Texture and transport in spray pyrolyzed TlBa2Ca2Cu3O9 thick films

J. E. Tkaczyk, J. A. Sutliff, J. A. DeLuca, P. J. Bednarczyk, and C. L. Briant
General Electric Research and Development, Schenectady, New York 12301

Z. L. Wang, A. Goyal, D. M. Kroeger, D. H. Lowndes, and E. D. Specht
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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The electron backscattering pattern technique has been applied to the microstructural investigation of Tl(1223) thick films formed by vapor-phase thallination of Ag-containing Ba–Ca–Cu–oxide precursors. For samples grown on polycrystalline YSZ, considerable biaxial alignment is found in localized, multigrain regions as wide as 100 μm or more. However, on scales above 1 mm the overall texture remains only uniaxial with the c-axes (i.e., [001]) aligned perpendicular to the plane of the substrate. On single-crystal KTaO3 an epitaxial relationship is evident which persists to the surface of a 3 μm thick film. Modest variations in the processing protocol yield films containing grains oriented with the c-axis in the plane, resulting in the degradation of transport properties. The data suggest a growth mode in which sparse nucleation occurs at the substrate followed by rapid lateral crystallization.

I. INTRODUCTION

Large-scale applications of high temperature superconductors (HTS) await the fabrication of long lengths of a suitable conductor. Critical current density of the order $10^4-10^5$ A/cm² at the service temperatures and fields appears necessary for many applications. However, long polycrystalline conductors contain grain boundaries which severely degrade the transport properties, especially in a magnetic field. The benefit of grain alignment was documented by experiments on bicrystals which showed good critical current density across small-angle grain boundaries,1 most recently in Tl(1223) thin-film bicrystals.2 Other researchers observed improved properties across special (so-called low Σ) grain boundaries.3 In Bi2Sr2Ca2Cu3Ox powder-in-tube tapes where c-axis grain alignment is obtained through mechanical processing, critical current densities over $10^4$ A/cm² at 77 K, zero field, have been obtained over lengths of the order of 100 m.4 This material serves as a paradigm for the brick-wall model which proposed an explanation of high critical current density in these uniaxially aligned materials.5 Significant enhancements above this current density level have been demonstrated in polycrystalline films of HTS materials where alignment of both the c-axes and a-axes has been achieved by the special preparation of a textured substrate.6 In these cases the critical current densities approach those of single crystal films. However, it appears difficult to prepare such substrates with lengths appropriate for large-scale applications.

Critical current densities above $10^5$ A/cm² at 77 K, zero field, were obtained in spray pyrolyzed Tl(1223) films formed on polycrystalline YSZ substrates.7,8 The observation of high critical current density in these thick films offered some optimism for large-scale applications using this chemical system. Although clearly textured with c-axis oriented perpendicular to the substrate, it was initially thought that the a-axis of this tetragonal structure was randomly oriented in the plane of the film. This belief was based on the random nature and fine grain structure of the substrate and also the absence of temperature gradients in the process. Subsequent texture analysis at points widely dispersed over the film surface using the electron backscattering pattern technique (EBSP) yielded pole figures consistent with this picture.9

However, further investigations using narrow beam x-ray diffraction indicated the presence of local in-plane texture in these films.10 Azimuthal phi-scans around the sample normal with spot size of the order 0.5 mm indicated concentrations of similar oriented grains. The angular spread of a-axis orientations within each colony was determined to be $\sim 10-15^\circ$. Measurements confirmed the random nature of a-axis orientations when averaged over the whole sample. Refined measurements were performed with a spot size approximately 0.1 mm wide and revealed a distribution of colony sizes from 0.1 mm up to the $\sim 1$ mm and established a correlation between colony structure and the critical current density value.11 These results suggest a model for current
transport which involves percolative transport across [001] tilt grain boundaries (i.e., boundaries containing the c-axis and transverse to the basal plane). In contrast, the brick-wall model emphasizes the conduction across basal plane (i.e., [001] twist) grain boundaries and relies on the enhancement factor due to the large area of basal plane boundaries in highly aspected grains.

In this report an investigation of the microstructure on length scales below that reported for the x-ray data is presented. Pole figures and orientation images generated from EBSP diffraction experiments confirm the colony microstructure down to the scale of the grain size and elucidate the nature of the colony boundary. Additional results for films grown on single crystal substrates and under alternate process conditions suggest a model for film growth and colony formation.

