Priority communication

Growth mechanism of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films on vicinal MgO

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YBa$_2$Cu$_3$O$_{7-\delta}$ thin films have been grown on vicinal MgO substrates by pulsed-laser ablation. The substrate topography has been shown to affect the microstructure of the film. The step edges act as preferential sites for island nucleation, controlling the in-plane alignment of the islands. The resulting microstructure consists of c-axis oriented grains which have a large aspect ratio. The formation of a well-defined substrate surface enables the growth of highly oriented YBa$_2$Cu$_3$O$_{7-\delta}$ films, on a substrate where there is a large lattice mismatch. The films have been characterized by both X-ray diffraction techniques and transmission electron microscopy.

1. Introduction

The effect of the substrate surface in controlling the microstructure of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films has already been demonstrated [1]. In that study, it was shown by X-ray pole-figure analysis that a high-temperature anneal of the substrate prior to film deposition led to better in-plane orientation of the grains — no high-angle grain boundaries were detected. However, for films deposited on substrates which had only been chemically polished or mechanically polished, a significant number of high-angle grain boundaries were produced. X-ray rocking curve and ion-channeling measurements [2] show that the crystalline perfection of films grown on annealed substrates was also improved. Studies using transmission electron microscopy (TEM) [3–6] have unequivocally demonstrated that steps on the substrate surface can act as preferential sites for island nucleation of YBa$_2$Cu$_3$O$_{7-\delta}$ and other oxide thin films. This phenomenon has been described as a form of graphoepitaxy [4]. For YBa$_2$Cu$_3$O$_{7-\delta}$ films grown on MgO, the islands were found to be epitaxial and aligned with their c-axis perpendicular to the film–substrate interface plane. To study further the effects of the substrate surface on film microstructure, YBa$_2$Cu$_3$O$_{7-\delta}$ thin films have been deposited onto vicinal MgO.

A vicinal surface is defined as one “approximating, resembling, or taking the place of a fundamental crystalline form or face” [7], or, in other words, a vicinal surface can be thought of in terms of terraces of low index with low surface energy and steps [8]. For MgO, which has the rocksalt structure, the lowest energy surface is (001), which is also the cleavage plane. Fig. 1 shows a schematic representation of a vicinal surface formed on MgO. The surface consists of (001) terraces, at an angle $\theta$ to the original substrate surface, which are bound by planar steps. The steps have a height $h$.

Fig. 1. Schematic representation of a stepped surface. The step height is $h$ and the angle of deviation from the low-energy (001) surface is $\theta$. (Redrawn after Tasker and Duffy [8].)

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This paper extends ideas introduced in an earlier paper [5], in which it was shown that YBa$_2$Cu$_3$O$_{7-\delta}$ thin films grown on vicinal MgO possessed both high transition temperatures and high critical currents. It was also shown that the film microstructure was somewhat different than that observed for films grown on (001)-oriented MgO. In this paper the microstructure of films grown on vicinal MgO will be presented and also a mechanism proposed to account for the observed microstructure.

2. Experimental

Vicinal surfaces were prepared in the following way: (001)-oriented MgO single-crystal substrates were polished about the (100) axis to the desired angle. The results reported in this paper are for a chosen angle of 5°, although a wide range of angles has been studied. After polishing, the substrates were cleaned in organic solvents and annealed in air at 1100–1200°C for up to 24 h. During the annealing procedure, the surface, which is misoriented with respect to the low energy (001) plane, rearranges to form a series of surface steps in order to lower the total surface energy of the system [10]. The surface now resembles that shown in the schematic in fig. 1.

