Transactions of the Materials Research Society of Japan 29[4] 1253-1256 (2004)

Investigation of Crystal Defects in YBCO Films by Post-Annealing of Precursor Films Including BaF_2

Ataru Ichinose[1], Akihiro Kikuchi[2], Takanobu Kiss[3], Kyoji Tachikawa[4], Shirabe Akita[1] and Kiyoshi Inoue[2]
[1]Central Research Institute of Electric Power Industry, Komae, Tokyo 201-8511 Japan
Fax: 81-3-3480-3401, e-mail: ai@criepi.denken.or.jp, akita@criepi.denken.or.jp
[2]National Institute for Materials Science, Tsukuba 305-0047, Japan
Fax: 81-298-59-2301, e-mail: KIKUCHI.Akihiro@nims.go.jp, INOUE.Kiyoshi@nims.go.jp
[3]Kyushu University, Fukuoka, Fukuoka 812-8581, Japan
Fax: 81-92-642-3963, e-mail: kisu@ees.kyushu-u.ac.jp
[4]Tokai University, Hiratsuka, Kanagawa 259-1292, Japan
Fax: 81-463-50-2096, e-mail: tacsuper@keyaki.cc.u-tokai.ac.jp

Precursor films are deposited on $SrTiO_3$ single crystals using Y, BaF_2 and Cu as evaporation sources at room temperature. The precursor films are subsequently annealed in a low-oxygen pressure atmosphere to obtain crystallized YBCO films. We intentionally do not introduce water vapor to a reaction chamber in the annealing process. The YBCO films indicate the c-axis orientation by x-ray diffraction. Characteristics of critical current density, J_c, vs. magnetic field (J_c-B) are measured as a function of temperature in magnetic field parallel and perpendicular to the film surface. The J_c value at 77 K in self-field is approximately 5 MA/cm^2. And the J_c value at 80 K in 10 T (B//ab-axis) is approximately 0.13 MA/cm^2. The Angular dependences of J_c are also measured at several magnetic fields. As a result, it is possible that some pinning center exists along the c-axis direction (perpendicular to the film surface). Therefore, we observe crystal defects such as twin boundaries, grain boundaries between a- and c-axis oriented grains and impurities using a transmission electron microscope (TEM). At a viewpoint of microstructure, we discuss whether these defects effectively work as pinning centers along the c-axis direction or not.

Key words: BaF_2, E-beam deposition, Microstructure, TEM, Critical current

1. INTRODUCTION

$YBa_2Cu_3O_{7-x}$ (YBCO)-coated conductors are expected to be useful for numerous applications of high-T_c superconductors. Several YBCO fabrication processes using starting materials including fluorine, the so-called fluorine processes, have been reported. The merits of fluorine processes are that they are relatively simple and it is considerably easy to obtain high-J_c YBCO films. The representative processes of the fluorine process are the BaF_2 ex situ process [1, 2], the TFA-MOD process [3, 4] and our process. In our process, the film deposition is similar to that in the BaF_2 ex situ process, which is deposited by co-evaporation of Y, BaF_2 and Cu. However, annealing conditions are very different from those of the other processes, which are a low-pressure atmosphere and introduction of only pure oxygen gas. Annealing conditions of the other process are approximately ambient atmosphere and introduction of oxygen gas, water vapor and inert gas such as nitrogen gas.

Our previous work [5, 6] revealed that YBCO films were obtained without introducing water vapor when the precursor films were annealed in a low-oxygen pressure atmosphere. The c-axis-oriented YBCO films were successfully prepared on $SrTiO_3$ substrates and Y_2O_3-buffered $SrTiO_3$ substrates. In the case of approximately 200 nm thick, the YBCO films almost grew up to the film surface when the temperature reached to the maximum annealing temperature [7]. It was found that the obtained YBCO films grew epitaxially according to the observation of cross-sectional transmission electron microscope (TEM) [8]. The layer structures corresponding to a unit cell along to the c-axis direction are clearly observed in the entire film thickness from the interface to the surface top. Furthermore, the columnar structures with different contrast were observed in the YBCO film cross-sectional TEM images, which is perpendicular to the film surface and has the typical distance of approximately 50 nm.

