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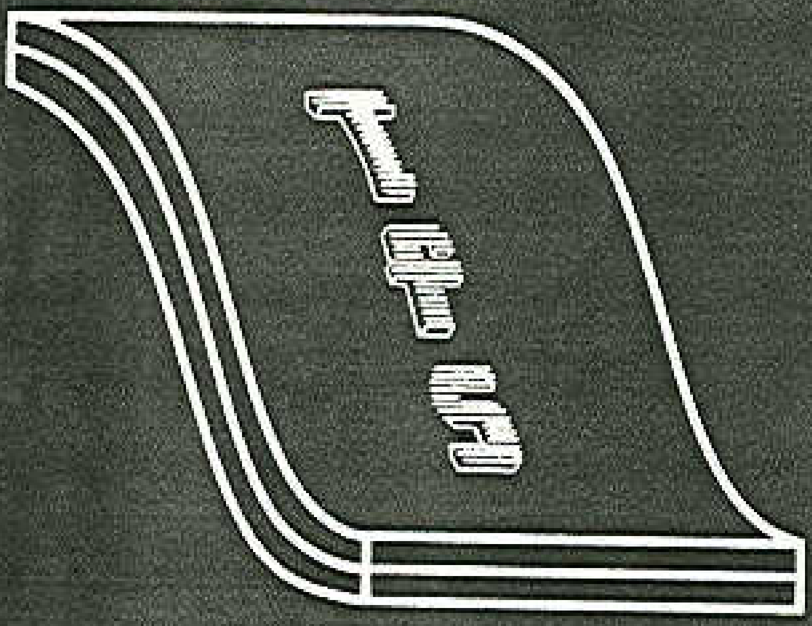

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$YBa_2Cu_3O_{7-x}$ THIN FILM GROWTH ON SINGLE CRYSTAL AND POLYCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA

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INTRODUCTION

A variety of single crystal substrate materials have proven useful in obtaining high-quality epitaxial $YBa_2Cu_3O_{7-x}$ (Y-123) thin films using several different growth techniques.[1-5] We have recently grown Y-123 thin films that routinely have $T_c > 90$ K and $J_c > 1MA/cm^2$ by pulsed-laser ablation of a stoichiometric, polycrystalline Y-123 target on single crystal substrates such as (100) $SrTiO_3$, $LaAlO_3$, $KTaO_3$ and yttria-stabilized zirconia (YSZ).[2] For many applications, however, single crystal substrates are not appropriate due in part to the substrate cost and/or the lack of substrates of appropriate dimensions and flexibility. 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, Tl-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] However, recent work has shown that the presence of large-angle grain boundaries in Y-123 causes a reduction in $J_c(H=0)$ by a factor of ~1/50.[12] It appears that a high degree of crystalline alignment is necessary to obtain critical current densities approaching those necessary for most high-temperature superconducting applications to be realized. This is partly a consequence of the anisotropy in these materials which requires that conduction in the superconducting state occurs primarily within the a-b planes.

In this paper, we report on the growth of Y-123 thin films on single crystal and randomly-oriented polycrystalline YSZ substrates. High quality epitaxial Y-123 thin films were grown on (100) YSZ in order to identify the factors that

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determine the optimum growth conditions for this substrate material. In addition, we have grown Y-123 thin films that are highly c-axis oriented with a zero resistance T_{co} between 85 K and 89 K on both rigid and flexible randomly-oriented polycrystalline YSZ. Critical current densities in excess of 10^4 A/cm^2 at 77 K in zero magnetic field were obtained for the films on rigid polycrystalline substrates. According to recent work, this value for J_c approaches what appears to be the upper limit for J_c when large-angle grain boundaries are present in the film.[12]

EXPERIMENTAL DESCRIPTION

The Y-123 thin films were grown in situ by pulsed-laser ablation as has been described elsewhere.[2,13] In brief, a KrF excimer laser beam [~350 mJ, 38ns full-width half-maximum (FWHM) pulse duration] was focused to a horizontal line on a ~25 mm diameter Y-123 rotating target. The focused energy density was determined to be 2.5–3.0 J/cm^2. The heated substrates were placed 6.5 cm from the Y-123 pellet. Film growth was carried out at substrate temperatures ranging from 620°C to 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. For critical current measurements, the films were patterned using standard photolithographic techniques to produce 100 μm × 3 mm bridges..

