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Microstructures of *a*-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films prepared by low temperature and template processes

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Highly *a*-axis oriented epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ have been prepared by both a low temperature process and also a self-template technique. Films deposited at low temperature showed good crystallinity whereas films grown on a template exhibited a high transition temperature into the superconducting state. Detailed transmission electron microscopic investigations have been performed on these two kinds of *a*-axis oriented films. Significant differences have been found in the microstructures of these films. The dominant defects formed in these films are misoriented grains which mainly show a *c*-axis orientation. The origin of the nucleation of misoriented grains is attributed to surface defects of the substrate. No boundary between the template layer and upper layer could be distinguished for films made by the self-template process. A thin *c*-axis intermediate layer with a thickness of 2–5 unit cells was observed at the interface between the *a*-axis film and the $SrTiO_3$ substrate for both kinds of films. The formation and influence of such an intermediate layer needs further study.

1. Introduction

Epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ (YBCO) with *a*-axis orientation have considerable potential in the development of multilayer superconducting devices. Considerable effort has been expended in order to prepare *a*-axis oriented thin films using different deposition processes [1–4]. The work reported to date has shown that it is difficult to obtain *a*-axis oriented films with a quality comparable to that of *c*-axis oriented epitaxial films. The techniques used to grow *a*-axis films have included lowering the deposition temperature, using a template layer of non-superconducting $PrBa_2Cu_3O_{7-\delta}$, and employing a varying temperature process, the so called 'self-template' technique [1–3, 5]. The low temperature process is relatively simple and may produce *a*-axis films with a very good crystallinity. However, the transition temperature into the superconducting state for films made by this technique is very low [3]. It is not clear why these highly crystalline films have such poor superconducting properties. An oxygen disorder and deficiency might contribute to the degradation of the superconducting properties [6]. In contrast, films grown on a template can have superconducting transitions approaching that of typical *c*-axis YBCO thin films, however they posses a relatively poor crystallinity.

In the self-template method, the initial nucleation and formation of the 'bulk' films are separated. In the first stage of deposition, nucleation is initiated at a low substrate temperature since this is favourable to the formation of an highly crystalline *a*-axis oriented YBCO layer. In the second stage, a high substrate temperature is used. The template layer formed in the early stage can act as a guide seed to force the films to grow with an *a*-axis orientation. Unfortunately, such a large variation in the deposition temperature introduces lattice strains and microstructural defects into the grown films.

An understanding of the correlation between the superconductivity and microstructural characteristics of these *a*-axis thin films is of practical significance. It would provide important information to further improve the quality of *a*-axis thin film. In this paper we describe the microstructural features of *a*-axis YBCO films revealed by transmission electron microscopy (TEM). The study was carried out mainly on cross-sectional TEM samples. Films made by both the low temperature and self-template processes are compared and discussed.

2. Experimental procedure

The YBCO thin films were grown using a modified off-axis rf-magnetron sputtering technique. Details of this deposition technique have been previously published [7]. Briefly, in addition to the usual off-axis sputtering technique, we have placed a copper plate facing the target at an angle of about 45°. This copper plate is earthed and covered by a thick YBCO layer. By using such a modification, most negative ions produced in the sputter plasma are accelerated toward the grounded plate and are neutralized. Since there is no electric field between the copper plate and the substrate heater (both on ground potential), the sputtered atoms will reach the substrate well thermalized. Hence the problem of film bombardment by oxygen negative ions has been significantly diminished. Moreover, the growth rate and the uniformity of the films are also found to be improved as compared with conventional off-axis sputtering.

A sintered stoichiometric YBCO ceramic disc with a diameter of 50 mm and a thickness of about 4 mm has been used as the sputtering target. All films were grown on single crystal substrates of $SrTiO_3$ (STO) with a (100) orientation. The surface of the substrates were well polished and cleaned. In order to fabricate oxide films, a mixture of argon and oxygen with a ratio of $Ar:O_2 \approx 2:1$ has been used. The total sputter pressure was about 6 Pa. The input rf-power was about 80 W which yields a power density of 4 W cm^{-2}. To improve the thermal contact between the heater and substrate, the substrates were stuck onto the heater with silver glue. The temperature of the substrate is measured by a k-type thermocouple which is inserted into the heater. Such measured values of the deposition temperature are believed to approach to the actual temperature on the substrate surface.

