Superconducting and Microstructural Properties of [001] Tilt $YBa_2Cu_3O_{7-\delta}$ Thick Film Grain Boundaries on $SrTiO_3$ Bicrystal Substrates

Qiang Li, Y. Zhu, V. F. Solovyov, H. J. Wiesmann, and M. Suenaga

***Abstract*—We present a study of superconducting and microstructural properties of [001] tilt $YBa_2Cu_3O_{7-\delta}$ (YBCO) thick film grain boundaries (GB) on $SrTiO_3$ bicrystal substrates prepared using BaF_2 ex-situ post deposition reaction process. For a 15° tilt boundary, multiple micro-bridges were patterned across the grain boundary at various locations. A large variation of local critical current density J_c was observed. Through local microstructural characterization of these GB bridges using transmission electron microscope (TEM), a direct correlation of local GB J_c with structure is identified.**

***Index Terms*—Critical current, Interface phenomena, Superconductors**

I. Introduction

Grain boundaries in high-T_c superconductors (HTS) are of paramount importance for large-scale applications like HTS cables and wires. In spite of the notable progress achieved in fundamental studies of transport properties across grain boundaries, the relationships between the superconducting properties and the microstructural properties are still poorly understood.

There are three key issues in the field of HTS grain boundary (GB) studies. The first is the angular dependence of grain boundary J_c^{GB}. In most HTS grain boundaries, J_c^{GB} decreases exponentially with misorientation angle θ, for θ approximately > 10 degree [1]. An exception is in the case of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) bicrystal [001] twist grain boundaries, where Li and coworkers observed an angle independent J_c^{GB} [2]. The second issue is the processing dependence of J_c^{GB}. There is more than a two order of magnitude difference in a typical value of J_c^{GB} for the same misorientation angle among several well-known processing techniques for $YBa_2Cu_3O_{7-\delta}$ (YBCO), such as pulsed laser deposition (PLD), liquid phase epitaxial, top-seed melt texture, and BaF_2 ex-situ post reaction. The third issue is the local J_c variation due to structural inhomogeneity along a single grain boundary. This problem is particularly severe in the case of the YBCO system, where micrometer-scale structural defects are typically observed for most processing conditions. The study of these problems is particularly inadequate. This is due to exceptional difficulties in preparing TEM specimens at the exact location of the patterned micro-bridge previously characterized in transport experiments. It is thus the purpose of this work to address the issue of local J_c^{GB} variation in YBCO.

In the present work, we prepared [001] tilt YBCO thick film grain boundaries on $SrTiO_3$ bicrystal substrates using BaF_2 ex-situ post reaction process. The choice of the BaF_2 process in the present study is motivated by the potential long length application of similarly fabricated YBCO thick film. Some advantages of this process are: 1) process being easily scaled up, 2) thick (more than 5 μm) films maintaining texture, 3) high J_c comparable to PLD films [3]. By using a focused laser-beam, multiple micro-bridges were patterned across the grain boundary at various selected locations with different optical morphology. After detailed transport measurements were performed, the local microstructures at those bridges, as well as along much larger section of the grain boundary films, were characterized in an advanced TEM. For a 15° tilt boundary, a large variation of local grain boundary J_c^{GB} was observed. We were also able to directly correlate local grain boundary microstructure with J_c^{GB}.

II. Experiment

A series of YBCO thick films were grown on $SrTiO_3$ bicrystal substrates consisting of a symmetric [001] tilt boundary. Films of thickness 0.5 – 1 μm were grown by e-beam deposition of pre-cursors including BaF_2 and followed by ex-situ post reaction at temperature of 735 °C [3]. The superconducting (SC) films have T_{co} = 90 - 91.5 K and intragranular J_c^{SC} of 1.2 - 2.5 × 10^6 A/cm^2 at 77 K and self-field. Along the grain boundary, each film was divided into 3-5 sections. One section about 1 mm wide was used as a TEM specimen to study the grain boundary microstructure on a much larger scale. On other sections, bridges with widths w = 3 – 100 μm were patterned across the boundaries for transport measurements. The location of the bridges was chosen based on optical microscopy.

Six probes in an in-line configuration were used for measuring the voltage-current (V-I) characteristics simultaneously across the grain boundary and intragrain superconducting films. Transport measurements were performed in an exchange-gas cryostat equipped with a 9 T superconducting magnet. Zero magnetic field (< 20 mG) environment was achieved using a compensating field to

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balance both ambient and remnant field in superconducting coils. To avoid self-heating, a bi-directional dc current sweep was used at high currents with a pulse of 100 ms width. Voltages were obtained over six orders of magnitude with a resolution of 1 nV, and averaged for both current directions several times to eliminate thermal EMF. Both intergrain (GB) J_c^{GB} and intragrain (SC) J_c^{SC} were determined using the electric criteria of 10 μV/cm.

