High quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films with controllable in-plane orientations grown on yttria-stabilized zirconia substrates

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The pulsed-laser deposition (PLD) technique was used to grow high $T_C$ superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films on both virgin and ion-bombarded yttria-stabilized zirconia (YSZ) substrates. To pattern high $T_C$ films for device applications, the ion milling technique is often used to turn virgin YSZ substrates into ion-bombarded substrates. Multilayered processes require the growth of high $T_C$ films on these ion-bombarded substrates. The purpose of this work was to investigate the growing conditions for these two kinds of substrate surfaces. We found that high quality $0^\circ$ in-plane orientation films can be grown on either substrate when the growth temperature is about $810 \text{ °C}$. The thin film grown at this temperature has $T_C$ of about 90.3 K and $J_C$ of about $4 \times 10^6 \text{ A cm}^{-2}$ at 77 K. On virgin substrates, the in-plane orientations of YBCO films grown within the temperature range of 790–730 °C exhibit a mixture of $0^\circ$ and $45^\circ$ domains. As the growth temperature decreases, the dominant orientation shifts gradually from $0^\circ$ to $45^\circ$. On the other hand, on ion-bombarded YSZ substrates, the in-plane orientation of YBCO films grown within the same temperature range shows that the $45^\circ$ domain is more prominent. Furthermore, $9^\circ$ subpeaks appear around the $0^\circ$ peak on ion-bombarded YSZ substrates. At a lower growth temperature of around 690 °C, only the $45^\circ$ domain exists on the virgin substrate, while a small amount of $0^\circ$ domain is present with the majority of $45^\circ$ domain on the ion-bombarded substrate. The $T_C$ and $J_C$ of the films grown at around 690 °C on virgin substrates are as good as films grown at high temperatures, despite the difference in the in-plane orientations. © 2006 American Institute of Physics.

I. INTRODUCTION

High $T_C$ superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films can be fabricated on many kinds of substrates, such as strontium titanate oxide (STO), MgO, Al$_2$O$_3$, yttria-stabilized zirconia (YSZ), etc.\textsuperscript{1–3} Many different fabrication methods also exist.\textsuperscript{4–7} Grain boundary Josephson junctions are important for superconducting devices, and there are several fabrication methods for these as well. The earliest grain-boundary junctions were the natural grain boundaries found in polycrystalline films\textsuperscript{8} and, thus, could be controllably fabricated.

IBM first developed bicrystalline grain boundary junctions in 1988. According to Hilgenkamp and Mannhart,\textsuperscript{3} the original goal of developing the bicrystalline grain boundary junctions was to study the influence of the grain boundaries on superconducting transport properties.\textsuperscript{3,5,10} However, a considerable number of subsequent research efforts have focused on applying this technique for making Josephson junction devices. From an applications point of view, the bicrystal technique suffers some drawbacks, such as difficulty extending to integrated circuit processing and the expensive-
The main goal of this work was to resolve these problems and to improve the fabrication process.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Surface morphologies of virgin substrates and ion-bombarded substrates

To pattern high $T_c$ films for device applications, an ion-milling technique is often used to turn virgin substrates into ion-bombarded YSZ substrates. It is necessary to grow high $T_c$ films on these ion-bombarded substrates for multilayered processes. The surface morphologies of virgin and ion-bombarded substrates are important factors for producing YBCO films. The virgin substrate is a single crystal with 10% yttria content, manufactured by Japan’s Shinkosha Company. We used a 3 cm ion source to etch the virgin substrate to create a rough surface. This 3 cm ion source contained tungsten filaments and graphite grids. The beam current and the argon pressure of the ion source were set at 5–6 mA and $5 \times 10^{-4}$ torr, respectively. Beam voltages of 300, 500, and 700 V accelerated the ion source. Adjusting the etching time to correct for voltage differences helped achieve an approximately constant etch depth. The atomic force microscopy (AFM) images show the smooth virgin substrate [Figs. 1(a)] and the holes and islands caused by ion etching [Figs. 1(b) and 1(c)]. The influence of the substrate texture on YBCO thin films is presented below.

