Y-Ba-Cu-O thin films grown on rigid and flexible polycrystalline yttria-stabilized zirconia by pulsed laser ablation

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In situ growth of highly oriented $YBa_2Cu_3O_{7-x}$ thin films (200–500 nm in thickness) has been obtained by pulsed KrF (248 nm) laser ablation on both rigid and flexible randomly oriented polycrystalline yttria-stabilized zirconia substrates. It is shown that *c*-axis-perpendicular $YBa_2Cu_3O_{7-x}$ films with a mosaic spread of only 1.0° can be grown on these randomly oriented polycrystalline substrates. Superconducting thin films were obtained with $T_c(R=0) \sim 89$ K on well-polished substrates. For the films deposited on the flexible substrates, the superconducting T_c is not degraded by repeated bending of the flexible substrate/film composite over a 2.25-cm-radius arc although the normal-state resistivity increases slightly, suggesting the creation of microcracks. The $YBa_2Cu_3O_{7-x}$ films grown on rigid polycrystalline yttria-stabilized zirconia substrates have a critical current density $J_c(H=0) \sim 1400$ A/cm^2 at 77 K.

I. INTRODUCTION

High-quality $YBa_2Cu_3O_{7-x}$ (Y-123) thin films have been obtained on single-crystal substrates using a variety of growth techniques.[1-5] In particular, we recently have shown that Y-123 thin films with $T_c > 90$ K and $J_c > 1$ MA/cm^2 can be obtained routinely by pulsed-laser ablation of a stoichiometric polycrystalline Y-123 target on single-crystal substrates such as (100) $SrTiO_3$, $KTaO_3$, and yttria-stabilized zirconia.[2] However, single-crystal substrates are expensive, are not available in the sizes and shapes needed for many applications, and generally lack the flexibility required of substrates to be used in fabricating high-current conductors. For this reason, a great deal of effort has been put into developing high-temperature superconducting conductors which would be more suitable for applications. These efforts have included Ag-sheathed Y-123, Ti-Ba-Ca-Cu-O, and Bi-Sr-Ca-Cu-O superconducting wires and tapes,[6-8] magnetically- and melt-textured bulk materials,[9,10] as well as Y-123 thin films on polycrystalline metallic substrates.[11] In all cases, some degree of crystalline alignment is believed to be necessary to obtain critical current densities approaching those required for most high-temperature superconducting applications.[12] This is a direct consequence of the high degree of anisotropy in these materials as conduction in the superconducting state occurs primarily within the *a-b* planes.

Substrate candidate materials must meet several criteria including little or no chemical reactivity with the superconducting material and reasonable compatibility with respect to thermal expansion, with lattice matching of course necessary for epitaxial growth. As mentioned above, yttria-stabilized zirconia (YSZ) is one of several ceramic materials that have been found to meet these criteria. Excellent Y-123 thin films have been obtained on YSZ using a variety of deposition techniques. In recent work, it has been shown that the reactivity between Y-123 and YSZ is minimal, especially at temperatures used for *in situ* thin-film growth ($\sim$700 °C), with a thin ($\sim$6 nm) $BaZrO_3$ intermediate layer formed between the Y-123 thin film and the substrate.[13] The thermal expansion coefficient of YSZ is only moderately lower than that for Y-123 [α(YSZ) $\sim$ 8 ppm/°C, α_{a-b} (Y-123) $\sim$ 13 ppm/°C at 20 °C]. With respect to epitaxial growth, though, the lattice mismatch between this cubic substrate ($a = 0.516$ nm) and orthorhombic Y-123 ($a = 0.382$ nm, $b = 0.389$ nm, $c = 1.168$ nm) is about 5.5% for (100) oriented YSZ even when the *a*- and *b*-axes of Y-123 are rotated by 45° about the *c* axis with respect to the crystal axes of YSZ. Of course, when considering nonepitaxial thin-film growth, lattice-matching criteria will be of little relevance.