Two types of polycrystalline YSZ substrates, rigid and flexible, were used in this study; they have been described in detail elsewhere.[13] The rigid (General Electric) substrates were 98% dense and 1–3 mm in thickness. The thin flexible sintered zirconia substrates (Corning) had thicknesses of 20–25 μm. Bend radii of less than 1 cm are possible without failure, and repeated bending does not appear to degrade the flexible substrates' mechanical properties.

RESULTS AND DISCUSSION

$YBa_2Cu_3O_{7-x}$ on Single Crystal (100) Yttria-Stabilized Zirconia

A systematic study was made of the in situ growth of Y-123 on (100) YSZ. Desirable substrate characteristics include little or no chemical reactivity with the superconducting film and reasonable compatability with respect to thermal expansion, with lattice matching normally considered necessary for epitaxial growth. In recent work, it has been shown that the reactivity between Y-123 and YSZ is minimal at temperatures often used for in situ thin film growth (~700°C), with only a thin (~6 nm) $BaZrO_3$ intermediate layer formed between the Y-123 thin film and the substrate.[14] The thermal expansion coefficient of YSZ is only moderately lower than that for Y-123 [α(YSZ) ~ 8 ppm/°C, α_{a-b}(Y-123) ~ 13 ppm at 20°C]. However, 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 approximately 5.5% for (100) oriented YSZ, if the a- and b-axes are rotated by 45° about the c-axis with respect to the crystal axes of YSZ.

Figure 1 shows the resistivity vs temperature for Y-123 films grown on (100) YSZ at various substrate temperatures. All films were thicker than

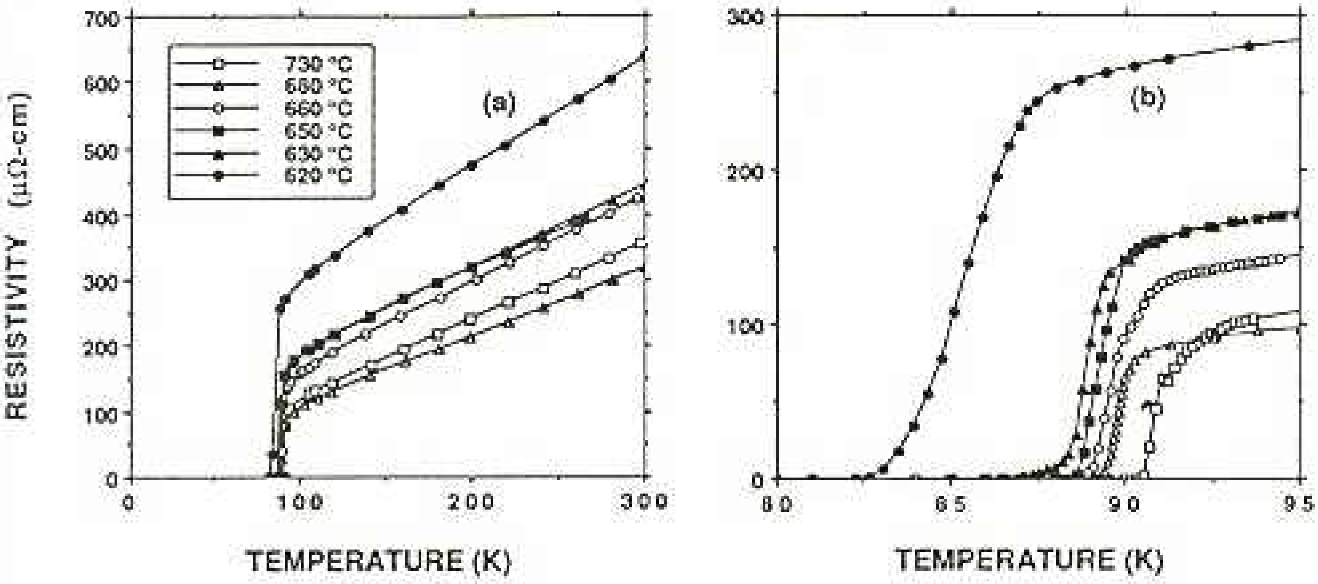


Figure 1. Resistivity vs temperature for Y-123 grown on (100) YSZ at various substrate temperatures. Minimum film thickness ~ 200 nm.