The films were formed by pulsed-laser ablation from a stoichiometric YBa$_2$Cu$_3$O$_{7-\delta}$ target. The exact details of the deposition technique have been reported in detail elsewhere [11]. Briefly, the films were deposited by focusing a KrF (248 nm) excimer laser onto the target pellet. The substrates were mounted on silver foil on the substrate stage. The temperature of the substrate stage was 670°C during deposition. Film deposition was performed in 400 mTorr of oxygen. The laser was operated at a pulse-repetition rate of 50 Hz and a fluence of $\sim$ 1 J/cm$^2$. The films produced had a thickness of 200–300 nm. The films were examined by TEM and by X-ray diffraction (XRD) using both standard 2θ analysis and pole figure measurements. Samples for TEM analysis were prepared using standard specimen preparation techniques. Briefly, for plan-view imaging, 3 mm discs were cored from the substrate using an ultrasonic disc-cutter. The discs were polished, from the substrate side only, to a thickness of 150 μm and then dimpled to 20 μm. All grinding and polishing was performed in nonaqueous media. The dimpled discs were ion-milled to perforation using 5 kV Ar$^+$ ions at an incident angle of 18°. During ion-milling the sample was cooled to liquid-nitrogen temperatures. All samples were examined at 120 keV using a JEM 1200EX.

3. Results

Fig. 2 shows a standard 2θ X-ray pattern obtained from a YBa$_2$Cu$_3$O$_{7-\delta}$ thin film grown on 5° vicinal MgO. From this pattern it can be seen that the film is oriented exclusively with its c-axis perpendicular to the plane of the substrate. The absence of peaks arising from the (001) planes of the substrate indicate that the grains are not aligned parallel to the [001] axis of the MgO. From rocking curve measurements, it was shown that there was a large mosaic spread indicating that some grains were misoriented towards the (001) direction of the substrate. Typical full width at half maximum (FWHM) measurements of the (005) YBa$_2$Cu$_3$O$_{7-\delta}$ peak were 1.71° for films grown on 5° vicinal MgO, compared to a FWHM of 0.30° for a film grown on annealed (001)-oriented MgO. However, there was no evidence for grains oriented parallel to the substrate [001]
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X-ray pole-figure analysis indicated that no high-angle grain boundaries were present in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown on 5° vicinal MgO. Fig. 3 shows an X-ray pole-figure recorded about the (102) peak of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The 4 distinct spots indicate that no large-angle rotations between domains are present in the film, i.e., the $a$- and $b$-crystal axes of the film are aligned with the substrate crystal axes in the interface plane.

The film microstructure was examined by TEM. Fig. 4 shows a plan-view, bright-field image illustrating the typical microstructure associated with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown on 5° vicinal MgO. The microstructure consists of $c$-axis oriented grains, which have a much larger aspect ratio than that more usually associated with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown on (001)-oriented MgO substrates. The grains are $>400 \text{ nm}$ in length and $\sim 100 \text{ nm}$ wide. $c$-Axis oriented grains in films grown on (001) substrates are usually equiaxed with a diameter of $\sim 400-800 \text{ nm}$ [4]. The predominant direction of the grain boundaries is shown by arrows in fig. 4a. The grains are

direction. This effect has also been observed by other workers [9]. It is interesting to note from this article that as the vicinal angle increased there was a reduction in the mosaic spread.
The following mechanism is proposed to explain the observed microstructure of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films grown on vicinal MgO substrates: the step edges act as preferential sites for island nucleation, as previously demonstrated in TEM studies of film nucleation and growth [4]. It is proposed that the steps not only control the position of island nucleation but also act to align the individual nuclei. During further deposition, grain growth occurs and the individual islands begin to coalesce to form an interconnected microstructure. Because the growing nuclei are aligned with the step edges, as they coalesce there is very little in-plane rotational misalignment, which would result in the formation of a mosaic structure. Instead, the islands coalesce to form an elongated grain. The grains would thus be elongated parallel to the step edges. Because of the parallel array of steps, as shown schematically in fig. 1, the misorientation of the grains perpendicular to the step direction is very small, which accounts for the absence in these films of high-angle grain boundaries, demonstrated by the X-ray pole-figure analysis.