In this paper, we report the results of a study on the deposition of Y-123 on randomly oriented polycrystalline YSZ substrates. Both rigid and flexible polycrystalline YSZ substrates are used for the first time. The most significant result of this work is that Y-123 thin films that are highly *c*-axis oriented and with a zero resistance $T_c \sim 89$ K can be obtained on very smooth and planar randomly oriented polycrystalline YSZ. However, even with this high degree of *c*-axis orientation, the critical current density at 77 K in zero

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magnetic field is only ~ 1400 A/cm^2, suggesting that either misorientation in the *a-b* plane or some other mechanism is limiting the critical current density.

II. EXPERIMENTAL DESCRIPTION

The Y-123 thin films were deposited *in situ* by means of pulsed-laser ablation under the same conditions by which excellent epitaxial Y-123 thin films were obtained on single-crystal substrates.[2] A KrF excimer laser beam (~ 350 mJ, 38 ns full-width half-maximum (FWHM) pulse duration) was focused to a horizontal line on a ~ 25-mm-diam Y-123 rotating target. The focused energy density was determined to be 2.5–3.0 J/cm^2. The focused line was scanned vertically in order to produce a deposition region within which films were more uniform in thickness and composition.[2] The substrates were bonded to a stainless steel heater surface at a distance of 6.5 cm from the Y-123 pellet. Film growth was carried out at a substrate temperature of 730 °C (calibrated by infrared thermometry) in an oxygen pressure of 200 mTorr. After deposition, the films were cooled in 600 Torr of oxygen at a rate of 10 °C/min in order to convert the as-deposited tetragonal films into fully superconducting orthorhombic Y-123 films. Film thicknesses ranged from 200–500 nm. For critical current measurements, the films were patterned using standard photolithographic techniques with a bridge width of 100 μm.

Two types of polycrystalline YSZ substrates, rigid and flexible, were used in this study. The rigid (General Electric) substrates were fabricated by cold pressing and sintering at 1400 °C for 4 h in air. The starting powders were obtained from Tosoh USA, Inc. These powders are stabilized with 3 mole % Y_2O_3 and have an average particle size of 26 nm. The major impurity is Na_2O (0.013% by weight). The sintered pellet was 98% dense with a diameter of 6.5 cm and 0.3-cm thickness. Film-growth substrates (~ 0.3 cm wide and ~ 1.5 cm long) were sectioned with a metal-bonded diamond saw. For some specimens copper lap polishing was followed by successively finer diamond powder polishing, down to a No. 3 final grit size (2–4-μm particle sizes). This resulted in smooth surface with occasional saw marks still visible. These substrates were put through the "epitaxial" polishing process that is normally used for single-crystal substrates at Oak Ridge, using a silicon oxide (Syton) slurry and standard automatic polishing machines. This resulted in very smooth and slightly rounded substrate surfaces.

Thin flexible sintered zirconia substrates (Corning) also were prepared using proprietary powder sheet-forming methods. These substrates had thicknesses of 20–25 μm and bend strengths > 1 GPa. Bend radii of less than 1 cm are possible without failure, and repeated bending does not appear to degrade the flexible substrates' mechanical properties. The grain size in the fired substrates was 0.1–0.6 μm; the local surface roughness reflected this grain-size distribution. Some of the flexible substrates also were lightly polished at Corning in order to study the effect of surface roughness on superconducting transport properties.

