Deposition-Temperature Dependence of Vortex Pinning Property in YBa$_2$Cu$_3$O$_7$+BaHfO$_3$ Films

Tomoya Horide$^{1}$, Kenta Torigoe$^{1,2}$, Ryusuke Kita$^{2}$, Ryota Nakamura$^{1,2}$, Manabu Ishimaru$^{1}$, Satoshi Awaji$^{3}$ and Kaname Matsumoto$^{1}$

$^{1}$Department of Materials Science and Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan
$^{2}$Graduate School of Integrated Science and Technology, Shizuoka University, Hamamatsu 432-8561, Japan
$^{3}$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Improvement of critical current density ($J_c$) in magnetic fields is required in YBa$_2$Cu$_3$O$_7$ films, and process parameters should be optimized for controlling pinning centers. In the present study, a deposition temperature was varied in pulsed laser deposition of YBa$_2$Cu$_3$O$_7$+BaHfO$_3$ films to control the nanorod structure, and its influence on $J_c$ was analyzed. The YBa$_2$Cu$_3$O$_7$+BaHfO$_3$ film deposited at 850°C exhibited pinning force maximum ($F_{p,max}$) as high as 413 GN/m$^3$ at 40 K, while the $F_{p,max}$ for the deposition temperature of 850°C at 77 K was smaller than that in the YBa$_2$Cu$_3$O$_7$+BaHfO$_3$ film deposited at 900°C. A critical temperature decreased and matching field increased with decreasing the deposition temperature. Increase in deposition temperature is effective in improving the $F_{p,max}$ in high temperatures, since the critical temperature and matching field dependences of $J_c$ value dominate the $F_{p,max}$. On the other hand, low deposition temperature improves the $F_{p,max}$ in low temperatures since the $F_p$ shift in accordance with matching field is dominant to the $F_{p,max}$. Thus, the deposition temperature should be set in pulsed laser deposition of YBa$_2$Cu$_3$O$_7$ films containing nanorods considering the $J_c$ variation with critical temperature and matching field.

[doi:10.2320/matertrans.MT-M2019303]

(Received October 17, 2019; Accepted December 16, 2019; Published February 25, 2020)

Keywords: YBa$_2$Cu$_3$O$_7$, vortex pinning, critical current density, nanorod, thin film

1. Introduction

For development of high-performance REBa$_2$Cu$_3$O$_7$ (REBCO; RE = Y, Nd, Sm, Gd etc.) superconducting tapes, improvement of critical current density ($J_c$) is required.$^{1)}$ Introduction of pinning centers can improve $J_c$, and nanocomposite structures containing nanorods or nanoparticles are effective in improving vortex pinning in REBCO superconducting tapes. Pulsed laser deposition (PLD)$^{2)}$ and metal organic chemical vapor deposition (MOCVD)$^{3)}$ are the most used method for fabricating REBCO tapes, and BaMO$_3$ (M = Zr, Sn, Hf etc.) nanorods$^{4,7)}$ which work as strong pinning centers, can be introduced into the REBCO tapes and films using these methods. The vortex pinning properties of nanorods are determined by several structural parameters such as nanorod density, length, interface structure, and strain etc. The nanorod density significantly affects the pinning properties in magnetic field, since the vortex density increases with increasing magnetic field.$^{8)}$ The length and tilt of nanorods determine the vortex volume which is accommodated by a nanorod, namely the pin potential. Furthermore, the interface structure affects an elementary pinning force.$^{9)}$ It has also been reported that the strain of matrix affects the critical temperature ($T_c$) by varying the oxygen vacancy formation energy.$^{10)}$ To achieve high $J_c$ in the REBCO tapes and films containing nanorods, the process parameters should be optimized to control these factors.

