Y–Ba–Cu–O thick film preparation using multistep KrF excimer laser deposition

K. Ebihara a, *, K. Shingai a, Y. Yamagata a, T. Ikegami a, A.M. Grishin b

a Department of Electrical and Computer Engineering, Kumamoto University, Kurokami, Kumamoto 860, Japan
b Department of Condensed Matter Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Abstract

Thick films of high-temperature superconductors (HTSC) have attracted much attention to a number of current-carrying applications such as current leads, interconnects, current limiters and cryotron-type switches. As the film thickness of HTSC films is increased using the conventional method of pulsed laser deposition, the surface morphology is degraded during the film deposition. This structural transition results in decreasing the critical current density with the film thickness. Here, a multistep deposition technique in the KrF excimer laser ablation is used to prepare Y–Ba–Cu–O thick films. The high-quality Y–Ba–Cu–O superconducting films of thickness of a few mm were formed by optimizing the processing conditions from the bottom to the surface of the film. The initial ultrathin layer of a few nm was prepared at the low repetition rate of 1 Hz at laser fluence 3 J cm⁻². Then, various repetition rates at the fluence 2 J cm⁻² were chosen for deposition of the intermediate layer and the surface layer, both with thicknesses of about 1 μm. It is shown that surface morphology and vertical growth are significantly dominated by the initial layer structure and the following deposition conditions. The thick films with high $T_c$ (zero) 89 K were obtained when the surface layer was prepared at a lower repetition rate under lower process temperature. The three step procedure prepared the superconducting thick films with the critical current density of $1.2 \times 10^6$ A cm⁻² (at 5 K). ©1997 Elsevier Science S.A.

Keywords: Y–Ba–Cu–O thick film; Multistep KrF excimer laser deposition

1. Introduction

High-temperature superconducting thick films capable of carrying a large current have attracted special interest in power electronic applications including current limiters, current rectifiers and large current leads. In last few years numerous researchers have observed that, when film thickness is more than 400–500 nanometers, the superconducting properties rapidly degrade. Pulsed laser deposition has been used to prepare YBa₂Cu₃O₇−ₓ (YBCO) thick films and the growth mechanism during the thick film deposition has been studied. Carim et al. reported that, as film thickness increased, the surface morphology changed from a primarily planar structure to the basket-weave morphology and that a transition from c-axis to a-axis oriented crystallites dominates [1]. Foltyn et al. have deposited YBCO films ranging from 0.0065 to 6.9 mm on yttria-stabilized zirconia (YSZ) substrates with an intermediate layer of CeO₂ [2]. As film thickness for these films is increased, critical current ($J_c$) decreases asymptotically to 1 MA cm⁻². Wu et al. also fabricated high current YBCO thick film (about 1.5 μm) of the heterostructure YBCO/CeO₂/YSZ/Ni which shows the superconducting properties of $J_c=2 \times 10^5$ A cm⁻² (at 77 K) and $T_c=90$ K [3]. They applied ion beam assisted deposition to formation of highly textured YSZ buffer layers on a Ni-based alloy (P211astelloy).

In this paper we report the deposition of YBCO thick films using a multistep pulsed laser process. It has been suggested that the majority conversion to a- (or b-) axis growth at a few hundred nanometers thickness may result from strain accumulation, small crystalline particles (second phase particles) on top of the films, droplets and so on. In addition to these, there is another dominant factor related to the film deposition conditions. The properties of the laser produced plasma plume and the oxides formation in gas phase are considered to be gradually changed while successive pulsed laser ablations make the thick film deposit layer by layer. Here we optimize the deposition
conditions by applying the multistep procedure to the pulsed laser deposition.

2. Experiment

A schematic of the experiment is shown in Fig. 1 [4]. A Lambda Physik excimer laser (LPX 305icc: \( \lambda = 248 \) nm, pulse width=20 ns, max. energy=850 mJ) was used to ablate the targets in a spherical deposition chamber (\( \phi = 400 \) mm). We have used a stoichiometric bulk pellet YBCO as the target for YBCO superconducting thin film preparation. The laser beam from 1 J cm\(^{-2}\) to 5 J cm\(^{-2}\) was made incident on the small area (2\( \times \)5 mm\(^2\)) of the pellet at an angle of 45\(^\circ\). The target was rotated at 12 rpm to avoid texturing of its surface. Oxygen gas was led into the chamber and total deposition pressure was in the range of 100–300 mTorr. The YBCO thin films were grown on the MgO(100) substrate placed at a distance 4–8 cm from the target surface. The substrate was heated up to 600–750 °C.

