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Processing, microstructures, and pinning properties of $REBa_2Cu_3O_{7-\delta}$ ($RE=$ Y and Gd) superconducting films

$REBa_2Cu_3O_{7-\delta}$ ($RE=$ Y and Gd) 초전도 박막의 공정, 미세구조 및 피닝특성 분석

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Abstract

Processing, microstructures, and pinning properties of \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) \((\text{RE}=\text{Y and Gd})\) superconducting films

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For practical applications of high temperature superconductor (HTS) coated conductors (CCs), high critical current density \((J_c)\) in high magnetic fields is desirable. To improve the HTS current-carrying capabilities in high fields, an inclusion of nano-sized particles into the HTS matrix is required. In this study, we characterized the flux pinning properties of \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) \((\text{REBCO, RE}=\text{Y and Gd})\) films by the pulsed laser deposition (PLD), metal-organic deposition (MOD), and reactive co-evaporation deposition & reaction (RCE-DR) processes. We also successfully fabricated GdBCO films with \( \text{Gd}_2\text{O}_3 \) additions on \( \text{CeO}_2\)-buffered \( \text{MgO} \) (100) substrate by PLD for systemic
study. On the basis of the results from systemic study, Gd$_2$O$_3$-doped GdBCO films were post-annealed in various temperatures and oxygen pressure ($P_{O_2}$) for improvement of their pinning properties. Finally, we summarized comparison of pinning properties and microstructures of REBCO films prepared by various methods. The major results are as the following.

First, our group have successfully fabricated Sn-doped REBCO films by MOD and PLD. Also, SuNAM Co. have successfully developed a new high-throughput process called RCE-DR for the fabrication of long-length high-$J_c$ GdBCO CCs on LaMnO$_3$ (LMO)-buffered IBAD MgO template. However, the flux pinning properties of those REBCO films are not fully identified yet. In this study, we fully identified the flux pinning properties of REBCO films fabricated by the PLD, MOD, and RCE-DR process. As a result, the 5 vol% Sn-doped GdBCO film on CeO$_2$-buffered IBAD MgO template by PLD exhibited the highest maximum pinning force density ($F_{p,max}$) values and the highest $J_c$, which is evidence that 5 vol% is the optimum content. In the case of MOD process, the Sn-doped YBCO film on SrTiO$_3$ (STO) (100) substrate exhibited enhanced $J_c$ and $F_{p,max}$ compared with undoped YBCO film. From the fast Fourier transform (FFT) patterns from high resolution-transmission electron microscope (HR-TEM) image and scanning transmission electron microscope-energy dispersive X-ray spectroscopy (STEM-EDS) analysis, we first reported the Sn-containing nanoparticles are not BaSnO$_3$ but YBa$_2$SnO$_{5.5}$ (YBSO). We also investigated the effect of the growth temperature on the microstructures and superconducting properties of GdBCO CCs deposited by the RCE-DR process on LMO-buffered IBAD MgO template. We employed three different growth temperatures of 840, 860 and
880°C. With decreasing the growth temperature, the $J_c$ at 65 and 77 K were improved due to enhanced pinning properties, which are attributable to refined Gd$_2$O$_3$ particles trapped in the GdBCO matrix. Analyses by transmission electron microscopy (TEM) revealed that the average particle size of Gd$_2$O$_3$ is 126.5 nm in the 840°C sample which is smaller than that of 171.4 nm in the 860°C sample and 217.8 nm in the 880°C sample. Interestingly, although (103) misoriented GdBCO grains existed together with biaxially textured grains in the film grown at 840°C, exhibited higher $J_c$ values in magnetic fields compared with other films composed of only biaxially textured grains, suggesting that the increase in $J_c$ due to pinning by refined Gd$_2$O$_3$ particles surpasses the degradation of $J_c$ by (103)-oriented grains present at the film surface.

