Graphoepitaxy of CeO_2 on MgO and its application to the fabrication of 45° grain boundary Josephson junctions of $YBa_2Cu_3O_{7-x}$

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(Received 12 December 1994; accepted for publication 26 June 1995)

We communicate a detailed study of the epitaxial growth of CeO_2 on MgO. The key feature of the growth is the dependence of the in-plane orientation of the CeO_2 epitaxial layer on the MgO surface morphology. Atomic force microscopic (AFM) measurements, x-ray analyses, as well as high-resolution transmission electron microscopy (HRTEM) investigations reveal that on rough substrates a cube-on-cube growth of CeO_2 on MgO occurs while on smooth substrates the CeO_2 unit cell is rotated around the surface normal by 45° with respect to the MgO unit cell when the deposition rate is low (~0.3 Å/s) during the first stages of growth. This growth mechanism can be used for a defined fabrication of 45° grain boundaries in the CeO_2 layer by controlling the surface roughness of the MgO substrate. This report demonstrates that these 45° grain boundaries may be used to fabricate $YBa_2Cu_3O_{7-x}$ Josephson junctions. © *1995 American Institute of Physics.*

I. INTRODUCTION

Grain boundaries in crystalline high temperature superconductors (HTS) can act as Josephson junctions. Their application in electronic devices makes it necessary to produce grain boundaries in a controllable and reproducible way. This can be realized by the deposition of an $YBa_2Cu_3O_{7-x}$ (YBaCuO) thin film over a substrate step,[1] by using bicrystals[2] and by the biepitaxial method.[3] In the biepitaxial method, a 45° grain boundary is produced by the controlled change of the in-plane orientation of an epitaxial YBaCuO film.

Up to now, many different combinations of materials have been used in the biepitaxial process. The process includes the deposition of a seed layer, patterning of the seed layer, and, subsequently, the deposition of a buffer layer and of the superconductor YBaCuO. The 45° grain boundary is formed at the boundary between the regions with and without seed layer.

This report communicates the dependence of the in-plane orientation of CeO_2 on MgO (100) with the morphology of substrate and the deposition rate. It can be used to produce well defined 45° grain boundaries, without any additional seed layer.

The relationship of an epitaxial layer on a substrate is determined by the interfacial energy and the lattice mismatch, which leads to strain energy. The layer orients itself in such a way that the lattice mismatch is small and the interfacial energy is minimized. Depending on the nature of substrate and film one or more epitaxial relations can be possible. The cluster nucleation depends on the substrate temperature and deposition rate and consequently both parameters can determine the epitaxial relationship. Additionally, the substrate surface morphology can influence the in-plane orientation of an epitaxial layer. Surface steps act as nucleation centers and can impose a certain in-plane orientation of the growing film. This mechanism is known as graphoepitaxy. Graphoepitaxially determined growth of oxides has been observed in the system YBaCuO on MgO and YBaCuO on yttria-stabilized zirconia (YSZ). Norton *et al.* and Pennycook *et al.* deduced from the fact that the interface between YBaCuO and MgO is incommensurable without localized strain fields that the epitaxial alignment of the YBaCuO grains is acquired at atomic steps.[4] Recent results of one of the authors indicate on the other hand that this can also be explained by a rearrangement process during initial growth without any graphoepitaxial mechanism.[5] Brorsson *et al.* showed that the in-plane alignment of YBaCuO on YSZ is sensitive to the surface morphology. Using YSZ substrates of different roughness they showed that the [110] YBaCuO//[100]YSZ orientation is promoted by a graphoepitaxial mechanism.[6]

MgO is a highly ionic insulating solid, crystallizing in the NaCl structure. It has low-energy, charge neutral (100) cleavage planes. The lattice constant of MgO is 4.2 Å. CeO_2 has a cubic fluorite-type structure with a lattice constant of 5.4 Å. The smallest epitaxial misfit of ~10% is achieved when the CeO_2 unit cell is rotated around the surface normal by 45° with respect to the MgO unit cell, i.e., with an in-plane orientation: CeO_2[110]//MgO[100].