To compare the structural characteristics of the template and the 'bulk' film, samples used for this work were grown by both the low deposition temperature and the self-template processes. The first kind of films were prepared at a heater temperature of about 650 °C and deposited with the usual sputter parameters stated above. The second kind of films were fabricated using the self-template process. A template layer was first grown at 650 °C and then the heater temperature was increased to about 750 °C within a few minutes at which point the upper layer was deposited. After the deposition process, oxygen with a 1×10^5 Pa pressure was introduced into the deposition chamber. The heater was then cooled down to about 450 °C over a period of about 15 min and at this point the heater was switched off and the sample was cooled down to room temperature.

X-ray diffraction was used to analyse the crystallinity and the orientation of the grown films. The local composition of the films was analysed by energy dispersive X-ray spectroscopy (EDS) analysis. Cross-sectional TEM samples were prepared by gluing two pieces of film together face to face using an epoxy resin. They were then cut with a diamond saw into thin slides and mechanically ground to about 30 μm in thickness. Finally the samples were further thinned by ion milling until perforation occurred. The images were observed using a Jeol JEM-2000FX TEM. Selected area electron diffraction as well as energy dispersive X-ray spectroscopy were used to determine the phase structure.

3. Results and discussion

The films made by the low temperature process and the self-template technique have been studied. The critical temperatures of the films grown at low deposition temperature were found to be 60–70 K. Such values are significantly lower than those of films grown by the self-template process. The latter showed typical transitions near 90 K. Before the superconducting transition, films grown at low temperature exhibited a semiconductive or very weak metallic behaviour as indicated by the ratio of the resistivity at room temperature to that at 100 K (RRR). The values of RRR are less than 1.2 whereas for films made by the self-template process it approaches 3. The normal state resistivity of these two types of films are also quite different. It has been found that there is a correlation between the superconducting properties and thickness of the upper layer (the layer deposited at high temperature), as is shown in Fig. 1.

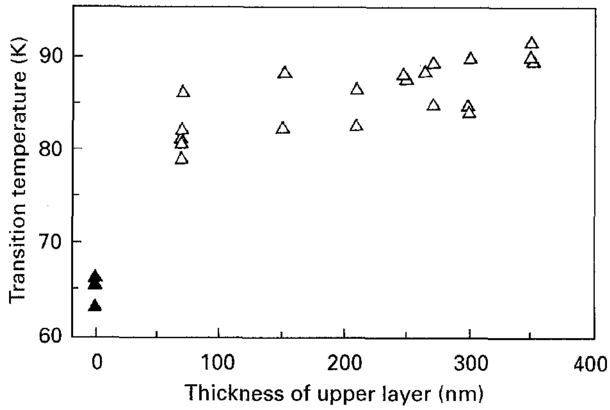
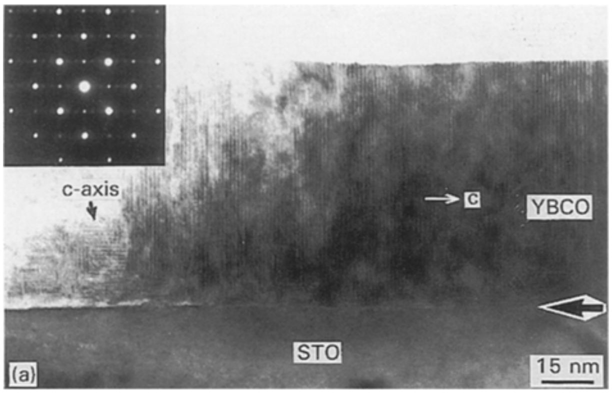


Figure 1 The transition temperature as functions of the thickness of the upper layer. The data for a zero thickness for the upper layer were measured on typical films deposited at low temperature. The data for films deposited at low temperature are represented by the symbol (▲) whilst those for the films made by a self template process are represented by the symbol (△).