Second, we tried to optimize the Gd$_2$O$_3$ additions in GdBCO films on CeO$_2$-buffered MgO (100) substrate. The Gd$_2$O$_3$-doped GdBCO films with various x mol% ($x = 0, 2, 4, 6, \text{ and } 10$) relative to GdBCO were prepared at 800°C with the $P_{O_2}$ of 300 mTorr by PLD. Among all samples, a 2 mol% Gd$_2$O$_3$-doped GdBCO film exhibited the highest $J_c$ value of 2.88 MA/cm$^2$ at 77 K and 4.72 MA/cm$^2$ at 65 K in 0 T, and also shows the $F_{p,max}$ values of 37.3 GN/m$^3$ near 2.8 T at 65 K and 11.3 GN/m$^3$ near 1.8 T at 77 K, evidencing that 2 mol% is the optimum Gd$_2$O$_3$ content. We also tried to enhance flux pinning properties of Gd$_2$O$_3$-doped GdBCO film by post-annealing process. According to our preliminary study on GdBCO CCs by RCE-DR, the flux pinning properties of GdBCO CCs were improved by post-annealing. Since the average particle size of Gd$_2$O$_3$ in GdBCO film by PLD can be refined, it must be attractive to study the effect of the post-annealing process on the GdBCO
films with Gd$_2$O$_3$ nanoparticles on a robust substrate. To identify the effect of the post-annealing process on the pinning properties of Gd$_2$O$_3$-doped GdBaCO films, we performed post-annealing in various temperature and PO$_2$. The $T_{c,\text{zero}}$ values of GdBaCO films annealed at 800 °C in the PO$_2$ of 10 mTorr are increased up to ~91.4 K. The angular dependence $J_c$ of GdBaCO film annealed at 800°C in 10 mTorr are slightly improved along the direction parallel to the $c$-axis compared with non-annealed 2 mol% Gd$_2$O$_3$-doped GdBaCO film, representing that it has $c$-axis correlated pinning centers. From TEM analysis, some defects along the $c$-axis of GdBaCO are observed in the post-annealed sample. It suggested that flux pinning along $c$-axis ($B//c$) in the post-annealed sample might be improved by the GdBa$_2$Cu$_4$O$_8$ (Gd124) type stacking faults filed up along the $c$-axis of GdBaCO matrix.

Third, we summarized comparison of pinning properties and microstructures of REBCO films prepared by PLD, MOD, metal-organic chemical vapor deposition (MOCVD), and RCE-DR. We compared exponent $\alpha$ value, $F_{p,max}$, minimum $J_c$ ($J_{c,\text{min}}$), angular dependence of $J_c$, and the shape & size of pinning centers for REBCO films. As a result, the flux pinning properties of REBCO films by PLD still exhibit much higher than other deposition method. Although the GdBaCO films by the RCE-DR process still indicate lower flux pinning properties, we suggest that improvement of pinning properties will be feasible by Gd$_2$O$_3$ refinement and post-annealing process through previous study of Gd$_2$O$_3$-doped GdBaCO films.

**Keywords:** REBa$_2$Cu$_3$O$_{7-\delta}$ (REBCO, RE=Y and Gd) films, Gd$_2$O$_3$-doped GdBaCO films, pulsed laser deposition (PLD), post-annealing process,
critical current density ($J_c$), maximum pinning force density ($F_{p,max}$)

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Chapter 1. General Introduction

1.1. High temperature superconductor coated conductors

Since discovery of HTS in 1986 [1], extensive R&D efforts have been advanced for electric power applications. As a result, Bi-Sr-Ca-Cu-O (BSCCO) superconductors with $T_c$ of 110 K, which is 1st generation HTS wire, have reached a practical applications. However, BSCCO wires have several disadvantage such as high cost from silver tube, low $J_c$ due to high angle boundaries, low irreversibility field ($H_{irr}$) at 77 K. [2, 3]. This low $H_{irr}$ prevents use of BSCCO at 77 K in any significant field and provides one of the key arguments for developing a 2nd generation HTS technology based on YBCO [3]. Up to now, Y or rare earth materials-based superconducting (Y or REBCO) wire is expected to be in practical uses for various applications such as magnet, motors, transformers, generators, transmission cables, and etc (Fig. 1.1 [4]).

The Y or REBCO system has anisotropic crystal structure (Fig 1.2). In these system, copper oxide planes form a common structural element, which is dominated the superconducting properties. Depending on stoichiometry, the crystallographic unit cell contains varying number of CuO$_2$ planes as well as CuO chain. The occupancy of chin oxygen site can vary from 0 to 1, corresponding to oxygen contents $\delta$ varying from 0 to 1 [5, 6]. At high temperature or when $\delta$ is between 0.6 and 1, the structure becomes tetragonal.
After oxygen annealing, the structures with oxygen content below 0.6 becomes a transition from tetragonal phase to orthorhombic phase. It is also well known that $REBCO$ superconductors tend to form $RE_{1+x}Ba_{2-x}Cu_{3}O_{7-\delta}$ type solid solutions because of the similarity in the ionic radii of $RE^{3+}$ and $Ba^{2+}$ [7, 8]. The lower $T_c$ values in contrast to the stoichiometric $REBCO$ can be attributed to the substitution of $RE^{3+}$ ions on $Ba^{2+}$ sites and the reduction of the carrier density to the CuO$_2$ planes [9].