In contrast, a nonrotated growth mode (cube-on-cube) with an in-plane orientation CeO_2[100]//MgO[100] results in a misfit of about 22%. However, a smaller misfit of 4% is calculated when the epitaxial growth is described in terms of domains, since three lattice parameters of CeO_2 match with

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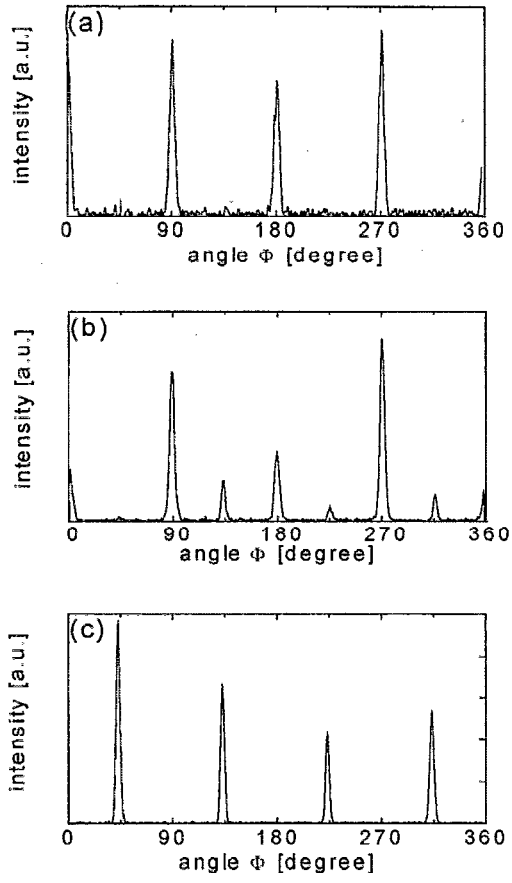

FIG. 1. X-ray ϕ scans of CeO_2 (420) on different (100) MgO substrates. (a) For a rough MgO substrate, (b) for a smooth substrate. 0° corresponds to a [100] substrate direction being parallel to the diffracting plane.

four of the MgO substrates. Therefore, the lattice mismatch strain in this orientation is large but the one associated with the domains is comparatively small.

Cube-on-cube and a multi-in-plane orientation of CeO_2 on MgO has been reported by many groups.[3,7] To our knowledge there are no previous reports of CeO_2 grown on MgO with a pure 45° rotation. Here, we report on our ability to induce both orientations of the CeO_2 on MgO in a controlled way. As a key factor, we regard the surface morphology of the substrate and the deposition rate during the first stages of growth.

II. EXPERIMENT

Thin films of CeO_2 and MgO were deposited on MgO by electron beam evaporation from pellets of CeO_2 or MgO. The deposition was performed at an oxygen partial pressure of $1-2\times10^{-4}$ mbar. Optimum crystalline quality was achieved at a substrate heater temperature of 900 °C for CeO_2 and 525 °C for MgO.

We deposited CeO_2 on three types of MgO substrates of different polishing, i.e., of different surface roughness.

The crystalline quality of the CeO_2 films was studied by Rutherford backscattering spectrometry (RBS) and channeling, using 1.4 meV He^+ ions incident normal to the sample surface. The orientation was studied by x-ray diffraction measurements. The surface quality was characterized by

