IEEE TRANSACTIONS ON MAGNETICS, VOL. 27, NO. 2, MARCH 1991

Properties of $YBa_2Cu_3O_{7-\delta}$ Thin Films Grown on Off-Axis-Cut MgO Substrates

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Abstract

A series of $YBa_2Cu_3O_{7-\delta}$ films has been reactively sputtered on off-axis-cut MgO substrates. All the films were oriented with the *c* axis normal to the substrate regardless of substrate orientation, indicating that growth dynamics is a major factor influencing film orientation on non-lattice-matched substrates. As the substrate orientation is moved off the [100] direction the films showed a decrease in transition temperature and showed properties indicative of an increased density of weak links. The films grown on high-angle substrates showed better properties than the films grown on low-angle substrates. Films grown on (110) MgO were as good as films grown on (100) MgO.

Introduction

The morphology of a $YBa_2Cu_3O_{7-\delta}$ thin film is important in determining the film's superconducting properties and the applications for which it is suitable. In particular, for high current density applications the transport current must be perpendicular to the *c* axis and the film must be either a single crystal or a highly aligned *c* axis film with mostly low angle grain boundaries. High angle grain boundaries form weak links which can degrade critical current densities and cause high sensitivity to magnetic fields.[1,2] In contrast, for applications for magnetic field detectors and optical detectors one may require a polycrystalline film with a high density of "high quality" weak links. In this paper we explore the possibility of altering the film morphology by growing on substrates which are cut off a principal crystalline axis. The hope is that this procedure may be a method of controllably altering the film morphology to produce weak linked films which are suitable for detector applications. In addition this type of study may lead to a better understanding of what factors determine the film orientation and morphology on non-lattice matched substrates. This information may yield insight into what will be required to produce completely oriented films on Si, Al_2O_3, and amorphous substrates.

There has been extensive study of the morphology of $YBa_2Cu_3O_{7-\delta}$ on (100) MgO.[3,4,5] Under most conditions, $YBa_2Cu_3O_{7-\delta}$ forms a mosaic structure in which the grains assume one of several epitactic orientations. The most common orientations are those with the *c* axis along an MgO [100] direction normal to the substrate and with the *a,b* axes along the MgO [100], [110], [120] or [130] direction in the plane of the substrate. This behavior is indicative of a weak epitaxy due to the large lattice mismatch of MgO and $YBa_2Cu_3O_{7-\delta}$. The naturally occurring mosaic structure then consists of *c* axis aligned grains which form high angle tilt boundaries (boundaries between grains with different in-plane orientations). These grain boundaries have been shown to form weak links with nearly ideal RSJ current-voltage (IV) characterisitcs.[2] Using the proper growth and substrate preparation one can obtain completely oriented *c* axis films on (100) MgO.[4] This paper extends this previous work to off-axis-cut MgO substrates.

Experimental

The films were grown by reactive dc magnetron sputtering from a stoichiometric $YBa_2Cu_3O_{7-\delta}$ target using a standard *in situ* process. The sputter geometry is a "slightly off-axis" geometry as shown in Fig. 1. A Taguchi optimization experiment[6] was performed for $YBa_2Cu_3O_{7-\delta}$ growth on MgO by varying the substrate temperature T_s, total pressure P_T ($Ar + O_2$), O_2 partial pressure P_{O_2}, and the gun height. The dc power was fixed at P = 120 W (dc voltage = 140 V). The optimum growth parameters in our system were determined to be: $T_s = 740°C$, $P_T = 31.9$ Pa (240 mTorr), $P_{O_2} = 12.8$ Pa (96 mTorr). These growth conditions consistently produced as-deposited films with zero resistance transition temperatures of $T_{co} = 88 - 91$ K on (100) $SrTiO_3$ and (100) $LaAlO_3$, and $T_{co} = 85 - 89$ K on (100) MgO. All sputtered films in this paper were fabricated using these deposition parameters. The deposition rates for this method are 0.5 - 1.0 nm/min, which are quite slow when compared to other deposition methods. All sputtered films were deposited for 6 h and were approximately 200 nm thick.