The films were characterized using X-ray diffraction, scanning electron microscopy (SEM), electron probe micro analysis (EPMA) and resistivity–temperature measurements. The magnetization was measured by a Quantum Design MPMS-2 SQUID magnetometer.

3. Results and discussion

3.1. Effect of initial deposition conditions on the thick film properties

The initial deposition forms the bottom ultrathin layer on the MgO(100) substrate. It is desirable for the crystallographic axes of the bottom thinner layer to have well-defined orientations with respect to the substrate. The crystalline structure of the bottom layer is responsible for the thick film properties. We investigate the effect of the initial deposition conditions for the bottom layer on the thick film properties. We prepared YBCO thick films consisting of the bottom ultra thin layer and the top (surface) layer. The bottom layer was deposited on the MgO substrate heated up to 710 °C at a oxygen pressure of 200 mTorr. The KrF excimer laser energy density was changed in the range of 1 J cm\(^{-2}\) to 5 J cm\(^{-2}\) at a laser repetition rate of 1 Hz. The following deposition for the surface thick film was kept at a laser energy density of 2 J cm\(^{-2}\) and a repetition rate of 10 Hz. The overall film thickness is about 1 mm including the bottom thin layer of about 2 nanometers. Fig. 2 shows the X-ray diffraction patterns for the deposited films. Fig. 2(b) shows that the film deposited at 3 J cm\(^{-2}\) has diffraction peaks (001) indicating a highly c-axis oriented film. The SEM micrograph for this sample showed a smooth surface with small particles. The zero resistivity critical temperature \( T_c \) of this thick film was 82.1 K. When we decrease the laser fluence to 1 J cm\(^{-2}\), the polycrystalline with diffraction peaks of (100), (200), (110) etc are observed as shown in Fig. 2(a). The ejected species from the target have insufficient energy for c-axis oriented structure. In the

![Fig. 1. Schematic of the pulsed laser ablation deposition system.](image)

![Fig. 2. X-ray diffraction patterns for YBCO thick films prepared by the two step procedure. Initial deposition conditions (a): 1 J cm\(^{-2}\), 1 Hz, 710 °C, 200 mTorr (b): 3 J cm\(^{-2}\), 1 Hz, 710 °C, 200 mTorr (c): 5 J cm\(^{-2}\), 1 Hz, 710 °C, 200 mTorr. Top surface layer deposition conditions: 10 Hz, 2 J cm\(^{-2}\), 710 °C.](image)
case of a higher laser fluence of 5 J cm\(^{-2}\), the surface morphology showed surface roughness due to a number of droplets. The X-ray diffraction pattern of the film shows the weak (001) peaks as shown in Fig. 2(c). The above result suggests that controlling the plasma plume by optimization of laser fluence is one of the techniques that can be used to improve quality of the thick films.

3.2. YBCO thick film preparation by three steps procedure

A three steps PLD process was attempted to fabricate YBCO thick films. Fig. 3 shows a typical deposition scheme consisting of a bottom ultrathin layer (about 2 nm), an intermediate layer (about 300 nm) and the surface thick layer (about 700 nm). Deposition conditions for each layer were changed to prepare high-quality superconducting thick films. In the initial deposition condition for the bottom layer we chose the same conditions as in Fig. 2(b). The intermediate layer was also prepared under the conditions of 10 Hz, 2 J cm\(^{-2}\) and 710°C. The top surface layer was fabricated using two different conditions: a lower repetition rate of 5 Hz or a low substrate temperature of 650°C. Fig. 4 shows the SEM micrograph for YBCO thick films by the three steps procedure. Fig. 4(a) is the SEM of the thick film prepared at 10 Hz and 710°C for both intermediate and surface layers. There are a number of particles on the surface resulting in the roughness in the thick film growth. This thick film shows the basket-weave morphology. When the laser repetition rate is decreased to 5 Hz, the particle number on the film surface abruptly decreases as shown in Fig. 4(b). This thick film showed highly c-axis orientation normal to the substrate. This suggests that low repetition rate improves the film quality due to suppression of generation of the particles.

Fig. 4(c) is a SEM image of the thick film consisting of the top layer prepared at lower substrate temperature 650°C and high repetition rate (10 Hz). It is clearly shown that there are needle-shaped a-axis outgrowths. The needles are a-axis regions which have been observed at lower substrate temperatures by others [5]. In spite of a high repetition rate, decreasing the substrate temperature makes a-axis growth enhance and c-axis growth reduce.