III. RESULTS AND DISCUSSION

The resistance-versus-temperature characteristics for Y-123 thin films on flexible polycrystalline, rigid polycrystalline, and (100) single-crystal YSZ substrates are shown in Fig. 1. Note that, for the film deposited on the single-crystal (100) YSZ substrate, the critical temperature is above 90 K ($R = 0$) with the normal-state resistivity extrapolating to near zero at 0 K which is indicative of an excellent epitaxial Y-123 thin film. The zero-resistance superconducting transition temperatures for films deposited on polycrystalline YSZ substrates are seen to be only slightly lower than for the single-crystal substrate. Note, however, that the critical temperature for the film deposited on the rigid polycrystalline YSZ is noticably higher than that for the film on the flexible substrate. In addition, the normal-state resistivity of the film deposited on the rigid polycrystalline substrate is significant-

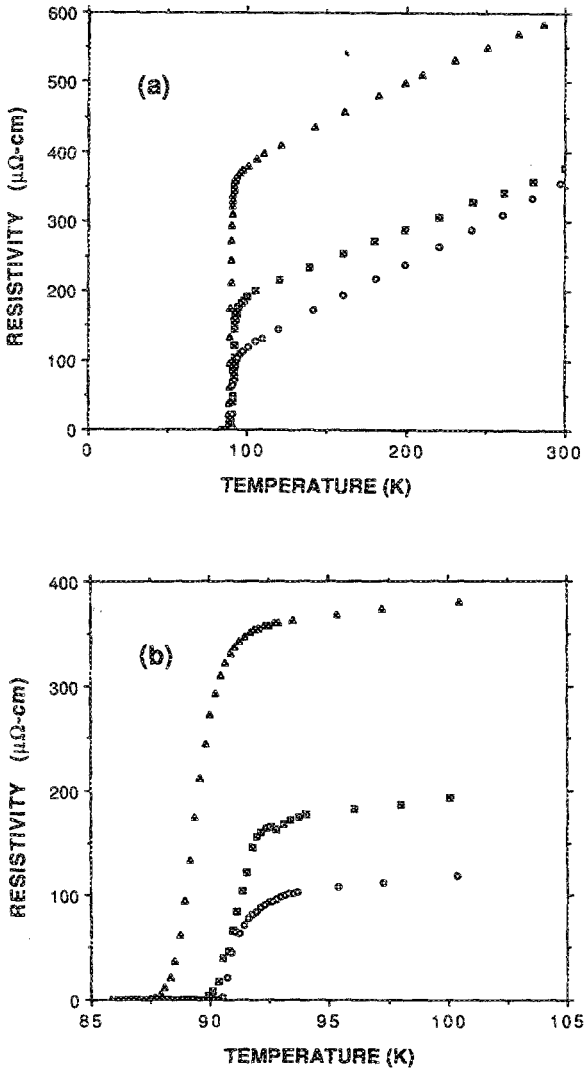


FIG. 1. Resistivity vs temperature for $YBa_2Cu_3O_{7-x}$ thin films grown on (○) (100) single crystal, (□) cold-pressed and sintered polycrystalline (GE), and (Δ) flexible polycrystalline (Corning) YSZ substrates for the temperature range (a) 0–300 K and (b) 85–105 K.

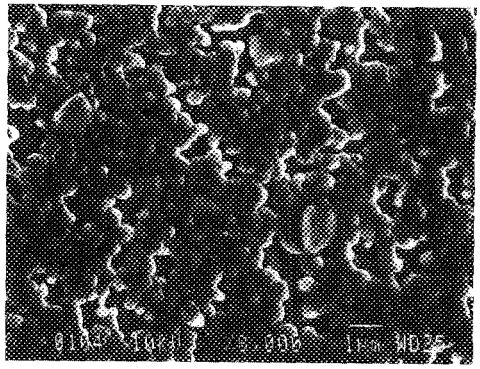
ly lower than for the film on flexible YSZ. This appears to be due primarily to the fact that the surface polish for the rigid polycrystalline substrate was of higher quality than that for the flexible substrate, thus demonstrating the importance of surface finish in obtaining high-quality films. Note that for the films deposited on both types of polycrystalline substrates, an extrapolation of the normal-state resistance curve to 0 K gives a nonzero resistance intercept. We have found this to be the case for *c*-axis-perpendicular Y-123 thin films that exhibit no in-plane epitaxial relationship.