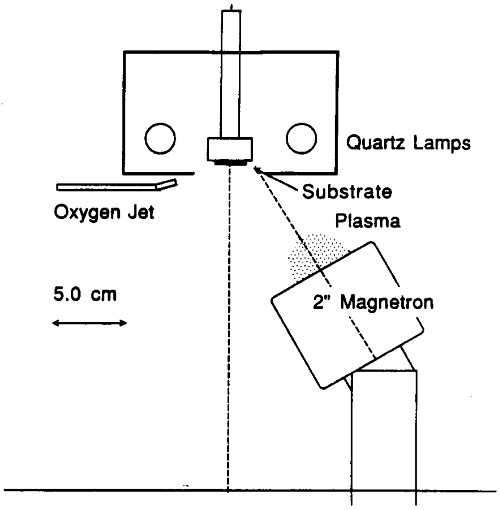


Figure 1. Schematic diagram of the sputter geometry. In this "slightly off axis" geometry the normals from the cathode just miss the substrate to avoid resputtering effects.

Manuscript received September 24, 1990.

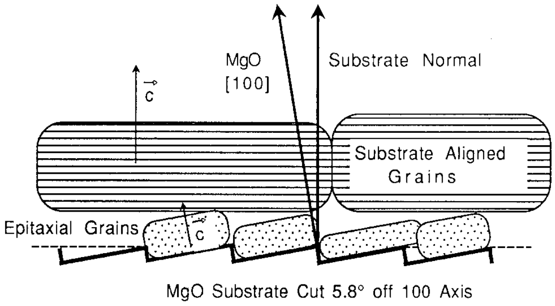


Figure 2. Schematic diagram of $YBa_2Cu_3O_{7-\delta}$ growth on a slightly off-axis-cut substrate. Small epitaxial grains nucleate at the substrate interface. These grains give way to large growth oriented grains which constitute the major part of the film volume.

In addition, some films were also produced by a standard laser ablation technique[7] to determine how the off-axis growth morphology depends on deposition techniques. These films were deposited using a tripled Nd:YAG laser at T_s=710°C, P_{O2} = 33.3 Pa (250 mTorr).

Two sets of substrates were used for this study. The first set consisted of commercially polished (100) MgO wafers. The second set of substrates consisted of MgO wafers cleaved or cut from a natural MgO crystal and then ground to various orientations. The substrate orientation will be specified by the angle between the substrate normal and the MgO [100] direction. The substrates were cut to keep the substrate normal in the [100] - [110] plane and therefore a 45° substrate will have a (110) orientation. These substrates were mechanically polished with a 1 μm diamond grit final polish and then heat treated by baking at 1100°C in flowing O_2 for 12 h. Since the MgO (100) surface is extremely stable it is expected, at least for low angle cuts, that the heat treatment will regrow the (100) MgO surface and form surface steps as shown schematically in Fig. 2. Although we have not yet explicitly determined the surface structure of our off-axis cut substrates, evidence for this type of regrowth has been demonstrated in TEM studies for similar regrowth conditions.[8]

Film Properties

X-ray diffraction measurements indicate that all of the films are predominantly oriented with the *c* axis normal to the substrate *regardless of substrate orientation.* An example of this can be seen in Fig. 3 where a rocking curve of the $YBa_2Cu_3O_{7-\delta}$ (003) peak is plotted along with a rocking curve of the MgO (200) peak for a film grown on a substrate cut 6.8° off the (100) axis. As seen most of the $YBa_2Cu_3O_{7-\delta}$ grains have their *c* axes aligned within 2° of the substrate normal (tilt angle of 0°), whereas only a small number of $YBa_2Cu_3O_{7-\delta}$ grains have their *c* axis aligned with the MgO [100] direction (shown by the small peak at 6.8° tilt angle). The grains that are aligned with the MgO [100] direction are probally small grains growing epitaxially at the MgO-$YBa_2Cu_3O_{7-\delta}$ interface. As the film grows, it is expected that the grains loose registry with the substrate and their orientation is determined by growth dynamics. This type of growth is shown schematically in Fig. 2. Similar observations on laser ablated $YBa_2Cu_3O_{7-\delta}$ on off-axis cut MgO have been recently made by Moeckly *et al.*[9] Typical rocking curve widths on the (007) peaks are shown below in Table 1. As the substrate orientation moves off the (100) orientation, the widths of the rocking curves on the *c* axis peaks at first increase. This indicates that the degree of *c* axis alignment decreases, as expected, when orienting influence of the substrate is absent. Somewhat surprisingly, at higher angles (above 10°) the films become better oriented, and the rocking curve widths decrease.

