Growth and properties of $YBa_2Cu_3O_7$ thin films on vicinal and polycrystalline MgO substrates

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We discuss the results of a study on the growth by laser ablation of $YBa_2Cu_3O_7$ thin films on polycrystalline and annealed vicinal (001) MgO substrates. In both instances the films were found to grow predominantly with the *c* axis normal to the plane of the substrate, regardless of the orientation of the MgO surface. In the case of the vicinal substrates the films were found to have superconducting properties comparable to those obtained with films grown on (001) oriented, annealed single-crystal substrates.

A recent study of the initial stages of growth of $YBa_2Cu_3O_7$ thin films on single-crystal MgO substrates, which are not well lattice matched to the cuprate superconductor, has indicated that this stage consists of island nucleation.[1–3] Moreover, the study indicated that at growth temperatures ~630 °C and above, the system exhibits a strong tendency to nucleate grains with the preferred orientation, i.e., with the *c* axis of the cuprate normal to the substrate. The surface topography of the substrate was also found to be important during the nucleation stage: steps produced on the substrate surface by predeposition annealing were found to act as preferred sites for nucleation. It has been proposed that the alignment of the nuclei with the steps increases the perfection of the alignment observed between the individual grains during the early stages of film growth.[3] Recent examinations of the effect of MgO surface preparation on the structural and superconducting properties of laser-ablated $YBa_2Cu_3O_7$ films have confirmed that substrate annealing is important in forming high quality films with good morphology at relatively low deposition temperatures.[4] This letter extends previous studies of $YBa_2Cu_3O_7$ thin-film growth on (001) oriented single-crystal MgO surfaces to the growth of cuprate films on vicinal and randomly oriented polycrystalline MgO surfaces.

All of the results discussed here were obtained from films deposited by laser ablation under idential conditions that have proven effective in our laboratory for the formation of high quality films with good morphology on (001) oriented MgO.[4] Briefly, these conditions include an excimer laser operating at 248 nm with a fluence of ~1 J/cm^2 and a repetition rate of 50 Hz. The deposition was carried out in a pure oxygen ambient of 400 mTorr with a substrate temperature of 670 °C.

The vicinal substrates were prepared as follows: single-crystal substrates, cleaved from a MgO boule, were polished about the (100) axis to the desired angle, which in these experiments ranged from 3° to 10° from the (001) normal. After polishing, the substrates were usually heated in air or oxygen to 1100–1200 °C for 12–24 h. When a surface of a crystalline material is prepared such that it is slightly misoriented with respect to a low-index plane and then annealed, surface steps will generally form so as to lower the total surface energy.[5] The annealing process has been shown to be important in yielding the best quality $YBa_2Cu_3O_7$ films.[4,6] The polycrystalline MgO substrates were cut and polished from bulk material obtained from Avco Speciality Materials, Inc. The material was formed by hot-pressing high-purity MgO grains having an average size of ~50 μm. X-ray analysis confirmed the random orientation of the material. The polycrystalline substrates were also thermally annealed after polishing.

Scanning electron micrographs of films grown under the above conditions on polycrystalline and on vicinal MgO substrates are shown in Fig. 1. Figure 1(a) illustrates the variation in morphology of $YBa_2Cu_3O_7$ grown on different MgO grains. The individual MgO grains can be clearly seen in the texture of the overlying film. The morphology seen in Fig. 1(b) is typical of that found in films grown on vicinal MgO. The film is relatively smooth and appears to be completely devoid of the characteristic narrow rectangular *a*-axis normal grains that are often found in films grown on unannealed, (001) oriented MgO.

Standard 2Θ x-ray analysis of the films grown on the vicinal substrates reveals that the *c* axis of the $YBa_2Cu_3O_7$ material is fully oriented normal to the plane of the substrate, not parallel to the (001) direction. Pole figure measurements show that these *c*-axis normal grains are in close registry with the principal axes of the MgO, with no high-angle tilt boundaries being evident to within the resolution of the measurement (~2%). For the polycrystalline substrates the 2Θ x-ray scans again indicate that the film is completely oriented with the *c* axis of the $YBa_2Cu_3O_7$ grains normal to the substrate despite the random orientation of the substrate surface.