The effect of surface polishing on film morphology and granularity is shown in Fig. 2. Figures 2(a) and 2(b) compare films deposited on unpolished and lightly polished flexible YSZ, respectively; the thin films deposited on polished substrates consistently exhibited superior electrical properties. Figure 2(c) shows a film deposited on the polished rigid polycrystalline YSZ substrate. The morphology observed for Y-123 thin films deposited on polished polycrystalline substrates is very similar to that for films grown on single-crystal (100) YSZ at this high temperature.

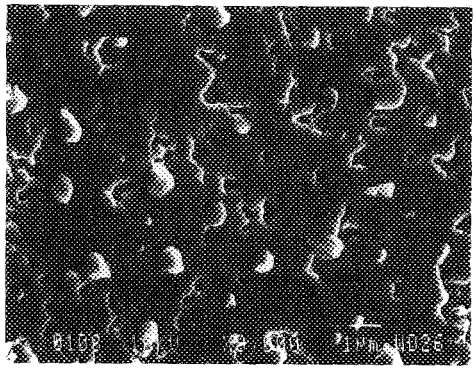
One obvious concern for Y-123 thin films grown on flexible substrates is whether the film/substrate structure remains superconducting and flexible after deposition. Figure 3 shows the resistance-versus-temperature plot for a ~450-nm-thick film deposited on a flexible YSZ substrate. After deposition, the sample was flexed over an arc of radius 2.25 cm with the film facing outward (i.e., placed in tension). The figure shows the observed resistance-versus-temperature behavior for the film before flexing, after flexing three times, and after flexing eighteen times. First note that after flexing three times the normal-state resistivity increases slightly. This suggests that, upon placing the film in tension through flexing, the strain is relieved through the formation of microcracks. Note also that for additional flexing (fifteen additional times) no further increase in the normal-state resistivity is observed, suggesting that the microcracks do not continue to form. As is also shown, virtually no degradation of the superconducting-transition temperature was observed upon flexing.

Because the flexible YSZ substrates were not highly polished, the Y-123 film quality was not very good. This is reflected in the slight depression of $T_c(R=0)$ as well as in the critical current densities, with J_c values at 56 K and 4.2 K (zero magnetic field) measured to be 800 and 10^4 A/cm^2, respectively. No attempt was made to observe the effect of flexing on J_c.

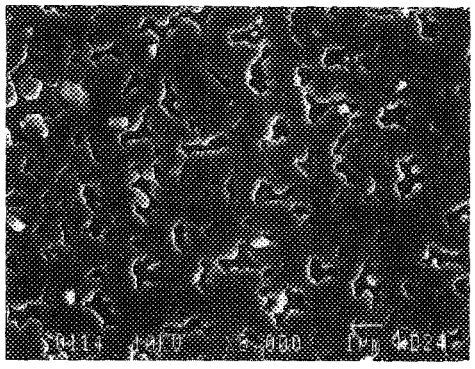
As mentioned earlier, improved crystallographic orientation of Y-123 material invariably leads to an increase in J_c with the most ordered materials (epitaxial single-crystal thin films) yielding critical currents above 10^6 A/cm^2 at 77 K. For randomly oriented polycrystalline substrates, of course, no large-scale film orientation originates from the crystal lattice of the substrate. However, large anisotropies in film-growth kinetics can result in partially oriented (textured) film growth. In Y-123, such an anisotropy exists, with crystal growth being much faster in the *a*-*b* plane than along the *c* axis. Based solely on the growth kinetics, *c*-axis-perpendicular growth should be favored on planar substrates. Randomly oriented polycrystalline substrates that



(a)



(b)



(c)

FIG. 2. SEM micrographs illustrating the effect of surface finish on the granularity of Y-123 films grown on (a) unpolished flexible, (b) polished flexible, and (c) polished rigid polycrystalline YSZ.