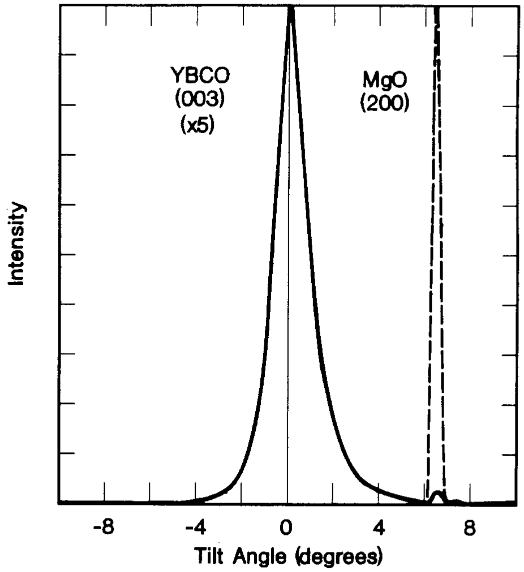


Figure 3. X-ray rocking curves of the $YBa_2Cu_3O_{7-\delta}$ (003) peak and the MgO (200) peak for a $YBa_2Cu_3O_{7-\delta}$ film grown on 6.8° MgO. Most of the film is oriented with the *c* axis parallel to the substrate normal. A small peak is seen at 6.8° off the substrate normal along the MgO [100] direction.

Table 1. (007) Rocking curve widths (FWHM)

Substrate orientation	0°	4.6°	6.8°	20°
Rocking width	0.30°	1.70°	1.60°	0.70°

Resistive transitions for films on 0° and 6.8° MgO substrates are shown in Fig. 4. The film on the off-axis-cut MgO has a lower transition temperature and a broader transition than the film grown on the oriented substrate. The dependence of the transition temperature on substrate orientation is summarized in Fig. 5 where the transition midpoint (T_{c50}) is plotted versus the substrates orientation. The bars on the data points denote the position of the zero resistance point (T_{co}) and the 90% resistance point (T_{c90}). The transition temperature seems to come back up at higher substrate orientations (>20°), showing a strong correlation with the rocking curve widths. As seen in Fig. 5, the sputtered films on substrates from the natural MgO crystal polished in-house have consistently lower transition temperatures than the films on the commercial (100) MgO. We have not yet identified the properties of the MgO or the surface preparation that are responsible for these differences. On a 45° substrate the film properties, at least for laser ablated films, are as good as those on (100) MgO.