Figure 2 is a typical bright-field image of the microstructure of the $YBa_2Cu_3O_7$ film grown on a single grain of polycrystalline MgO showing twins and grain boundaries in the film. On each individual grain a highly *c*-axis oriented film was obtained; no evidence of any *a*-axis oriented material could be discerned. The grains are typically 250–300 nm in diameter and have a shape very similar to that observed for $YBa_2Cu_3O_7$ thin films grown on single-crystal (001) oriented MgO. To determine the crystallographic relationship between the grains, selected area diffraction (SAD) patterns were examined. A number of the grains

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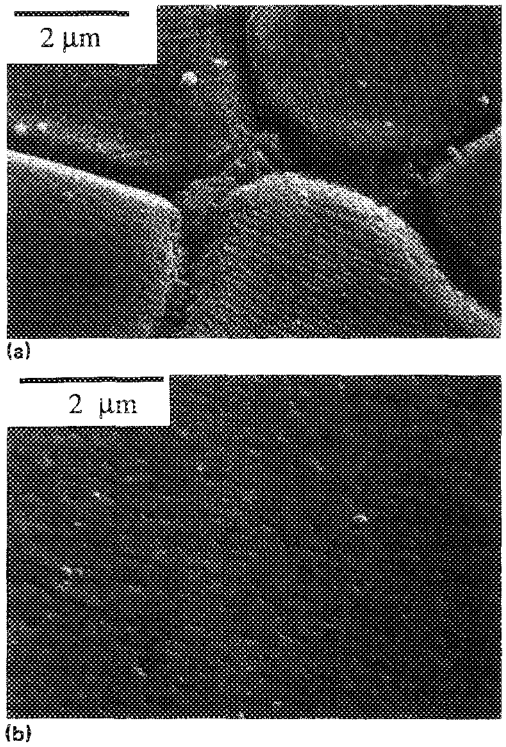

FIG. 1. (a) Scanning electron micrograph (SEM) of a $YBa_2Cu_3O_7$ film grown by laser ablation on a polycrystalline MgO substrate. The MgO grains are clearly evident in the microstructure of the film; (b) SEM micrograph of a $YBa_2Cu_3O_7$ film grown on vicinal (5°) MgO

were rotationally misoriented by only very small amounts; however, misorientations corresponding to rotations of 29° and 6.5° about the [001] zone axis were frequently observed. Both of these grain boundaries have been observed in $YBa_2Cu_3O_7$ thin films deposited by laser ablation onto (001) oriented single-crystal MgO.[3,7] Where growth of the film occurred on adjacent MgO grains, there appeared in many cases to be only slight rotational misalignment across the boundary; however, in some instances rotations of ~45° were measured. This particular rotation corresponds to orientations very similar to $\Sigma = 29$ special high-angle grain boundaries in cubic materials.[3,8]

The morphology of $YBa_2Cu_3O_7$ thin films on vicinal

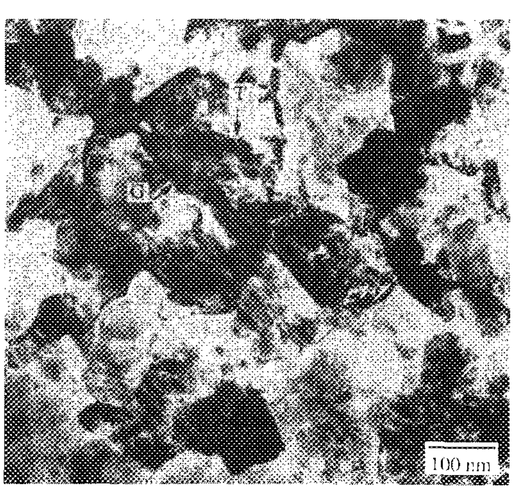

FIG. 2. Bright-field image of a $YBa_2Cu_3O_7$ thin film on polycrystalline MgO. Examples of twin boundaries (T) and grain boundaries (G) within the films are shown.