After transport measurements, the samples were subjeted to microstructural characterizations. Two types of TEM specimens were prepared. The first type was prepared with the thinned area for TEM study on each specimen falling exactly on the grain boundary bridge after final ion milling. The second type was prepared on the reserved 1 mm wide film section. Using sequential milling, a large portion of grain boundary on the 1 mm wide strip may be characterized to reveal the structural variation of the grain boundary. For simplicity, we will describe a detailed transport and microstructural characterization of a 15° [001] tilt grain boundary at various locations.

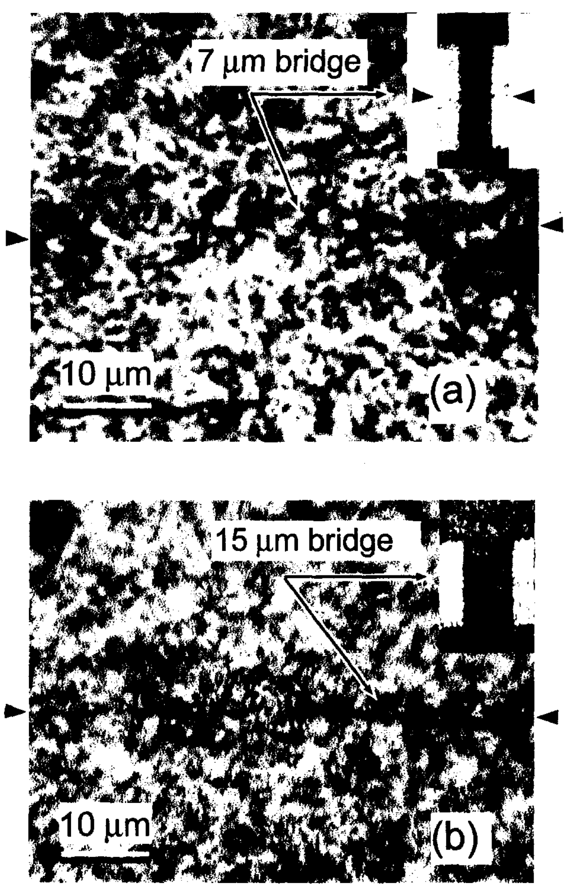

Fig. 1. Optical images of a 15° [001] tilt YBCO thick films in the vicinity of the selected area for bridges before patterning. Grain boundary is indicated by the pair of black arrowheads. (a) Bridges of width 77 μm, 17 μm, and 7 μm (illustrated as an inset) across the grain boundary were sequentially patterned in the area indicated by the long arrow; (b) A 15 μm wide bridge (inset) across the grain boundary was patterned in the area indicated by the long arrow.

Fig. 1 shows optical images of the 15° tilt YBCO thick film grain boundary in the vicinity of the selected area for bridges before patterning. In Fig. 1a, an area with relatively uniform morphology across the grain boundary under optical microscope was selected. A 77 μm wide bridge (sample A) was first patterned across the grain boundary at the position indicated by the long arrow, followed by transport measurements. To check the uniformity, we sequentially reduced the width of the bridge to 17 μm (sample B) and 7 μm (sample C) for further transport characterization. In Fig. 1b, an area with apparent intergrowth was selected using optical microscope. A 15 μm wide bridge (sample E) was patterned for transport measurements at the position indicated by the long arrow.

III. Transport Properties

Like most films that we studied with misorientation angles ranging from 4° to 24°, we found a very small depression of T_c at the grain boundary for this 15° tilt YBCO film. The intragrain T_c^{SC} of the superconducting film is 91.2 K. The grain boundary T_c^{GB} is 90.05 K, the resistance across the grain boundary dropping more than 5 orders of magnitude below the normal state value. A typical value of intragrain J_c^{SC} was observed in this film, 1.83×10^6 A/cm^2 at 77 K. J_c^{SC} was obtained from the V-I characteristics measured on a 7.2 μm bridge pattern on one side of grain boundary.