Supply of atoms from the plume, surface diffusion, nucleation and growth occur under non-equilibrium conditions in the case of PLD. Deposition temperature, laser condition, target composition etc. should be optimized to control these phenomena, when high quality single phase films are fabricated using PLD.$^{11-13)}$ The growth of nanocomposite film is more complicated, because the nanocomposite structure is formed with complex process comprising diffusion of atoms, nucleation and growth of matrix and second phase, and coalescence of the islands. The nanorod structure is significantly changed by the PLD conditions such as the deposition temperature and the deposition rate as well as the selection of matrix and nanorod material. In order to control the nanorod structure in REBCO, RE = Y, Nd, Sm, Eu, Gd etc. for matrix, and M = Zr, Hf, Sn etc. for nanorod have been investigated. Furthermore, it has been reported that the nanorod structure and the $J_c$ characteristics are controlled by changing the PLD conditions. Among them, the deposition temperature is one of the most important parameters. It has been reported that the size, density, and length of nanorods strongly depend on the deposition temperature: The nanorods are cut and tilted$^{14,15)}$ and the density of the nanorods is increased$^{16)}$ with lowering the deposition temperature. These indicate that the deposition temperature should be optimized to control the nanorod structure and to achieve high $J_c$.

In this study, we focus on the deposition temperature in fabricating YBa$_2$Cu$_3$O$_7$+BaHfO$_3$ (YBCO+BHO) films using PLD. A magnetic field dependence of $J_c$ significantly varied with the deposition temperature, and high $J_c$ values were obtained at 40 K in the film prepared at moderately low temperature. We analyze the $J_c$ values based on $T_c$ and matching field, and the deposition-temperature dependence of vortex pinning is discussed in the YBCO+BHO films. Based on the results, structure and process designs on nanorod are discussed to achieve high $J_c$ in YBCO+BMO films.
2. Experimental

Sample preparation was performed using PLD. The target was a YBCO+BHO mixed target, whose BHO content was fixed at 4.7 vol%. The oxygen partial pressure was 26 Pa, and the film thickness is shown in Table 1. The deposition temperature was varied between 830°C and 900°C. After the deposition, the films were cooled to 200°C in an oxygen atmosphere of 55000 Pa in 1 hour, and the films were removed from the chamber at 100°C or below. Here, YBCO+BHO(X) means a YBCO+BHO film prepared at X°C. Transmission electron microscopy (TEM) observation was performed to clarify the nanorod structure. A bridge having a width of 90 µm and a length of 1 mm was formed on the films by photolithography and H3PO4 wet etching, and superconducting properties were evaluated using Physical Property Measurement System. Tc and irreversible temperature (Tirr) were evaluated by measuring a temperature dependence of electrical resistance. A current density-electric field (J-E) curve was measured to evaluate Jc. Furthermore, the Jc in the YBCO+BHO(850) was measured in temperatures of 65 K and 40 K and magnetic fields up to 16 T using the 20 T superconducting magnet in Institute of Materials Research, Tohoku University. The magnetic field angles for the magnetic fields parallel to the ab plane and the c-axis are defined as -90° and 0°, respectively. 1 µV/cm was used as a criterion to determine the Jc and Tirr. Furthermore, the n value was obtained in the range of 10–100 µV/cm assuming the relationship of E ∼ Jn.

3. Results

The cross-sectional TEM image of the YBCO+BHO(850) is shown in Fig. 1. The nanorods with a spacing of 15–20 nm and a diameter of ~6 nm are elongated through the film thickness. The matching field (Bφ) is roughly estimated to be ~6.8 T from the spacing of the nanorods. From a report on deposition-temperature dependence of the nanorod structure, 15) it is considered that the nanorods are elongated through the thickness at the deposition temperatures higher than 850°C.