These $REBCO$ materials were successfully fabricated by various deposition methods such as pulsed laser deposition (PLD), metal organic deposition (MOD), metal organic chemical deposition (MOCVD), and reactive co-evaporation deposition & reaction (RCE-DR) on flexible metal substrate (Fig 1.3 [10]), called as CCs. Details of deposition methods of $REBCO$ films will be explained below in 1.2. Recent efforts for 2nd generation HTS CCs are focused on increasing their length and performance. To achieve large current carrying property, high $J_c$ in high magnetic field is still required, and it is very important to understand the flux pinning properties that determine $J_c$.

To enhance the performance of $REBCO$ CCs in magnetic field, it is very effective to incorporate the artificial defects, of which size is comparable to the very short in-plane coherence length ($\xi \sim 1.5$-2 nm) [3], into the superconducting matrix act as flux pinning centers. As such an effort, many research groups tried to improve pinning properties of REBCO CCs by introducing nano-sized second phases into the superconducting matrix. Further details of type of defects and materials of pinning centers will be explained below in 1.3.
1.2. Fabrication technologies of REBCO films

In this chapter, the fabrication technologies of long-length REBCO CCs, including PLD, MOD, MOCVD, and RCE-DR are briefly introduced. Table 1.1 shows key parameters of the CCs among manufacturers [11]. The basic principles of each method are summarized in the following subsections.

1.2.1. Pulsed laser deposition (PLD)

PLD is a kind of the physical vapor deposition (PVD), carried out in a vacuum system, which widely used in the development of the CC technology. In the late 1980s, PLD was popularized as a fast and reproducible oxide film growth technique through its success in growing in-situ epitaxial HTS films [12]. As shown in Fig. 1.4, PLD system includes a laser source such as an ArF (λ =193 nm), KrF (λ = 248 nm), and XeF (λ =260 nm) eximer layer or a Nd:YAG (λ = 355 nm) laser, an optical system which contains an aperture, a mirror and a focusing lens. It also includes a vacuum chamber which has a heater, a heating stage, and a rotating target holder. Pulsed laser typically generated from laser source is focused on the target, and then transfers the substance into the substrate. PLD has proven remarkably effective at yielding epitaxial films. Up to now, several companies (Bruker, Fujikura, SuperOx, and Sumitomo) have fabricated REBCO CCs by PLD and scaled up to production long length [13-17]. Fujikura Ltd. is famous companies to produce REBCO CCs by the PLD method. In 2014, they reported GdBCO CCs of $I_c$ value over 600 A/cm-
width at 77 K with length up to 1 km [18].

1.2.2. Metal-organic deposition (MOD)

The MOD process for fabrication of REBCO films has been investigated as an alternative to expensive PVD process using high vacuum system [19, 20]. The MOD process is considered to be cost-effective for the fabrication of long length high-$I_c$ YBCO CCs [21, 22]. The trifluoroacetic acid (TFA)-MOD process of YBCO films was first reported by A.Gupta et al. in 1988 [23]. In spite of a great success with the TFA-MOD method, it has been a challenging problem to produce MOD-processed CCSs with $I_c$ because thick film fabrication required for high-$I_c$ is uneasy with the TFA-MOD process due to a macroscopic crack formation in thick films and also a long decomposition time of organic components. To overcome these problems, fluorine-free precursor solutions for YBCO CCs have been investigated, and some approaches were reported effective [24-26]. In MOD process, the precursor film is deposited on a substrate using a coating solution and dried. The precursor film is thermally decomposed and fired it into a superconducting phase in ambient pressure. With a single coating step it is possible to achieve 0.8 μm effective REBCO thickness, but the coating and decomposition processes can be repeated multiple times to achieve thicker layers and thus increase the overall critical current. From now on, the technology have developed commercial REBCO HTS CCs by AMSC Co., Ltd., reporting the property of YBCO CCs with $I_c$ value of 466 A/cm-width at 77 K with length up to 540 m in 2010 [27]
1.2.3. Metal-organic chemical vapor deposition (MOCVD)

A chemical vapor deposition (CVD) technique using $\beta$-diketon metal chelates as source materials is commonly called MOCVD [28]. Organic precursors are used for Y (or other rare-earth materials), Ba, and Cu. In the first step, the liquid precursors are vaporized at a constant temperature. The vaporized precursors then flow in a carrier gas of argon and oxygen and are injected onto a hot substrate. The MOCVD process provides a number of advantages, including simple refill of precursors (which are maintained outside the vacuum chamber), double-sided coating (non-line-of-sight coating), and the ability to modify film composition continuously during growth [29]. However, there are several drawbacks which are the slow growth rate and high price of precursor materials. Superpower Inc. is well-known for fabricating REBCO CCs by the MOCVD process. They reported that the YBCO CCs are available in lengths greater than 1,065 m with minimum 282 A/cm-width in 2009 [30].