II. PROCEDURE

Textured Tl(1223) films are formed by the reaction or precursor films at 860 °C with Tl2O vapor in a two-zone reactor. The fabrication details are described in a previous communication, but a brief summary follows. Polycrystalline, yttria-stabilized zirconia substrates (3% Y2O3) are sprayed with an ultrasonically nebulized nitrate solution having cation stoichiometry Ba2Ca2Cu3O10.37. Substrate temperature during deposition was 275 °C. The nitrate films are deposited as twelve layers with intermediate partial decompositions at 650 °C for 5 min between deposition of each layer. The nitrate films are then fully decomposed in flowing oxygen using a stepped temperature ramp with final temperature 850 °C followed immediately by a furnace cool.

The resulting oxide precursor are then thallinated in a two-zone reactor in which the temperature ramps of the sample and Tl2O3 source zones are independently controlled. An oxygen flow of approximately 10 sccm is passed through a baffled chamber containing the source and provides convective transport of Tl2O vapor to the sample. The final thallium content of the reacted films is influenced by the partial pressure of thallium oxide during this process. The relation between source temperature and partial pressure of Tl2O has been reported by Holstein.

The temperature protocol for the sample zone was identical for all the samples studied and consists of a 40 min ramp from 400 to 860 °C, a soak at 860 °C for 58 min and a furnace cool. Three types of films (types A, B, and C) are obtained, depending on the particular temperature protocol of the source zone. For types A and B, thallium vapor pressure is appreciable only during the latter 34 min of the soak period during which the source zone is maintained at a temperature Ts.

The temperature protocol of the source zone consists of a 64 min ramp from 400 °C to Ts, a soak at Ts for 34 min, and a furnace cool in concert with the sample zone. The thallium content of the reacted films is determined gravimetrically and is indicated by an average index, x, in the formula TlBa2Ca2Cu3Oy.

Below 720 °C, little reaction occurred. Type A films were obtained for Ts in the range 725–730 °C. In this temperature range, the thallium content 0.70 < x < 0.85 increases relatively slowly as a function of Ts. At temperatures above 730 °C, significant changes in microstructure and degradation electrical properties were observed. Type B films were obtained for Ts in the range 730–735 °C where 0.85 > x > 1.00. At still higher Ts, a phase mixture of 1223 and 2223 was obtained, but these were not characterized further. Finally, type C films were obtained by introducing thallium vapor during the sample warming in addition to the soak period. For example, the temperature protocol of the source zone consists of a 40 min ramp from 400 °C to 725 °C, a soak at 725 for 54 min, and a furnace cool. Following thallination, all samples were patterned for four-point transport measurements and then post-annealed for 8 h at 600 °C in an oxygen ambient.

The EBSP technique for electron diffraction in a scanning electron microscope (SEM) is a useful tool for determination of phase content and microtexture. The technique is sensitive only to the crystalline lattice in the top ~100 nm of the sample. Diffraction patterns were obtained either from the native surface or from polished planar sections. Polished samples have a larger percentage area that produces indexable diffraction patterns and are preferred for orientation imaging. The diffraction patterns were imaged on a phosphor screen and video recorded. These patterns were later retrieved from video tape and analyzed on a personal computer using software developed by Schmidt. The analysis of each pattern gave a crystallographic orientation expressible either as Euler angles or a rotation matrix. The data were used to generate pole figures and orientation images. Pole figures are most useful for displaying the clustering of orientations regardless of spatial information. Orientation images (or maps) display orientation information in direct correspondence to position on the sample. In accord with standard metallographic practice, the pole figures were equal angle projections of only the upper hemisphere. A particular difficulty encountered with this convention, however, was the sensitivity of the {100} pole figure to small angular misalignments between the sample and calibration crystal.

Two modes of data acquisition were performed. In the first, the sample was translated under the diffraction spot. This mode best maintains the diffraction geometry and allows measurements over large regions of the sample (>1000 μm). The second mode of operation consisted of electronically moving the electron beam over a region small enough so that the change in diffraction...
geometry is negligible. This method has the attractive feature that it retains precise information about the position of the spot on the sample as it is imaged in the SEM.

III. EXPERIMENTAL RESULTS

Figure 1 compares the microstructures of the native surface for three films of nominal thickness 3 μm. Figures 1(a), 1(b) and 1(c) typify the different microstructures obtained from the process variations A, B, and C described above. The corresponding average transport properties are listed in Table I. X-ray diffraction traces indicate the dominance of (1223) phase in each of these films.

