Control of the in-plane epitaxy for bi-epitaxial grain boundary junctions using a new multilayer structure

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In order to obtain 100% bi-epitaxial 45° grain boundary junctions of YBa2Cu3O7 (YBCO), we have systematically examined the in-plane epitaxy of CeO2 films grown on MgO substrates. The inevitable presence of CeO2[110]∥MgO[100] causes mixtures of in-plane rotation of 0° and 45° between YBCO/CeO2/MgO and YBCO/MgO. We have further developed a new structure, namely YBCO/CeO2/Yttria-stabilized ZrO2/MgO and YBCO/MgO boundary, so that 100% in-plane rotation of 45° can be routinely obtained. The model of the in-plane epitaxial relationship between the multilayers using near coincident site lattices was proposed. The critical current density of the junctions made on the boundary is 3×10^5 A/cm² at 77 K, while the order of the Jc of YBCO films on both sides of the grain boundary is 10^6 A/cm². The current-voltage characteristics of the junctions show resistively shunted junction behavior. The better epitaxy of our new structure can lead to a better control of grain boundary critical current density. © 1995 American Institute of Physics.

I. INTRODUCTION

Most microelectronics applications of high Tc superconductors require the process of controllable Josephson junctions with S-N-S or weak-link structures. Among the existing weak-link geometries, the grain boundary junctions work well and have reasonable high IcRn products at the temperature near Tc, though the microscopic mechanism is not yet clear. While the bi-crystalline grain boundary junctions of various angles give reproducible results for basic investigations, the bi-epitaxial process that creates the 45° grain boundary junction provides the possibility for integrated circuits and attracts immense attention. The bi-epitaxial grain boundary junction was first developed by Conductus, using SrTiO3 as a base layer, MgO a seed layer, and CeO2 a buffer layer. In their case, the fluorite structure of CeO2 makes it possible to be grown as a template layer on poorly matched layer, such as MgO, to rotate the in-plane orientation of subsequent YBa2Cu3O7 (YBCO) films to 45° with respect to the crystalline axis of the base layer. There was also a report of an in-plane rotation of 18° between YBCO/CeO2 and YBCO on MgO. To control and understand the in-plane alignment of the template layer and the substrate layer is important for achieving optimal transport properties as well as tailoring the in-plane crystallography of YBCO films to make the desired grain boundary. In this article, we have systematically analyzed the texturing of CeO2 on MgO, and found it difficult to obtain 100% bi-epitaxial 45° grain boundary junctions of YBCO on MgO using CeO2 as template layer. We further developed a new structure, namely YBCO/CeO2/

yttria-stabilized (YSZ) ZrO2/MgO and YBCO/MgO boundary, so that 100% in-plane rotation of 45° can be routinely obtained.

For the growth of CeO2 on MgO, our results showed that though the films consist of more than 95% of CeO2[100]∥MgO[100], a small percentage of CeO2[110]∥MgO[100] (about 5%) was always present, which may in turn affect the electrical characteristics of the grain boundary junctions. Similar results were also observed by Wu et al. On the other hand, YSZ films grown on MgO(001) were 100% c-axis oriented with in-plane [100] parallel to MgO[100], due to the large lattice mismatch for the other orientations. YSZ has the same crystal structure as that of CeO2 with a smaller lattice constant. This makes it more favorable for controllable epitaxy on MgO. It is known that the growth of YBCO films on YSZ results in two different in-plane epitaxial states of c-axis oriented films, we therefore use CeO2 as heteroepitaxial buffer layers to control the epitaxy of YBCO on YSZ. The results of the in-plane epitaxial relationships between CeO2, YSZ, and MgO are consistent with a model using the near coincident site lattices (NCSL) by considering the oxygen sublattices rather than the simple cubic to cubic match.

II. EXPERIMENTAL PROCEDURES

The multilayer films were prepared by pulsed laser ablation using KrF excimer laser (248 nm, 30 ns pulse width). The YSZ film was grown by laser ablating a single crystal YSZ with energy density of about 2.2 J/cm². The CeO2 film was subsequently grown on YSZ and/or directly on MgO by laser ablating a pressed CeO2 powder target sintered in
1400 °C O₂ for 12 h. The films were then patterned by standard photolithography and Ar ion milling. We then grew a YBCO layer on both the exposed MgO surface and on the patterned CeO₂/YSZ and/or CeO₂. The laser energy for both CeO₂ and YBCO targets was about 1.5 J/cm². The target to substrate distance was fixed at 4 cm. The oxygen pressure and substrate temperature during the deposition of YBCO films was 400 mTorr and 730 °C, respectively. For the growth of YSZ and CeO₂ films, the substrate temperature was varied between 730 and 780 °C in 200–400 mTorr oxygen atmosphere. The thickness of YSZ and CeO₂ was typically about 400 and 300 Å, respectively.