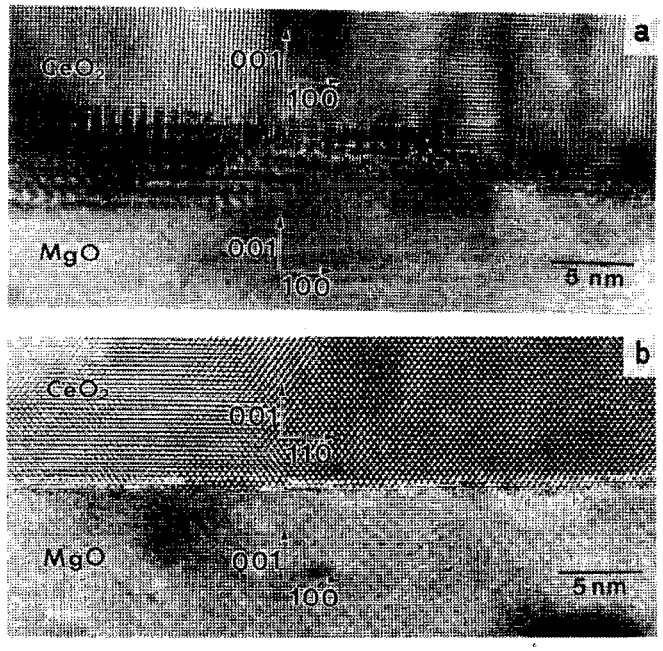

FIG. 2. Cross sectional lattice fringe images of two CeO_2 films grown on a rough MgO substrate (a) and on a smooth substrate (b). The different orientations of the CeO_2 with respect to the MgO are indicated by arrows.

cross sectional lattice fringe transmission electron microscopy (TEM) and noncontact atomic force microscopy. All CeO_2 films were of high crystalline quality. A minimum yield in the channeling spectra in the [100] direction of less than 5% was measured. X-ray measurements of the (004) CeO_2 reflex showed a rocking curve width of 0.5° to 1°, independent of the in-plane orientation of the film.

III. RESULTS AND DISCUSSION

The deposition of CeO_2 on smooth MgO substrates without a controllable deposition rate does not ensure reproducibility. Cube-on-cube films are obtained when deposition rate in the first stage of deposition is high whereas the 45° rotated growth occurs for low deposition rate. A shutter was placed to fix the deposition rate. A low deposition rate of about 0.3 Å/s warrants 45° rotated growth. A mixture of both orientations is observable when the deposition rate is higher. In the following we present investigations of CeO_2 films grown with a low deposition rate of about 0.3 Å/s.

Figure 1 shows x-ray diffraction ϕ scans of CeO_2 (420) reflections of films deposited on the three different MgO substrates with different polishing. The spectra reveal different in-plane orientations of CeO_2 on the different substrates: a pure cube-on-cube growth [Fig. 1(a)]; a mixture of a cube-on-cube and a 45° rotated growth [Fig. 1(b)]; and a pure 45° rotated growth occurs [Fig. 1(c)].

The cross sectional lattice fringe image of cube-on-cube oriented CeO_2 on MgO [Fig. 2(a)] shows Moiré fringes at the interface due to a superposition of CeO_2 and MgO in the viewing direction. The spacing of these fringes is in accordance with the values calculated from the lattice parameters of MgO and CeO_2. Therefore, it can be concluded that the interface of the cube-on-cube oriented CeO_2 and MgO is

wavy with a roughness up to 8 nm. In contrast, the interface between the 45° rotated CeO_2 and the MgO substrate is very smooth [Fig. 2(a)]. No steps higher than one unit cell of MgO can be observed. This is confirmed by AFM measurements. Height variations of only 0.4 nm were measured.[8]

Substrates, where both CeO_2 orientations were observed, have an intermediate roughness. We measured a typical height variation of 0.8 nm and higher by AFM.

Since all films were grown under the same conditions, we conclude that the orientation of the CeO_2 films is strongly dependent on the surface morphology, too. Two competing in-plane orientations of CeO_2 on [100]MgO are possible. The orientation $[110]CeO_2//[100]MgO$ has a slightly lower interfacial energy than the $[100]CeO_2//[100]MgO$ orientation. In the initial stage of the deposition of CeO_2 on MgO, nucleation can occur on terraces and at surface steps. If nucleation occurs on terraces, the growth of $[110]CeO_2$ is favored due to the lower interfacial energy. In contrast, a nucleation at steps will result in a cube-on-cube orientation. Therefore the deposition rate, step height, and step density on the surface determine the in-plane orientation of CeO_2 on MgO (100). Steps on MgO form an additional surface for the nuclei, which may change the interfacial energy in favor of the cube-on-cube growth. Therefore the step height and step density on the surface determine the in-plane orientation of CeO_2 on MgO.