The critical current density, J_c, at 77 K and in a self-field is quite high, approximately 5 MA/cm^2 [7]. In the case of a magnetic field parallel to the film surface, J_c at 80 K is higher than 0.1 MA/cm^2 up to the magnetic field of 12 T. In the case of magnetic field perpendicular to the film surface, the reduction of J_c occurs as a common J_c-B property of the high-T_c superconductors. The results are also compared with the properties of the YBCO film deposited by a pulse laser deposition (PLD). The magnetic field, B_{GL}, where a finite electric resistance appears with decreasing electrical field, is slightly better than in the YBCO film obtained by PLD, indicating that the J_c-B properties in the high magnetic field are also excellent. Furthermore, the differences of the field angle dependences of J_c are revealed between the present YBCO film and the PLD-YBCO film. Some kinds of pinning center along to the c-axis direction appear to exist in the only YBCO film prepared by annealing of the precursor film. We discuss pinning centers in the

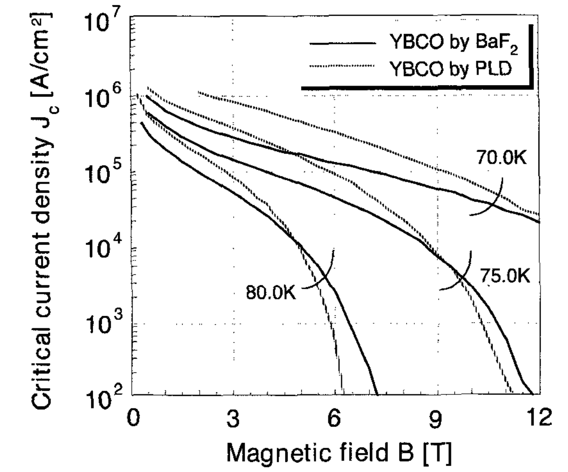

Fig. 1 Critical current densities vs magnetic fields for the YBCO film prepared by no-additional-water annealing of precursor film and the PLD-YBCO films.

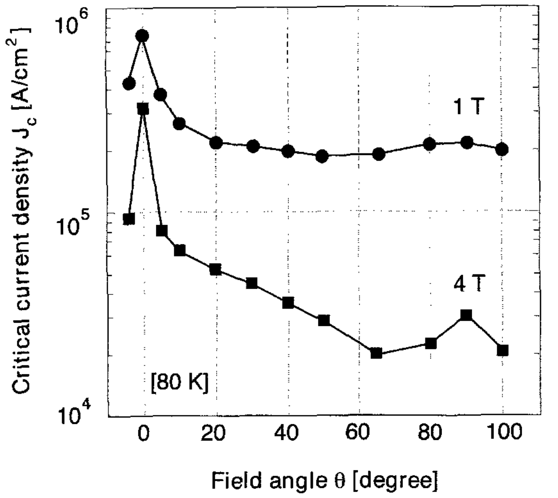

Fig.2 Field angle dependences of the critical current density at 80 K in 1 T and 4 T.

YBCO films from the viewpoint of microstructures.

2. EXPERIMENTAL PROCEDURES

Precursor films were deposited on $SrTiO_3$ single crystals at room temperature by a co-evaporation technique using Y, BaF_2 and Cu as evaporation sources. The precursor films were subsequently annealed under a low pressure of oxygen atmosphere. Pure oxygen gas was introduced near the samples, but water vapor was not introduced into the reaction chamber. The annealing period at the maximum temperature is 30 minutes. After that, the temperature was reduced to approximately 550°C, and pure oxygen gas was introduced until the chamber pressure was 100 Torr, to fully oxidize YBCO films, keeping the temperature at 550°C.