Figure 2 shows a magnetic field dependence of Jc at 77 K in the films. When the deposition temperature was 850–900°C, the Jc at 0 T was about 2 MA/cm². On the other hand, the Jc for YBCO+BHO(830) was 0.3 MA/cm² at 0 T. The YBCO+BHO(850) and YBCO+BHO(900) films exhibit almost the same Jc-B curves, and the Jc decreases above 4 T. In the YBCO+BHO(850), the magnetic field dependence of Jc is different from those in the YBCO+BHO(890) and

<table>
<thead>
<tr>
<th>Parameters of the YBCO+BHO films prepared in the present study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness /nm</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>YBCO+BHO(900)</td>
</tr>
<tr>
<td>YBCO+BHO(890)</td>
</tr>
<tr>
<td>YBCO+BHO(850)</td>
</tr>
<tr>
<td>YBCO+BHO(830)</td>
</tr>
</tbody>
</table>

Fig. 1 TEM image of the YBCO+BHO(850) film.
YBCO+BHO(900), and $J_c$ starts to decrease at 6 T. Furthermore, the magnetic field dependence of the global pinning force ($F_p = J_c \times B$) is shown in Fig. 2(b). The $F_p$ for deposition temperatures of 890°C and 900°C exhibits the maximum value at 4 T, and the largest value at 77 K in this study is 19.3 GN/m$^3$ in the YBCO+BHO(900). The YBCO+BHO(850) exhibits a $F_{p,max}$ (maximum value of $F_p$) of 15.1 GN/m$^3$ at 6 T. On the other hand, in the YBCO+BHO(830), the $J_c$ and $F_p$ at 77 K are one or more orders smaller than those in the other films. Thus, it was found that the $J_c$ at 77 K strongly depends on the deposition temperature, and the $F_{p,max}$ at 77 K decreases with lowering the deposition temperature. Table 1 also shows the $J_c$ of 20 K and 9 T. At high temperature (77 K) and low magnetic field, the YBCO+BHO(900) exhibits a high $J_c$, but $J_c$ becomes higher in the YBCO+BHO(850) with decreasing temperature and with increasing magnetic field. In the YBCO+BHO(830), the $J_c$ at 77 K is extremely small, but the $J_c$ at 20 K and 9 T is comparable to that in the other films.

From the results in Fig. 2, high $J_c$ is expected at low temperature and high magnetic field in the YBCO+BHO(850). The $J_c$ characteristics of YBCO+BHO(850) at 65 K and 40 K are shown in Fig. 3. The $F_p$ of YBCO+BHO(850) exhibits the maximum at 7–8 T in temperatures of 65 K and 40 K. These are almost the same as the magnetic field at which $F_{p,max}$ was observed at 77 K, showing that the matching field determines the $F_{p,max}$ and the peak field. The value of $F_{p,max}$ is 103 GN/m$^3$ at 65 K and 413 GN/m$^3$ at 40 K. Figure 3 also shows an angular dependence of the $J_c$ at 65 K in the YBCO+BHO(850). A large c-axis peak in the YBCO+BHO(850) shows that the nanorod worked as a strong c-axis correlated pinning centers.

The matching field ($B_m$) and $T_c$ are important parameters for $J_c$ characteristics. Figure 4 shows a resistance-temperature ($R-T$) curve of the films. The resistance started to decrease near 90 K, and became zero at 88–83 K. Sharp superconducting transition was observed around 88 K for the YBCO+BHO(900) and the YBCO+BHO(890). However, the YBCO+BHO(850) and YBCO+BHO(830) films exhibited a two-step superconducting transition, and this tendency was remarkable in the YBCO+BHO(830). It is considered that the two-step transition is caused by a compositional deviation due to the deposition at the low temperature. The deposition-temperature dependence of $T_{c0}$ is shown in Fig. 4(b). As is observed in the $R-T$ curves, $T_{c0}$ decreases with decreasing the deposition temperature, and the significant decrease in $T_{c0}$ is caused by the two-step superconducting transition. $T_{ir}$-$B$ and $(1 - T_{ir}/T_c)$-$B$ curves are shown in Fig. 5(a) and (b). $T_{ir}$ decreases with increasing magnetic field, but its tendency varies after exhibiting a shoulder at $\sim 3.5$–7 T. The $T_{ir}$-$B$ behavior for the high magnetic field side and for the low magnetic field side does not depend on the deposition temperature, but the magnetic field at which the shoulder is observed strongly depends on the deposition temperature. It is known that the shoulder is observed at $B_m$ in $T_{ir}$-$B$ curve.8)
values determined from the TEM and the $T_{\text{irr}}$ shoulder may be due to the accuracy for measuring the nanorod spacing in the cross-sectional observation. Furthermore, the $F_p$ peak in low temperature may possibly be affected by contribution of the random pinning. Also in the previous report, the $T_c$ has decreased and the $B_\Phi$ has increased with decreasing the deposition temperature in YBCO+BHO.\textsuperscript{17} The difference between the present and previous results are due to slight difference in controlling the substrate temperature and the growth rate, but it seems that the present tendency of $T_c$ and $B_\Phi$ to the deposition temperature is similar to that in the previous report.

