Growth of $YBa_2Cu_3O_7$ thin films on MgO: The effect of substrate preparation

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We discuss the results of a study of the effect of substrate preparation on the microstructure and superconductive properties of $YBa_2Cu_3O_7$ thin films formed by laser ablation on (001) MgO substrates. Thermal annealing of the substrates is found to be highly effective in producing at fairly low growth temperatures (670 °C), epitaxial, *c*-axis normal films with good superconductive properties. Alternative surface treatments result in the formation of large angle tilt boundaries and inferior superconductive properties.

Since the initial demonstrations of epitaxial[1] and *in situ*[2] growth of $YBa_2Cu_3O_7$ thin films there has been notable progress in the ability to produce high quality cuprate superconductor thin films,[3] particularly epitaxial films grown on lattice-matched substrates. It would be highly desirable if this success could be readily extended to other non-lattice-matched substrates and if the film morphology could be significantly improved to better facilitate conventional lithographic processing.

MgO is an excellent substrate material with which to investigate some of the key issues of $YBa_2Cu_3O_7$ thin film nucleation and growth. It is well established that at normal growth temperatures there are no obscuring chemical reactions between the film and the MgO substrate.[4] Promising results in obtaining high quality *c*-axis normal films have been reported with MgO for some time,[5] despite the more than 9% lattice mismatch. Recently, studies[6] using transmission electron microscopy to examine the nucleation phase of $YBa_2Cu_3O_7$ growth on MgO substrates have shown that the initial stage of deposition proceeds via an island growth mechanism and that it is highly favorable for these islands to nucleate at the edge of steps formed on the (001) surface of the MgO substrate. Here we report the results of an investigation of the effect of MgO surface preparation on the superconducting properties of YBCO thin films grown by laser ablation. We show that under the currently optimum conditions, essentially single-crystal films can be obtained at comparatively low deposition temperatures (670 °C) on MgO and that the films are rather smooth and have dc superconductive transport properties that can be in the same range ($J_c \sim 4$–6×10^6 A/cm^2 at 77 K) as those obtained using $SrTiO_3$ and $LaAlO_3$ substrates.

The films in this study were all deposited by laser ablation from a slightly Cu-rich YBCO target onto the (100) surface of MgO single-crystal substrates, all cut and polished from the same boule. The laser deposition was carried out using identical conditions which our experience has shown to be effective for the low-temperature ($\leqslant 700$ °C) growth of good YBCO films. These conditions include an excimer laser operating at 248 nm with a pulse energy of 80–90 mJ and a repetition rate of 50 Hz. The deposition was carried out in a pure oxygen ambient of 400 mTorr and with a substrate to target spacing of 4 cm.

All the substrates were mechanically polished to a nominally scratch-free optical finish with 1/4 or 1 μm diamond grit. One group of substrates was then simply chemically cleaned prior to mounting into the vacuum system, one group was chemically polished in a hot phosphoric acid etch, which is expected to yield an atomically smooth surface, and the third group was heated in air or oxygen to 1100–1200 °C for 12–24 h, a process that should result in the formation of a high density of atomic steps on the substrate surface.[7] In all cases the substrates were mounted into the ablation chamber and coated by 10 000 laser pulses to a thickness of approximately 200 nm.

Typical thin-film resistance versus temperature (R vs T) curves for these three different substrate conditions are shown in Fig. 1. In all cases we have found that films grown on the chemically polished substrates have a higher thin-film resistance, a nonzero R vs T intercept at $T = 0$, and a significantly lower T_c. There is less difference between the resistance of the films grown on the mechanically polished and on the annealed substrates, although films on the mechanically polished substrates usually do have a measureably lower T_c, as illustrated by Fig. 1.