The crystal alignment of YBCO films was measured by XRD θ-2θ scans and φ-scans. The cross-sectional TEM images and the plan-view TEM images were obtained using a HITACHI HF-2000 microscope. The TEM samples are prepared by cutting and milling using a focused ion beam. Extend E-J properties were measured by a standard four-probe method at various conditions of B, T and θ. Magnetic field was applied up to 12 T. The sample was rotated to change the direction of the applied magnetic field. θ was defined by the angle from the film surface. Namely, θ =0° is parallel to the film surface.

3. RESULTS

Fig. 1 shows J_c-B properties under magnetic fields up to 12 T applied perpendicular to the film surface at the measurement temperatures of 70, 75 and 80 K. Reference J_c-B curves for 70, 75 and 80 K also, shown in Fig. 1 are for the YBCO film deposited by PLD on a $SrTiO_3$ substrate [8]. The both film thickness are approximately 200 nm. The J_c values in the higher magnetic fields of 12 T (70 K), 9 T (75 K) and 5T (80 K) are almost the same in YBCO films prepared by the present process and by the PLD process. However, J_c differences between the present YBCO film and the PLD-YBCO are clearly observed in low and medium magnetic fields. The typical curve of the J_c-B properties for the YBCO films obtained by the present process is S-shaped. The change of the curvature of the J_c-B properties by magnetic fields depends on the temperature. On the other hands, when the magnetic fields applied parallel to the film surface, the J_c-B properties are the almost the same in the PLD-YBCO.

The magnetic–field angle dependencies of J_c are also measured at the temperature of 80 K and the magnetic field of 1 T, showing in Fig. 2. In general, the J_c is decreasing with increasing the angle of the applied-magnetic field. For example, the PLD-YBCO as the reference film in Fig. 1 is not observed a peak at the 90 degrees. However, a broad peak at the 90 degrees is clearly observed in Fig. 2, indicating that some kinds of pinning center exists in the YBCO film, which is effective in the direction perpendicular to the film surface.

The magnetic–field-angle dependences of J_c are also measured at the temperature of 80 K in the magnetic fields of 1 T and 4 T, as shown in Fig. 2. In general, J_c decreases with increasing angle of applied magnetic field. For example, the reference PLD-YBCO in Fig. 1 does not exhibit J_c increase at 90 degrees. However, a broad peak at 90 degrees is observed in Fig. 2, indicating that some kinds of pinning centers exist in the YBCO film, which are effective in the direction perpendicular to the film surface. The magnetic field of 4 T is almost the crossover point of J_c at 80 K between the both YBCO films, indicating that the good J_c-B properties in higher magnetic field as shown in Fig. 1 appear to result from some kinds of pinning centers perpendicular to the film surface.

Previous works were on the microstructures of the YBCO films, as observed in cross-sectional TEM images [3]. This time, we also observed the plan-view TEM images of the YBCO films. A large-area plan-view TEM image is shown in Fig. 3. Many twin boundaries, some a-axis-oriented grains and impurity grains are observed. It is found that the columnar structures observed as a kind of crystal defect in the cross-sectional TEM image results from the twin boundaries, because the columnar structures and the twin boundaries matched perfectly. Furthermore, impurity grains observed in the cross-sectional TEM image and in the plan-view TEM image are circles of approximately 50