Since the surface roughness has been identified as the decisive parameter for the in-plane alignment, we tried different surface treatments in order to control this orientation. A similar approach has been used by Chew *et al.*[9] They changed the in-plane orientation of *c*-axis YBaCuO on (001) MgO substrates by a preceding low-temperature argon milling process. YBaCuO films grown on milled regions of the substrate showed a film axis rotated 45° with respect to films grown on untreated regions. They speculated that the ion milling breaks the step structure of the surface. Therefore, the morphological driving force is lowered and the in-plane orientation of YBaCuO is switched from YBaCuO(100) to YBaCuO(110) parallel to (100) MgO. Unfortunately, they could not reproduce their results.[10]

In contrast to Chew *et al.* we started with smooth substrates, and used several techniques to roughen the surface in order to change the orientation of CeO_2. Both, Ar-ion milling (500 V, 0.5 mA/cm^2 for 3 min) and Ce implantation (50 keV ions incident 50° relative to the sample surface with doses ranging from 5×10^{12} to 10^{15}/cm^2) resulted in a change in orientation of the CeO_2 film. However, a residual amount of 5% to 10% of 45° rotated grains in cube-on-cube aligned CeO_2 was still observed. Therefore, both techniques need further improvements.

Another approach does not use any of the above-mentioned surface treatments. Instead, the homoepitaxy of MgO on MgO substrates serves as a roughening step. The homoepitaxy of MgO proceeds via island growth. The high density of these islands reliably provides the necessary reference steps for the desired cube-on-cube growth. Figures 3(a) and 3(b) show AFM measurements, which illustrate the change of the surface morphology of a smooth MgO surface due to the deposition of 40 nm MgO. The initially very smooth substrate, with a height variation of about 0.4 nm [Fig. 3(a)] is changed into a rough surface, with a height variation of more than 3 nm [Fig. 3(b)]. The three-dimensional growth of MgO on MgO leads to a very high density of rectangular islands, whose edges are oriented in the (100) direction. Therefore, graphoepitaxial nucleation of CeO_2 at these steps determines the orientation of the CeO_2

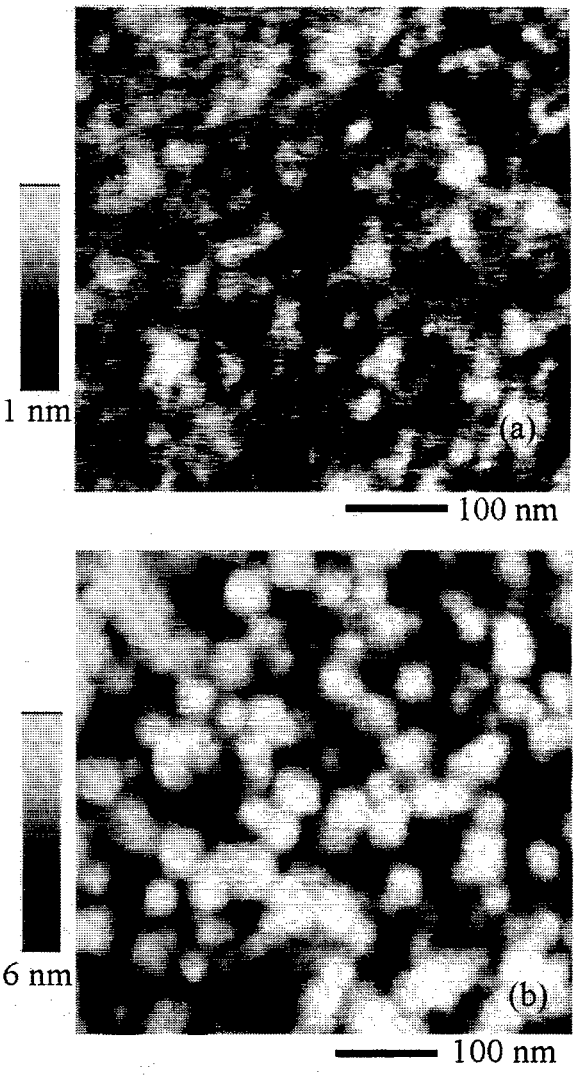

FIG. 3. AFM measurements of a smooth MgO substrate (a) and of a smooth substrate covered homoepitaxially with 40 nm MgO (b). In (b) the edges of the picture are parallel to [100] directions of MgO.

