GROWTH AND PROPERTIES OF $YBa_2Cu_3O_7$ THIN FILMS ON NON-LATTICE-MATCHED AND POLYCRYSTALLINE SUBSTRATES

B. H. Moeckly, D. K. Lathrop, S. E. Russek, R. A. Buhrman
M. G. Norton, and C. B. Carter
Cornell University
Ithaca, New York 14853-2501

Abstract

We have investigated the nature of the in-situ growth of *c*-axis normal $YBa_2Cu_3O_7$ thin films on non-lattice-matched, vicinal, and polycrystalline MgO substrates, and on buffer layers of MgO. We find that the preparation of the MgO surface determines the structural and transport properties of the films. In particular, we are able to reproducibly grow films exhibiting either weak link behavior of very high critical current densities. We will discuss the variation of the thin film microstructure, oxygen content, and superconductive properties with the changes in the thin film crystal structure that result from the different growth situations.

Introduction

The growth of high quality $YBa_2Cu_3O_7$ thin films on a few single-crystal substrates has been demonstrated for some time.[1] However, it has become clear that for several potential applications it would be highly desirable to obtain films of sufficient quality on various other, perhaps non-lattice-matched or polycrystalline, substrates. It is also apparent that in attempting to probe the mechanisms responsible for the superconducting behavior of the high T_c materials, it is necessary to understand the fundamental materials properties of these cuprates. Thus, a dual motivation lies behind the work to be presented here.

Our choice of substrate material for these experiments is MgO; it is inexpensive, does not react with the film[2], has reasonable microwave properties, can be readily deposited as a buffer layer, and is transparent in the infrared. As a first step, it is necessary to understand the initial stages of thin-film growth on MgO. Recent studies using transmission electron microscopy[3] (TEM) to examine the nucleation phase have indicated that growth occurs via an island mechanism and that there is a strong tendency for these islands to nucleate at the edges of steps on the MgO surface. This study has clearly demonstrated the importance of surface quality and preparation in controlling the growth habit of high T_c thin films. This paper reports the results of the effect of the MgO orientation and surface preparation on the superconductive properties of YBCO thin films.

The films employed in this study were deposited by laser ablation under identical conditions. A pulsed excimer laser operating at the KrF line (248 nm) was operated at a repetition rate of 50 Hz and a fluence of ~1J/cm^2. The substrates were clamped to a Haynes alloy heater block located 4 cm from the YBCO target. A silver foil underlying the substrate was used to promote thermal contact. Deposition was carried out with a stage temperature of 670 °C in a pure oxygen ambient of 400 mTorr.

Effect of Surface Treatment of Single-Crystal MgO Substrates

In the first set of experiments, the surface of single-crystal (100) MgO substrates was prepared by different methods; the effect of this surface treatment on the deposited YBCO film was examined by various structural and electrical measurements.[4,5] The substrates were cleaved from a MgO boule and then mechanically polished to an optical finish with 1/4 or 1 μm diamond grit. The first group of substrates was then not further altered beyond chemical cleaning of the surface. A second group was chemically polished using a hot phosphoric acid etch which is expected to yield an atomically smooth surface. The third group was annealed at high temperature (1100-1200 °C) for 12-24 hours for the purpose of forming steps in the substrate surface. And lastly, substrates comprising a fourth group were polished about the (100) axis to an angle of 3° to 10° from the (100) normal (vicinal substrates). This group was also thermally annealed with the objective of creating a high density of surface steps.

Standard 2Θ x-ray analysis of the films in each group indicates that they all consist of *c*-axis normal oriented grains. Note that the *c*-axis of the films is normal to the plane of the substrate surface, not nesessarily parallel to the MgO (100) direction. The *c*-axis lattice constants range from 11.68Å to 11.72Å with no difference between the different substrate groups.