In order to examine the crystallinity and phase structure formed in these films, X-ray diffraction has been performed on a number of samples. In addition, the quality of the epitaxy of these films has been further studied by measuring the full width at half maximum (FWHM) of the rocking curves. Both types of films show a high degree of *a*-axis orientation. The diffraction patterns always reveal a highly oriented structure with the *a*-axis perpendicular to the substrate surface. For films grown at low deposition temperature, only the (l00) peaks and the substrate peaks are visible in the diffraction pattern. No reflections due to either random crystallographic orientations or to secondary phases have been observed in the X-ray diffraction experiments. The FWHM of the (100) peak on the rocking curve is found to be less than 0.25 °, indicating a good crystallinity.

In contrast, films grown by the self-template process showed relatively larger FWHM values, ranging between 0.33–0.45°, depending on the thickness of the upper layer. The appearance of very small (00l) peaks on the X-ray diffraction pattern indicates that a small amount of *c*-axis grains have been formed in the film although *a*-axis epitaxy is dominant. However, abrupt superconducting transitions near 90 K have been obtained for many films deposited by the template method.



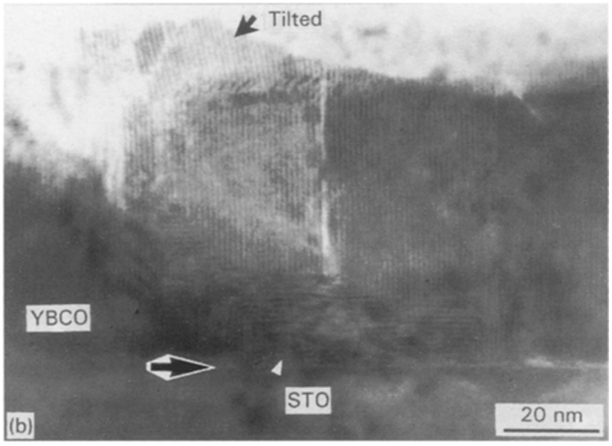


Figure 2 (a) Cross-sectional TEM micrograph of a film deposited at low temperature. The inset is the related selected area electron diffraction pattern. (b) TEM image showing a large *c*-axis nucleus on the STO substrate and a tilted YBCO *a*-axis grain with a tilt angle of $\sim 8°$.

The microstructures studies by TEM confirm the above observations. A typical cross-sectional TEM image of a film deposited at low temperature and the related selected area diffraction pattern are shown in Fig. 2a. The thickness of this film is about 70 nm. As can be seen from the micrograph, the growth with *a*-axis orientation is of high quality. Very few structural defects such as stacking faults and dislocations, which are very common in *c*-axis YBCO thin films, can be found. The most commonly observed defects in the TEM images are small misoriented grains, mainly with *c*-axis orientational although no $(00l)$ peaks have been observed in the X-ray diffraction spectra. Sometimes such grains have a tilted orientation with a small angle to the *a*-axis. A typical grain of tilted YBCO is shown in Fig. 2b. The tilt angle is about 8°. Near the interface between the film and the STO substrate there is a large *c*-axis nucleus or grain which is indicated by a white arrow head in the picture. It seems that those misoriented grains were nucleated near the film/substrate interface, if not directly on the surface of the STO substrate.

As can be seen from the TEM pictures, we have found a thin intermediate layer formed at the film/substrate interface. Such as intermediate layer seems to consist of *c*-axis oriented structures. The occurrence of an intermediate layer is a common feature for *c*-axis YBCO films deposited on a ZrO_2 substrate [8,9]. It is believed that such an intermediate layer is due to interaction between YBCO and the ZrO_2 substrate, producing $BaZrO_3$. However the existence of an intermediate layer between *c*-axis oriented YBCO and an STO substrate has been seldom reported to date. Such an intermediate layer could be due to the growth dynamics rather than an interaction. Our observation would suggest that the *c*-axis oriented intermediate layer was first nucleated and formed on the (100) surface of STO. The thickness of such a layer is between 2–5 unit cells but some grains could be larger, such as the one indicated by the black arrow on Fig. 2b. Subsequently the *a*-axis oriented film is formed and grown on the intermediate layer. At the moment it is uncertain whether this is a common phenomenon for the growth of *a*-axis YBCO thin films. As mentioned previously, such a *c*-axis oriented intermediate layer might be further developed to a large grain size.