Fig. 2 shows the temperature dependence of J_c^{GB} at various locations along the 15° [001] tilt YBCO thick film grain boundary. The solid square shown in the figure is the data for the intragrain J_c^{SC}. The solid circles are the data taken on a 1 mm wide film strip across the grain boundary. Since the 1 mm width is orders of magnitude larger than the scale of structural inhomogeneity, the value of J_c measured on this film strip may be taken as the averaged value of J_c^{GB} for

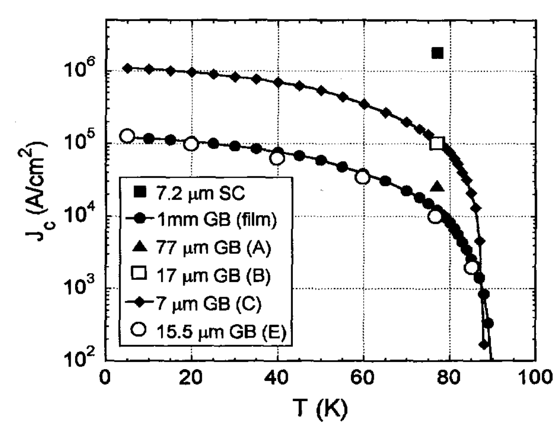

Fig. 2. Temperature (T) dependence of critical current density J_c at various locations along a 15° [001] tilt YBCO thick film grain boundary. The solid square is the data for the intragrain J_c^{SC}.

this 15° [001] tilt boundary. Thus, at 77K, the average J_c^{GB} is about 1.21×10^4 A/cm^2, which is more than two orders of magnitude lower than the intragrain J_c^{SC}.

Large local variations of J_c^{GB} are demonstrated in Fig. 2. At locations B and C, local J_c^{GB} is almost an order of magnitude higher than the averaged J_c^{GB}. It is apparent that transport properties are relatively uniform on a scale of 20 μm, since grain boundary critical current I_c^{GB} at bridges C and B (through width reduction at the same location) scales quite well with width. At larger length scales, this uniformity is lost. This is demonstrated by the much lower value of J_c^{GB} for a 77 μm wide bridge A patterned on the same location before bridges B and C. In a huge contrast, we found the value of J_c^{GB} for bridge E is about one order of magnitude lower than that for bridges B and C. At bridge E, an apparent intergrowth (shown in Fig. 1b) was identified by optical microscope prior to transport measurements. The lowest value of J_c^{GB} found at bridge E is surprisingly close to the average value of J_c^{GB} determined on a 1 mm wide strip. This finding suggests that the majority of this 15° tilt grain boundary is likely made of regions with poor transport properties similar to that at bridge E.

For bridge C, the local J_c^{GB} is 1.05×10^5 A/cm^2. It is among the highest J_c^{GB} values reported so far for 15° [001] tilt YBCO gain boundaries made by various processing methods. To determine whether or not bridge C is still a weak link, we applied magnetic field parallel to the common c-axis, which is also parallel to the interface plane. The results presented in Fig. 3, show magnetic field dependence of local J_c^{GB} for bridge C measured at various temperatures. J_c^{GB} dropped 50% at mere 30 G applied field, which indeed suggests weak-coupling behavior of this grain boundary. The observed field dependence does not display a regular Fraunhofer or diffraction pattern for a uniform short Josephson junction, and likely this suggests structural inhomogeneity of the grain boundary on bridge C at sub-micron scale.

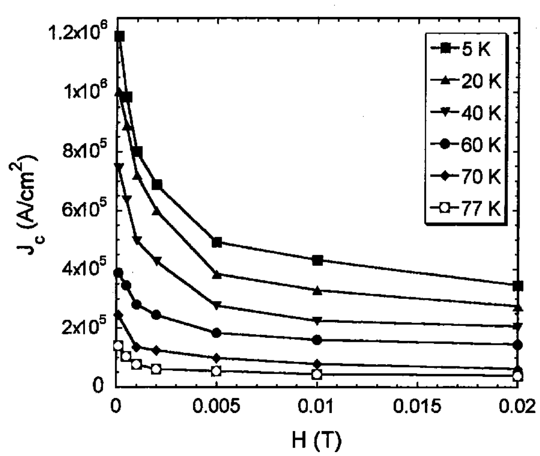

Fig. 3. Magnetic field (H) dependence of J_c^{GB} at bridge C across a 15° [001] tilt YBCO thick film grain boundary