X-ray pole figure analysis has proven to be an invaluable tool in identifying an important effect of surface preparation on film structure and transport properties. As Fig. 1 illustrates, films grown on the chemically-polished substrates contain a large number of YBCO grains which are rotated in the *a-b* plane with respect to the substrate. These tilt boundaries are seen at approximately 45°, 27°, 16°, 9°, and smaller angles, all of which can be accounted for by preferred epitaxial relations between the film and the MgO surface.[2,3] For the mechanically-polished substrates, the pole figures indicate a 10-20% density of rotated grains occurring at predominantly 45°. Finally, for the annealed (100) MgO and vicinal substrates, the pole figure analysis presents no evidence of any high-angle tilt boundaries, i.e. all the film's grains are in registry with the *a* and *b* axes of the MgO.

X-ray rocking curve measurements yield further information on the crystalline quality of the various films. Typical full width at half maximum (FWHM) measurements of the (005) YBCO line are 0.30° for a film grown on an annealed substrate, 0.72° for a mechanically-polished substrate, 1.02° for a chemically-polished substrate, and 1.71° for an annealed vicinal substrate.

Ion channeling measurements emphasize this trend in improved crystalline quality as the substrate surface is altered; typical measured values of χ_{min} are 62% for a film on a chemically-

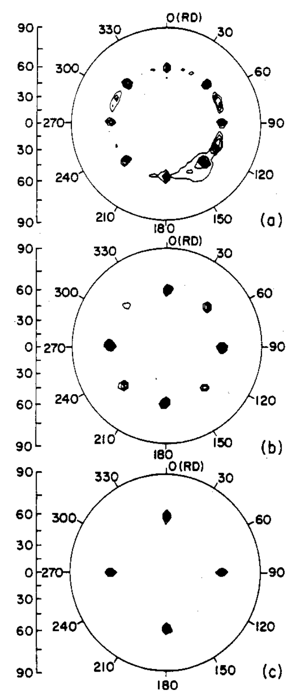

Figure 1. Typical x-ray pole figures taken about the (102) peak for YBCO thin films deposited by laser ablation onto (a) a chemically-polished MgO substrate, (b) a mechanically-polished substrate, and (c) a thermally annealed substrate.

Manuscript received September 24, 1990.

0018-9464/91/0300-1017$01.00 © 1991 IEEE

polished substrate, 18.7% for a mechanically-polished substrate, and 18.0% for an annealed non-vicinal substrate. Information on the oxygen disorder in the films has been obtained using high-energy oxygen resonance Rutherford backscattering spectroscopy.[6] Oxygen disorder is high at the O sites ($\chi_{min,O}$=92% on chemically-polished substrates) but is improved by appropriate predeposition substrate surface treatment ($\chi_{min,O}$=63-65% for mechanically-polished and annealed substrates).

The materials properties of the films have been further investigated using TEM.[3,5] These studies show that the grain structure of the films grown on chemically-polished, mechanically-polished, and annealed (100) MgO films is quite similar, consisting of ~1μm-sized *c*-axis grains whose rotational misaligment corresponds to that seen in the x-ray pole figure studies. Films grown on the vicinal surfaces, however, show a different morphology. These films consist of primarily *c*-axis oriented grains which have a much larger aspect ratio than those observed in films on other substrates. These grains appear highly oriented with respect to rotations about the [001] zone axis. The shape and alignment of these grains in films grown on vicinal MgO is believed to be the result of nucleation and growth at step edges on the substrate surface.

The normal-state resistivities of the films grown on chemically-polished substrates were up to a factor of two higher than films grown on the other single crystal substrates; this observaton is consistent with the channeling and rocking curve results. Typical thin-film resistance vs. temperature (R vs. T) curves for these various substrate preparations are shown in Fig. 2. In all cases films grown on the chemically-polished substrates have a non-zero R vs. T intercept and a significantly lower T_c. There is less difference between the other three substrate preparations, though films grown on mechanically-polished substrates usually have a lower T_c on average.

