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TEM investigation of $YBa_2Cu_3O_7$ thin films on $SrTiO_3$ bicrystals

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Abstract

$YBa_2Cu_3O_7$ films in *c*-axis orientation on bicrystalline $SrTiO_3$ substrates are investigated by TEM. The films and the substrates are examined in cross-section and in plane view. The grain boundary of the bicrystal substrate contains (110) faceted voids, but is otherwise straight on a nanometer scale. Contrary to this, the film grain boundary is not straight. The deviation from a straight grain boundary can be up to 100 nm for a 100 nm thick film. The deviation from the intended position of the YBCO grain boundary can already occur at the film/substrate interface where it can be as much as ±50 nm.

1. Introduction

An important future application of high-temperature superconductors in electronics will be their use as Josephson junctions. For *c*-axis oriented $YBa_2Cu_3O_7$ (YBCO) different types of Josephson junctions have been reported, e.g. ramp junction [1], junctions based on a multicomponent template layer (e.g. bi-epitaxial AlO_3/MgO or $NdGaO_3$/YSZ) [2,3] or a bicrystal [4,5].

The ramp type and the template-layer type junctions can in principle be made in large quantities which make them potential candidates for use in devices. However, the bicrystal technique allows one to control the macroscopical angle freely, thus allowing determination of the dependence of the critical current density (J_c) across the grain boundary (GB) as a function of the macroscopic angle. Dimos et al. performed such a study which showed that J_c is strongly correlated with the macroscopic tilt angle [4]. Compared to the bicrystals, the grain boundary in the ramp type junction is difficult to control whereas in the template layer type junction the macroscopic angle is fixed given a chosen materials system.

Dimos et al. have prepared bicrystal type junctions by growing a thin film of YBCO on bicrystalline $SrTiO_3$ substrates. Based on the assumption that the GB of the YBCO "follows" the GB of the substrate Dimos et al. made thin strips across the grain boundary over which they measured J_c. An important question in this respect is whether the GB of the YBCO film really "follows" the GB of the substrate. In order to test this for the symmetrical grain boundaries a TEM study was started on which some preliminary results were reported earlier [6] on the actual location of the GB in the YBCO thin films grown on various $SrTiO_3$ bicrystalline substrates with symmetrical grain boundaries having angles of 36.8°, 53.2° and 67°. As will be shown in this paper the grain boundary of the film deviates in general strongly from the intended straight plane.

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2. Experimental

Fused/sintered $SrTiO_3$ bicrystals were purchased from a commercial source (WAKO BUSSAN CO, Ltd.). The grain boundary is intended to be a pure symmetrical [001] tilt boundary, in this case with a common *c*-axis. Bicrystals with a [001] rotation angle of 36.8°, 53.2° and 67° [1] respectively were used. The geometries of these grain boundaries are shown in Fig. 1, as well as the convention of notation used in this text. In this notation each angle is associated with only one habit plane being the plane contained within the measured angle. The indices 1 and 2 refer to the crystal one and crystal two, respectively. In the following the short term "GB_{SrTiO_3} plane" will be used for the grain-boundary plane of the bicrystalline $SrTiO_3$ substrate. In general the plane which is shared by the two crystals can be described by specifying the planes in each of the two crystals which is parallel with the common boundary plane. For $\Omega = 36.8°$, 53.2° and 67° one then has the notation $(310)_1 \| (310)_2$ (theoretical angle is 36.87°), $(210)_1 \| (210)_2$ (theoretical angle is 53.13°) and $(320)_1 \| (320)_2$ (theoretical angle is 67.38°).

C-axis YBCO films were grown by laser ablation and sputtering on the $SrTiO_3$ bicrystalline substrates.

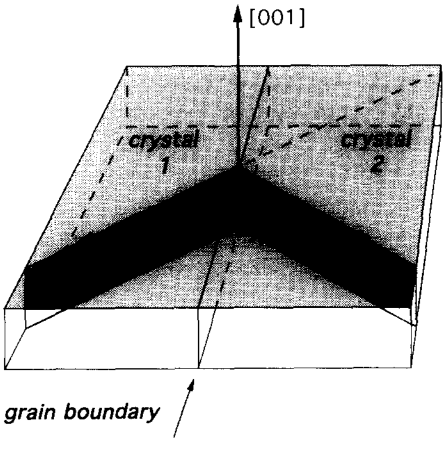

Fig. 1. A schematic figure of the bicrystal grain boundary which defines the notation used in this work.

[1] The manufacturer of the bicrystal substrate indicated an angle of 66°. However, it was measured to be 67° and will be referred to as such.

Electron microscopy was performed with a Philips CM30ST-FEG operated at 300 kV.