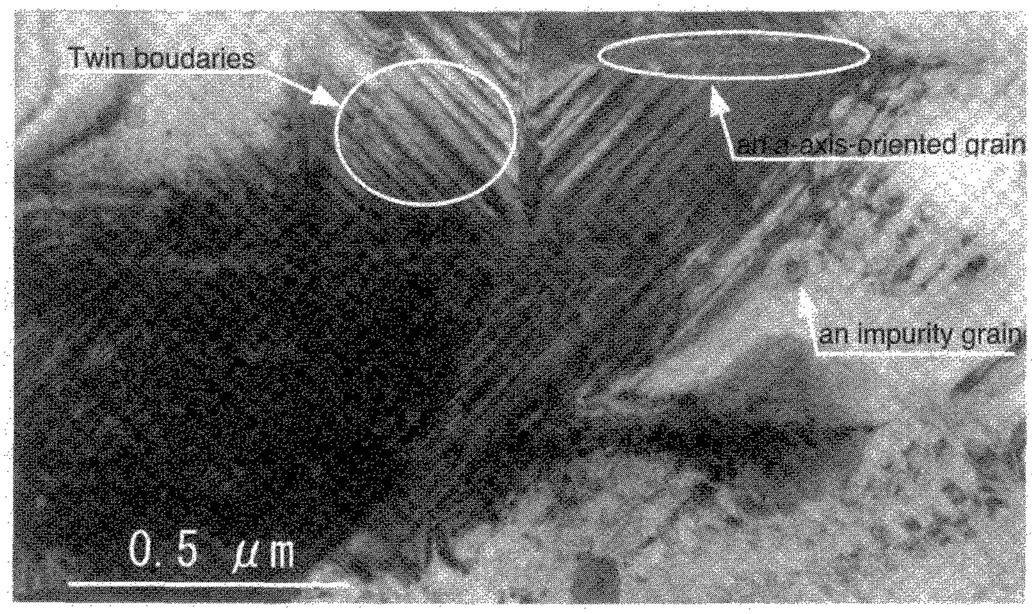

Fig. 3 Plan-view TEM images of the YBCO films.

nm diameter, indicating that the shape of the impurity grains is a sphere.

4. DISCUSSION

We discuss whether crystal defects function as effective pinning centers perpendicular to the film surface. According to the TEM observation, twin boundaries, a-axis-oriented grains and impurity grains exist in the YBCO films. Impurity grains in the three defects only have an isotropic structure and the distribution is random and infrequent, suggesting that the impurity grains are not effective on pinning centers perpendicular to the film surface. Twin boundaries and a-axis-oriented grains are clearly crystal defects perpendicular to the film surface, indicating that these defects have possibility of the effective pinning centers perpendicular to the film surface.

The twin boundaries are generally observed in the YBCO films regardless of the fabrication method. Therefore, there are many reports which are discussed the twin boundaries as the pinning centers. In bulk samples, the twin boundaries are generally believed to work as the pinning centers [9, 10]. However, the J_c value of bulk samples is not so high in comparison with the J_c level of 10^5-10^6 A/cm^2 for film samples, which is usually the level of 10^4 A/cm^2. The pinning effect of the twin boundaries in film samples has been still studied. Yamazaki et al. reported the pinning effect of twin boundaries using unidirectionally twinned YBCO films, resulting that the experimental results did not indicate the evidence of strong pinning centers for twin boundaries [11]. The highest Jc is obtained when twin boundaries are at 45 degrees for the transport current. The Jc parallel and perpendicular to twin boundaries are almost the same. Moreover, Safar et al. reported that twin boundaries worked as effective pinning centers at high magnetic fields [12]. In this case, twin boundaries are mosaic and the difference of J_c in higher magnetic field than approximately 4 T is obtained in the case of 45 degrees for twin boundaries and the case of parallel / perpendicular to twin boundaries. The J_c at 45 degrees for twin boundaries is a factor of two higher parallel / perpendicular to twin boundaries. This experimental result, that is the highest J_c at 45 degrees for twin boundaries, is the same with Yamazaki's result. Furthermore, in the comparison between the present YBCO film and the PLD-YBCO film, the both YBCO film thickness is almost the same to be 200 nm and the both substrates are $SrTiO_3$ single crystals. However, the some kinds of pinning center perpendicular to the film surface exist in the present YBCO, while these do not exit in the PLD-YBCO, indicating that it is difficult to explain these results using twin boundary effect as the pinning centers.