B. Preparation of films

A Lambda Physik LPX 100 excimer laser, with a pulse width of 30 ns and a wavelength of 248 nm, was used to grow the YBCO thin films. First, we varied laser energy density, oxygen pressure, and the distance between the target and holder to optimize the YBCO superconducting properties on the virgin substrate. Next, in the deposition temperature range of 660–810 °C, we compared the films deposited on ion-bombarded substrates with those on smooth substrates. In this temperature region, all films deposited on either kind of substrate were $c$-axis films. The oxygen pressure and the laser energy density were fixed at 320 mTorr and 1.5 J cm$^{-2}$, respectively. The distance between the target and holder was 39 mm. We used a four-circle x-ray diffractometer with a Cu Kα source to detect the YBCO {103} and YSZ {202} x-ray peaks and to distinguish between different in-plane orientations. We expected the 0° orientation to dominate at high temperatures and the 45° orientation to dominate at low temperatures.5

FIG. 1. The surface morphology determined by an AFM on (a) a smooth virgin substrate and [(b) and (c)] after the substrate bombarded with ions. The ion damage can create holes as in (b) or islands of terraces as in (c).

FIG. 2. The x-ray Φ-scan spectra for films grown at 810 °C on (a) a virgin substrate and (b) an ion-bombarded substrate.
Since the ion-milling process is an essential tool in most device fabrication processes, as addressed in Sec. II A, study of the films grown on ion-bombarded substrates should reflect these same conditions. At the high end of our growth temperature range, around 810 °C, we found that there are no differences between films on virgin substrates and ion-bombarded substrates as shown in Figs. 2(a) and 2(b). They both have the pure 0° orientations.

For films grown at 790 °C, a small amount of the 45° domain appears, as indicated by the presence of small peaks at 45° and 135° on the virgin substrate in Fig. 3(a). On the ion-bombarded substrate, in addition to the presence of the 45° domain, broad satellite peaks appear at ±9° around the 0° peak, shown in Fig. 3(b).

For films grown at 730 °C, Fig. 4(a) shows that the 0° domain and the 45° domain are about equally abundant on virgin substrate. However, on ion-bombarded substrates, the 45° domain is prominent, shown in Fig. 4(b).

Figure 5(a) shows a pure 45° orientation in the film grown on the virgin substrate when the growth temperature is lowered to 690 °C. However, on the ion-bombarded substrate, Fig. 5(b) shows a small amount of 0° domain among the dominant 45° orientation.

Interestingly, at even lower growth temperatures of around 660 °C, a small 0° peak reappears on the virgin substrate, as shown in Fig. 6(a). The reason for the reappearance of the 0° peak is unclear at present. However, it is consistent that the 0° peak becomes much more pronounced for the ion-bombarded substrate, as shown in Fig. 6(b).
Table I summarizes our x-ray Φ-scan results for films grown at different temperatures. In addition to the x-ray Φ-scan spectra, we also measured θ-2θ spectra. Two examples are shown in Fig. 7. The results show that the films grown in the temperature range of 660–810 °C are all pure c-axis films, while those grown at approximately 630 °C have a small amount of a-axis domains mixed with the predominant c-axis domains. The inset of Fig. 7(a) shows a small broad peak, which is indicative of the formation of the interface compound BaZrO$_3$ at high temperatures. This peak is absent for films grown at lower temperature, as shown in Fig. 7(b).

We found that films deposited at 810 °C or above are all in-plane 0° oriented, regardless of the substrate surface conditions. However, some previous experimental results were somewhat inconsistent. To investigate this further, we varied the distance between the laser target and holder, with affixed laser energy density at 1.5 J cm$^{-2}$ and temperature at 810 °C. To our surprise, when the target to holder distance was reduced from 39 to 36 mm, we found a pronounced 45° peak in the Φ-scan spectrum shown in Fig. 8(b).

Since plasma heating increases the effective temperature of the virgin substrate, the outcome should be a pure 0° peak. Thus, our results clearly indicate that physical damages due to the incident plume do not have sufficient time to anneal even at 810 °C.

Moreover, we also varied the oxygen pressure while keeping the distance between target and holder fixed at 39 mm, laser energy density at 1.5 J cm$^{-2}$, and temperature at 790 °C. As the oxygen pressure was lowered from 320 mtorr [Fig. 9(a)] to 280 mtorr [Fig. 9(b)], we again observed similar Φ-scan patterns when the plasma plume touched the substrate. In addition, the 9° orientation appeared again in this process.