4. Discussion

Table 2 compares the present results with the high $J_c$ values reported in literatures.\textsuperscript{18–20} The $F_{p,\text{max}}$ value of 15 GN/m\textsuperscript{3} at 77 K is not so large compared with the results in the previous reports. On the other hand, the $F_{p,\text{max}}$ values of 400–407 GN/m\textsuperscript{3} have been observed in SmBCO+BHO at 40 K.\textsuperscript{18,19} and the present $F_{p,\text{max}}$ value of 413 GN/m\textsuperscript{3} at 40 K is one of the highest values. Thus, the high $F_{p,\text{max}}$ was successfully obtained especially at 40 K in the present YBCO+BHO(850). The reason for the high $F_{p,\text{max}}$ value is discussed based on $T_c$ and $B_\Phi$.

4.1 Magnetic field dependence of $J_c$

At 77 K, the $F_{p,\text{max}}$ for the YBCO+BHO(900) and YBCO+BHO(890) was larger than that for the YBCO+BHO(850). The size of nanorod decreases with decreasing the deposition temperature, and the diameter of nanorod was about 6 nm in the YBCO+BHO(850). When the nanorod size is smaller than the vortex size, the vortex volume which is accommodated by a nanorod may determine the pin potential. However, the $J_c(0 \text{T})$ obtained from the pin potential is much larger than the experimental value, suggesting that not only the depinning from the nanorod but also vortex excitation such as half loop or double kink determine the $J_c$.\textsuperscript{21} Actually, the $J_c(0 \text{T})$ at 77 K is comparable in the YBCO+BHO(900), YBCO+BHO(890), and YBCO+BHO(850), and the difference in nanorod size does not affect the $J_c(0 \text{T})$. The previous study also showed that the effect of nanorod size decreases with decreasing temperature, and the effect of nanorod size disappears below 77 K.\textsuperscript{22} The result in this study is consistent with this previous conclusion. Thus, the influence

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c / \text{K}$</th>
<th>$B_\Phi / \text{T}$</th>
<th>$F_{p,\text{max}} (77 \text{K}) / \text{GN/m}^3$</th>
<th>Peak field (77 K) / T</th>
<th>$F_{p,\text{max}} (40 \text{K}) / \text{GN/m}^3$</th>
<th>Peak field (40 K) / T</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO+BHO(850)</td>
<td>86.1</td>
<td>6.8</td>
<td>15.1</td>
<td>6</td>
<td>413</td>
<td>8</td>
</tr>
<tr>
<td>SmBCO+BHO(18)</td>
<td>91.1</td>
<td>5.8</td>
<td>32.5</td>
<td>5</td>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>SmBCO+BHO(19)</td>
<td>91</td>
<td>9.9</td>
<td>14.2</td>
<td>6</td>
<td>407</td>
<td>10</td>
</tr>
<tr>
<td>GdBCO+BHO(20)</td>
<td>89.1</td>
<td>4.1</td>
<td>22.5</td>
<td>5.5</td>
<td>285</td>
<td>7</td>
</tr>
<tr>
<td>(Gd,Y)BCO+20%Zr(3)</td>
<td>90</td>
<td></td>
<td>22*</td>
<td>3-5*</td>
<td>365*</td>
<td>5-9*</td>
</tr>
</tbody>
</table>