200 nm. From the behavior of the normal-state resistivity, it is clear that superior Y-123 thin films are obtained at substrate temperatures in the range of 680°C to 730°C, with film quality degrading for substrate temperatures lower than 680°C. Poor films were obtained for substrate temperatures at or below 620°C. Figure 1(b) shows that a thick Y-123 film grown at 730°C has a higher T_c than films grown at lower temperatures. However, resistivity measurements for films of thickness 60 nm show that the films grown at 680°C are vastly superior to those at 730°C. As shown in Fig. 2, the normal-state and superconducting behavior of the film of thickness 53 nm deposited at 730°C is quite poor, apparently because of the interaction between Y-123 and YSZ at this temperature. The formation of this interaction layer seriously degrades the properties of very thin (~50 nm) Y-123 thin films deposited on YSZ at 730°C. For a growth temperature of 680°C, however, a 62 nm thick film was obtained with $T_{c0} > 90$ K, although the normal-state resistivity is seen to be somewhat higher than for the 344 nm thick Y-123 film. Apparently, the interaction between Y-123 and YSZ is substantially reduced at 680°C. We conclude that a deposition temperature of 680°C (at 200 mTorr oxygen) is near the optimum growth temperature for Y-123 on (100) YSZ when considering both substrate interaction ($BaZrO_3$ formation) and low resistivity, high T_c, c-axis perpendicular growth.

Further evidence for significant substrate/thin film interaction can be seen in the SEM micrographs shown in Fig. 3. For the 53 nm thick Y-123 film, one can see regions where a smooth Y-123 layer gives way to an underlying phase which resembles the a-axis perpendicular material seen in post-annealed Y-123 thin films. This is in agreement with Tietz et al. whose transmission electron microscopy studies revealed that an intermediate layer consisting of $BaZrO_3$ was followed by a Y-123 layer of mixed orientation before giving way to c-axis perpendicular material. This intermediate layer apparently encompasses enough of the 53 nm Y-123 thin film to prevent a continuous superconducting path through the film. For the 152 nm thick film there is no visible evidence of this intermediate layer at the film surface. However, the high resistivity of this film suggests that a significant fraction of its thickness involves this intermediate layer. For films greater than 220 nm, the normal-state resistivity