In comparison with films deposited at a low temperature, the *a*-axis oriented films made by the self-template method revealed relatively poor crystallinity. Various structural defects are visible on TEM images. Fig. 3a presents a cross-sectional TEM view showing a large *c*-axis grain. The selected area diffraction pattern shows reflections from both *a*- and *c*-axis structures. It can be clearly seen that such a grain was directly grown on the STO substrate. It should also be noted that the STO substrate under this grain is not flat. This might be the origin for the nucleation of misoriented grains. Fig. 3b shows another similar case: a large *c*-axis grain and related diffraction pattern. The matching of YBCO and STO is YBCO [100]//STO [100]. Namely the incident direction of the electron beam is parallel to the [100] of the grain. The photo clearly shows that the grain is located on a hollow in the STO substrate. We have frequently observed that such misoriented grains, particularly large grains, are nucleated on a substrate surface defect.

Fig. 4a demonstrates two adjacent *c*-axis grains embedded in the *a*-axis film. From the electron diffraction pattern it is simple to observe that the orientations of these two grains are different. The [110] direction of the left hand grain is parallel to the incident direction of the electron beam whereas the right hand one has its [100] direction parallel to the electron beam. Also there is a tilt angle of $\sim 5°$ between the *c*-axes of the two adjacent grains. In addition to the *c*-axis grains other kinds of structural defects such as gaps, precipitates, etc., have also been observed in TEM studies, as is shown in Fig. 4(b and c). We have found that there are some small precipitates with typical sizes of about 10 nm produced in the film. These small grains are oxide compounds, most probably Y_2O_3.

It should be pointed out that we have not observed any significant boundary caused by the variation of deposition temperature during the film growth. Namely, we cannot clearly distinguish the template layer from the upper layer on the cross-sectional TEM images although they were grown at quite different deposition temperatures. On the other hand, intermediate layer like *a*-axis structure can also be found

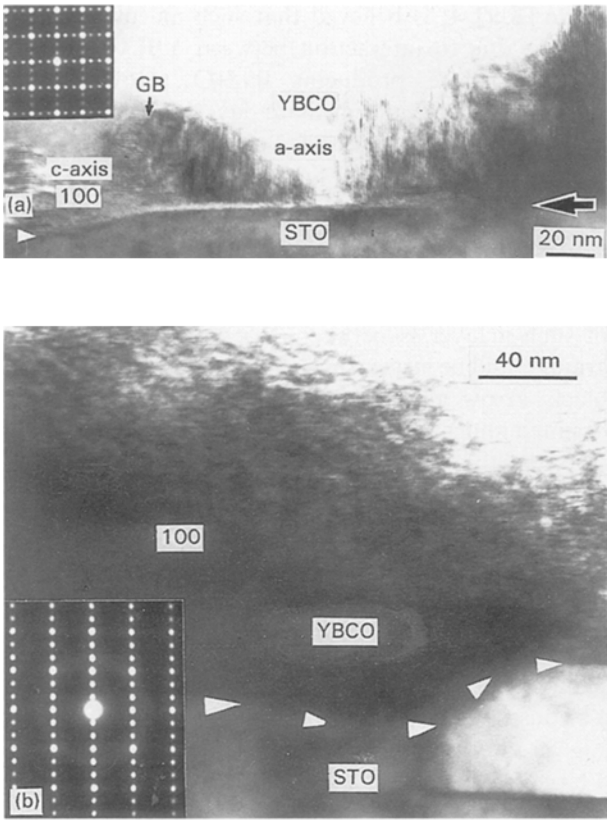


Figure 3 (a) TEM cross-sectional view for a film grown by the self-template process. The electron diffraction pattern shows a mixture of *a*- and *c*-axis structures. Please note that some *c*-axis structures are formed at the interface. (b) Two adjacent *c*-axis grains in an *a*-axis oriented film grown on a template. There is an angle of about 5° between the axes of these two grains.

for films made by the self-template method, as indicated by the black arrow in Fig. 3a. A more detailed investigation on this intermediate layer using high resolution TEM is in progress.