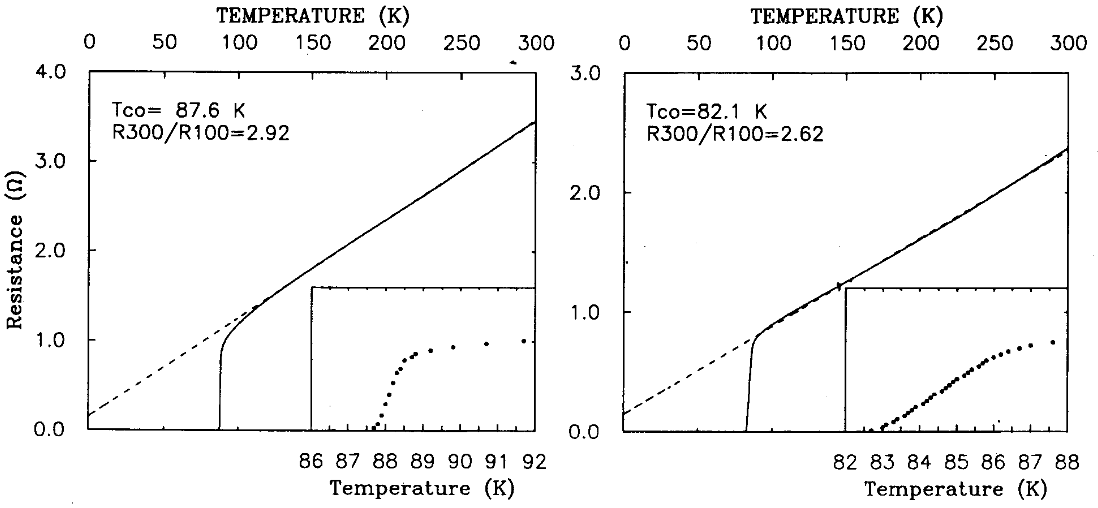


Figure 4. Resistive transitions of $YBa_2Cu_3O_{7-\delta}$ films on (100) MgO and 6.8° MgO substrates. The films on off axis-cut substrates show a marked reduction in transition temperature and an increase in transition width.

SEM micrographs of $YBa_2Cu_3O_{7-\delta}$ films on 0°, 4.6°, and 20° substrates are shown in Fig. 6. Both the 0° and 20° films show a smooth dense morphology. The films on low angle substrates, however, have a rough platelet-like morphology exemplified by that shown in figure 6b. The SEM pictures suggest that films on low angle substrates (1°-10°) have a large amount of disorder in the in-plane orientation as well as the small amount of variation in the *c* axis orientation seen in the rocking curves. Also seen in the SEM photographs is the presence of a large number of voids in several of the films. The number of voids observed in the films on the natural crystal MgO subtrates is considerably larger than that seen on the commercial substrates. The number of voids does not seem to correlate with the orientation of the substrate and the number of voids seen in laser ablated films on the same substrates is considerably less. The SEM studies further show that there are considerably fewer long *a* axis grains in the films on off-axis-cut MgO.

Discussion

The observation that the films grow with the *c* axis normal to the substrate, regardless of the orientation of the substrate normal, indicates that growth dynamics is more important that substrate interaction in determining the orientation of these films. It is known from the aspect ratio of *a* axis grains that the growth rate in the *a* (or *b*) direction is 10 to 100 times faster than growth in the *c* direction. Grains with their *c* axis aligned to the substrate normal will have rapid continual growth since surface diffusion can continually support growth in the fast direction. Grains growing epitaxially at the substrate interface will have their growth impeded when the *a* axis face meets a substrate step or when it grows out of the substrate plane (see figure 2). On the low angle substrates the *epitaxial* grains that nucleate at the substrate surface will frustrate the alignment of the *substrate-normal* grains. This may account for the rough platelet-like morphology seen in the SEM photos and the broad superconducting transitions. On the higher angle films, we anticipate that fewer epitaxial grains will nucleate and the substrate normal grains will have better alignment thus accounting for the smoother texture and less broad transitions.

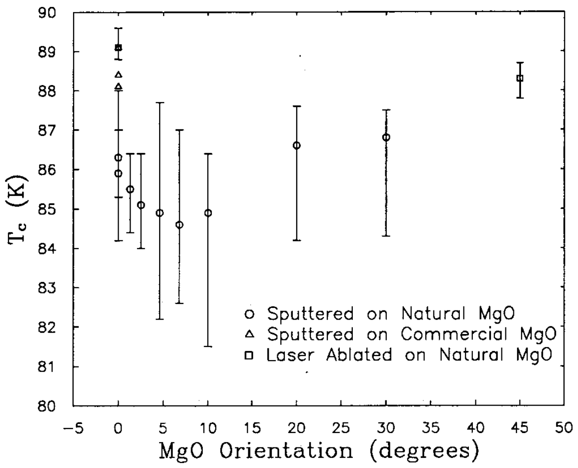
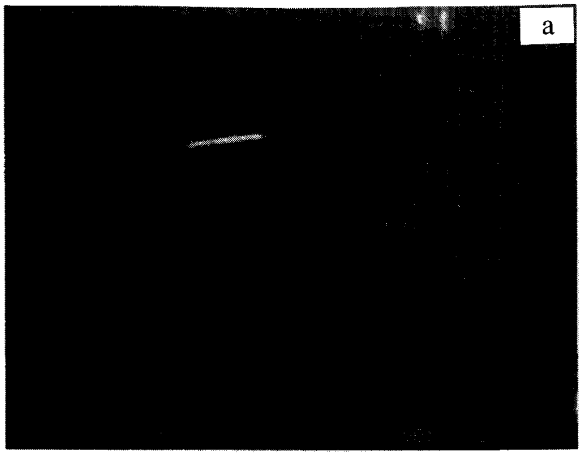