Fig. 5 shows the resistivity–temperature curves for the

![Fig. 4. SEM micrographs for thick films prepared by the three steps deposition procedure under various surface layer deposition conditions. Bottom deposition condition: 1 Hz, 3 J cm\(^{-2}\), 710°C. Intermediate layer deposition conditions: 10 Hz, 2 J cm\(^{-2}\), 710°C. Top surface deposition conditions: (a) 10 Hz, 2 J cm\(^{-2}\), 710°C; (b) 5 Hz, 2 J cm\(^{-2}\), 710°C; (c) 10 Hz, 2 J cm\(^{-2}\), 650°C.]

same samples as in Fig. 4. The sample (b) corresponding to Fig. 5(b) has the superconducting transition at \(T_c\) (zero) = 88.2 K. Although the sample (c) also shows slightly higher normal resistivity comparing with the sample (b), the superconducting transition for the sample
(c) occurs at $T_c(\text{zero})=89.5$ K. The superconducting properties of the sample (a) prepared with the two step procedure were degraded by the surface roughness caused by the particles. The thick film has a 5 times higher normal resistivity and a low transition temperature of $T_c(\text{zero})=82.1$ K. It is shown that the multistep thick film preparation provides the improved superconducting properties by optimizing the deposition conditions for each layer.

3.3. Estimate of critical current density of YBCO thick films

Very often the transport measurements in thick superconducting films lead to wrong results. Structural or compositional nonuniformities lead to the stratification of the transport current. Regions of extremely high current thus interlace with regions of near zero current [6]. The calculated value of the critical current $J_c$, which is determined by the normalization over total film cross-section, thus is found to be underestimated. In magnetic measurements the measured value of magnetization is proportional to the transversal size of a film and the maximum value of the diamagnetic currents induced in a film plane. Therefore, the magnetization measurements using SQUID was used to estimate the critical current $J_c$ in prepared YBCO thick films. The temperature dependency of magnetization is shown in Fig. 6. The Bean model has been applied to determine critical current density [7]. According to this model, the critical current density is proportional to the remnant magnetic moment. The analysis of this technique gives volumetric critical current results many orders of magnitude larger than the transport measurements [8]. Samples A and B were prepared by the three steps procedure and sample C by the two steps procedure as shown in Table 1. A high critical transition temperature of 80 K was achieved for the YBCO thick film by the three steps process. In order to quantify the preferential c-axis orientation we have measured the rocking curves for the neighboring MgO-200 and YBCO-006 reflections. The widths of the rocking curves for the sample A are narrow, with the full width at half-maximum FWHM=0.906° and 0.117° for YBCO and MgO respectively. The Bean model analysis provides the current density of $1.2 \times 10^6$ A cm$^{-2}$ (at 5 K) for the magnetization curve of the sample A. A gradual increase of the magnetization with temperature up to 70 K is a distinctive feature for the thick film A. This is caused by the layered structure of the YBCO thick film.

4. Conclusion

The multistep laser deposition technique was applied to prepare the Y-Ba-Cu-O thick films with a thickness of about 1 mm. The processing conditions were optimized vertically from the bottom to the surface. In particular, careful control of the laser repetition rate, laser fluence and substrate temperature for the initial bottom layer and the deposition near 0.4–0.5 mm dominated the Y-Ba-Cu-O thick film properties. The deposited Y-Ba-Cu-O thick films with a thickness of about 1 mm have the superconducting properties of zero-resistivity critical temperature 88 K and critical current density of $10^6$ A cm$^{-2}$ (at 5 K).

This work was partly performed by the cooperative research program with Kyushu Electric Power Co.Inc.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Superconducting properties of YBCO thick films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Bottom</td>
</tr>
<tr>
<td>A</td>
<td>1 Hz</td>
</tr>
<tr>
<td></td>
<td>680 °C</td>
</tr>
<tr>
<td>B</td>
<td>1 Hz</td>
</tr>
<tr>
<td></td>
<td>680 °C</td>
</tr>
<tr>
<td>C</td>
<td>1 Hz</td>
</tr>
<tr>
<td></td>
<td>680 °C</td>
</tr>
</tbody>
</table>

References


Fig. 6. Temperature dependence of magnetization for YBCO thick films. The deposition conditions are indicated in Table 1.