The samples were investigated by TEM in plane view (both film and substrate) and in cross-section. For the plane-view studies of the film or of the substrate the as-received samples were mechanically back-thinned to < 10 μm and then ion milled. The cross-section specimens were made by grinding the sample to less than 10 μm following a previously reported procedure [7] and finally ion milled carefully until the grain-boundary area was electron transparent.

3. Results

3.1. Substrate grain boundary

The substrate grain boundaries (GB's), for $\Omega = 36.8°$, 53.2° and 67°, are found to be straight except for some voids on the grain boundary and steps of a few atomic layers. An example of the straight GB with a few voids is shown in Fig. 2. The microscopic roughness in the GB is only of the order a few unit cells of $SrTiO_3$.

The 67° GB corresponds locally (20 nm) to a $\Sigma 13$ GB (here and in the following it is assumed that YBCO can be approximated with a tetragonal structure, thus the term Σ- GB can be used). A high-resolution image of a $\Sigma 13$ GB is shown in Fig. 3. In this GB the bicrystals share a common (320) plane. Theoretically the $\Sigma 13$ GB is related to a tilt angle of 67.38°. From the diffraction pattern the macroscopic angle is found to be ≈ 67° which is in agreement with the combination of a $\Sigma 13$ GB (67.38°) with some occasional steps of a few atomic steps.

The $\Omega = 53.2°$ GB corresponds to the theoretical $\Sigma 5$ GB with a tilt angle of 53.13°. In this $\Sigma 5$ GB the two crystals share a common (210) plane. From the diffraction pattern the macroscopic angle is measured to be ≈ 53° in good agreement with the intended angle. The alternative $\Sigma 5$ GB, related to the angle 53.13°, was investigated in plane view in but only a specimen section which contained both the whole YBCO film (15 nm) and some of the substrate. This also indicated that the flatness of the 36.8° GB of the substrate is comparable to the 53.2° GB.

The three bicrystals show apart from the intended

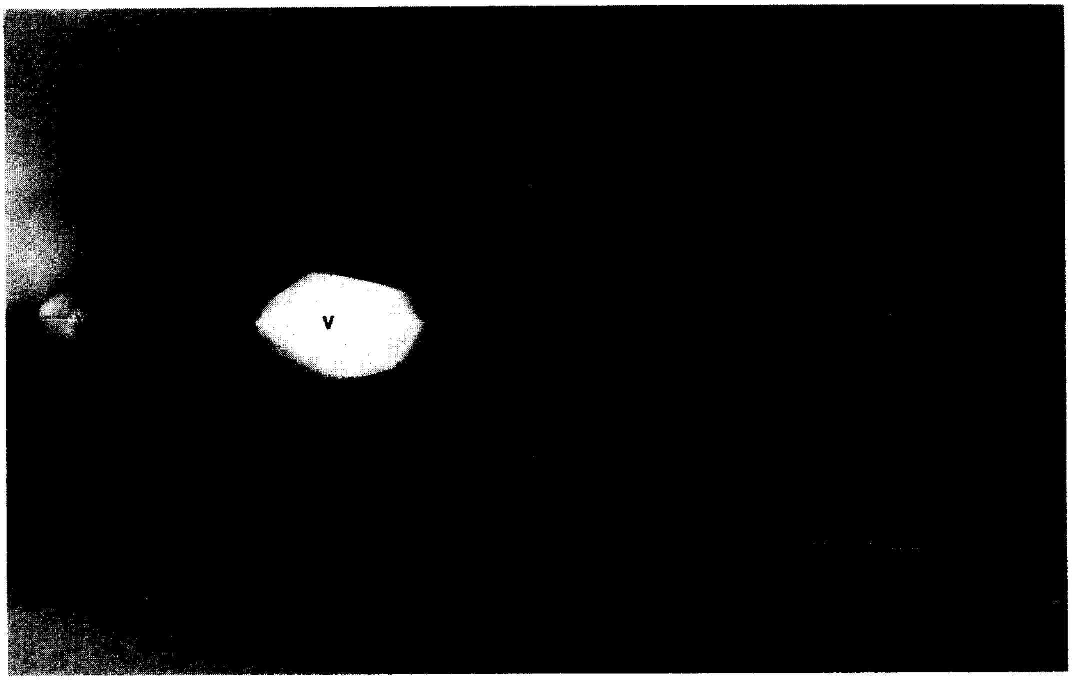

Fig. 2. An [001] low-magnification plane view image of the substrate GB with $\Omega=67°$. The GB (marked GB) is straight and exhibits only little strain contrast. The voids are indicated with a "v".

