Effect of Mg(OH)$_2$ on YBa$_2$Cu$_3$O$_7$ thin film on MgO substrate studied by atomic force microscope

B. I. Kim, J. W. Hong, G. T. Jeong, and S. H. Moon
Department of Physics, Seoul National University, Seoul 151-742, Korea
D. H. Lee and T. U. Shim
Memory Division, Samsung Electronics, Suwon 440-600, Korea
Z. G. Khim
Department of Physics, Seoul National University, Seoul 151-742, Korea

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We observed the surface degradation of MgO single-crystal substrates stored in humid air after cleavage by atomic force microscope. Annealing at 1000°C in dry oxygen removed local defects though residual subgrain structure remains. The morphology of YBa$_2$Cu$_3$O$_{7-£}$ (YBCO) films on the annealed and degraded substrates reflects these changes of the density, $J_c$. We confirmed that the annealing process of degraded substrate improves the film quality by measuring transition temperature $T_c$ and critical current $J_c$ of each film.

I. INTRODUCTION

Since the discovery of high-temperature oxide superconductors (HTSC), the MgO crystal has been widely used as a substrate for the HTSC thin films because of good lattice matching and low chemical reactivity with HTSC. However, it is well known that the surface morphology and roughness of the substrate strongly influence the growth and electrical properties of the film deposited on it. Although MgO is widely used as a substrate for HTSC thin film, it is also known to form hydroxide or carbonate at the surface due to chemisorption of H$_2$O or CO$_2$ in air, which will certainly degrade the quality of the HTSC film deposited on it. Consequently, study of the formation of hydroxide and the effect of oxygen annealing on the MgO substrate is quite important for the high-quality HTSC film deposition.

In the present article, we report the study of the formation of hydroxide on the cleaved MgO single-crystal substrate and its effects on YBCO film deposited on the substrate using atomic force microscopy (AFM). Effects of oxygen annealing on the surface morphology of substrate and film were studied.

II. EXPERIMENT

MgO substrates used in this study were cleaved along the (100) plane with a chisel and then cleaned with acetone and ethanol using an ultrasonic cleaner ten minutes in each solvent. This cleaning process was repeated before each experiment. The surface roughness of all the samples was investigated with AFM in air at room temperature. All surface images were obtained in the constant force mode with force of 1–2 nN. The material of the cantilever (Park Scientific Instrument, microlever) used in this experiment is Si$_3$N$_4$. Data were recorded in real time with a computer and displayed as 64 color gray scales without any smoothing processing.

For the formation of magnesium hydroxide, MgO substrates were stored in air with humidity of 100% for several days. The change of surface morphology of the MgO substrate was observed by AFM. To see the effect of annealing on the surface morphology, one of the degraded MgO substrates was annealed in a furnace at 1000°C for 2 h. Subsequently, the substrate was annealed in flowing dry oxygen at a flow rate of 200 cc/min for three hours. After this process, the furnace was slowly cooled down to room temperature.

YBCO films were deposited on degraded and annealed substrates at the same time with a magnetron sputtering system. The substrate temperature during film deposition was 725°C and the partial pressure of oxygen was about 50 mTorr. The deposition rate was about 20–30 Å/min and the thickness of the film deposited was about 2000–3000 Å. After holding the substrate temperature at 450°C in 600 Torr oxygen environment for 2 h, the film was cooled down to room temperature.

We measured the transition temperature $T_c$ and critical current density $J_c$. Structural properties of the film deposited on the degraded or annealed substrates are also studied to investigate the influence of the substrate surface morphology on the film quality.

III. RESULTS AND DISCUSSIONS

MgO single crystals studied in this work are of 99.9% purity and were cleaved along the (100) plane.

The AFM image of the MgO single crystal right after cleavage indicates that the surface roughness is less than 30 Å as shown in Fig. 1. One can observe tiny spots with a diameter of ~150 Å which are possibly due to an impurity phase and cleavage steps with height of ~1000 Å. After storing the MgO crystal in humid air of 100% humidity for three days, we observed appearance of another phase of round shape with diameter around 1000–2000 Å and height of ~100 Å as shown in Fig. 2(a). After six days of storing in humid air, many small spots with size of 50–300 Å developed around the larger round shape [Fig. 2(b)]. This implies that MgO single-crystal surfaces suffer strong chemisorption and reaction with water vapor and this agrees with the result of other earlier study. MgO crystal stored in a dry air box, however, did not show any hillocks except small spots of...
Fig. 1. AFM images of cleaved MgO substrate (3.3×3.3 μm², z scale 28 nm/div.). Tiny spots with a diameter of ~150 Å which are possibly due to an impurity phase and cleavage steps with height of ~1000 Å.

Fig. 2. (a) AFM image of cleaved MgO substrate after three days in a humid air (1.1×1.1 μm², z scale 2.4 nm/div.) Another phase of round shape with diameter around 1000–2000 Å and height of ~150 Å appeared. (b) AFM image of cleaved MgO substrate after six days in a humid air (1.1×1.1 μm², z scale 4.1 nm/div.). Many small spots with size of 50–300 Å developed around the larger round shape.

Fig. 3. AFM image of annealed MgO substrate: (a) Pyramidal structures with a diameter of about 1800 Å and height of about 150 Å were shown. Many pits (marked by arrow) with a diameter ranging from 0.1 to 2 μm and a depth of about 100–300 Å were observed (5.0×5.0 μm², z scale 31 nm/div.). (b) Sometimes an image of bar shape (marked by arrow) with typical length of 0.3 μm, width of 0.1 μm, and height of 100 Å aligned perpendicularly to each other on MgO(100) plane appeared (1.1×1.1 μm², z scale 14 nm/div.). Small structures shown in Fig. 2 have disappeared. (c) The steps with height of 50 Å and terrace width of 400 Å around these structures appeared (1.1×1.1 μm², z scale 13 nm/div.).