X-ray analyses of our films indicate that they consist of all *c*-axis normal oriented grains. In rare instances scanning electron microscope examinations do reveal a small density of the readily identifiable grains that have their *c* axis in the plane of the film. The *c*-axis lattice constants for the films range from 11.68 to 11.72 Å with no discernible difference between the different substrates. X-ray pole figure analysis has proven useful for identifying what we feel to be a major factor contributing to differences in the films. As shown in Fig. 2 films grown on the chemically polished substrates have a strong mosaic pattern, with the $YBa_2Cu_3O_7$ grains assuming a number of different preferred *a-b* rotations to the substrate. The most common of these rotations is centered on 45° followed by 27°,16°, 9°, and smaller angles, all of which can be at least approximately accounted for by various epitaxial relations between the film and the (100) MgO surface.[5,6] For the mechanically polished substrates, the pole figure study indicates a 10–20% density of 45° rotated grains with the remainder of the film being in registry with the principal axes of the

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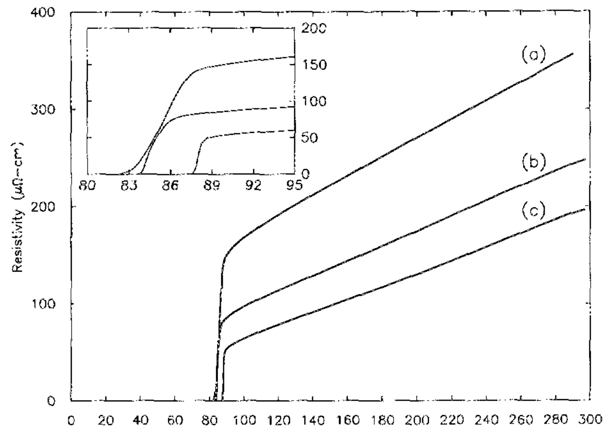

FIG. 1. Resistivity vs temperature curves for typical examples of films grown on (a) a chemically polished (001) MgO substrate, (b) a MgO substrate that has been mechanically polished only, and (c) a thermally annealed MgO substrate.

MgO. For the films grown on the high-temperature annealed substrates, pole figure analysis presents no evidence of any large angle tilt boundaries. X-ray rocking curve measurements made on representative films yield full width at half maximum (FWHM) measurements on the (005) line that vary from 1.02° for a film grown on a chemically polished substrate, to 0.72° for a mechanically polished substrate, to 0.30° for an annealed substrate.

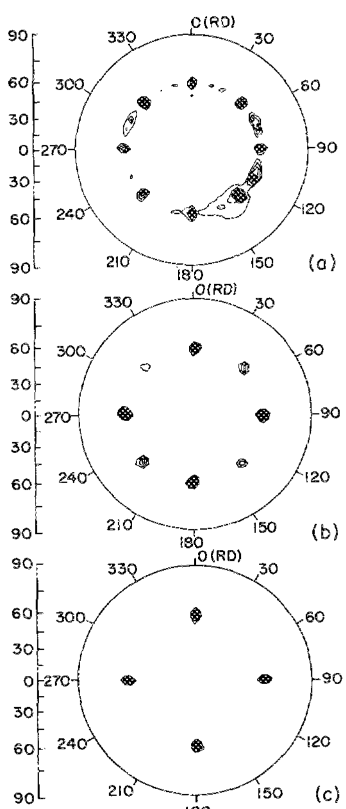

FIG. 2. Typical x-ray pole figures taken about the (102) peak for $YBa_2Cu_3O_7$ thin films deposited by laser ablation onto (a) a chemically polished MgO substrate, (b) a mechanically polished substrate, and (c) a thermally annealed substrate.