4. Conclusions

Highly *a*-axis oriented epitaxial thin films of YBCO have been prepared by both a low temperature deposition process and a self-template technique. Films deposited at low temperature showed good crystallinity whereas films grown on a template exhibited a high transition temperature. The microstructures of these films has been investigated by using TEM. Differences in the microstructures of these two kinds of *a*-axis films have been found and discussed. The dominant structural defects in the *a*-axis films are misoriented grains, mainly with *c*-axis orientation. The origin of such grains may be attributed to substrate surface defects. No significant boundary between the template layer and upper layer could be distinguished although they were grown at quite different deposition temperatures. On the other hand, a thin *c*-axis intermediate layer with a thickness of 2–5 unit cells has been observed at the interface between the *a*-axis YBCO film and the STO substrate. It is not clear whether such an intermediate layer is a common feature for growing *a*-axis YBCO thin films on STO substrates. The formation of such an intermediate layer and its influence on the growth of *a*-axis oriented YBCO thin films needs to be further studied.

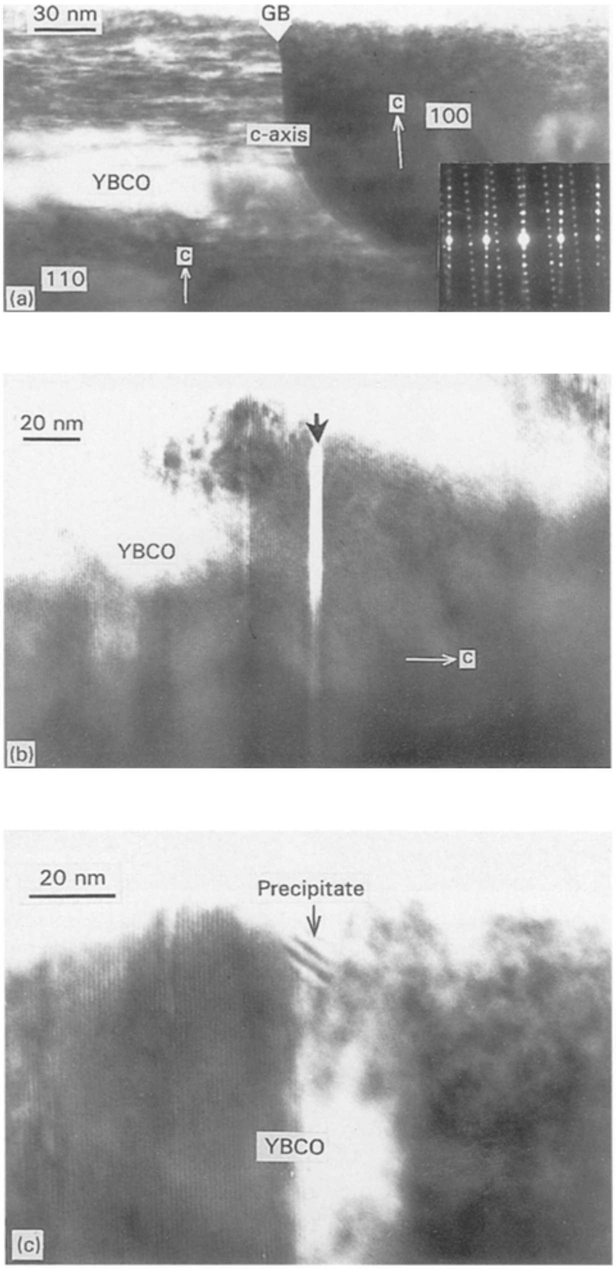


Figure 4 Various defects appeared in films prepared by self-template process: (a) Micrograph of two adjacent misoriented grains embedded in the *a*-axis film. The orientation of these two grains is different. The [110] direction of the left hand grain is parallel to the electron beam. Meanwhile the one at the right hand side has [100] parallel to the beam. The angle between the two *c*-axes is about 5°. (b) A gap formed in such *a*-axis films as denoted by the black arrow. (c) A small precipitate with a size about 10 nm, probably being a grain of Y_2O_3.

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