As seen in Fig. 1(a), type A samples obtained using the nominal process show a somewhat porous, plate-like morphology, and this is typically associated with high critical current density. Rounded nodules at the top surface with diameter 1–2 μm were identified as silver particles with energy dispersive spectroscopy (EDS). Most of the remaining structure was identified as the (1223) phase. In Fig. 1, comparison is made of the secondary electron (above) and backscattered electron (below) images of the surface of a type A sample. The backscattered scanning electron image indicates a number of round particles less than 1 μm in diameter on the surface of the plates. The differing contrasts in the secondary and backscattered images suggest these to be inclusions of relatively low mean atomic number. Similar features were observed for type B and C films. TEM studies of similar films indicated the presence of some nonsuperconducting oxide inclusions.15

In order to develop a sense of the grain size in this material, continuous EBSP line scans were performed

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FIG. 1. Scanning electron micrographs of the unpolished surfaces of three samples typical of types A, B, and C processing on polycrystalline YSZ. Figure (a) compares secondary electron (above) and backscattered electron (below) images of the surface of a type A sample. Figures (b) and (c) are secondary electron images for types B and C, respectively.

TABLE I. Transport properties for three process protocols.

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_c$ (K)</th>
<th>Resistivity ($\mu\Omega\cdot$cm)</th>
<th>$J_c$ (77 K, 0 T) (kA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>105–108</td>
<td>500–700</td>
<td>60–100</td>
</tr>
<tr>
<td>Type B</td>
<td>105–108</td>
<td>750–900</td>
<td>15–45</td>
</tr>
<tr>
<td>Type C</td>
<td>108–111</td>
<td>1500–2500</td>
<td>2–10</td>
</tr>
</tbody>
</table>

along polished planar sections. Small but discrete shifts in the crystallographic orientations, of either the $a$- or $c$-axes, were identified with a passing from one grain to the next. Double images consisting of the superposition of diffraction patterns from two crystallographic orientations were often observed in the transition regions, and these were associated with an encounter with a grain boundary. These shifts and double images were encountered with spatial frequency in the scale of $2–10\ \mu$m. In previous studies, SEM images of fracture surfaces and TEM images show structures which suggest plate-like grains $3–10\ \mu$m in the plane of the plates and $0.5–2\ \mu$m through the thickness.\textsuperscript{5,10} Together, these observations suggest that the surface features shown in Fig. 1(a) are indicative of grains in the bulk of the film and are not purely a surface phenomenon.

Type B films fabricated with thallium contents in excess of $x = 0.85$ are accompanied by the appearance of fan-like structures such as shown in Fig. 1(b). These isolated structures are separated by regions with the plate-like morphology seen in the type A films. The segments that collectively make up the fans are seen to be as large as $100\ \mu$m in length. EBSP analysis along individual segments indicates each filament to be a single crystal $1223$ plate with the $c$-axis in the plane of the film with some tendency for $110$ normal to the film. Type B films generally have a degraded critical current density as compared to those films with slightly lower thallium content in which the fans are absent. At still higher thallium contents (i.e., above $x = 1.0$), a mixture of $1223$ and $2223$ phases is detected by x-ray diffraction measurements and the critical current density remains poor.

The microstructure seen in Fig. 1(c) is typical of that obtained when precursor films are prematurely exposed to thallium oxide vapor during warming to the reaction temperature. Elongated grains are seen to be uniformly interspersed with plate-like structures. The x-ray diffraction pattern is dominated by the $(001)$ reflections, but there are additional reflections from misaligned grains. Individual electron backscattered patterns confirm that the elongated structures are $1223$ grain with $c$-axis oriented along the surface. Although the transition temperatures are largely unaffected, these pre-reacted samples are characterized by a high normal state resistivity and poor critical current density.

Plotted in Fig. 2 is the dependence of the critical current density on magnetic field for the three types of films. For type C films the critical current density is degraded by a factor of 20 from its zero field value by a 0.01T field applied from the zero-field-cooled condition. The critical current density shows significant hysteresis. Types A and B show much weaker dependence on magnetic field and little or no hysteresis.

Figure 3 shows an SEM micrograph of a film formed on a single crystal KTaO$_3$ using the type A thallination process. Transgranular cracks seen in the film are along the $\{100\}$ planes and probably occur due to differential contraction during cooling. The apparent size of the surface features is larger than on YSZ and there is evidence in the shapes of an epitaxial influence of the
substrate. There is a tendency for rectangular shapes with boundaries that follow the (100) directions.