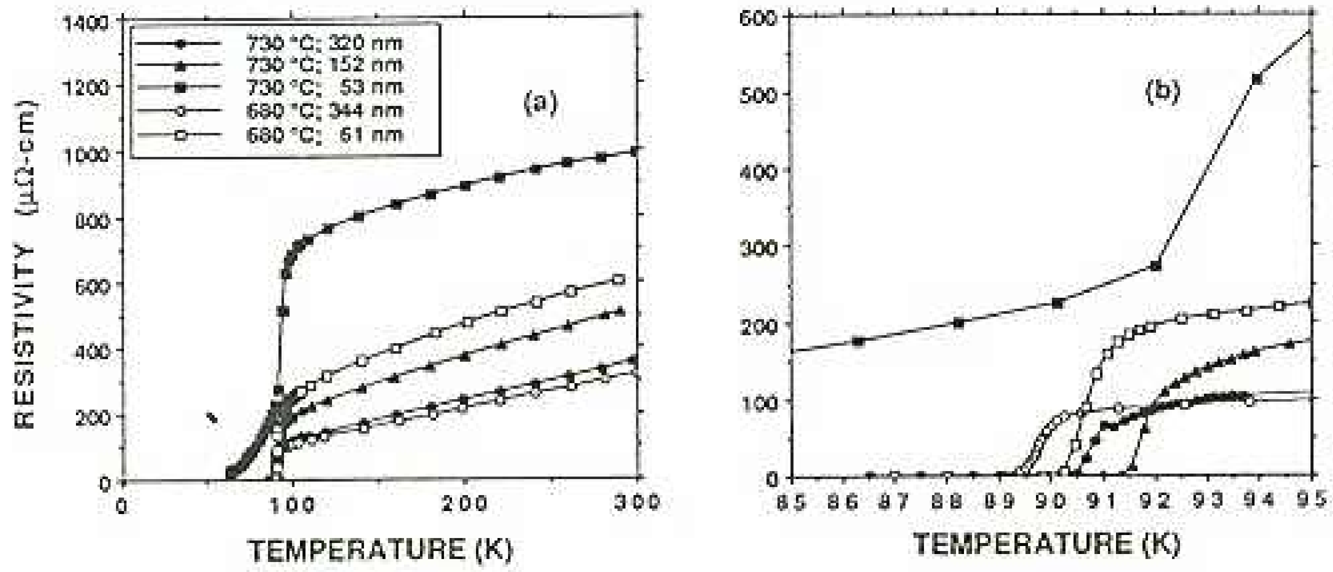


Figure 2. Resistivity vs temperature for Y-123 films of varying thickness grown on (100) YSZ at 680°C and 730°C.

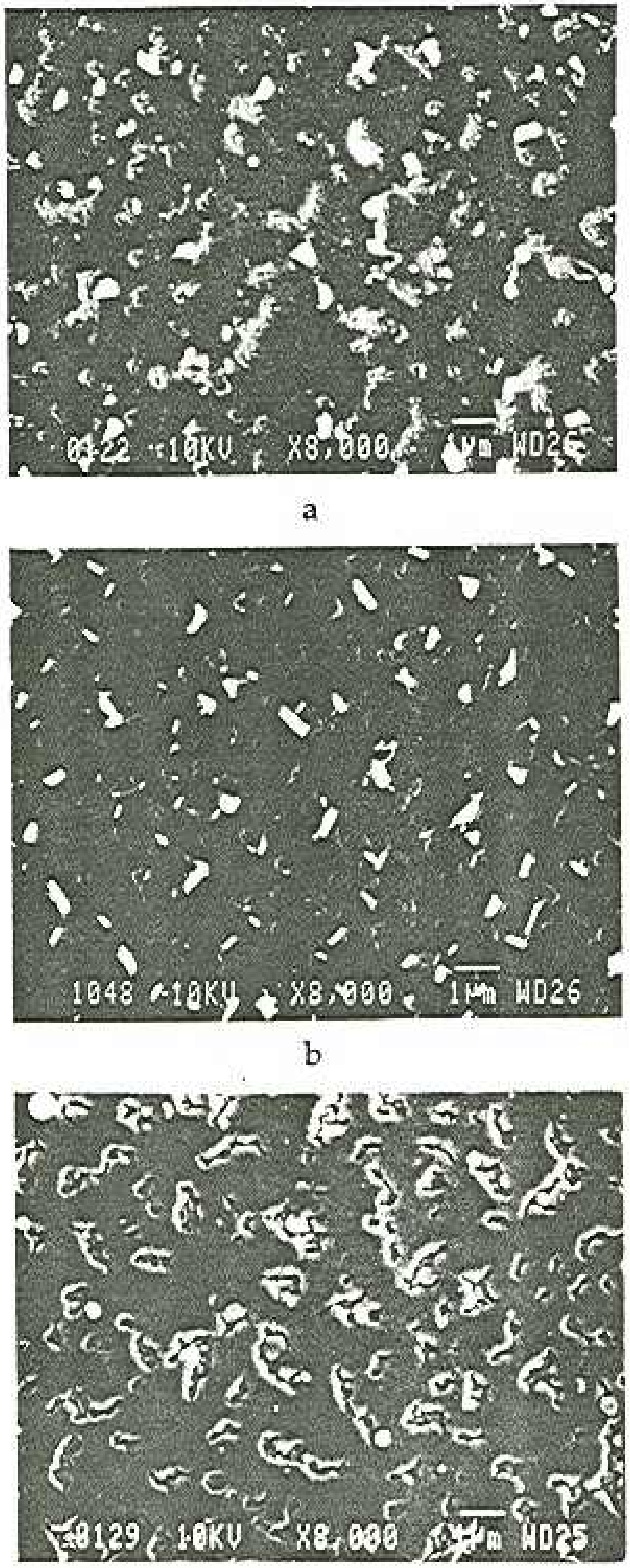
is quite low, suggesting that this intermediate layer terminates at some fixed thickness. It is interesting to note that, as seen in Fig. 3(c), the surface appears quite rough, with holes partially through films as thick as 220 nm. A similar behavior was observed for Y-123 thin films grown on $SrTiO_3$ and $KTaO_3$ at 730°C.[2] Nevertheless, films with this morphology exhibit excellent superconducting and normal-state properties.