The transport properties of the films were measured by forming microbridge patterns in the film using standard photolithographic and inert-ion etching processes. Superconducting weak-link behavior is invariably exhibited in such microbridges formed in films on chemically-polished substrates. Fig. 3a shows one such current-voltage (I-V) characteristic obtained at 4.2K from a 1μm wide x 3μm long microstructure. The occurrence of this weak link behavior is attributed to the presence of high-angle tilt boundaries in the film. The critical current densities J_c of these weak links range from less then 10^4 A/cm^2 to more than 10^5 A/cm^2 at 4.2K and are 10 to 50 times lower at 77K.

Microbridge transport measurements of the films on mechanically-polished, annealed, and vicinal substrates yield values of J_c which are 2 to 3 orders of magnitude higher than the values found for films on chemically-polished substrates. The highest J_c's are found in microbridges of films on annealed substrates; the values range from 4 to 6x10^6 A/cm^2 at 77K and are approximately 10 times higher at 4.2K. The shape of the I-Vs in this case (see Fig. 3b) is

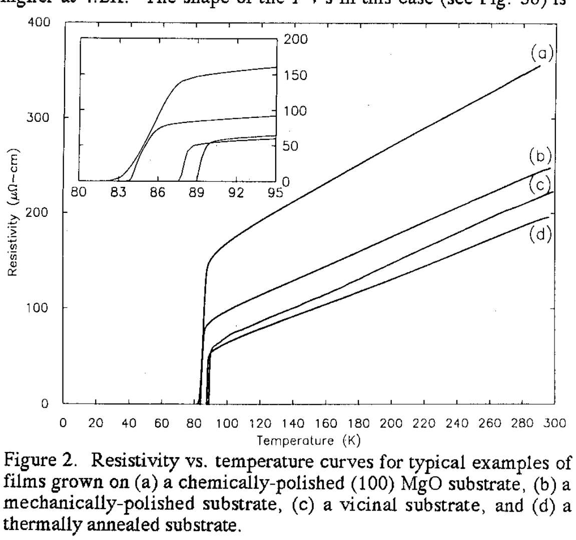

Figure 2. Resistivity vs. temperature curves for typical examples of films grown on (a) a chemically-polished (100) MgO substrate, (b) a mechanically-polished substrate, (c) a vicinal substrate, and (d) a thermally annealed substrate.

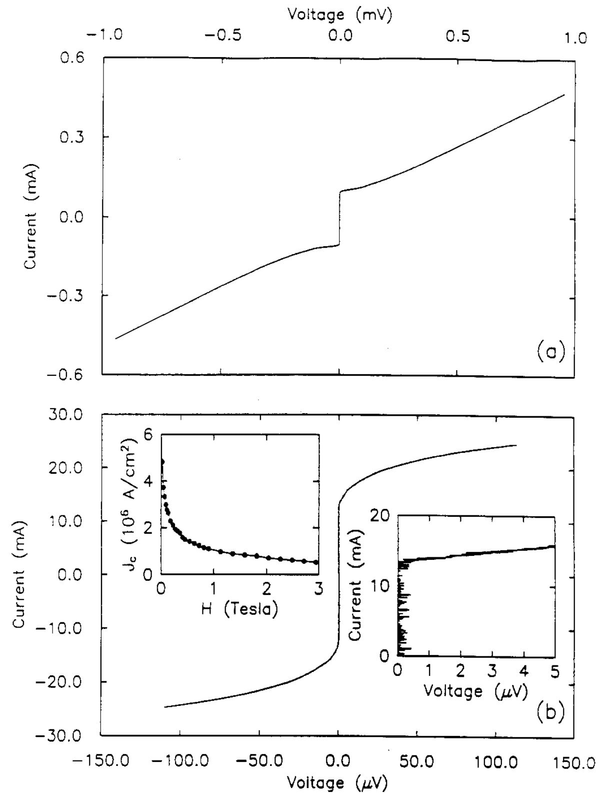

Figure 3. (a) The I-V characteristic at 4.2K of a ~1μm wide, 3μm long microbridge fabricated in a YBCO thin film grown on a chemically-polished substrate. (b) The I-V characteristic of a 1.3μm wide, 2 μm long microbridge at 77K for a film grown on a thermally annealed (100) MgO substrate. The right inset is an expanded view of the abrupt onset of the non-zero 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.