The pole figures in Fig. 4 were obtained using EBSP analysis of type A processed samples on two different substrates, polycrystalline YSZ and single crystal KTaO₃. Data were acquired from a 5 × 5 mm area of the unpolished surface by moving the sample under the electron beam. The {001} pole figures show c-axis alignment with the smaller spread in orientations for the film on the single crystal. However, the most striking difference is in the {100} pole figure. For the single crystal substrate, the strong clustering of points is evidence for a [100]:[100] epitaxial relationship in accord with the oriented grain morphology seen in the SEM micrograph. For the polycrystalline YSZ substrate, the points are uniformly distributed, indicating no preferred orientation of the a-axes in the plane of the film over this 5 × 5 mm area.

However, as mentioned in the introduction, x-ray diffraction measurements give indications of local in-plane alignment on spatial scales of the order 0.1–1 mm. This motivated EBSP investigations on smaller scales and additional data were acquired for type A processed films deposited on polycrystalline substrates. Initial measurements have been presented elsewhere.¹⁶ The following data set is statistically more intensive in that over 200 points were analyzed for each pole figure construction and two magnifications of the same region were analyzed.

Figure 5 shows the {100} pole figures obtained from the polished surface of a type A film. At lower magnification an area of 67 μm × 200 μm is imaged. The relatively uniform angular distribution of points within any one quadrant indicates a relatively random distribution. However, at higher magnification (100) pole figures were obtained from the polished surface of a polycrystalline film. In the low and high magnification images, (a) and (b), data were obtained from an area of 67 × 200 μm² and 20 × 70 μm², respectively. The upper hemisphere of the equal angle projection is shown.
distribution of $\alpha$-axis orientations in the nondegenerate range between $0$ and $90^\circ$. At higher magnification, an area $20 \, \mu\text{m} \times 70 \, \mu\text{m}$ contained within the larger area was imaged. In each quadrant of the pole figure, three groupings of in-plane orientations are observed, confirming the presence of local alignment. The nonuniform distribution of points between quadrants is indicative of a systematic tilt of the $c$-axis from the normal direction. This few degrees tilt is believed to be an artifact derived from misorientation of the calibration crystal and sample.

Orientation images were constructed by associating the output of the EBSP analysis with the position of the analyzing beam on the sample surface. Figure 6 shows the images obtained at these two magnifications. In each case, the projection of the $c$-axis onto the plane of the substrate surface (i.e., R-T plane) is plotted. Because of the fourfold symmetry of the crystal structure, the angle in the R-T plane was chosen to lie within the first quadrant, $0$–$90^\circ$. The fine-line rectangle drawn in Fig. 6(a) indicates the region in which the higher magnification data were taken. There is good correspondence between the data taken at the two magnifications.

IV. DISCUSSION

Using the EBSP technique we have been able to measure the orientation of the 1223 lattice as a function of position in a number of films. This has allowed us to probe both the extent of 1223 grains as well as microtexture of grain ensembles. Orientation maps containing about 200 points, such as presented in Fig. 6, are the present state-of-the-art for a tetragonal material. These maps can be paired with traditional microstructural observation techniques to generate a more complete understanding of the microstructure and its relationship to the electrical transport properties.

Inspection of the surface morphology in Fig. 1 for the type A films reveals plate-like surface structures that are about $5$–$10 \, \mu\text{m}$ in size characterized by an irregular, curvilinear boundary with evidence of terraced steps and necking between neighboring plates. EBSP analysis indicates that these regions contain primarily the 1223 phase. Evidence from a combination of EBSP line scans, and contrast observed in SEM images of fracture surfaces and TEM images, indicate these surface features to be associated with grains in the bulk of the film.

The continuous lines in Fig. 6(b) are drawn so as to lie across large and abrupt changes in orientation. Changes as much as $45^\circ$ are encountered across these boundaries in a distance of only $5$–$10 \, \mu\text{m}$. As such these lines appear to define regions of grains with similar alignment which we refer to as “colonies” in accord with the terminology adapted by previous work.\textsuperscript{10} The three orientational groupings on the pole figure [Fig. 5(b)] are clearly identified as individual colonies on the map. The angular scatter within any group is about $15^\circ$. In the lower magnification map of Fig. 6(a), a more uniform population of angles in the nondegenerate range $0$–$90^\circ$ is evident. The selection of colony boundaries becomes more difficult, in part because the spatial scale becomes too coarse. However, in some areas abrupt changes in orientation are still evident. Regions as large as $50 \, \mu\text{m}$ or more show shared orientation, but there is also a tendency for gradual change of grain orientation across these larger regions.