Fig. 3. An [001] high-resolution plane-view image of the $SrTiO_3$ substrate GB with $\Omega=67°$. A step of the order of a few unit cells can be observed at the GB (marked S). The periodicity (1.4 nm) parallel with the GB corresponding to a $\Sigma 13$ GB is indicated.

[001] tilt also a small additional tilt (< 1°) about a direction perpendicular to the *c*-axis as was evident from changes in the electron diffraction pattern when passing the GB_{SrTiO_3} plane.

3.2. Voids in the substrate

The voids are found to have mainly (110) facets (see Fig. 2) whereas occasionally (100) facets are observed. The voids are almost symmetrical around the GB and the sizes range from 10 nm up to 100 nm. They are distributed randomly in the GB_{SrTiO_3} plane as deduced from plane view, cross-section and stereo imaging. This implies, as is indeed observed, a possibility of the presence of faceted grooves in the intersection of the GB_{SrTiO_3} and the surface, due to the presence of a void at the location where the $SrTiO_3$ bicrystal was cut.

3.3. Film grain boundary

Figs. 4 and 5 show low-magnification images of the YBCO film GB with $\Omega = 53.2°$ and 67°, respectively. In both cases it can be observed that the boundary deviates from a straight line. This deviation is found to be up to ±100 nm in this 100 nm thick film. In the 53.2° GB the straight parts of the GB can be up to 200 nm long whereas in the 67° GB the longest straight part is only of the order 100 nm.

In order to determine whether the deviation from a straight GB_{SrTiO_3} occurs also at the substrate/film interface or is generated further from the interface or is generated further from the interface a 15 nm thick YBCO film was investigated. A plane-view image of the thin YBCO film GB with $\Omega = 36.8°$ is shown in Fig. 6. Moiré fringes are present at some locations near the GB_{SrTiO_3} due to an overlap in the viewing direction of the $(SrTiO_3)_1$ lattice and the $(YBCO)_2$ lattice (or vice versa). With the lattice parameters being 0.39 nm and 0.385 nm, respectively, and given the orientation of the $SrTiO_3$ and YBCO lattices, the spacing of the moiré fringes can be calculated to be 0.61 nm. The orientation of these 0.61 nm fringes should be parallel and perpendicular to the GB, respectively. Both these spacings and the two perpendicular orientations are observed in the experimental

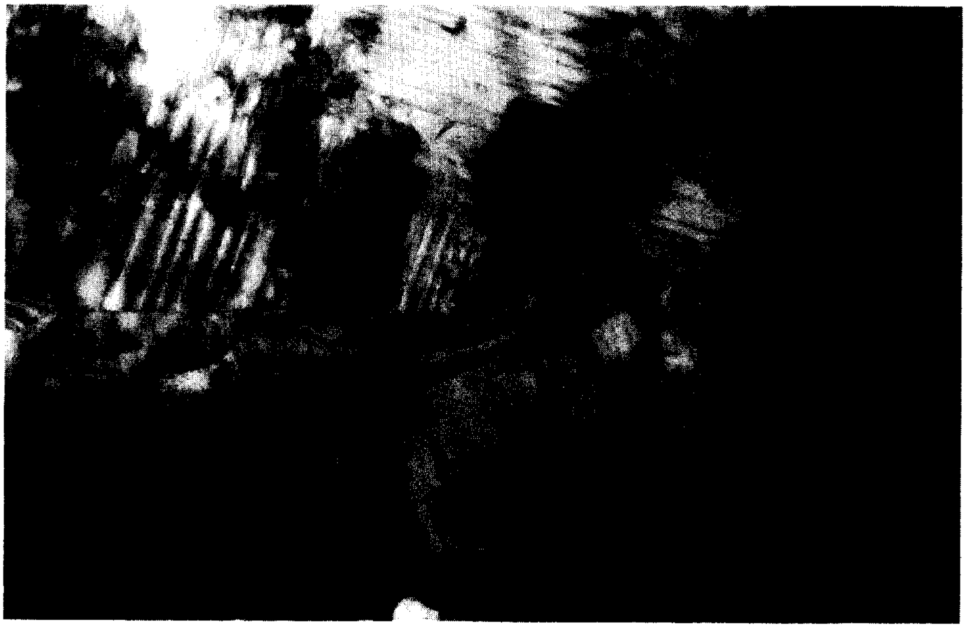

Fig. 4. An [001] low-magnification plane-view image of the 100 nm thick $YBa_2Cu_3O_7$ film GB with $\Omega = 53.2°$. The substrate has been ion milled away. The GB (marked GB) is zig-zagging, resulting in facets other than the intended (210) facet.