A dependence of $B_\Phi$ on the deposition temperature is shown in Fig. 5(c), demonstrating that the nanorod spacing decreases as the diffusion length decreases with lowering the deposition temperature. The difference between the $B_\Phi$
of nanorod size is not dominant to the difference of $J_c$ in this study.

The $B_\theta$ dependence of $J_c(B)/J_c(0 \ T)$ is discussed. In Fig. 2, $J_c(B < B_\theta)/J_c(0 \ T)$ is large in the YBCO+BHO(900) whose $B_\theta$ is small. It has been reported that $J_c(B < B_\theta)/J_c(0 \ T)$ decreases with increasing $B_\theta$ in YBCO+BMO. When the vortices move between the nanorods by the double kink or half loop excitation, the vortex excitation becomes more significant with increasing $B_\theta$ that is, with decreasing the nanorod spacing. The vortex motion has been discussed based on the $n$ value and creep analysis. The $n$ values at 77 K and 2 T are shown in Table 1, indicating that the $n$ value is small for low deposition temperature. The result on $n$ value also supports the conclusion that the vortex excitation becomes significant in the case of narrow nanorod-spacing, namely the case of low deposition temperature.

On the other hand, when $B_\theta$ increases, it becomes possible to pin high-density vortices, so high $J_c$ can be maintained even in high magnetic fields. $J_c$ is almost constant at 1–7 T in the YBCO+BHO(850) because there are sufficient pinning sites. When the magnetic field increases and all the pinning centers are occupied by vortices, the vortices are pinned by elastic interaction between vortices, and $J_c$ decreases rapidly. Since the region of single vortex pinning by the nanorods was extended to high magnetic field, $F_{p,max}$ shifted to the high magnetic field, and as a result, the $F_{p,max}$ at low temperature became large in the YBCO+BHO(850).

### 4.2 Influence of $T_c$ on nanorod pinning

It is expected that $T_c$ also significantly affects $J_c$. Figure 6(a) shows a $T_c$ dependence of $J_c(77 \ K, 0 \ T)$ in the YBCO+BMO films. In addition to the results of this study, the results of the literature which is shown in Table 2 are also shown. The results for the films with different $B_\theta$ are compared in Fig. 6(a), since the $J_c(0 \ T)$ is not affected by the matching field. In order to take account of the two-step transition, $T_{cstr}$ was obtained by extrapolating the sharp decrease in $R$-$T$ curve at $T < T_{onset}$ to $R = 0$. $T_{0}$ is determined by the weakest point along the superconducting path. On the other hand, $T_{cstr}$ represents the superconducting transition with excluding anomaly of the inhomogeneously weakened point. $J_c$ is given by the voltage generation when current flows in the entire superconducting region, suggesting that $T_{cstr}$, not $T_{0}$ is suitable parameter for discussing $J_c$. Actually, it has already been discussed that the $J_c$ values can be explained by $T_{cstr}$ rather than $T_{0}$. Although some results deviated from the tendency, the $J_c(77 \ K, 0 \ T)$ tends to increase with increasing $T_c$ regardless of the sample. The reason for the deviation in some samples is reduction in effective current flowing path, or the change in nanorod shape (e.g. the inclined growth of nanorod at low deposition temperature). Furthermore, Fig. 6(b) shows the $J_c(40 \ K, 3 \ T)$-$T_c$ ($T_{cstr}$) for the samples in the present study, the samples reported in the previous studies, and the samples reported in Table 2. Because the in-field $J_c$ is strongly affected by matching field, Fig. 6(b) shows the results for $B_\theta = 4–7 \ T$. Here, the result in Ref. 19 is excluded from Fig. 6(b) because its $B_\theta$ of ~10 T is slightly larger than the $B_\theta$ in Fig. 6(b). Similarly to the $J_c(77 \ K, 0 \ T)$, the $J_c(40 \ K, 3 \ T)$ decreases with decreasing $T_c$ ($T_{cstr}$).