![FIG. 7.](image1.png) (a) At high temperature 810 °C, there will be obvious BaZrO$_3$ interface. (b) At temperature 690 °C, there is no BaZrO$_3$ interface.

![FIG. 8.](image2.png) (a) Film deposited on virgin substrate with 39 mm between target and holder at temperature 810 °C. (b) Film deposited on virgin substrate with 36 mm between target and holder at temperature 810 °C.

![FIG. 9.](image3.png) (a) Film deposited on virgin substrate with oxygen pressure of 320 mtorr at 790 °C. (b) Film deposited on virgin substrate with oxygen pressure of 280 mtorr at 790 °C.
We conclude that the plasma plume damages the substrate and produces films similar to those deposited on ion-bombarded substrate at a lower growth temperature. The effective temperature rise due to plasma heating is not the major factor. Thus it is crucial to minimize in situ plume damage for better and more reproducible film quality.

C. Transport properties of the YBCO film

We used the YBCO films from Table I to study two transport properties: resistance and critical current. We obtained the resistivity and transition temperature of the YBCO film by using the standard four-probe method. The resulting curves of pure 0° orientation and pure 45° orientation are shown in Figs. 10(a) and 10(b) respectively.

From these $R$-$T$ measurements, we determined the superconducting transition temperatures for films deposited on the two kinds of substrate surfaces and at different growth temperatures in Table II. The general trend of lower $T_C$ with lower growth temperature for both kinds of substrate surfaces agrees with previous work. However, in our case, the $T_C$ range is much smaller.

We used a superconducting quantum interference device (SQUID) magnetometer to measure $M$-$H$ curves, and employed the Bean model to estimate the $J_C$ values of the films. The dimensions of all the samples are practically identical, with dimensions of 4 mm, 4 mm, and 0.3 μm in length, width, and thickness, respectively. Some $M$-$H$ curves are shown in Fig. 11.

The resulting $J_C$ at 5 K and 77 K are tabulated in Table III. It is clear from this table and Table I that the $J_C$ is quite high for films of either pure orientation on virgin substrates. The $J_C$ deteriorates when there are mixed domains. The ion-bombarded surface is also detrimental to films deposited at

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$T_C$ (onset)</th>
<th>$T_C$ (onset)</th>
</tr>
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<tbody>
<tr>
<td>810 °C</td>
<td>89.1 K</td>
<td>90.3 K</td>
</tr>
<tr>
<td>790 °C</td>
<td>88.5 K</td>
<td>91.5 K</td>
</tr>
<tr>
<td>730 °C</td>
<td>86.1 K</td>
<td>90 K</td>
</tr>
<tr>
<td>710 °C</td>
<td>86.7 K</td>
<td>88.7 K</td>
</tr>
<tr>
<td>690 °C</td>
<td>85.9 K</td>
<td>88 K</td>
</tr>
<tr>
<td>660 °C</td>
<td>84.5 K</td>
<td>89.1 K</td>
</tr>
</tbody>
</table>

TABLE II. List $T_C$ at different temperature.
lower temperatures. Thus, $J_C$ is much more sensitive to large-angle grain boundaries in the films, as expected from $d$-wave superconductivity.

### III. CONCLUSION

The AFM pictures show that the ion-milling process makes the surface rougher, which has profound effects on the YBCO films on YSZ substrates, especially in the temperature range of 730 to 790 °C. At higher temperatures of about 810 °C, we show that the film deposited on ion-bombarded substrates is as good as the one deposited on virgin substrates, indicating that the damaged surface can heal at higher temperatures.

In addition, *in situ* damages can be produced by the plasma plume at any temperature. These damages cannot be observed easily with the naked eye and apparently do have sufficient time to heal at high deposition temperatures. Thus it is very important to prevent plume-induced damage during fabrication processes.

Our transport measurements show that we can obtain high $T_C$ and $J_C$ for pure 0° films on either virgin or ion-bombarded surfaces of YSZ substrates. On the other hand, we can have high $J_C$ for pure 45° films only on virgin substrates. These results are important for designing reproducible biepitaxial grain boundary junctions for various applications.

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