Four-circle x-ray diffraction was utilized to investigate the orientation of Y-123 thin films on (100) YSZ. They were found to be c-axis perpendicular with a mosaic spread ~0.9°. As has been reported,[14] the best lattice match of Y-123 to (100) YSZ (actually ~5.5% mismatch) would occur if the in-plane Y-123 <110> coincided with the in-plane YSZ <100>, equivalent to a 45° rotation of the Y-123 a- and b- axes about the c-axis with respect to the crystal axes of YSZ. However, we find two distinct types of in-plane orientation for Y-123 on (100) YSZ, with the in-plane YSZ <100> coinciding with either the Y-123 <100> or <110>. It is unclear at this time what factors determine in-plane orientation.

We have carried out critical current density measurements for Y-123 films on (100) YSZ with J_c(77 K, H=O) ~1.8 MA/cm^2 and J_c (4.2 K, H=O) ~15 MA/cm^2, results that are indicative of high quality epitaxial thin films.[2] The magnetic field dependence of J_c is very similar to what has been reported for Y-123 on (100) $SrTiO_3$, with J_c less sensitive to magnetic field if H is parallel to the a-b plane as opposed to H parallel to the c-axis.[15]

Y-123 on Polycrystalline YSZ

Single crystal substrates are expensive, are not available in the sizes and shapes needed for many applications, and generally lack the flexibility required of high current conductors. However, they have the advantage that a high degree of orientation of Y-123 invariably leads to an increase in J_c, with the most ordered material (epitaxial thin films) yielding J_c ~ 10^6 A/cm^2 at 77 K. For randomly-oriented polycrystalline substrates, there is little film-orientinginfluence from the crystal lattice of the substrate. However, a large



a

b

c

Figure 3. SEM micrographs of Y-123 grown on (100) YSZ at 730°C, to thicknesses of 53nm (a), 152 nm (b), and 220 nm (c).

anisotropy in growth kinetics can result in partially oriented films. For Y-123, such an anisotropy exists as crystal growth is much faster in the a-b plane than along the c-axis. Based solely on growth kinetics, c-axis perpendicular growth should be favored on planar substrates. Randomly-oriented polycrystalline substrates which are planar and well polished, such as the rigid polycrystalline YSZ specimens, provide a good system to observe to what extent kinetics are able to dictate film orientation. Four-circle diffractometer x-ray data for Y-123 films grown on randomly-oriented polycrystalline rigid YSZ substrates indicate that the films are highly oriented with the c-axis perpendicular to the substrate surface.[13] The rocking curve for the (006) peak had a width of only 1.0 degrees, comparable to that found for Y-123 on (100) YSZ. This high degree of orientation of Y-123 on a randomly-oriented polycrystalline substrate illustrates how strongly growth kinetics initially favor growth in the a-b plane, resulting in c-axis perpendicular thin films. We 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. However, as expected, no in-plane epitaxial alignment was observed, indicating that large-angle grain boundaries exist in these films.

Figure 4 illustrates the effect of deposition temperature on both the normal-state resistivity and the superconducting transition temperature for Y-123 films thicker than 250 nm on rigid, polycrystalline YSZ substrates. The best Y-123 films were obtained at 730°C with the normal-state resistivity rising and T_{c0} falling with decreasing deposition temperature. As will be discussed later, these measures of Y-123 film quality do not correlate with the critical current densities, since the highest J_c values were obtained for the films grown at 680°C. It appears that both the normal-state resistivity and T_{c0} are controlled predominately by the intragrain quality, which is better at higher deposition temperatures, while J_c is determined primarily by the properties of the grain boundaries.

