GROWTH AND PROPERTIES OF YBa2Cu3Oy THIN FILMS ON NON-LATTICE-MATCHED AND POLYCRYSTALLINE SUBSTRATES

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Abstract

We have investigated the nature of the in-situ growth of c-axis normal YBa2Cu3Oy 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 YBa2Cu3Oy thin films on a few single-crystal substrates has been demonstrated for some time. 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 Tc 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, 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 (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 coalesce under identical conditions. A pulsed excimer laser operating at the KrF line (248 nm) was operated at a repetition rate of 50 Hz and an energy fluence of 1 J/cm². The substrates were clamped to a Haynes alloy heater block located 4 cm from the YBCO target. 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.

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. The substrates were cleaned 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 10% phosphoric acid etch which is expected to yield an atomically smooth surface. The third group was 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 necessarily parallel to the MgO (100) direction. The c-axis lattice constants range from 11.68 Å to 11.72 Å 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 45º, 27º, 16º, 9º, and smaller angles, all of which can be accounted for by preferred epitaxial relations between the film and the MgO surface. For the chemically-polished substrates, the pole figures indicate a 10-20% density of rotated grains occurring at predominately 45º. 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 0.30º for a film grown on an annealed substrate, 0.72º for a mechanically-polished substrate, 1.02º for a chemically-polished substrate, and 1.71º 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 χmin are 62% for a film on a chemically-polished MgO substrate, 72% for a mechanically-polished MgO substrate, and 100% for a thermally annealed MgO substrate.

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.
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. Oxygen disorder is high at the O sites (92%) on chemically-polished substrates. Fig. 3a shows one such current-voltage (I-V) characteristic obtained at 4.2K from a 1pm wide x 3pm long microbridge fabricated in a YBCO thin 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.

Figure 3. (a) The I-V characteristic at 4.2K of a 1pm wide, 3pm long microbridge fabricated in a YBCO thin 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 3$\times$10^6 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, $J_c = 3$-5$\times$10^5 A/cm^2. 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. 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 substrates 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 grain. 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 microscopy (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 12 K 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 $10^5$ to $10^6$ A/cm² at 4.2 K. 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 discrepancy 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 is 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 Al₂O₃ 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. Here we discuss results of our preliminary experiments.

We have deposited films of MgO onto (1010) α-Al₂O₃ 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, that the orientation of the deposited MgO with respect to the substrate is (110) MgO || (110) Al₂O₃. 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. 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 85K 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/cm² at 77K. It is believed these values are among the highest reported for YBCO films 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-

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**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 (1010) α-Al₂O₃ with an intermediate (110) MgO buffer layer. The inset shows the x-ray pole figure of the film.

**Figure 6.** The $R$ vs. $T$ curve of one of these films is shown in Fig. 6. The zero-resistance $T_c$ is 85K which is typical of our results so far. The resistivity is also comparable to our better films.
Table 1. A summary of the results of the structural and superconductive measurements made on YBa2Cu3O7 films deposited on various MgO substrate surfaces. All the films were deposited by laser ablation using the same deposition parameters.

<table>
<thead>
<tr>
<th>MgO substrate</th>
<th>Pole figure analysis</th>
<th>RBS analysis</th>
<th>Rocking curve analysis on (005) peak (FWHM)</th>
<th>( T_c(R=0) ) (K)</th>
<th>( J_c ) at 77K (10^6 A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically polished</td>
<td>16°, 27°, 45° TB, 62% small angle TB</td>
<td>62%</td>
<td>1.0°</td>
<td>325-350</td>
<td>82.5-84</td>
</tr>
<tr>
<td>Mechanically polished</td>
<td>45° TB, 63% small angle TB</td>
<td>63%</td>
<td>0.7°</td>
<td>140-250</td>
<td>83-86</td>
</tr>
<tr>
<td>Annealed</td>
<td>No high angle TB, 18°, 65%</td>
<td>0.3°</td>
<td>200-230</td>
<td>87.5-88.5</td>
<td>3.4-6.0</td>
</tr>
<tr>
<td>Vicinal</td>
<td>No high angle TB, 18°, 65%</td>
<td>1.71°</td>
<td>200-300</td>
<td>83-89</td>
<td>5.2-3</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buffer layer on sapphire</td>
<td>No high angle TB</td>
<td>0.93°</td>
<td>350-400</td>
<td>82-87</td>
<td>0.1-1.2</td>
</tr>
</tbody>
</table>

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.

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References

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