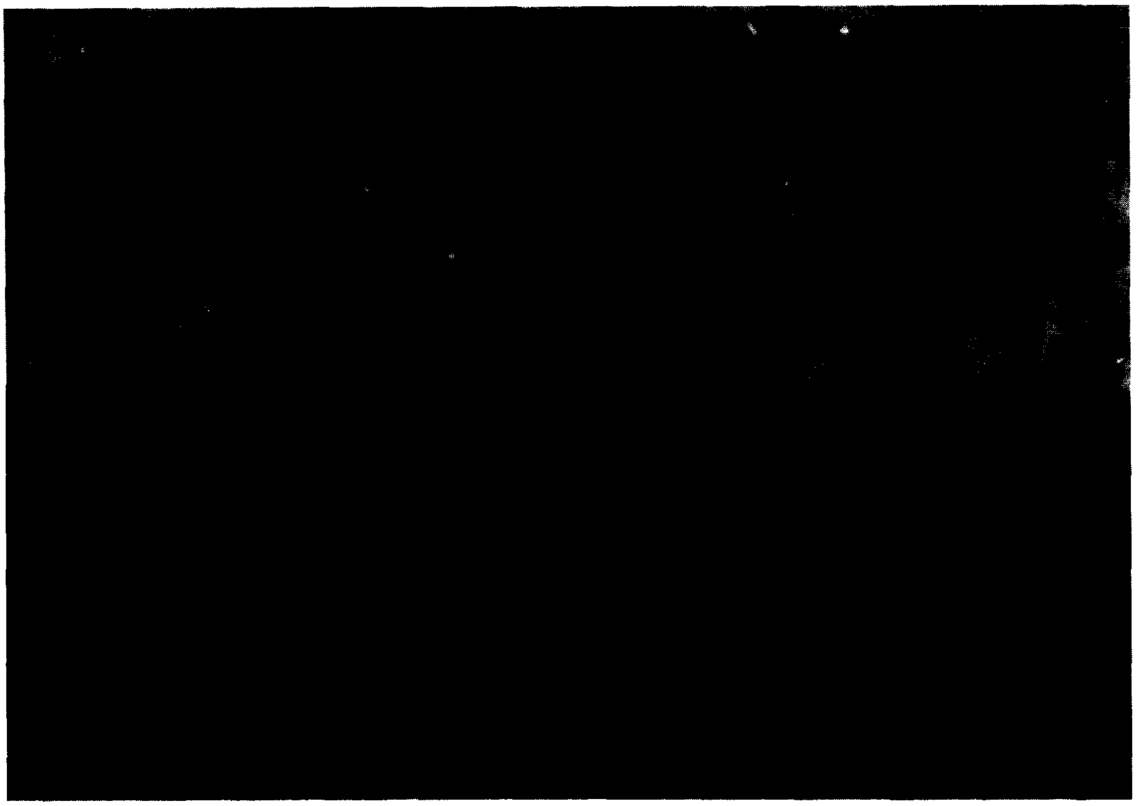

Fig. 5. A low-magnification plane-view image of the YBCO film GB with $\Omega = 67°$. The substrate has been ion milled away. The viewing direction is slightly tilted away from the [001] zone axis in order to improve the contrast between the two sides.

image. The extent of the YBCO film crossing is 15 nm in the image but is in other places found to be up to 50 nm.

Fig. 7 shows a plane-view high-resolution image of a 100 nm thick film GB with $\Omega = 53.2°$. The specimen is about 20 nm thick and is a section close to the surface. The image of the GB is mostly sharp which implies that the YBCO film GB is not strongly inclined in the viewing direction. The film GB deviates from the straight GB_{SrTiO_3} plane. The film GB shows specific facets. The dominant facet is the symmetrical (210) GB which corresponds to the GB_{SrTiO_3}. Another frequently observed facet is the other symmetrical GB where the $(310)_1$ of crystal 1 is parallel to the $(310)_2$ of crystal 2. The angle between the common (310) and the common (210) GB is 45°. A third observed GB is one in which $(100)_1$ is parallel with $(430)_2$ or vice versa $((430)_1 \| (100)_2)$. This GB is asymmetrical. The angle between this GB and the "normal" (210) GB is measured to be about 26° in agreement with the theoretical angle of 26.56°.