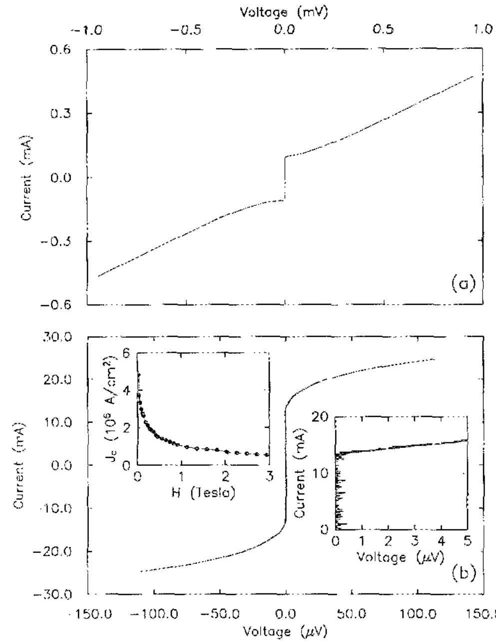

FIG. 3. (a) *I-V* characteristic taken at 4.2 K of an ~1-μm-wide, 3-μm-long microbridge fabricated in a $YBa_2Cu_3O_7$thin film grown on a chemically polished substrate. (b) *I-V* characteristic of a 1.3-μm-wide, 2-μm-long microbridge taken at 77 K for a film grown on a thermally annealed substrate. The right inset gives an expanded view of the abrupt onset of the nonzero voltage regime. The left inset shows the effect of magnetic field on the critical current of the microbridge. The field is applied normal to the plane of the film, i.e. parallel to the *c* axis.

Ion channeling measurements show a clear trend in improved crystalline quality as one goes from a film grown on the chemically polished substrate ($\chi_{\rm min} = 62\%$) to a film on a mechanically polished substrate ($\chi_{\rm min} = 18.7\%$) to a film grown on the most favorable, annealed substrate ($\chi_{\rm min} = 18.0\%$). With the recent development of high-energy oxygen resonance Rutherford backscattering spectroscopy[8] it is now possible to obtain information on the oxygen stoichiometry and, using resonant channeling, the oxygen disorder in the films. With the latter we have found that all of the films exhibit considerably higher disorder at the O sites, but again this disorder is highest for the chemically polished substrates ($\chi_{\rm min,O} = 92\%$) and lowest for the mechanically polished and annealed substrates ($\chi_{\rm min,O} = 63$–65%).

Microbridges formed from films on chemically polished substrates invariably exhibit superconducting weak link behavior such as that illustrated by the current-voltage (*I-V*) characteristic shown in Fig. 3(a). These data were taken at 4.2 K from a 1-μm-wide×3-μm-long microstructure. The occurrence of such weak links is in general accord with the assumption that each large angle tilt boundary in the film exhibits weak link behavior. We find that J_c of these weak links ranges from less than 10^4 A/cm^2 to greater than 10^5 A/cm^2 at 4.2 K. At 77 K the J_c's are typically 10 to 50 times lower than that found at 4.2 K. The normal-state conductance per unit area of these grain boundary weak links ranges approximately from $1\times10^7/\Omega$ cm^2 to $5\times10^8/\Omega$ cm^2 and, as is generally the

TABLE I. Summary of the results of the structural and superconductive measurements made on films deposited on MgO substrates having three different substrate preparations. All the films were deposited by laser ablation using the same deposition parameters.

Substrate treatment	Pole figure analysis: observed tilt boundaries	RBS analysis $\chi_{\min,\,total}$ $\chi_{\min,\,O}$	Rocking curve analysis on (005) peak (FWHM)	ρ(300 K) ($\mu\Omega$ cm)	$T_c(R=0)$ (K)	J_c at 77 K (10^6 A/cm^2)
Chemically polished	16°,27°,45° TB; small angle TB	62% 92%	1.02°	327–356	82.5–84	0.0032–0.025
Mechanically polished	45° TB; small angle TB	18.7% 63%	0.72°	140–248	83–86	0.5–3.3
Annealed	No large angle TB	18.0% 65%	0.30°	196–231	87.5–88.5	3.4–6.0

case for YBCO thin-film weak links, is at least approximately temperature independent.