1.2.4. Reactive co-evaporation deposition & reaction (RCE-DR)

The method for reactive co-evaporation (RCE) of YBCO films was first elegantly implemented in an oscillatory manner by Kinder and co-workers [31]. Recently, SuNAM developed a novel RCE-DR process to fabricate high performance GdBCO CCs on LaMnO$_3$-buffered IBAD MgO templates with extremely high throughput [32-34]. The RCE-DR is basically a two-step process. In this process, an amorphous GdBCO precursor film was first deposited by e-beam evaporation at 400°C. The deposition rate of each
material was controlled by the QCM and automatic control program. The amorphous film had the cation ratio of Gd : Ba : Cu ≈ 1 : 1 : 2.5. This cation ratio was chosen to incorporate a high content of Gd$_2$O$_3$ particles in the GdBCO matrix. Then, as-deposited amorphous film was passed through a tube furnace at 860 °C with two different oxygen pressure zones. The first passing zone had lower $P_{O_2}$ of $10^{-5}$ Torr and the second zone had higher one of 150 mTorr where the amorphous film was fast converted into the GdBCO film (Fig. 1.5). High deposition rates owing to highly efficient e-beam co-evaporation at low temperatures and low oxygen partial pressures, followed by a fast conversion of the amorphous phase into the superconducting phase at high temperatures and high oxygen pressures, are the key features of SuNAM’s RCE-DR process. Unlike other co-evaporation processes such as RCE- cyclic deposition and reaction (CDR) or evaporation using drum in dual chamber (EDDC) requiring multiple cycles of deposition and conversion [35, 36], SuNAM’s RCE-DR process was designed to form a superconducting layer by a single pass in which the amorphous glassy phase previously deposited by co-evaporation is rapidly converted into the superconducting phase at once. In 2014, SuNAM reported GdBCO CCs of minimum $I_c$ value over 535 A/cm-width at 77 K with length up to 978 m [37].

1.3. Flux pinning mechanism

The $RE$BCO materials are type-II superconductor which do not exhibit the Meissner-Ochsenfeld effect. When an electrical current flows into a
superconductor, no resistance or voltage is generated under critical current ($I_c$). However, a finite resistance is generated when the current becomes larger than $I_c$. It is because quantized flux lines, whose core part is in a normal state, enter the superconductor and are moved by the Lorenz force that is the product of the applied magnetic field and the current (Fig. 1.6). The current flows also normal core in the flux-flow state. To increase the $J_c$, we have to pin the flux lines by introducing appropriate defects, where flux lines stay stably. Therefore, Vortex pinning technology holds the key for improving $J_c$. Many types of crystalline defects, such as fine precipitates of non-superconducting phases, dislocations [39-43], oxygen vacancies [44, 45], twin boundaries [46, 47], and so on, act as pinning centers. However, $J_c$ rapidly decreases as the temperature increases under magnetic fields. The main reasons for this $J_c$ depression are the intrinsic crystalline anisotropy of HTS and the thermal fluctuations.

To obtain the high-$J_c$, strong pinning centers should be introduced over the whole length of the CCs to prevent vortices from moving by the Lorentz force. In consequence, vortex pinning control by introducing nano-sized second phases into the superconducting matrix is very effective. K. Matsumoto et al. [48] have reported classification of artificial pinning centers (APCs). Schematic views of APCs in the YBCO films are presented in Fig.1.7. When the crystalline defects that can be used as APCs are classified by the dimension, there are many kinds of defects as follows; 1D-APCs such as dislocations and columnar defects [49]; two-dimensional APCs (2D-APCs) such as small angle grain boundaries [43, 50], anti-phase boundaries [51] and surfaces of large precipitates [52]; 3D-APCs such as
nanoparticles and second phases of the scale of \( \xi \) or more. Additionally, the defects smaller than \( \xi \), such as vacancies [53], cation disorder [54] or dilute doping [55], should be classified into zero-dimensional APCs (0D-APCs). Also combinations are possible, such as 1D-APCs + 3DAPCs [56]. The reciprocal orientation of the APCs and matrix is also to be taken into account: APCs can be parallel, usually, or perpendicular to the c-axis of the superconducting film [57], or isotropic [58, 59], or have complex orientations like interconnected networks [60] or perpendicular + parallel assemblages [61]. These sentences excerpted parts of his paper [48]. Fig. 1.8 shows configuration of a pinned vortex by 1D-APCs or 3D-APCs. In the case of nanorods (1D-APCs), a zigzag state of the vortex line comes to stabilize in energy as the direction of the magnetic field is tilted from the direction of nanorod, and the portion pinned by the nanorods is shortened. When the current is energized in this configuration, the vortex line comes free from the nanorod by the small Lorentz force, leading to the decrease of \( J_c \). In the case of nanoparticles (3D-APCs), however, vortex line is pinned by the randomly distributed. Therefore, 3D-APCs shows more gradual isotropic behavior than 1D-APCs.
References