The growth process leading to the microstructure described above is undoubtedly complex. Under the type A reaction protocol, precursor films are exposed to a significant partial pressure of thallium vapor only after having reached the reaction temperature of $860 \, ^\circ\text{C}$. The observation of strong texture appears to rely on the rather abrupt introduction of thallium into the precursor mix under conditions where the 1223 phase is thermodynamically favored. One must avoid the formation and growth of nuclei in the bulk of the film. The two specific processing variants (i.e., types B and C) which yield films of mixed orientation involved excessive thallium partial pressure during some part of the process.

FIG. 6. Orientation images were constructed from EBSP data by plotting the projection of the $\alpha$-axis into the plane of the substrate. Both low (a) and high (b) magnifications are shown. The inset rectangle in (a) denotes the area where the higher magnification data were obtained. The continuous lines in (b) are guides to the eye chosen to follow colony boundaries.
Similarly, in the fabrication of Tl(2212) films, Ginley et al.\textsuperscript{17} have reported sensitivity of the microstructural orientation to the specific processing configuration. Films of mixed orientation were obtained when the precursor film was placed in contact with a thallinating pellet. Nucleation was observed at both the substrate and free surface. In contrast, epitaxially oriented films were obtained when processed in the open configuration. More recently, success with formation of the 1223 phase by pellet thallination is accomplished by taking appropriate measures to keep the thallium vapor pressure low during processing, either by careful selection of the pellet composition\textsuperscript{18} or by reduced temperature processing.\textsuperscript{19} It is interesting to note that the specific fan-type microstructure and properties of the type B films are reproduced in the former study.

Based on the strong crystallographic texture and rounded grain morphology found in these high \(J_c\) films, the presence of some transient liquid phase during the thallination of the precursor has been suggested in a previous publication.\textsuperscript{7} The complete lack of texture and grain growth in films not containing Ag suggests the participation of Ag in some type of eutectic interaction with the precursor matrix and Tl\(_2\)O vapor. During crystallization of the 1223 phase, the Ag is excluded from the growing 1223 grains and agglomerates as nodules identifiable in SEM micrographs. A similar role for Ag is reported for other HTS systems\textsuperscript{20} and for the preparation of large-grain semiconductor materials on amorphous or ceramic substrates.\textsuperscript{21} Recent investigations of films quenched at the start of thallium incorporation have begun to elucidate the specific chemistry of the melting and nucleation process.\textsuperscript{15}

The observation of an overall c-axis texture in type A films and, more convincingly, epitaxy on single crystal KTaO\(_3\), suggests that the 1223 phase grows from the substrate up. A similar scenario has been demonstrated by Lanham et al. for epitaxial Tl\(_2\)Ba\(_2\)CaCu\(_2\)O\(_8\) films formed by post-annealing of laser ablated precursors on LaAlO\(_3\).\textsuperscript{22} A related situation exists for Bi(2223)/Ag types where c-axis texture first develops at the Ag interface.\textsuperscript{23} In these systems the liquids have been identified and the dissolution of Ag in this liquid verified.\textsuperscript{24} Strongly anisotropic surface energy and substrate interaction energies provide known mechanisms for the formation of plate-like grains with macroscopic uniaxial texture.\textsuperscript{25} The additional observation of local in-plane texture suggests that the solidification is initiated at a relatively sparse number of nuclei. A combination of high growth rates along in-plane directions and a few heterogeneous nuclei located at the substrate can be expected to yield the characteristic colony microstructure observed in these films. Such a process requires a combination of good homogeneity and low supersaturation conditions to avoid homogeneous nucleation.

V. CONCLUSIONS

By pairing the orientational maps and EBSP line scans with the microstructural observations, we provide evidence that there are two spatial scales corresponding to grains and colonies. Within the grains, the orientation is constant to within the resolution of the EBSP measurement (\(\pm 0.5^\circ\)). Within the colonies the orientation is distributed to about 15\(^\circ\). The rate of data acquisition and analysis available at the time of this investigation allows sampling at a relatively coarse spatial scale. Rapid advances in software and hardware promise that much more detailed maps will be soon available. A more confident separation of grain and colony boundaries will then be possible. The detailed information so obtained will be particularly relevant to questions concerning current transport in polycrystalline HTS materials.

Scale-up of this fabrication process to longer lengths requires an understanding of the role that processing has in developing this unique microstructure. The control of the Tl\(_2\)O vapor pressure and correct sequencing of exposure was identified as a necessary condition to achieve texturing and strong grain boundary coupling associated with high critical current density. The available data suggest a mechanism for colony formation in which sparse nucleation at the film/substrate interface is followed by rapid lateral growth.

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