are planar and well polished, such as the rigid polycrystalline YSZ specimens, provide a good system to observe the extent to which kinetics are able to dictate film orientation for Y-123. Figure 4 shows four-circle diffractometer x-ray diffraction data for a Y-123 film grown on a randomly oriented polycrystalline-rigid YSZ substrate. A Θ–2Θ scan along a plane containing the surface normal produced only (00*l*) peaks, indicating that the film is highly oriented with its *c* axis perpendicular to the substrate surface. Some measure of the degree of orientation of the Y-123 thin film can be found

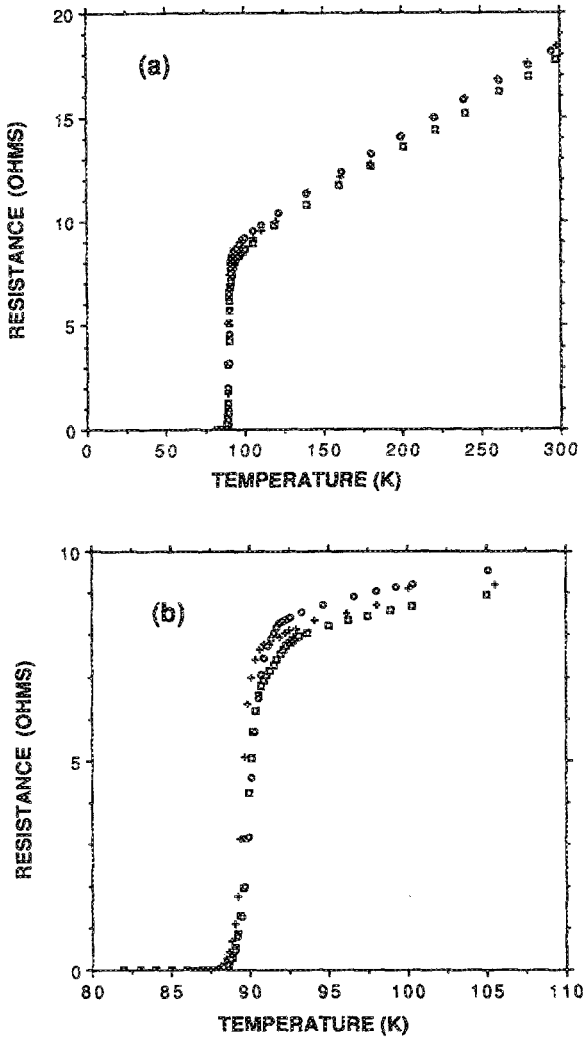


FIG. 3. Resistance vs temperature for $YBa_2Cu_3O_{7-x}$ thin film on flexible YSZ. Data are shown for the film/substrate structure before flexing (□), after flexing 3 times (+), and after flexing 18 times (○) for the temperature range of (a) 0–300 K and (b) 80–110 K.