Microbridges formed in the films grown on the mechanically polished and on the annealed substrates typically yield values of J_c which are two to three orders of magnitude higher than the values found for the above films. For the annealed substrates measured values of microbridge J_c's at 77 K range from 4 to 6×10^6 A/cm^2, and the I-V's have the characteristic nonlinear flux-creep behavior illustrated in Fig. 3(b). This is in sharp contrast to the weak link behavior of the microbridges on the chemically polished substrates. The inset in Fig. 3(b) shows the variation at 77 K of J_c with magnetic field (H applied parallel to the c axis) for a microbridge on an annealed substrate. As illustrated by the figure, the behavior of these microbridges is similar to that found with epitaxial films grown on $SrTiO_3$ substrates at considerably higher deposition temperatures[9] and is indicative of the presence of comparably strong pinning in the film.[10] Microbridges in films grown on mechanically polished substrates typically exhibit a J_c of the order of 3×10^6 A/cm^2 at 77 K, slightly below that found with the annealed substrate. However, in some instances a J_c is found that is about an order of magnitude lower, $J_c\sim$ 3–5×10^5 A/cm^2 at 77 K. This occurence is consistent with the above-mentioned x-ray pole figure analysis which indicates an $\sim$15% density of 45° tilt boundaries. Such anomalies have not yet been seen in the films on the annealed substrates for which the pole figure measurements do not reveal any large angle boundaries (to within the 2% resolution of the measurement), but of course only a limited amount of film area has actually been sampled in the transport measurements.

Collectively, these structural and transport measurements, which are summarized in Table I, clearly indicate the importance of surface preparation in obtaining a nucleation stage which will result in high quality YBCO films on non-lattice-matched substrates. A high density of atomic-scale surface steps appears to be the key to a successful growth process on MgO; this should also be the case for other non-lattice-matched substrates that may be of technological interest.

These comparative growth studies emphasize the strong dependence of the crystalline quality of the YBCO thin film grains on the epitaxial relation of the nucleus to the substrate. Apparently the orientation of a YBCO grain in one of the less favorable (13° 27.5°, etc.) epitaxial positions results in the grain growing with a much greater degree of atomic disorder. Thus not only does improper nucleation result in detrimental effects from the presence of large angle tilt boundaries, but the superconductive (and normal state) properties of the grown misoriented grains are themselves significantly degraded, resulting in a particularly strong diminution of J_c at the grain boundaries as illustrated in Fig. 3(a) and Table I.

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[1] P. Chaudhari, R. H. Koch, R. B. Laibowitz, T. R. McGuire, and R. J. Gambino, Phys. Rev. Lett. **58**, 1343 (1987).

[2] D. K. Lathrop, S. E. Russek, and R. A. Buhrman, Appl. Phys. Lett. **51**, 1554 (1987).

[3] See, for example, numerous papers in Mater. Res. Soc. Symp. Proc. **169**, (in press).

[4] Lisa A. Tietz, C. Barry Carter, Daniel K. Lathrop, Stephen E. Russek, Robert A. Buhrman, and Joseph R. Michael, J. Mater. Res. 4, 1072 (1989).

[5] Q. Li, O. Meyer, X. X. Xi, J. Geerk, and G. Linker, Appl. Phys. Lett. **55**, 310 (1989); X. X. Xi, G. Linker, O. Meyer, E. Nold, B. Obst, F. Ratzel, R. Smithey, B. Strehau, F. Weschenfelder, and J. Geerk, Z. Phys. B **74**, 13 (1989).

[6] M. G. Norton, L. A. Tietz, S. R. Summerfelt, and C. B. Carter, Appl. Phys. Lett. **55**, 2348 (1989); M.G. Norton, L. A. Tietz, S. R. Summerfelt, and C. B. Carter, Mater. Res. Soc. Symp. Proc. **169** (in press); M. G. Norton, C. B. Carter, B. H. Moeckly, S. E. Russek, and R. A. Buhrman, Proc. of the Conference on the Science and Technology of Thin-Film Superconductors, Denver, CO (in press).

[7] M. G. Norton, S. R. Summerfelt, and C. B. Carter, Appl. Phys. Lett. **56**, 2246 (1990).

[8] B. Planpain, P. Revesz, L. R. Doolittle, K. H. Purser, and J. W. Mayer, Nucl. Instrum. Methods B **34**, 459 (1988).

[9] B. Roas, L Schultz, and G. Saemann-Ischenko, Phys. Rev. Lett. **64**, 479 (1990).

[10] C. T. Rogers, S. Gregory, T. Venkatesan, B. J. Wilkens, X. D. Wu, A. Inam, B. Dutta, and M. S. Hegde, Appl. Phys. Lett. **54**, 2038 (1989).