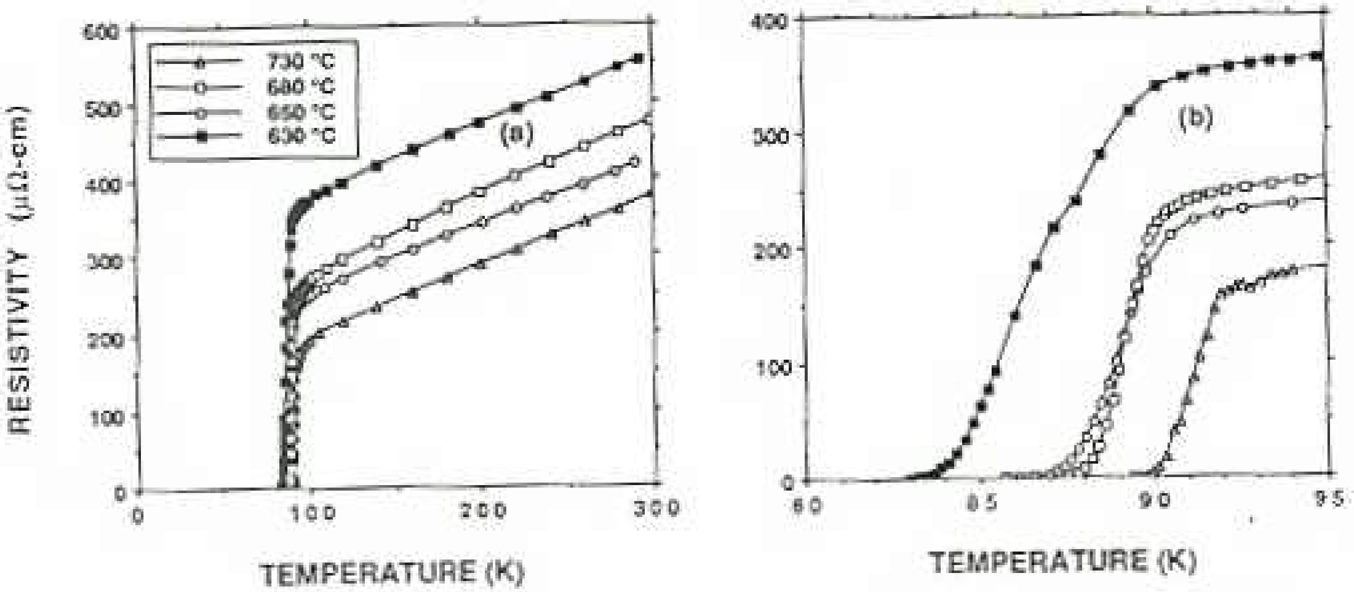


Figure 4. Resistivity vs temperature for Y-123 grown on rigid polycrystalline YSZ at various substrate temperatures.

Figure 5(a) shows J_c (T) for Y-123 thin films grown on rigid, polycrystalline YSZ substrates at 680°C and 730°C. At 77 K, $J_c(H=0)$ is only 1400 A/cm^2 for the film deposited at 730°C while the film deposited at 680°C has $J_c(77\ K, H=0) = 11{,}000$ A/cm^2. This high value of $J_c(77K)$ approaches the intrinsic value determined by Dimos et al. for large-angle grain boundaries in Y-123 thin films.[12] This dramatic dependence of J_c on deposition temperature may be related to the interaction between Y-123 and YSZ that forms $BaZrO_3$. The temperature range over which J_c changes rapidly is the same as that for which the intermediate $BaZrO_3$ layer degrades the superconducting properties of very thin (~50 nm) Y-123 films grown on single crystal (100) YSZ, as was discussed earlier. For the case of c-axis perpendicular polycrystalline Y-123 thin films (no alignment of the a- and b- axes), the $BaZrO_3$ would not be restricted to the YSZ/Y-123 interface but could diffuse rapidly along the grain boundaries, degrading inter-granular conduction. At lower growth temperatures, the degree of substrate/film interaction is reduced, along with the rate of diffusion along the Y-123 grain boundaries, resulting in improved coupling of the supercurrent between individual grains. This leads to higher J_c in spite of the fact that the lower temperature probably results in lower intragranular J_c.