50–300 Å up to a week. Thus it is believed that the observed round shape structure of size 1000–2000 Å on MgO surface is magnesium hydroxide [Mg(OH)₂] and the small spot of size 50–300 Å is magnesium carbonate (MgCO₃).

AFM image of annealed MgO substrate shows a pyramid-like structure with a lateral size of about 1800 Å and height of about 150 Å as shown in Figs. 3(a)–3(c). In some regions many pits with a diameter ranging from 0.1 to 2 μm and a depth of about 100–300 Å exist as marked by arrows in Fig.
3(a). This phenomenon of the pits seems to be consistent with pore migration and coalescence. The total number of pyramidal structures on an annealed substrate for a scan area $5\times5 \, \mu m^2$ is about 390. The average concentration of a pyramidal structure is about 15/\mu m^2.

Figures 3(b) and 3(c) show details of the pyramidalike structure and the state of the annealed MgO surface. One can also observe rather sporadically distributed bar shape structures with typical length of 0.3 \mu m, width of 0.1 \mu m, and height of 100 \AA{} aligned perpendicularly to each other on the MgO(100) plane was observed marked by arrows in Fig. 3(b). At present, we do not have any reasonable explanation on the observed two aligning directions and their orthogonal. The remarkable effect of annealing is that small structures on the degraded surface as shown in Fig. 2 have disappeared. This seems to be due to local reconstruction and dissociation of MgCO$_3$ caused during annealing process. If this is right, annealing temperature as high as the melting temperature will be required to reconstruct pyramidalike structures as shown in Fig. 3. The observed steps with height of 50 \AA{} and terrace width of 400 \AA{} around these structures support this fact [Fig. 3(c)]. The remaining structure should be magnesium hydroxide judging from the fact that the size is the same as the larger structure of Fig. 2. This is consistent with other earlier studies.

Images of YBCO film deposited by dc magnetron sputtering on a degraded MgO substrate stored in humid air [Fig. 4(a)] and on an annealed MgO substrate [Fig. 4(b)] show a number of hillock structures. The roughness of both the films is about 300 A. The number of hillocks of the film on a degraded MgO substrate is larger than that of the film on an annealed substrate. It seems that the size of each hillock in Fig. 4(a) varies from 0.1 to 1.5 \mu m due to variation of the concentration of the pyramidal structure discussed in Fig. 3(a). It is certain that the film morphology was strongly influenced by the substrate morphology. The large number of hillocks observed in a film deposited on a degraded MgO crystal is due to the small structure which was removed during annealing.

Images of a YBCO film deposited on a freshly cleaved MgO [Fig. 5(a)] and on a commercially polished MgO [Fig. 5(b)] show that the film roughness is about 100 A and the grain size is about 0.3–0.4 \mu m. Although no distinct hill with a screw dislocation image was identified in our AFM observation, the island may correspond to a growth hill with a screw dislocation because the size of one island is equivalent.
to that of one growth hill with a screw dislocation. Comparing the images of YBCO films deposited on an annealed MgO substrate with that of a film on a fresh MgO substrate, we can see that the rough surface of the film is due to a larger structure remaining even after annealing process.

X-ray diffraction patterns exhibit a (001) orientation of YBCO films. We measure the critical current density $J_c$ of the film by a commercial superconducting quantum interference device magnetometer (Quantum Design Inc.). Critical current density $J_c$ by Bean’s critical model. In Table I, measured $J_c$ and $T_c$. The critical current density of YBCO film on an annealed MgO substrate shows an increase of 60 times compared to that of film on a degraded MgO substrate. Critical current density of YBCO film on an annealed substrate is at least one order of magnitude smaller than that of YBCO film on a polished MgO film. The granular structure of the film on a degraded or annealed substrate causes a rather weak coupling between grains seems to be the cause for the low $J_c$ observed in YBCO films.

### Table I. Critical current density $J_c$ and critical temperature $T_c$ of YBCO films on MgO.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$J_c$ (A/cm²) at 10 K</th>
<th>$J_c$ (A/cm²) at 0.2 K</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>$4.8 \times 10^6$</td>
<td>$3.5 \times 10^5$</td>
<td>87</td>
</tr>
<tr>
<td>Annealed</td>
<td>$9.1 \times 10^6$</td>
<td>$7.6 \times 10^5$</td>
<td>89</td>
</tr>
<tr>
<td>Degraded</td>
<td>$1.5 \times 10^6$</td>
<td>$1.2 \times 10^5$</td>
<td>84</td>
</tr>
</tbody>
</table>

### IV. CONCLUSION

We observed the surface degradation of MgO surface through formation of Mg(OH)$_2$ and MgCO$_3$ directly with AFM. Annealing at 1000 °C in dry oxygen removes local defects but a residual subgrain structure remains. The trace of chemical reaction and surface reconstruction on annealed MgO could be observed. The morphology of YBCO films on the annealed and degraded substrates seems to be related to these changes of the substrates. The superconducting transition temperature of the film on an annealed substrate is comparable to that of the film on a commercially polished substrate, while that of the film on the degraded substrate is lower by more than 5 K. One can improve the morphology as well as the electrical property of the film by annealing the degraded MgO substrate stored in air, as can be seen in the $J_c$ measurement. It seems that the microstructure on the degraded surface, which was removed during annealing, makes film quality poor. The degraded MgO substrate without any treatments such as annealing and polishing did not result in high-quality YBCO films.