The film thickness was determined by a surface profilometer as well as Rutherford backscattering spectroscopy (RBS). The resistivity and critical temperature of YBCO films were measured by the standard van der Pauw method. The critical current densities were determined by transport method. The film structure was investigated by a four-circle diffractometer with Cu Kα radiation. In-plane texturing was examined by rotating the sample about the substrate normal from planes that are not parallel to the substrate surface (i.e., φ scan). The diffraction intensities of φ scan were collected from the (103) family of peaks for YBCO films, and from (202) family peaks for YSZ, CeO₂, and MgO.

III. RESULTS AND DISCUSSION

A. YBCO/CeO₂/MgO

Figure 1 shows θ-2θ x-ray scan for a CeO₂ film grown on a (001) MgO substrate. The in-plane orientation of CeO₂ with respect to the MgO substrate was further investigated by x-ray φ scan. We found that the films consist of more than 95% of CeO₂[100][MgO][100], and less than 5% of CeO₂[110][MgO][100], judged by x-ray peak intensity. Figure 2 is the x-ray φ scan of YBCO/CeO₂ films grown on MgO(001). The deposition condition was 400 mTorr oxygen pressure and 730 and 750 °C substrate temperature for YBCO and CeO₂, respectively. A small percentage of CeO₂[100][MgO][100], indicated as the CeO₂(202) peaks shifted by 45° in φ from MgO(202) peak, is always present. We have tried several different growth conditions, but it is difficult to obtain 100% of CeO₂[100][MgO][100]. Moreover, no evidence of 18° in-plane rotation was found, despite of considerable amount of effort.

In order to understand the observed results, we considered a model that includes the oxygen sublattices in the (001) face of CeO₂ for the in-plane epitaxial relationship between CeO₂ and MgO. Figure 3 is the schematic representation of the (001) plan views of CeO₂ and MgO, with indication of all the NCSl possible for the epitaxial film growth. In the case of CeO₂[100][MgO][100], it was believed that the CeO₂ (a = 5.42 Å) has a simple cubic to cubic match with respect to MgO (a = 4.21 Å) with the lattice mismatch of more than 20%. However, such a lattice misfit seems to be too large to accommodate for the epitaxial growth. Therefore, we pro-

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posed that, as shown in the case (a) of Fig. 3, two Mg–Mg (or O–O) spacing of MgO coincide with three O–O spacing of CeO₂, which has misfits of about 3.48%. For the CeO₂[110][MgO[100], shown in the case (b) of Fig. 3, the lattice mismatch between the Mg–Mg and Ce–Ce is 9%. Table I lists the corresponding misfits for three different in-plane orientations. The preferred in-plane epitaxy of CeO₂[100][MgO[100] can be attributed to its smaller lattice mismatch than that of CeO₂[110][MgO[100]. On the other hand, for the 18° in-plane rotation, as the marked two possible NCSL's in the case (c) of Fig. 3, the lattice mismatch is about 1.74%. This misfit is less than those of the other two orientations. However, the lattice symmetry of the NCSL is entirely different between the (001) face of CeO₂ and MgO, which may be the reason for the absence of the 18° rotation.

It is difficult to prohibit the growth of the CeO₂[110][MgO[100] although the lattice mismatch of which is as large as 9%. This inevitable texture hence influences the epitaxial growth of YBCO on CeO₂/MgO. As seen from the φ scan of YBCO in Fig. 2, a small fraction of the peaks occurring at 45° shifted from the MgO peaks indicates the existence of mixed orientation of the films. $T_c$ ($R=0$) of the YBCO films is about 90 K. The critical current density, $J_c$, measured at 77 K is $7 \times 10^5$ A/cm². The reduction in $J_c$ is believed to originate from the high angle grain boundary. Moreover, the artificial boundary between YBCO/CeO₂/ MgO and YBCO/MgO will thus consist of an in-plane angle of 45° and a small fraction of 0°; the characteristics of the junction made from the boundary can be affected.

**B. YBCO/CeO₂/YSZ/MgO**

To control the epitaxy of YBCO films and obtain a complete in-plane rotation of 45° between YBCO and MgO substrates, we have grown YSZ as a seed layer on MgO prior to depositing CeO₂. The YSZ films grown at the substrate temperature higher than 760 °C were 100% c-axis oriented with in-plane [100] parallel to MgO[100]. Figure 4 is the typical φ scan of YBCO/CeO₂/YSZ layers on MgO. All the YSZ[202] peaks clearly coincide with those of MgO(202). No evidence of YSZ[110][MgO[100] was found. The result is reproducible under the oxygen pressure of 200–400 mTorr at a temperature higher than 760 °C. Lower deposition temperature lead to films of majority YSZ[100][MgO[100] orientation with the presence of a small fraction of 18° in-plane rotation.