3.4. GB in film growth direction

Figs. 8(a), (b) and (c) show an about 70 nm thick cross-section of a 67° GB. The image 8(a) is taken along the $\langle 210 \rangle_1$ in order to highlight one side of the film. From Fig. 8(a) it is clear that the film GB deviates from a straight boundary also in the growth direction. This is in agreement with the broadening of the GB observed in some areas in plane-view specimens (see Figs. 7 and 9) due to the fact that the GB is not parallel with the viewing direction. Image 8(b) shows that no secondary phase is present at the film GB. Image 8(c) shows that the YBCO film is continuous across the GB_{SrTiO_3}. The dark contrast seen in the substrate GB indicates that the substrate GB is affected by the deposition of the YBCO film. This

Fig. 6. An [001] high-resolution plane-view image of a 53.2° GB. The section contains the 15 nm YBCO film superposed on the $SrTiO_3$ substrate. A moiré interference is observed (marked M) due to crossing of the YBCO film over the $SrTiO_3$ substrate GB. The magnitude of the crossing in this image is 15 nm.

can be explained by some in-diffusion of Ba forming $BaTiO_3$ with the lattice spacing 0.40 nm. The dark contrast in this part of the bicrystal can be caused by a difference in the scattering potential (Ba instead of Sr) or strain.

3.5. *Effect of grooves/voids*

In general the GB in the YBCO film is free of any second phases. However some *a*-axis grains are observed around grooves in the GB_{SrTiO_3}. Fig. 9 is a plane-view image of a 67° GB where some *a*-axis grains can be observed which are probably nucleated due to the presence of a groove on the substrate GB. In other areas *a*-axis grains were found to coincide with contrast features (polygon shadows) which are believed to be related to the grooves in the substrate GB. In the plane view specimen of the 15 nm thick film faceted holes were observed to exist in both the YBCO film and the $SrTiO_3$ substrate which indicates that there are indeed grooves present at the GB surface.

4. Discussion

4.1. *Nomenclature*

In the present study of symmetrical tilt boundaries the notation is based on the bicrystalline $SrTiO_3$ system. For a pure symmetrical tilt boundary with a common *c*-axis one can specify a rotation angle around [001] which can be associated with a Σ. Here Σ is a measure of the volume of the unit cell of the coincident site lattice in units of the original unit cell e.g. $\Sigma5$ or $\Sigma13$.

Disregarding a possible in-plane rigid-body translation (a translation of $\frac{1}{2}d_{310}=0.62$ nm was in fact observed by TEM [8] in a 36.8° symmetrical boundary in a $SrTiO_3$ bicrystal) a rotation about [001] leads to two distinct symmetrical GB's on a microscopic