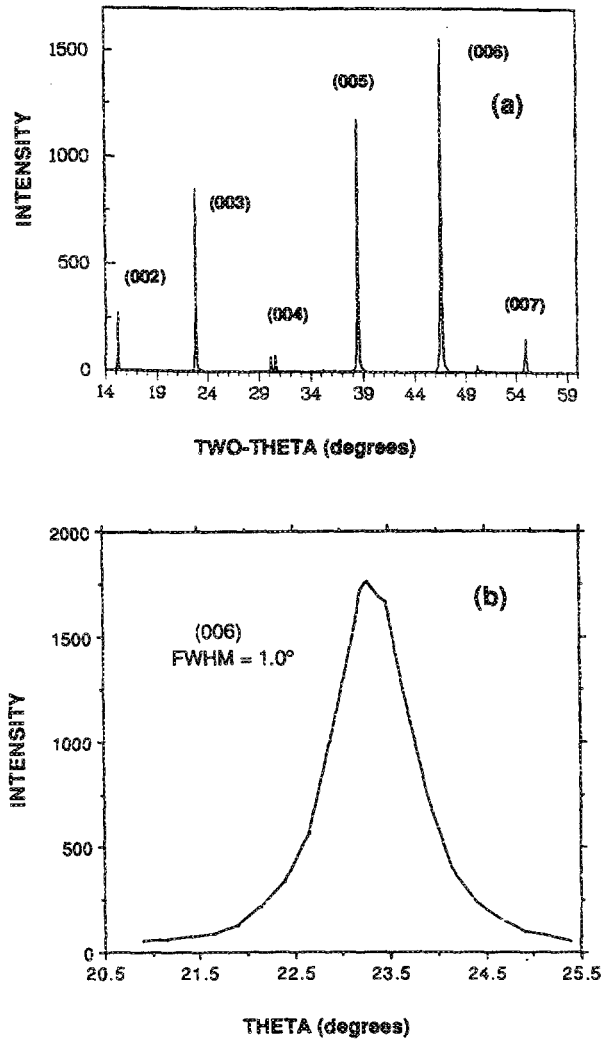


FIG. 4. Diffracted x ray intensity for an $YBa_2Cu_3O_{7-x}$ film on rigid polycrystalline YSZ. (a) x ray intensity vs 2θ, showing only (00l) peaks from the film. Also shown (b) is the rocking curve for the θ-scan through the (006) peak. The mosaic spread is approximately 1.0 degree.

by observing that the rocking curve for the (006) peak, shown in Fig. 4(b), has a width of only 1.0°. For comparison, the typical mosaic spead for an epitaxial Y-123 thin film on (100) $SrTiO_3$ is 0.2° and usually is dictated by the mosaic spread of the nominally single crystal substrate itself. It is interesting to note that, for Y-123 grown on randomly aligned single-crystal YSZ that was cut 10° away from the (001) direction, the x-ray diffraction peak width was 1.5°.[14] The high degree of orientation of the Y-123 film grown on our randomly oriented polycrystalline substrates illustrates how strongly growth kinetics must initially favor growth in the a-b plane, resulting in highly c-axis-perpendicular-oriented thin films. We also note that the (00l) peaks are evenly spaced, indicating that the film is not strained. From the locations of the peaks, the c-axis lattice parameter was determined to be 11.681 ± 0.002 Å, consistent with complete oxidation. As expected, no in-plane epitaxy was observed for these films.

For c-axis-aligned Y-123 thin films, one would expect some improvement in J_c over that observed for randomly oriented bulk Y-123. Figure 5 shows that this is true to some extent. The critical current density is shown as a function of temperature in zero magnetic field for a Y-123 thin film on rigid polycrystalline YSZ. For comparison with other work, $J_c(H = 0, 77\ \text{K}) = 1400\ \text{A/cm}^2$ for our films on rigid polycrystalline YSZ substrates; for Y-123 epitaxial thin films on single-crystal (100) YSZ, $J_c(H = 0, 77\ \text{K}) = 2\ \text{MA/cm}^2$. Figure 5 also shows the magnetic field dependence of J_c measured at 70 K for a polycrystalline Y-123 thin film deposited on a rigid polycrystalline YSZ substrate. The magnetic field direction was perpendicular to the current and to the film's c axis. This data compares favorably with results recently reported by Okada *et al.* for Y-123 superconducting tapes.[8] As with the tapes, however, the results for the polycrystalline films show that J_c decreases rapidly with increasing field strength. Some degree of hysteresis of J_c also was observed in the thin films, indicating flux trapping in the grains. This behavior was not observed for epitaxial Y-123 thin films deposited on $SrTiO_3$, for which only twin boundaries exist with no large-angle grain boundaries. It is unclear at this