Figure 5(b) shows the magnetic field dependence of J_c at 77 K for a Y-123 thin film grown on rigid, polycrystalline YSZ at 680°C. $J_c(H)$ is anisotropic, being highest for H perpendicular to the film c-axis (parallel to the a-b planes). For the c-axis oriented Y-123 film, the grain boundaries should be predominately oriented parallel to the c-axis. With H parallel to the c-axis, it is also parallel to most of these grain boundaries. This leads to enhanced decoupling of the grains with subsequent reduction in J_c. For H perpendicular to the c-axis, the magnetic field is not as effective in decoupling the grains as it is not parallel to all of the grain boundaries. For H perpendicular to the c-axis and perpendicular to the current flow, J_c drops to 1800 A/cm^2 at 1 kOe and to 460 A/cm^2 at 10 kOe. This data compares favorably with results recently reported by Okada et al. for Y-123 superconducting tapes.[8] As with the tapes, however, J_c decreases rapidly with increasing magnetic field strength. Some degree of hysteresis of J_c also was observed in the thin films, indicating flux trapping . The field dependence of J_c shows that weak link behavior is present.

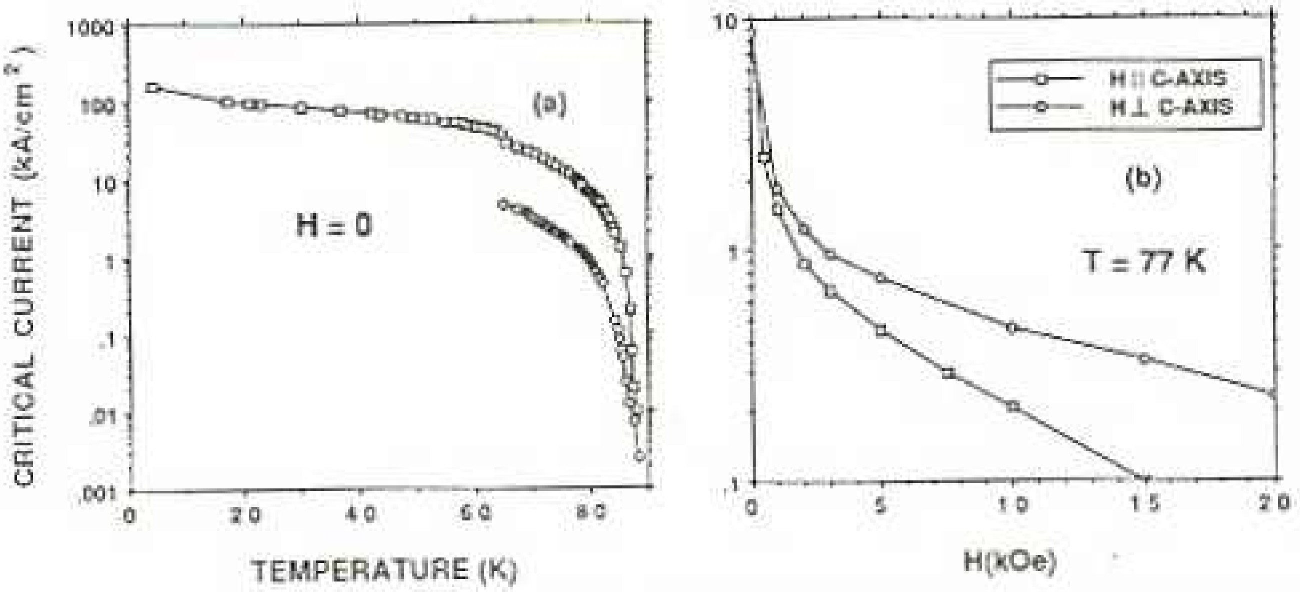


Figure 5. Critical current measurements for Y-123 on rigid, polycrystalline YSZ showing (a) $J_c(T, H=0)$ for films grown at 680°C (❑) and 730°C (o); Also shown (b) is J_c (77 K) vs magnetic field for a film grown at 680°C.