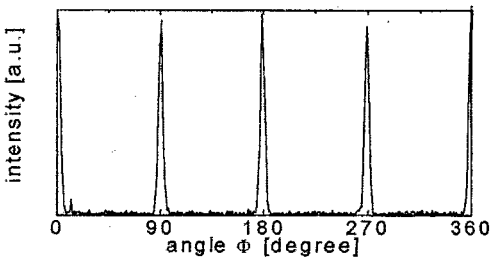

FIG. 4. X-ray ϕ scans of CeO_2 (420) on a smooth (100) MgO substrate covered homoepitaxially with 40 nm MgO. 0° corresponds to a [100] substrate direction being parallel to the diffracting plane.

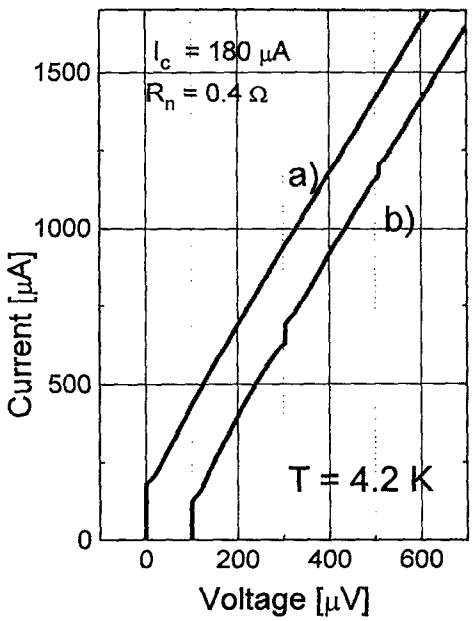

FIG. 5. IVC of a 10-μm-wide 45° grain boundary junction at 4.2 K (a) without external rf current and (b) with microwave irridation at 98.9 GHz. For clarity, curve (b) is displaced horizontally.

films. This is shown by the ϕ scan in Fig. 4. It corresponds to a CeO_2 layer deposited on a smooth MgO substrate covered homoepitaxially with 40 nm MgO. Only reflexes belonging to a cube-on-cube orientation of CeO_2 on MgO are observable.

For 45° grain boundary Josephson junctions, both CeO_2 orientations on one substrate are required. We achieved this goal by positioning a shadow mask over the substrate to cover half of it prior to the MgO deposition. The resulting MgO edge is smooth and flat. Thus, we expect that step edges do not form. After MgO deposition, the substrate is totally covered by CeO_2. The CeO_2 grows 45° rotated on the smooth part of the substrate, while on the rough part—covered homoepitaxially with MgO—it grows cube-on-cube. Therefore a 45° grain boundary in CeO_2 is formed at the boundary of both regions. This grain boundary is transferred into the YBaCuO film, grown on top of the CeO_2 film.

Across these grain boundaries we patterned narrow bridges, using standard photolithography and ion milling. Below T_c, these microbridges form Josephson junctions. A typical current voltage curve is depicted in Fig. 5. It shows a IV curve of a 10-μm-wide and a 200-nm-thick YBaCuO bridge containing the grain boundary at 4.2 K with (b) and without (a) microwave irridation (f=100 GHz). At the expected voltage spacing of about 200 μV well defined rf-induced steps are visible, proving the phase-locking of the Josephson oscillations with the external rf radiation. The I_cR_n products of the junctions are in the range of 30 to 90 μV at 4.2 K, which is comparable with I_cR_n products of 45° grain boundary Josephson junctions on MgO substrates.[3,9]

IV. SUMMARY AND CONCLUSION

In summary, we have shown that the in-plane orientation of CeO_2 on MgO is determined by the deposition rate and the surface roughness of the MgO substrate. By depositing the film at low deposition rate during the first stages of growth and controlling the surface roughness it is possible to create 45° grain boundaries in CeO_2. These grain boundaries can be used to fabricate YBaCuO Josephson junctions.

ACKNOWLEDGMENT

One of the authors (F. S.) acknowledges the support of a grant from Direction General de Investigacion Cientifica y Tecnica.

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