indicative of non-linear flux-creep behavior, in marked contrast to the weak-link behavior of chemically-polished-substrate films. Evidence for strong pinning in these films is provided by the variation of J_c with magnetic field, illustrated in the inset of Fig. 3b. Microbridges in films on mechanically-polished and annealed vicinal films typically exhibit J_c's in the range 0.5 to 3x10^6 A/cm^2 at 77K, slightly lower than the annealed-substrate films. However, in some instances, microbridges in the mechanically-polished films yield a J_c which is about an order of magnitude lower, J_c ~ 3-5x10^5 A/cm^2 at 77K. This result is consistent with the x-ray pole figure data, which indicate a ~15% density of 45° tilt boundaries.

Growth on Polycrystalline MgO

Results of the experiments discussed above prompted a study of YBCO thin films grown on randomly-oriented polycrystalline MgO substrates.[5] The material for this experiment, obtained from Avco Specialty Materials, Inc., consisted of hot-pressed, high-purity MgO grains having an average size of ~50μm. Substrates were cut and polished from this bulk material and then thermally annealed as described above. The random orientation of the material was confirmed by x-ray diffraction.

X-ray analysis of films grown on these polycrystalline subtrates again indicated complete *c*-axis orientation normal to the surface of the substrate. This fact is perhaps surprising given the randomly oriented nature of the MgO grains. The orientation of the substrate surface does appear to have an effect on the morphology of the YBCO film, however. Fig. 4 is a scanning electron micrograph of a film grown on a polycrystalline MgO substrate; the individual

MgO grains of the annealed substrate can be clearly seen in the texture of the overlying film.

X-ray pole figures cannot be used in this case to determine the orientation of the YBCO grains with respect to their underlying MgO grain. However, transmission electron micsoscopy (TEM) may be employed to search for *a-b* rotations in an area of the film which grows atop a single MgO grain. These TEM studies find that many of the YBCO grains are aligned; however, misorientations corresponding to rotations of 29° and 6.5° about the [001] zone axis were frequently observed. Observation of an area of the film grown across a MgO grain boundary revealed rotations of ~45° in some instances, although in many cases there was only slight rotational misalignment across the boundary.

The resistivity of the polycrystalline-substrate films was significantly higher than that measured for all other films. In addition, the zero-resistance T_c of these films was typically 78K, which is 10 to 12K below that generally obtained with YBCO films grown on annealed (100) MgO substrates.

Microbridges patterned in these films occasionally spanned a MgO grain boundary so that the effect of such a substrate grain boundary of the superconductive properties of the YBCO film could be examined. The J_c of the films for these microbridges was quite low, typically ranging from 10^4 to 10^5 A/cm^2 at 4.2K. Values of J_c approximately 10 times higher have been observed; these values are obtained from microbridges which are localized on a single MgO grain. The *I-V* characteristics of the microbridges are not as well described by the RSJ model as are the *I-V*s found in microbridges with similar J_c's but which are formed in films containing high-angle tilt boundaries as described previously. This discrepency may be explained by the existence of a series array of weak links in the microbridge or by flux creep arising from very weak pinning in the region. It's clear that the presence of the substrate grain boundaries severely degrades the superconductive properties of the YBCO film. This degradation may be due not only to the creation of high-angle tilt boundaries in the film, but also to atomic disorder present within the grains of the film resulting from misoriented film growth near substrate grain boundaries.

Growth on Al_2O_3 With a MgO Buffer Layer

The encouraging results of our studies of film growth on polycrystalline MgO and single-crystal MgO with varying surface preparations has convinced us of the feasibility of growing high quality YBCO films on buffer layers of MgO deposited on other substrate materials. Growth of YBCO thin films on buffer layers of various materials has been attempted with widely varying success for some time.[7] Here we discuss results of our preliminary experiments.

