquid N₂ (75 K), and low pressure liquid N₂ (64 K and 70 K) temperatures.

RESULTS AND DISCUSSION

Ion beam backscattering of the annealed films which had alkaline earth fluoride salts overcoated onto them showed no residual fluoride to be present. Sufficient residual water vapor is present during the anneal to react with the fluorine and remove it as HF vapor.

The XRD of the annealed films showed the su-
perconducting phase formed to be Tl₂Ba₂Ca₁₂Cu₂O₈.
The c-axis orientation of the films on LaAlO₃ is similar
to that for films reported previously. However, close examination of the annealed precursor films
\( (Ba₄.₈₅Ca₀.₁₅Cu₂.₀O₇) \) showed their c-axis lengths to be approximately 2% shorter than the literature value. Further small additions of Ba (\( \text{preanneal composition of} \ (Ba₄.₈₅Ca₁₅₀Cu₂.₀O₇) \) to the films finally increased the c-axis values to match those in the literature.

Pole figure analysis of the films showed distinct maxima for the (105) peak. The maxima are regularly spaced at \( z = 0°, 90°, 180°, \) and \( 270° \). This indicates the films have good in-plane a-axis orientation.

The DI screening of the films showed that the films which were most deficient in the alkaline earth metals (~10% low relative to a 2212 composition) had transition temperature onsets ranging from 85 to 100 K. The corresponding transition widths varied from 4 to 35 K. Increasing only the calcium content of the films to a Ca:Cu ratio of 1:2 increased the onset transition temperatures to over 100 K and decreased the transition widths to 2 K, or less. Further additions of barium to the films caused no further decrease in the transition widths but did slightly increase the onset transition temperatures to above 105 K. Figure 1 illustrates an optimum DI vs temperature for a film whose preannealed stoichiometry was \( Ba₄.₈₅Ca₁₅₀Cu₂.₀O₇ \).

The dependence of \( J_c \) on applied field direction at 75 K is shown in Fig. 2 for fields parallel and perpendicular to the c-axis. These \( J_c(\mathbf{H}) \) values at liquid nitrogen temperature are the highest that were obtained in this study. The \( J_c(\mathbf{H}) \) values for a film whose preannealed composition was \( Ba₄.₈₅Ca₁₅₀Cu₂.₀O₇ \). The \( J_c(\mathbf{H}) \) value at 0.6 T, 75 K value is 1.38*10⁵ amps/cm². The \( J_c(\mathbf{H}) \) value at 0.7 T, 75 K value is 1000 amps/cm². This large anisotropy in \( J_c(\mathbf{H}) \) at liquid nitrogen temperatures for Tl-based superconductors has been noted by other investigators.\(^6\)