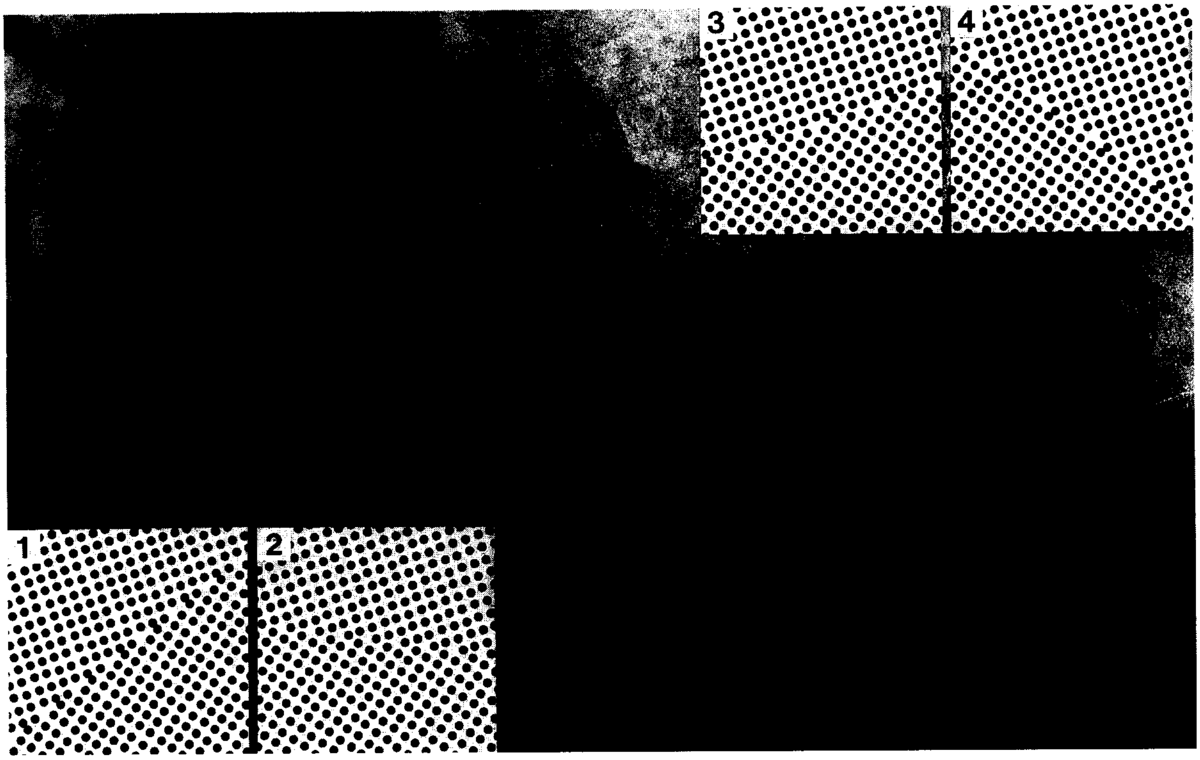

Fig. 7. An [001] high-resolution plane-view image showing the different GB facets which is seen in the 53.2° YBCO GB. The insets give a schematic representation of the different facets. The "normal" GB corresponds to inset number 2.

(structural) scale. These two GB planes are separated by an angle of 45°. Given that it is a pure symmetrical tilt boundary, the GB is completely determined by giving the physical acute angle Ω (0°–90°) between $[100]_1$ and $[100]_2$ which contains the GB as defined in Fig. 1. When the GB is asymmetrical it is necessary to specify the GB plane. The latter is done conveniently (also for the symmetrical case) by specifying the plane in each of the two crystals which is parallel with the GB plane, e.g. $(210)_1 \| (210)_2$ (symmetrical) or $(430)_1 \| (100)_2$ (asymmetrical). One can also use the notation $\Sigma 5$ {210} or $\Sigma 5$ {430}‖{100}. $\Sigma 5$ can be associated with two symmetrical GB's with the complementary angles $\Omega = 36.87°$ and $\Omega = 53.13°$. $\Sigma 13$ can be associated with the two symmetrical GB's having the complementary angles $\Omega = 22.62°$ and $\Omega = 67.38°$.

It should be emphasized that the two symmetrical grain boundaries which are complementary to each other are in fact different on an atomic scale which means that electrical measurements in principle need to be carried out on the whole range from 0° to 90°. Even if there is no direct difference in band-structure calculation of the two atomically different GB's (as can be seen in the insets in Fig. 7), the GB may still show a different susceptibility to GB defects or GB oxygen diffusion which will influence the electrical properties.

4.2. Substrate

The bicrystalline substrates (67° and 53.2°) have a smooth (nanometer scale) grain boundary with randomly distributed voids. In the voids apart from the most common (110) facets also a small fraction of (100) facets was observed. The (110) facets in a void can be up to 50 nm long which depends mainly on the size of the voids (up to 100 nm).

The random distribution of the voids result in the presence of some voids at the surface, resulting in a faceted groove. Grooves with (110) facets were found to trigger the nucleation of YBCO grains with an ori-

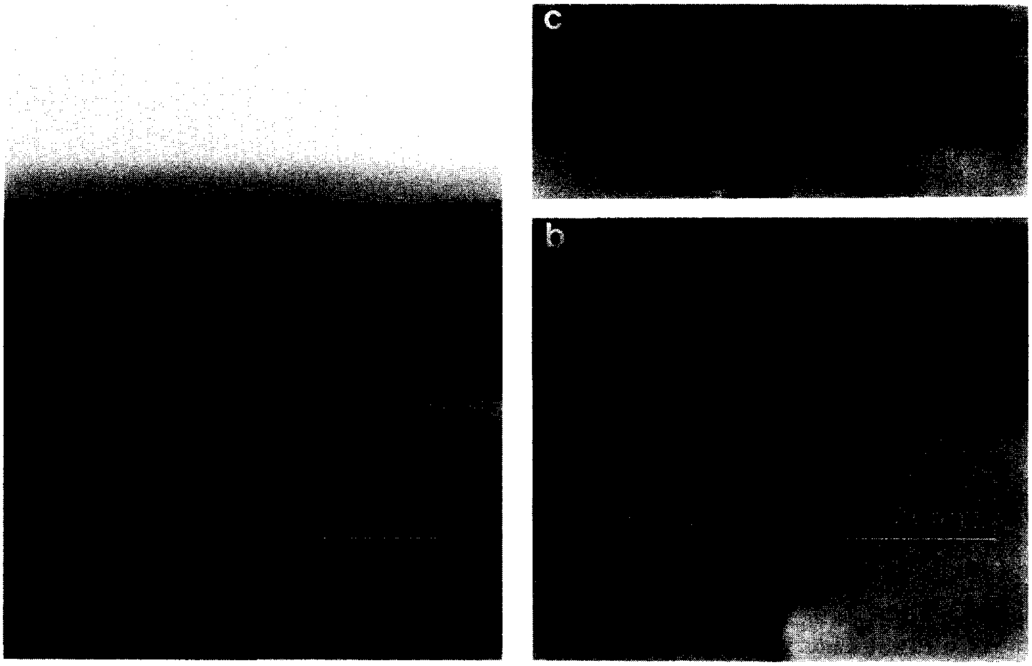

Fig. 8. Cross-section images of a 67° GB, (a) taken along the [210] direction of the crystal on the left side in order to differentiate the two YBCO films; (b) taken parallel to the substrate GB_{SrTiO3} such that the contrast across the boundary is symmetric in order to see whether the YBCO film continues across the GB_{SrTiO3} without interruption from secondary phases. (c) An enlargement of the framed area in (b) showing that the film is continuous.