We have deposited films of MgO onto $(10\bar{1}0)\ \alpha\text{-}Al_2O_3$ substrates by laser ablation. Our targets are single-crystal MgO, and deposition takes place with a substrate temperature of 450 °C and an oxygen pressure of ~10 mTorr. We find, as reported by others[8], that the orientation of the deposited MgO with respect to the substrate is (110) MgO || $(10\bar{1}0)\ Al_2O_3$. As our ablation system is equipped with a four-target palette, we were able to deposit films of YBCO in situ on top of these buffer layers. To our knowledge, this is the first report of the growth of YBCO thin films on MgO buffer layers of the (110) orientation.

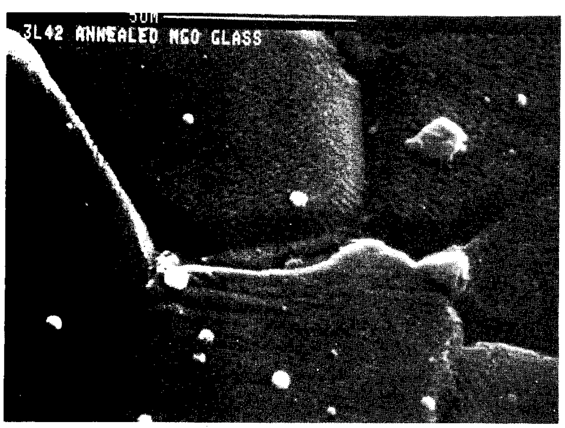

Figure 4. Scanning electron micrograph (SEM) of a YBCO film grown by laser ablation on a polycrystalline MgO substrate.

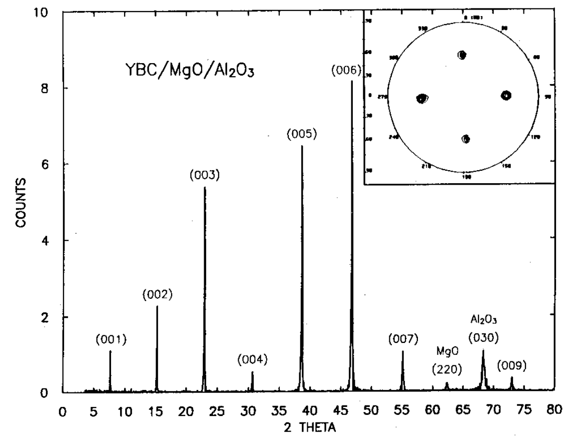

Figure 5. X-ray diffraction 2Θ pattern for a YBCO film grown on $(10\bar{1}0)\ \alpha\text{-}Al_2O_3$ with an intermediate (110) MgO buffer layer. The inset shows the x-ray pole figure of the film.

As shown in Fig. 5, x-ray 2Θ analysis reveals that the films are completely *c*-axis normal oriented, with no indication of *a*-axis growth. In addition, pole figure analysis shows that the YBCO films are completely aligned; there is no evidence of rotated grains (see inset of Fig. 5). This is a very promising observation, confirming the idea that YBCO films grown on buffer layers may be of high quality.

An *R* vs. *T* curve of one of these films is shown in Fig. 6. The zero-resistance T_c is 86K which is typical of our results so far. The resistivity is also comparable to our better films.

Transport measurements of microbridges patterned in a single initial film have yielded values of J_c of $>10^6$ A/cm^2 at 77K. It is believed these values are among the highest reported for YBCO films grown on MgO buffer layers. The *I-V* characteristic of a microbridge is shown in the inset of Fig. 6. Again, the flux-creep behavior typical of high J_c films is observed.