Another possibility of the pinning centers along to the c-axis direction is the a-axis-oriented grain. The a-axis-oriented grains in the c-axis-oriented matrix were reported to be effective pinning centers [13]. These grains have a rectangular shape in the plan-view TEM image. The longer side of the rectangular grains has two possible directions in the YBCO films, indicating that the longer side is parallel to the superconducting current flow, as shown in Fig. 4 (a) or perpendicular to the superconducting current flow, as shown in Fig. 4 (b). In both cases, the longer size is parallel to the <100>$SrTiO_3$ substrate. Stripes in the YBCO grains show the a-b plane of YBCO. According to the cross-sectional TEM image, the interface between the a-axis grains and the c-axis grains is perpendicular to the film surface and very sharp. The conceptual models of the pinning center along to the c-axis direction and the interrupt of superconducting current flow are shown in Fig. 4 (a) and 4 (b), respectively. In the case of Fig. 4 (a), although Lorentz force affects the magnetic fluxes, it is difficult for the penetrated magnetic fluxes to move across the YBCO films. Because this configuration of the a-axis oriented grains and the magnetic flux is the same as the case of the magnetic field applied in parallel to the film surface of the c-axis-oriented YBCO film. Moreover, it is known that the capability of superconducting current in the b-

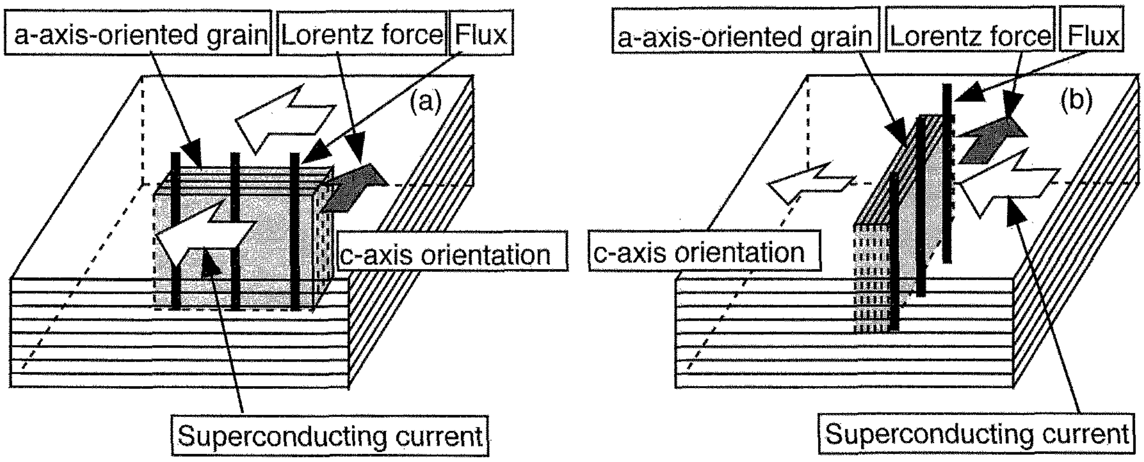

Fig. 4 Conceptual models of the pinning centers along to the c-axis direction (a) and the interrupt of superconducting current flow (b).

axis direction is much greater than that in the c-axis direction. In the a-axis-oriented grains shown in Fig. 4 (a), the superconducting current flows parallel to the b-axis direction of the YBCO films. Therefore, we concluded that the a-axis-oriented grains have enough possibility of the pinning centers along to the c-axis direction.

On the other hand, in the case of configuration shown in Fig. 4 (b), magnetic fluxes at the interface between a-axis- and c-axis-oriented grains can easily move due to a Lorentz force. Moreover, the a-axis-oriented grains interrupt the superconducting current because of anisotropic superconductivity between the a-/ b-axis directions and the c-axis direction, indicating that the effective cross-sectional area of current flow decreases. As a result, J_c reducton occurs when magnetic fluxes penetrate perpendicular to the surface of YBCO films. We concluded that the a-axis-oriented grains play two possible roles of a pinning center of magnetic flux parallel to the c-axis direction and an interrupt of superconducting current flow. According to the XRD measurements, the probabilities of the two distributions of the a-axis-oriented grains are almost the same at the present.