entation different from the intended c-axis orientation, and usually it is found to be an a-axis grain. This is expected because the (110) facet (in fact (101) or (011)) has an angle of inclination with respect to the (001) plane equal to 45°. TEM investigations on such rather steep surface inclinations showed that the YBCO film tend to nucleate a-axis grain on these [9].

4.3. Film

The YBCO film GB can deviate from the GB_{SrTiO3} plane right from the YBCO/$SrTiO_3$ interface and it can change orientation along the film growth direction. The zig-zagging of the GB is more dominant for the 67° GB along the substrate surface normal as well as in the film plane. Large parts of the 36.8° and the 53.2° [001] rotational GB are straight and oriented as the (underlying) substrate GB. The observation in all three specimens of the in-plane deviation of the film GB from the substrate GB is in agreement with STM and TEM work performed on asymmetrical bicrystalline YSZ substrate [10]. The deviation of the GB from the substrate normal in the film growth direction, as found in cross-section, implies that the maximum deviation from the intended position will increase with increasing film thickness. In plane view a moiré interference is observed in a significant part of the 67° GB indicating an overlap between the YBCO film from both sides of the boundary with respect to the viewing direction. Taken together with the deviation observed in cross-section the moiré interference is an indication of an inclined boundary. For the 53.2° GB only a small amount of inclined boundary is present whereas for the 36.8° GB no clearly detectable inclined GB is observed, the latter may be due the small thickness of the film (15 nm).

A $\Sigma5$ GB represents many different grain boundaries because the $\Sigma5$ notation describes only the orientation relation between the two grains and not the orientation of the GB. The two $\Sigma5$ GB's we investigated are the two symmetrical $\Sigma5$ GB's. The first investigated $\Sigma5$ GB is the GB with $\Omega = 53.2°$ with a 100 nm thick film. In this specimen three different $\Sigma5$ GB's are present. The "main" GB found is similar to

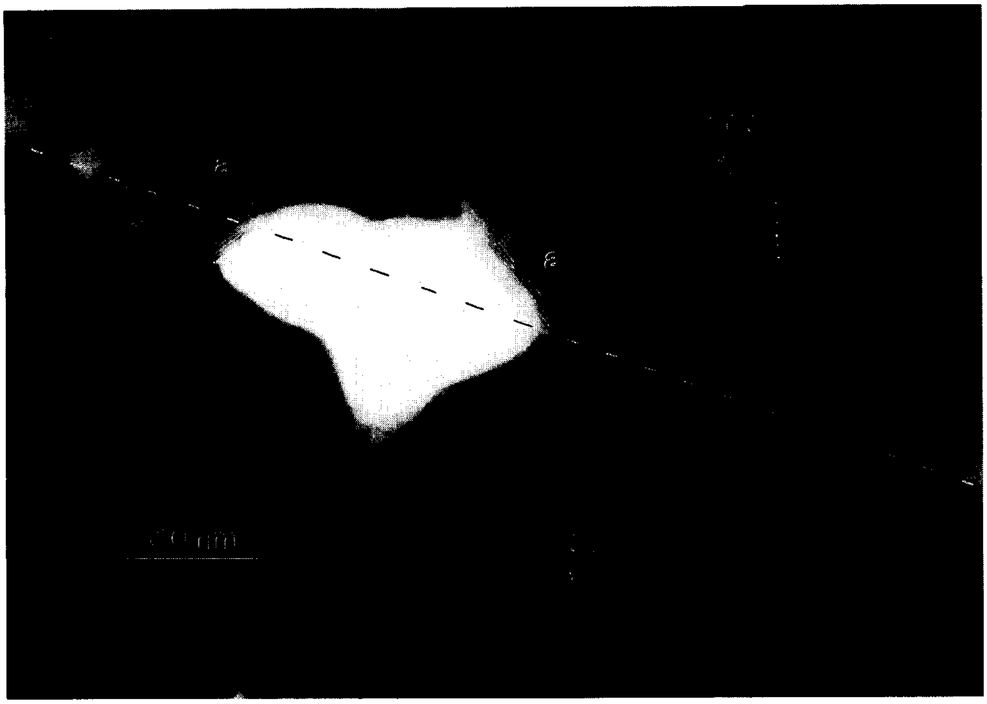

Fig. 9. A plane-view image of the 67° YBCO film GB. The image shows a hole in the film of a size of about 50 nm. Next to the hole two a-axis oriented grains (marked "a") have nucleated. Also a complementary symmetrical GB can be seen (indicated with a " c").