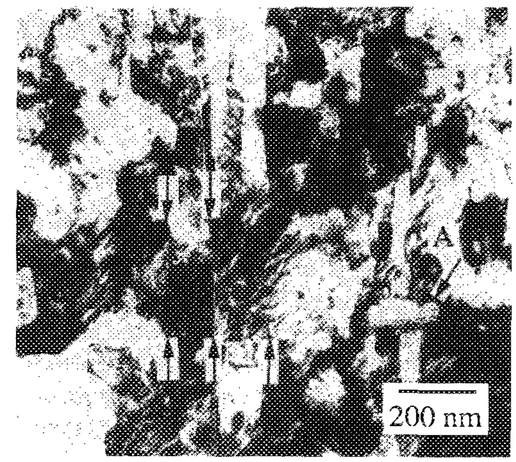

FIG. 3. Bright-field image of $YBa_2Cu_3O_7$ thin film grown on vicinal (5°) MgO. The arrows indicate the predominant direction of the grain boundaries. Grain A is oriented with its a (or b) axis perpendicular to the substrate plane.

MgO shows some differences from that seen for films grown on either polycrystalline or single-crystal MgO substrates. Figure 3 shows a typical bright-field image of a $YBa_2Cu_3O_7$ thin film on vicinal MgO where the misorientation angle of the substrate was 5°. The microstructure consists mainly of c-axis oriented grains which have a much larger aspect ratio than those more frequently observed. The predominant direction of the grain boundaries is indicated in Fig. 3. These grains appeared highly oriented with respect to rotations about the [001] zone axis. Some more typical "equiaxed" grains were also observed in the film, as was a small fraction of a-axis oriented grains. The morphology observed for film growth on vicinal MgO is believed to be the result of nucleation and growth at step edges on the substrate surface. The highly anisotropic growth of $YBa_2Cu_3O_7$ films, fastest along the a-b direction, results in rapid grain growth parallel to the step edges, leading to the formation of the elongated c-axis oriented grains. The microstructure development of $YBa_2Cu_3O_7$ thin films on vicinal MgO surfaces is at present being examined in more detail and will be published elsewhere.[9]

The transport properties of the films grown on vicinal and polycrystalline MgO were measured by forming microbridge patterns in the film using standard photolithography and inert-ion etching processes. In the case of the films grown on the polycrystalline substrates, some microbridges spanned MgO grain boundaries so that the effect of such a substrate grain boundary on the superconducting properties of the $YBa_2Cu_3O_7$ film could be examined. For the films grown on vicinal substrates, the transport measurements were made perpendicular to the long direction of the grains as that was expected to be the direction in which the surface steps would most likely influence supercurrent flow. However, from transmission electron microscopy analysis it appeared that only slight misorientations between grains occurred in this direction. Consequently, transport measurements in the orthogonal direction are under way.

The zero-resistance transition temperature for the films grown on the polycrystalline MgO substrates was typically