### 4.3 Nanorod structure design for improving $F_{p,max}$

These analyses show that the $F_{p,max}$ is determined by the $B_\theta$ dependence of $J_c(B < B_\theta)/J_c(0 \ T)$, the peak shift of $F_{p,max}$, and the $T_c$ effect. The $F_{p,max}$ at 77 K in the present study was smaller than those in the literature which is discussed in Table 2. Both the $T_c$ dependence of $J_c$ value and $B_\theta$ dependence of $J_c(B < B_\theta)/J_c(0 \ T)$ significantly affect the $F_{p,max}$ in high temperatures near 77 K. The $F_{p,max}$ shifts to high magnetic field due to large $B_\theta$ in the YBCO+BHO(850), but this cannot compensate the effect of $T_c$ and $J_c(B < B_\theta)/J_c(0 \ T)$. Therefore, in order to obtain high $F_{p,max}$ in high temperatures, moderate (or low) matching field and high $T_c$ are required, and this situation can be achieved by increasing the deposition temperature.

On the other hand, the high $F_{p,max}$ at 40 K was obtained for the deposition temperature of 850°C in spite of low $T_c$ ($T_{cstr}$). In this study, the $F_{p,max}$ was observed in slightly higher magnetic field in the YBCO+BHO(850) than in the previous reports. The high $F_{p,max}$ was obtained in the YBCO+BHO(850) because the peak shift in $F_\theta$ dominantly increased $F_{p,max}$. This indicates that the $F_{p,max}$ in low temperatures can be enhanced by increasing $B_\theta$ even if $T_c$ is slightly lowered. This is achieved by moderately low deposition-temperature.

Thus, this study demonstrates that the $J_c$ characteristics can be controlled by changing $B_\theta$ and $T_c$, and that optimization of $B_\theta$ and $T_c$ is needed depending on temperature and magnetic field for $J_c$ measurement. Furthermore, structure control such as the hybrid pinning and the control of interface and...
strain at the atomic scale is promising for further improvement of $J_c$.

5. Summary

The YBCO+BHO films were prepared using PLD, where the deposition temperature was changed between 830 and 900°C to control the nanorod structure. The highest $F_{p,\text{max}}$ at 77 K ($= 19.3 \text{ GN/m}^2$) was obtained for the deposition temperature of 900°C, but the high $F_{p,\text{max}}$ at 40 K was 413 GN/m$^2$ in the film deposited at 850°C. As the deposition temperature decreased, $T_c$ decreased and $B_{\Phi}$ increased. The films with high $T_c$ and low $B_{\Phi}$ can achieve high $F_{p,\text{max}}$ in high temperatures such as 77 K, while the film with high $B_{\Phi}$ exhibits high $F_{p,\text{max}}$ at low temperatures such as 40 K even if the $T_c$ is slightly low. While the former situation of high $T_c$ and low $B_{\Phi}$ is achieved in high deposition temperature, the latter situation of slightly low $T_c$ and high $B_{\Phi}$ is achieved in moderately low deposition temperature. Depending on temperature and magnetic field for measurement and application, the deposition temperature should be varied based on $T_c$ and $B_{\Phi}$ to enhance the $J_c$.

Acknowledgements

This work was partially supported by Grant-in-Aid for Scientific Research (B) (18H01478). The measurement was partially performed at High Field Laboratory for Superconducting Materials Institute for Materials Research, Tohoku University (17H0047).

REFERENCES