Figure 5. Transition temperatures of a series of sputtered $YBa_2Cu_3O_{7-\delta}$ films on substrates of various orientations. The points denote the transition midpoint. The bars denote the zero resistance temperature and the 90% resistance temperature. Also shown are the transitions temperatures for some laser ablated films on similar substrates. High quality films can be grown on (110) MgO.

The broad transitions in the films deposited on off-axis-cut MgO are tentatively attributed to weak links due to in-plane misalignment. TEM and J_c(H) measurements to further establish the film morphologies and the character of the weak links are currently under way. We hope that such films can be made with a high density of weak links (between *c* axis aligned grains) for detector applications.



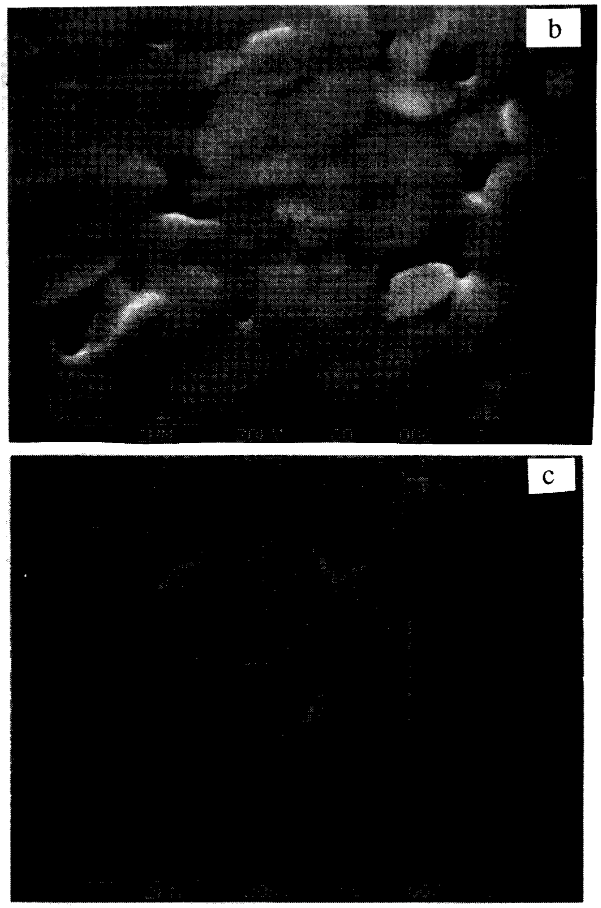


Figure 6. SEM micrographs of $YBa_2Cu_3O_{7-\delta}$ films on: (a) (100) MgO, (b) 6.8° MgO, (c) 20° MgO. The films grown on low angle MgO (0° - 10°) show a rough platelet-like structure seen in 6b.

Our results on sputtered films differ slightly from those of Moeckly *et al.* on laser ablated $YBa_2Cu_3O_{7-\delta}$ films on off-axis-cut MgO. Moeckly *et al.* observed a high degree of in-plane alignment and high J_c values for films deposited on 5° MgO. They attributed the in-plane alignment to grapho-epitaxy. Clearly more information is needed to establish what factors, including deposition technique and surface preparation, determine in-plane alignment. It has been established that it should be possible to obtain *c* axis films on most non-lattice matched (non-reactive) substrates. To obtain in-plane alignment will require further control over film growth.

Acknowledgements

We acknowledge R. H. Ono and J. M. Beall for help in the deposition of the laser ablated films. We thank D. Balzar and H. M. Ledbetter for their help in the X-ray diffraction measurements. We also thank C. C. Clickner for considerable technical assistance and A. Roshko for helpful discussions. B. Jeanneret acknowledges the Swiss NSF for financial support.

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