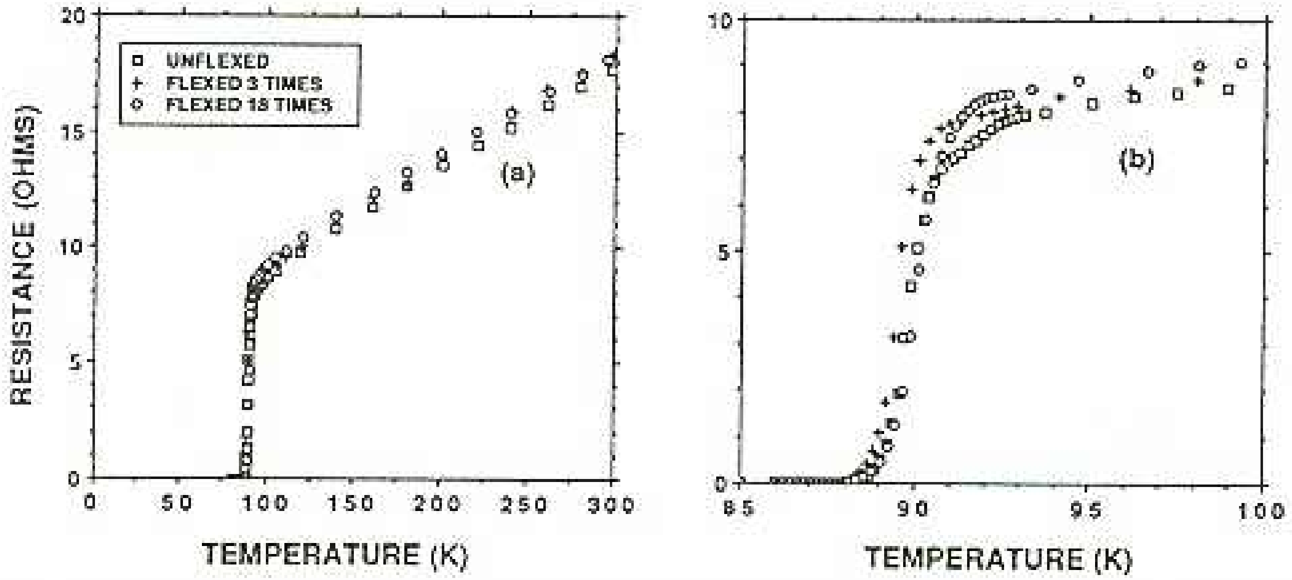


Figure 6. Resistance vs temperature for Y-123 thin films on flexible, polycrystaline YSZ. Data are shown for the film/substrate structure before flexing (o), after flexing 3 times (+), and after flexing 18 times (o).

Some Y-123 film growth experiments also were done on flexible YSZ substrates. An obvious concern is whether the film/substrate structure remains superconducting and flexible after film growth. Figure 6 shows resistance vs temperature for a ~450 nm-thick film grown on flexible YSZ at 730°C. After growth the sample was flexed over an arc of radius 2.25 cm with the film facing outward (i.e., placed in tension). After flexing three times, the normal state resistivity increased slightly. This suggests that, upon placing the film in tension through flexing, the strain is relieved through the formation of microcracks. Additional flexing (up to fifteen times), caused no further increase in the normal state resistivity, suggesting that the microcracks do not continue to form. Virtually no degradation of T_{co} was caused by flexing. Because the flexible YSZ substrates were not well polished, the Y-123 film quality was not good. This is reflected in the depression of $T_c(R=0)$ and by the $J_c(H=O)$ values at 56 K and 4.2 K of 800 and 10^4 A/cm^2, respectively. No attempt was made to observe the effect of flexing on J_c.

SUMMARY

We have shown that Y-123 superconducting thin films can be grown on randomly-oriented polycrystalline YSZ substrates with $85\ K < T_{co} < 89\ K$ and $J_c > 10^4$ A/cm^2 at 77 K. This J_c value approaches the $\sim 4\text{-}8 \times 10^4$ A/cm^2 limit expected for films containing random, large-angle grain boundaries on the basis of recent experiments using bicrystalline thin films.[12] It appears that for Y-123 films on single crystal YSZ, the upper limit for the growth temperature is determined by the Y-123/YSZ interaction. For polycrystalline films, grain boundary diffusion of film/substrate interaction products must be considered, emphasizing the importance of lower temperature Y-123 growth. Our experiments show that partially oriented, c-axis-perpendicular films can be grown even under conditions such that growth kinetics alone are responsible for determining the Y-123 thin film orientation, without strong epitaxial influence from the substrate. However, significant improvement of critical current densities for c-axis perpendicular Y-123 polycrystalline thin films will require a significant degree of grain alignment in the a-b plane.

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