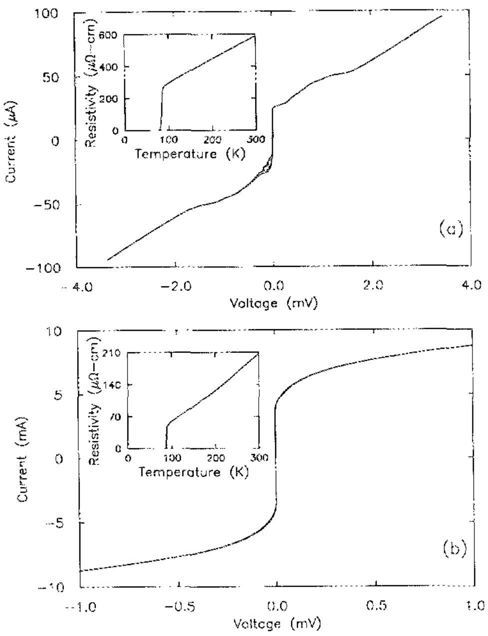

FIG. 4. (a) *I-V* characteristic of an ~1-μm-wide, ~3-μm-long $YBa_2Cu_3O_7$ thin-film microbridge that spans a substrate grain boundary in a polycrystalline MgO substrate. The data were taken at 4.2 K. The inset shows the temperature dependence of the normal-state resistivity of the $YBa_2Cu_3O_7$ film. (b) *I-V* characteristic at 77 K of a thin-film microbridge formed in a $YBa_2Cu_3O_7$ thin film grown on vicinal (5°) MgO. The microbridge current flows perpendicular to the surface steps. J_c for the microbridge is $\sim 2\times 10^6$ A/cm^2 at 77 K. The inset shows the temperature-dependent resistivity of the film.

78 K, which is 10 to 12 K below that generally obtained with $YBa_2Cu_3O_7$ films grown on annealed (001) MgO substrates. The critical current density J_c of the films was quite low for microbridges which spanned a grain boundary in the MgO substrate, typically ranging from 10^4 to 10^5 A/cm^2 at 4.2 K. J_c values approximately ten times higher have been observed, but it is believed these values were obtained from microbridges which are localized on a single MgO grain. The current-voltage (*I-V*) characteristics of the microbridges, as illustrated in Fig. 4(a), are generally nonlinear and do not closely approximate the resistively shunted junction-like *I-V*'s that are typically found in microbridges with similar J_c's but which are formed in large-grained films containing high-angle tilt boundaries grown on (001) substrates.[4] This difference can be attributed to either the presence of a series array of weak links in the microbridge, or, if the effective penetration depth is small enough to support multiple vortex states, to flux creep arising from very weak pinning in the microbridge region. Whatever the explanation for the *I-V* characteristic, the practical effect of the substrate grain boundary is to severely attenuate the superconducting properties of the $YBa_2Cu_3O_7$ film. This attenuation is almost certainly due in part to the creation of high-angle tilt boundaries in the film, but it may also be due to atomic disorder internal to the grains of the $YBa_2Cu_3O_7$ film which results from misoriented film growth near grain boundaries in the substrate.

The superconducting properties of the films grown on the 3°–5° vicinal substrates are considerably better than those obtained with the polycrystalline MgO. Normal-state resistivities are essentially the same (~200 μΩ cm) as those measured for high quality films on (001) substrates, and zero-resistance T_c's typically range from 86 to 90 K. Microbridge J_c measurements at 77 K yield values ranging from 0.4 to 2.3×10^6 A/cm^2, which are slightly lower than the best values obtained to date on annealed (001) oriented MgO substrates.[4] As illustrated by Fig. 4(b), the *I-V* characteristics are typical of the abrupt onset of flux creep across the microbridge above a well-defined critical depinning current. Measurements of transport properties in magnetic fields are in progress and will be reported elsewhere.

These studies have demonstrated that *c*-axis oriented films can grow on a randomly oriented substrate surface. This observation indicates that it is the highly anisotropic growth of $YBa_2Cu_3O_7$ that is influential in determining film orientation. During the early stages of growth the initial nuclei are oriented with their *c* axis perpendicular to the substrate surface; rapid growth then occurs laterally in the *a-b* plane. This mechanism may explain the recent results of Kennedy *et al.*,[10] who have shown that promising results may be obtained using amorphous or very fine grained MgO substrates. The importance of the anisotropic growth of $YBa_2Cu_3O_7$ is further demonstrated by the growth on vicinal surfaces. In this case, the film nucleates preferentially at ledges on the substrate surface, an example of graphoepitaxy. The nuclei then grow rapidly in a direction parallel to the step edges, thereby producing the observed morphology.

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