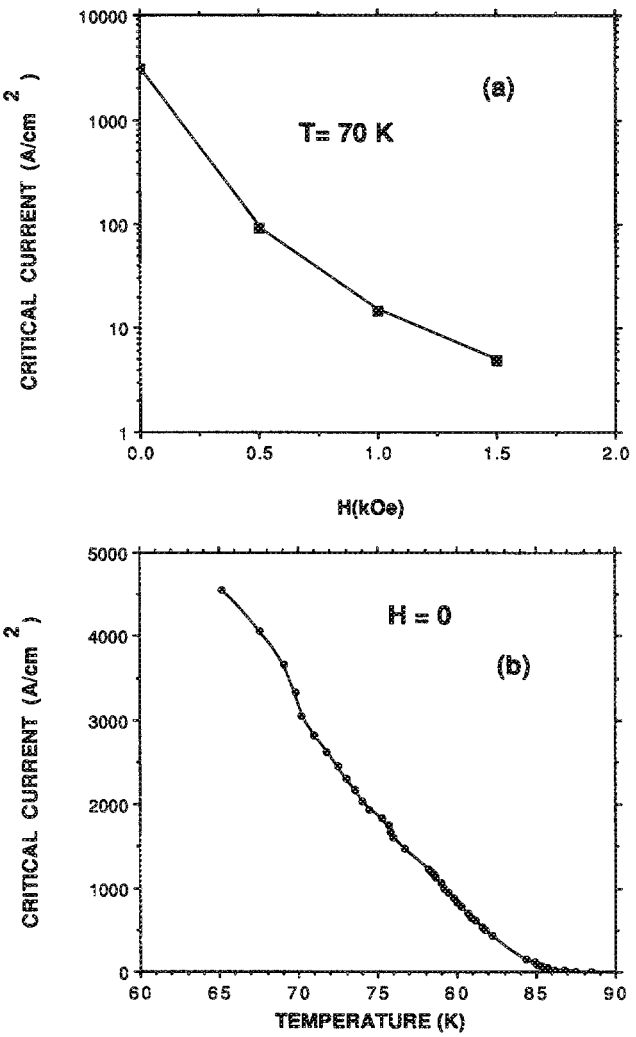


FIG. 5. Critical current density vs (a) magnetic field, measured at $T = 70$ K, for an $YBa_2Cu_3O_{7-x}$ film grown on rigid polycrystalline YSZ. The magnetic field was applied perpendicular to the current transport direction; both were perpendicular to the c axis of the $YBa_2Cu_3O_{7-x}$ film. Also shown (b) is J_c vs temperature in zero-applied magnetic field.

time why J_c for c-axis-oriented Y-123 thin films is still somewhat lower than might be anticipated from the results of recent experiments using bicrystals.[12] We know that large-angle grain boundaries exist in our films as no alignment is achieved with respect to the a and b axes. The experiments by Dimos *et al.* systematically addressed the effect of grain-boundary angle on critical current densities across the boundary, and lead one to expect J_c to decrease by a factor of ~ 100 with respect to epitaxial Y-123 thin films instead of the reduction by a factor of ~ 1000 that we observe. It would appear that some factor other than the grain-boundary angle is responsible for the reduced critical currents. We cannot rule out the possibility that $BaZrO_3$ formed at the Y-123/YSZ interface diffuses along grain boundaries to further limit conduction. Present work is aimed at exploring this possibility.

IV. SUMMARY

In summary, growth of Y-123 superconducting films on both rigid and flexible polycrystalline YSZ substrates appears potentially useful. The size and shape of the polycrystalline substrates needed for specific applications is not constrained, as it is with single-crystal substrates, and flexible substrates can be obtained and used. We have shown that Y-123 superconducting thin films grown on randomly oriented polycrystalline YSZ substrates have $T_c \sim 89$ K and J_c (77 K) ~ 1400 A/cm^2. One interesting observation is that well-oriented c-axis-perpendicular growth can be achieved when growth kinetics alone are responsible for determining the orientation of the Y-123 thin film without strong epitaxial influence from the substrate. However, it does appear that c-axis-perpendicular orientation alone is not sufficient to obtain high critical current densities. There is some uncertainty whether the presence of large angular misorientations of adjacent grains is solely responsible for the reduction of J_c that we find in films grown on polycrystalline YSZ. Chemical diffusion along large-angle grain boundaries may play a role and is being studied.

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