5. CONCLUSIONS

We prepared YBCO films by no-additional-water annealing of the precursor films deposited from Y, BaF_2 and Cu at room temperature. The YBCO films exhibit good J_c-B properties. The broad peak of J_c increase is observed at 90 degrees in addition to the large peak at 0 degree in the measurement of the dependences of J_c on the applied magnetic field angle to the film surface. This result suggested that some kind of pinning centers exists perpendicular to the film surface in the YBCO films. According to the cross-sectional and plan-view TEM observations, twin boundaries, impurity grains and a-axis-oriented grains are observed as crystal defects. The a-axis-oriented grains are considered to cause Jc reduction when a relatively small magnetic field is applied perpendicular to the film surface, and a work as the pinning centers oriented perpendicular to the film surface.

ACKNOWLEDGMENTS

We would like to thank Shigeo Sunaga of Electric Power Techno Systems Co. Ltd. for his help with the film growth. TEM sample preparation and TEM observation were performed at Hitachi Science System Ltd.

REFERENCES

[1] V.F. Solovyov, H.J. Wiesmann, M. Suenaga and R. Feenstra. *Physica* C **309**, pp. 269-274 (1998).
[2] V.F. Solovyov, H.J.Wiesmann, L-J. Wu, Y. Ahu and M. Suenaga, *Appl. Phys. Letters* **76**, pp. 1911-1913 (2000).
[3] A. Gupta, R. Jagannathan, E.I. Cooper, E.A. Giess, J.I. Landman, and B.W. Hussey, *Appl. Phys. Letters* **52**, pp. 2077-2079 (1988).
[4] P.C. McIntyre, M.J. Cima and M.F. Ng, *J. Appl. Phys.* **68**, pp. 4183-4187 (1990).
[5] A. Ichinose, A. Kikuchi, K. Tachikawa and S. Akita, *IEEE transactions on Applied Superconductivity* **11**, pp. 2913-2916 (2001).
[6] A. Ichinose, A. Kikuchi, K. Tachikawa and S. Akita, *Superconductor Science and Technology* **15**, pp. 262-268 (2002).
[7] A. Ichinose, T. Kiss, A. Kikuchi, K. Tachikawa, S. Akita, and K. Inoue, *Superconductor Science and Technology* **16**, pp. 398-401 (2003).
[8] M. Inoue, S. Nishimura, T. Kuga, M. Kikuchi, T. Kiss, M. Takeo, T. Matsushita, Y. Iijima, K. Kakimoto, T. Saitoh, S. Awaji, K. Watanabe and Y. Shiohara, *Physica C* **372-376**, pp. 794-797 (2002).
[9] E.M. Gyorgy, R.B. van Dover, L.F. Schneemeyer A.E. White, H.M. O'Bryan, F. Hellman, *Appl. Phys. Lett.* **56**, pp. 2465-2467 (1990).
[10] H. Fujimoto, T. Taguchi M. Murakami and N. Koshizuka, *Phsica C* **211**, pp. 393-403 (1993).
[11] H. Yamasaki, Y. Nakagawa, A. Sawa, H. Obara and K. Develos, Physica C 342-376, pp. 1885-1889 (2002).
[12] H. Safar, S. Foltyn, H. Kung, M.P. Maley, J.O. Willis, P. Arendt, and X.D. Wu, *Appl. Phys. Letters* **68**, pp. 1853-1855 (1996).
[13] H. Fuke, H. Yoshino, M. Yamazaki, T.D. Thanh, S. Nakamura, K. Ando and Y. Kobayashi, *Appl. Phys. Lett.* **60**, pp. 2686-2688 (1992).

(Received October 13, 2003; Accepted March 5, 2004)