The alignment of the c-axis of the film with the substrate normal rather than the substrate crystallographic direction is somewhat surprising. This observation indicates that growth of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films on vicinal surfaces is a form of graphoepitaxy, in which the topography of the substrate surface controls the film microstructure. It is not conventional heteroepitaxy, where the lattice parameter and crystal structure of the substrate controls the film microstructure. The effect is that the steps cause alignment, but the YBa$_2$Cu$_3$O$_{7-\delta}$ has a strong tendency to grow most rapidly in directions normal to the c-axis. The result is that the misfit at the interface is accommodated in part by a tilt boundary which is superimposed on the interphase interface. Such a mechanism is common in both other oxide systems [14] and has recently been reported for metals [15]. In the situation where there is no lattice rotation, the lattice misfit, $f$, can be calculated from the equation;

$$f = \frac{(a_s - a_o)}{a_o},$$

where the stress-free lattice parameters of the substrate and overgrowth are $a_s$ and $a_o$, respectively [16]. For the situation where the lattice planes of the overgrowth are rotated, the modified lattice parameter for the film becomes $a_m$, where $a_m = a_o / \cos \theta$ as shown in fig. 6, therefore the lattice misfit, $f$, now becomes;

$$f = \frac{(a_s - a_m)}{a_m}. \quad (2)$$
The calculated misfit for different angles of rotation is shown in table 1. From table 1 it can be seen that the lattice misfit decreases with increasing angle of rotation of the tilt boundary. It has been observed that the FWHM decreases for films grown on vicinal MgO where the vicinal angle is $> 10^\circ$ [9]. A possible reason for this observation is that the mismatch is significantly reduced at these high angles thereby favoring, on energetic grounds, growth parallel to the substrate normal. Other factors may influence the distribution of tilt angles which are seen in the X-ray rocking-curve measurements. Of particular importance may be the substrate temperature, which has been shown to affect the surface mobility of the ablated species [17]. It was reported in the above referenced study on metal films [15] that the tilt angle exhibited a weak dependence on growth temperature.

No comparable study has been performed on the growth of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films on a more closely lattice matched substrate, e.g. SrTiO$_3$ or LaAlO$_3$. However, growth of YBa$_2$Cu$_3$O$_{7-\delta}$ on a rough SrTiO$_3$ substrate showed that the c-axis of the film was aligned with the SrTiO$_3$ (001) crystallographic direction on areas inclined a few degrees from the (001) direction [18]. This cited study was not a comprehensive examination of film growth on misoriented surfaces, but may provide an insight into film growth on vicinal surfaces where there is not a large lattice mis-

Table 1

<table>
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<tr>
<th>Angle of rotation (deg)</th>
<th>Misfit (%)</th>
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<tr>
<td>0</td>
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<td>3.43</td>
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$^a$ Calculated from eq. (2).

match. For the systems YBa$_2$Cu$_3$O$_{7-\delta}$/SrTiO$_3$ and YBa$_2$Cu$_3$O$_{7-\delta}$/LaAlO$_3$, where the lattice misfit is 2.3% and $-1.1\%$, respectively, there may be no reason based on energetic considerations for formation of the tilt boundary at the interface. This hypothesis is being investigated as part of the continuing study of the growth of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films.

Further work is in progress to examine the nature of the film–substrate interface on an atomic scale using high-resolution electron microscopy. These studies should reveal the local structure of the film at the step edge and provide a more detailed understanding of the interface structure. Another aspect of this research is to study film growth on non-lattice matched substrates (e.g. MgO) which have been patterned using lithographic techniques as a means to control film growth.

5. Conclusion

In conclusion, highly oriented YBa$_2$Cu$_3$O$_{7-\delta}$ thin films have been grown on vicinal MgO substrates by pulsed-laser ablation. The topography of the substrate surface controls the nucleation and growth of the films, thereby enabling formation of YBa$_2$Cu$_3$O$_{7-\delta}$ thin films on a non-lattice matched substrate without the creation of high-angle grain boundaries. A model has been proposed to explain the observed orientation effect, wherein the misfit at the film–substrate interface is relieved by the formation of a tilt boundary.
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