Conclusion

The structural and transport measurements of YBCO films grown on various MgO surfaces are summarized in Table 1. These measurements clearly indicate the importance of obtaining a nucleation stage which will result in high-quality YBCO on non-

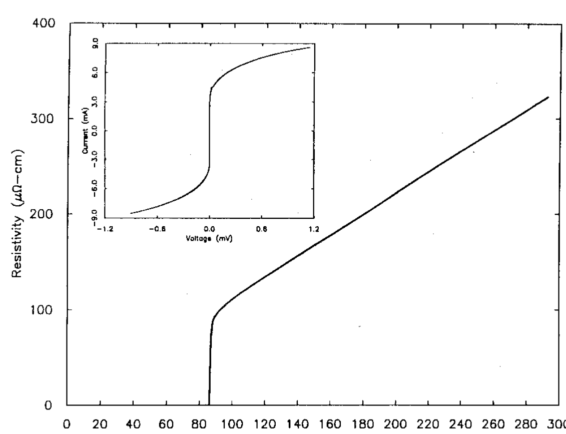

Figure 6. The *R* vs. *T* curve for a YBCO film grown on (110) MgO on Al_2O_3. The inset shows the film's *I-V* characteristic.

Table 1. A summary of the results of the structural and superconductive measurements made on $YBa_2Cu_3O_7$ films deposited on various MgO substrate surfaces. All the films were deposited by laser ablation using the same deposition parameters.

MgO substrate	Pole figure analysis: observed tilt boundaries	RBS analysis $\chi_{min,\ total}$ $\chi_{min,\ O}$	Rocking curve analysis on (005) peak (FWHM)	ρ(300K) (μΩ-cm)	$T_c(R=0)$ (K)	J_c at 77K (10^6 A/cm^2)
Chemically polished	16°, 27°, 45° TB; small angle TB	62% 92%	1.02°	325–350	82.5–84	0.0032-0.025
Mechanically polished	45°TB; small angle TB	18.7% 63%	0.72°	140–250	83–86	0.5-3.3
Annealed	No high angle TB	18.0% 65%	0.30°	200–230	87.5–88.5	3.4-6.0
Vicinal	No high angle TB	____	1.71°	200–300	83–89	.5-2.3
Polycrystalline	____	____	____	400–750	73–79	0.0027- 0.5 (4.2K)
Buffer layer on sapphire	No high angle TB	____	0.93°	350–400	82–87	0.1–1.2

lattice-matched substrates. Such considerations are of prime importance when the low-temperature growth of the cuprate superconductors is required in order to obtain a morphology which facilitates the use of lithographic processing and the growth of multilayer structures. To this end, these studies have emphasized the significance of the role which the method of graphioepitaxy may play in obtaining the desired film quality under restrictive conditions.

We wish to acknowledge many helpful conversations with D. H. Shin and J. Silcox. This research was supported by the Defense Advanced Research Projects Agency and by the Office of Naval Research. Additional support was provided by the National Science Foundation through use of the equipment and assistance of the staff of the National Nanofabrication Facility at Cornell and through use of the facilities of the Cornell University Materials Science Center. BHM acknowledges the support of a Department of Education fellowship.

References

1. See for example numerous papers in these proceedings; also see *Mat. Res. Soc. Symp. Proc.*, 169, 1989.

2. L. A. Tietz, C. B. Carter, D. K. Lathrop, S. E. Russek, R. A. Buhrman and J. R. Michael, *Jour Mat. Res.*, 4, 1072, 1989.

3. 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, *Mat. Res. Soc. Symp. Proc.* 169, 1989; 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, 1990, in press.

4. B. H. Moeckly, S. E. Russek, D. K. Lathrop, R. A. Buhrman, J. Li and J. W. Mayer, to be published in *Appl. Phys. Lett.*, 56, 1990.

5. B. H. Moeckly, S. E. Russek, D. K. Lathrop, R. A. Buhrman, M. G. Norton and C. B. Carter, submitted to *Appl. Phys. Lett.*

6. B. Planpain, P. Revesz, L. R. Doolittle, K. H. Purser and J. W. Mayer, *Nucl. Instr. and Meth.* B34, 459, 1988.

7. See for example A. B. Berezin, C. W. Yuan, and A. L. deLozanne, *Appl. Phys. Lett.* 57, 90,1990; S. Witanachchi, S. Patel, D. T. Shaw and H. S. Kwok, *Appl. Phys. Lett.* 55, 295, 1989.

8. J. Talvacchio, G. R. Wagner and H. C. Pohl, *Physica C*, 162-164, 1989.