Table I lists the corresponding misfits for three different in-plane orientations. The lattice mismatch between YSZ and MgO, for different orientations, are listed in Table I. YSZ has the same fluorite structure as CeO₂ but a smaller lattice constant ($a=5.14$ Å). Therefore, the lattice mismatch for the orientations of YSZ[100][MgO[100] and YSZ[110][MgO[100] are larger than those of CeO₂[100][MgO[100] and CeO₂[110][MgO[100], respectively.

![Diagram of CeO₂ and MgO orientations](image-url)

**FIG. 3.** Schematic representation of the [001] plan views of single layer slices of CeO₂ and MgO. Solid boxes (a) indicate the near coincident site lattice (NCSL) for CeO₂[100][MgO[100]. Dashed boxes (b) indicate the NCSL for CeO₂[110][MgO[100]. Dot lines (c) outline the NCSL for in-plane 18° rotation.

| Lattice mismatch | $a$ | $φ=0°$ | $φ=45°$ | $φ=18°$
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<tr>
<td>CeO₂</td>
<td>5.42 Å</td>
<td>3.48%</td>
<td>9.00%</td>
<td>1.74%</td>
</tr>
<tr>
<td>YSZ</td>
<td>5.14 Å</td>
<td>8.45%</td>
<td>13.69%</td>
<td>3.50%</td>
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**TABLE I.** The lattice mismatch between films and MgO substrate. The lattice constant $a$ of MgO is 4.21 Å, $φ$ refers the angle between [100] of the film and substrate.
FIG. 4. X-ray \( \phi \) scan of a YBCO/CeO\(_2\)/YSZ film on MgO(001) substrate.

YBCO grown on CeO\(_2\)/YSZ/MgO is 90 K, as shown in Fig. 5, while that of YBCO grown on MgO is 88 K. The critical current density \( (J_c) \) of YBCO on CeO\(_2\)/YSZ/MgO measured at 77 K is \( 3.4 \times 10^6 \) A/cm\(^2\), which is superior to that of YBCO on CeO\(_2\)/MgO.

C. Junction characteristics

Since YBCO films directly grown on MgO results in YBCO[100][MgO][100], the YBCO films grown on CeO\(_2\)/YSZ/MgO is to rotate by 45° relative to the YBCO grown on MgO. The CeO\(_2\)/YSZ layers were patterned by photolithography and Ar ion beam etching before the deposition of YBCO film. A complete in-plane rotation of 45° was thus obtained between YBCO/CeO\(_2\)/YSZ/MgO and YBCO/MgO boundary. The schematic view of this new multilayer structure is shown in Fig. 6. The critical current density of the microbridge formed across the boundary between YBCO/CeO\(_2\)/YSZ/MgO and YBCO/MgO is \( 3 \times 10^3 \) A/cm\(^2\) at 77 K. The current-voltage characteristics of the microbridge, with 9 \( \mu \)m in width and 2400 Å in YBCO film thickness, is shown in Fig. 7. The data exhibit resistively...
shunted Josephson junction behavior. These characteristics hold the promise for the superconducting quantum interference device (SQUID) fabrication.

IV. CONCLUSIONS

In this article we demonstrate that the creation of a 100% bi-epitaxial 45° grain boundary junctions of YBCO is impossible if one simply uses the CeO$_2$ as a template layer. The films consist of more than 95% of CeO$_2[100]|MgO[100]$, and about 5% of CeO$_2[110]|MgO[100]$. We have modeled the epitaxial relationships and correlated the observed results with the in-plane lattice mismatch. The inevitable presence of CeO$_2[110]|MgO[100]$ causes mixtures of 45° and 0° in-plane rotations between YBCO/CeO$_2/MgO$ and YBCO/MgO, and thus affects the transport properties of the YBCO films and the characteristics of the bi-epitaxial grain boundary junctions. We have further developed a new structure for bi-epitaxial grain boundary junction of YBCO using YSZ, CeO$_2$, and MgO as the seed layer, the buffer layer, and the substrate, respectively. YSZ films grown on MgO[100] were 100% a-axis oriented with in-plane [100] parallel to MgO[100]. The CeO$_2$ heteroepitaxial buffer layers were used to control the epitaxy of YBCO on YSZ. An 100% in-plane rotation of 45° was thus obtained between YBCO/CeO$_2$/YSZ/MgO and YBCO/MgO.

$T_c (R=0)$ of YBCO grown on CeO$_2$/YSZ/MgO is 90 K, while that of YBCO grown on MgO is 88 K. The critical current density of the microbridge formed across the boundary between YBCO/CeO$_2$/YSZ/MgO and YBCO/MgO is $3 \times 10^3$ A/cm$^2$ at 77 K, while the order of the $J_c$ of YBCO films on the both sides of the grain boundary is $10^6$ A/cm$^2$. The fabrication of SQUID based on such artificial grain boundary junction is in process. The better epitaxy of the new structure can lead to a better control of grain boundary critical current density which may be the key to the SQUID fabrication.

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