IV. Grain Boundary Microstructures

The sections containing grain boundary bridge C and E, as well as 1 mm film strip were isolated for TEM specimens by wire-saw. Preparing TEM specimens on the microbridges is difficult, because the TEM thin region must fall exactly on the bridge. The specimen must be repeatedly ion-milled and checked in an optical microscope. We were successful making a TEM specimen on bridge E, while most of bridge C was milled away. In addition, a large crack developed in the grain boundary area of bridge C, probably due to excessive milling. Fig. 4 shows the scanning TEM (STEM) image of the 15° [001] tilt YBCO thick film grain boundary at bridge E. The orientation of the grains on each side can be easily discerned from the respective twins. The grain boundary area is indicated between the linked arrowheads. In the boundary area, we found a number of a-axis oriented intergrowth grains. The intergrowth and adjacent matrix grains effectively form 90° sub-grain boundaries with respect to c-axis. It is not surprising that with this kind of grain boundary interface the bridge E has very low intergrain J_c^{GB}.

Using sequential milling, we were able to examine a large portion of the 15° [001] tilt grain boundary on the 1 mm wide strip. A-axis orientated intergrowth was found in the majority (over 80%) of the grain boundary, with various degrees of misorientation angle between the intergrowth and matrix grains. These intergrowth are likely the barriers to transport critical current. It is our belief that intergrowth at the grain boundary is responsible for the average J_c^{GB} being two orders of magnitude lower than the intragranular J_c^{SC}.

Fig. 4. TEM image of a 15° [001] tilt YBCO thick film grain boundary at bridge E, where a-axis orientated intergrowth was found. The round and rectangular shaped precipitates are Y_2O_3 and CuO, respectively, normally presented in films produced by the BaF_2 process.

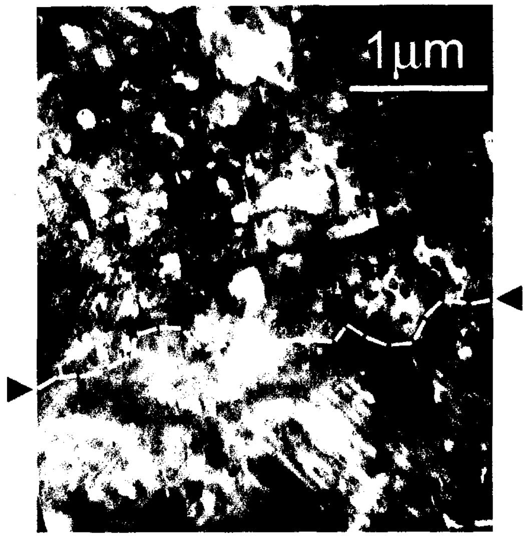

Fig. 5. TEM image of a 15° [001] tilt YBCO thick film grain boundary where no intergrowth was found. The white dashed line is a drawing along the interface showing the meandering pattern of the grain boundary.

In some regions along this 15^0 [001] tilt grain boundary, no intergrowth was found. An example of such a region is illustrated in Fig. 5, which was taken from the 1 mm wide grain boundary film strip. The white dashed line is drawn as a guide along the interface, showing the meandering pattern of the grain boundary. The grain boundary meander in the non-intergrowth area is on the order of 0.5 µm. Though we were unable to make a TEM specimen on bridge C, we suspect that the structure shown in Fig. 5 may be similar to that of the grain boundary on bridge C. This suggestion is further supported by the optical microscopic observation in the vicinity of bridge C. Relatively continuous and uniform morphology was observed across the grain boundary shown in Fig. 1a, contrasted to an apparent intergrowth shown in Fig. 1b. It is remarkable that the grain boundaries with this type of microstructure can carry critical current densities as high as 10^5 A/cm^2 at 77 K, and 10^6 A/cm^2 at 5 K, respectively.

V. Conclusions

In conclusion, [001] tilt YBCO thick film grain boundaries were fabricated on $SrTiO_3$ bicrystal substrates by using the BaF_2 ex-situ post reaction process. We performed extensive transport and microstructural studies on a 15° tilt boundary at various locations along the grain boundary. The average grain boundary J_c^{GB} is about two orders of magnitude lower than the intragranular J_c^{SC}. This low value of J_c^{GB} is due to a-axis oriented intergrowth along most of the grain boundary length. However, substantially higher value of J_c^{GB} was found at locations where no intergrowth was found. Instead, grain boundary meandering at scale of 0.5 µm was observed. It is quite remarkable that portions of a 15° tilt grain boundary carry an impressive high $J_c^{GB} \approx 10^5$ A/cm^2 at 77 K and self-field. If the intergrowth at grain boundary can be eliminated by appropriately adjusting process conditions, the BaF_2 method may yet produce films transporting high intergrain J_c^{GB} at moderate high misorientation angle.

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