the underlying substrate GB where the two crystals share a (210) plane, i.e. $(210)_1 \| (210)_2$. This GB is flat on a scale up to 200 nm along the GB. Two other facets are found, one where $(310)_1 \| (310)_2$ and one where $(100)_1 \| (100)_2$ or vice versa ($(430)_1 \| (100)_2$). The facets which deviate from the "main" facet only extend up to a length of about 30 nm. The $(100)_1 \| (430)_2$ (and $(430)_1 \| (100)_2$) asymmetrical GB's are such that the GB is parallel with the (100) plane of one of the crystals. With the $\Sigma 5$ orientation relation between both crystals the (430) plane of one crystal will be exactly parallel to the (100) plane of the other crystal. This means that this GB can occur together with the two symmetrical GB's without any additional dislocations.

The sample with a film thickness of 15 nm and $\Omega = 36.8°$ is also a $\Sigma 5$ GB. Here, however, the "main" facet observed is the $(310)_1 \| (310)_2$ which corresponds to the GB facet of the underlying substrate. The other symmetrical GB where $(210)_1 \| (210)_2$ (or vice versa) is found when the GB deviates from the "main" GB. As long as no other facets are present the specific GB where $(120)_1 \| (210)_2$ must occur in pair with the (perpendicular) GB where $(210)_1 \| (120)_2$ in order to compensate a deviation. No GB's having on one side the (100) facet are clearly observed. However, it is most likely that the $(100)_1 \| (430)_2$ is in fact present in a small amount or that it would develop if the film were thicker. The reason the low fraction of (100) facets is probably their less favourable grain-boundary energy compared to those of the two symmetrical boundaries.

A $\Sigma 13$ GB has a theoretical $\Omega = 67.38°$. Experimentally the angle is measured from diffraction patterns to be 67°. In this sample the "main" facet is found to be a GB where $(320)_1 \| (320)_2$ which corresponds to the underlying substrate and to a $\Sigma 13$ GB. This facet is observed to be up to 100 nm long. The complementary $(510)_1 \| (510)_2$ GB is also observed. A GB with on one side a (100) plane is not observed which perhaps can be related to a GB energy consideration. Theoretically the GB which contains a $(100)_1$ plane in crystal 1 will need a $(12\,5\,0)_2$ plane in crystal 2 which is a rather high index plane which will result in a high GB energy. By creating the low-index planes $(100)_1 \| (520)_2$ or $(100)_1 \| (730)_2$ the GB energy can be lowered but this requires rotation angles of $\Omega=68.2°$ (for the (520)) and $\Omega=66.8°$ (for the (730)), respectively. This implies a local misalignment of YBCO lattice of 0.8° or 0.6° which in turn has to be compensated by dislocations to obtain the 67.38°.

In the three cases studied, the average size of a facets is about 50 nm which implies for a strip line having a width of 1 μm one would have 20 separate grain boundaries. On top of this, misoriented grains of the same order of size can occur due to the presence of grooves at the GB whereas these grooves can also lead to holes in YBCO film GB. If the electrical properties for the different facets are different, which is quite likely, the electrical properties over thin strips will show a variation depending on the ratio of the various GB facets occurring in those strips. The presence of yet more GB facets along the YBCO film *c*-axis direction will increase the scatter in the electrical properties. Added to this variation the presence of grooves in the Josephson junction area can result in strong deviating electrical properties or even be deleterious to a device.

Dimes et al. did their measurement on approximately 10 μm narrow lines [4]. This is almost two orders of magnitude larger than the size of the GB faceting, *a*-axis grains and holes. As such their experiment only probed an averaged of the GB microstructure and did not clearly see the possible fluctuations due to different electrical properties of the different microstructure.

5. Conclusion

The TEM study shows that the YBCO film GB deviates considerably from the substrate GB_{SrTiO_3} in spite of an initially straight substrate GB. The film GB is composed of various facets with an average length in the order of 50 nm. Furthermore grooves in the GB surface can lead to unwanted *a*-axis grains and holes on a 100 nm scale. The roughness of the film GB as well as the possible presence of voids will make it difficult to get a reproducible fabrication of Josephson junctions by thin strips across the grain boundary.

Acknowledgements

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