Table 1.1. Fabrication process and template of industrial coated conductors [11].

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Technique</th>
<th>Substrate</th>
<th>Buffer layers</th>
<th>HTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMSC</td>
<td>RABITS/MOD</td>
<td>NiW</td>
<td>Y$_2$O$_3$/YSZ/CoO$_2$</td>
<td>Y123</td>
</tr>
<tr>
<td>SuperPower</td>
<td>IBAD/MOCVD</td>
<td>Hastelloy</td>
<td>Al$_2$O$_3$/Y$_2$O$_3$/MgO/LaMnO$_3$</td>
<td>Gd123</td>
</tr>
<tr>
<td>Bruker</td>
<td>ABAD/PLD</td>
<td>Stainless steel</td>
<td>YSZ/CoO$_2$</td>
<td>Y123</td>
</tr>
<tr>
<td>Fujikura</td>
<td>IBAD/PLD</td>
<td>Hastelloy</td>
<td>Al$_2$O$_3$/Y$_2$O$_3$/MgO/CoO$_2$</td>
<td>Gd123</td>
</tr>
<tr>
<td>SupeOx</td>
<td>IBAD/PLD</td>
<td>Hastelloy</td>
<td>Al$_2$O$_3$/Y$_2$O$_3$/MgO/CoO$_2$</td>
<td>Gd123</td>
</tr>
<tr>
<td>Sumitomo$^p$</td>
<td>RABITS/PLD</td>
<td>NiW</td>
<td>CrO$_2$/YSZ/CoO$_2$</td>
<td>Gd123</td>
</tr>
<tr>
<td>SuNAM</td>
<td>IBAD/RCE</td>
<td>Hastelloy or stainless steel</td>
<td>Al$_2$O$_3$/Y$_2$O$_3$/MgO/CoO$_2$</td>
<td>Gd123</td>
</tr>
<tr>
<td>STI$^p$</td>
<td>IBAD/RCE</td>
<td>Hastelloy</td>
<td>Y$_2$O$_3$/Al$_2$O$_3$/MgO</td>
<td>Y123</td>
</tr>
</tbody>
</table>

$^p$ As yet marketplace conductor.
Fig. 1.1. Electric applications of superconducting materials as a function of magnetic field [4].
Fig. 1.2. Crystal structure of $REBCO$. 

- CuO chain
- BaO layer
- CuO$_2$ plane (conduction plane)
- Y or Gd
- CuO$_2$ plane (conduction plane)
- BaO layer
- CuO chain

- : Y or Gd
- : Ba
- : Cu
- : O
Fig. 1.3. A schematic of the architecture for REBCO CCs [10].
Fig. 1.4. A schematic of PLD system.
Fig. 1.5. A schematic of the RCE-DR process and the program of the automated deposition control [34].
Fig. 1.6. Quantized flux lines and flux pinning [38].
Fig. 1.7. Sketch of the dimensionality of artificial pinning centers (APCs): 1D-APCs, 2D-APCs, and 3D-APCs. [48].
Fig. 1.8. Comparison of the configuration of a pinned vortex by 1D-APCs or 3D-APCs: (a) the zigzag state of the vortex line when the magnetic field is applied tilted from the direction of 1D-APCs, (b) the vortex line which is pinned by the randomly distributed 3D-APCs in the tilted magnetic field. [48].
Chapter 2. Flux pinning characterization of REBCO (RE=Y and Gd) films

2.1. Introduction

The 2G HTS CCs, based on REBCO thin film technology, are approaching a commercialization threshold. However, high $J_c$ in high magnetic field is still required for many electrical power applications. The field dependency of $J_c$, except the field applied parallel to the $ab$-plane of REBCO, is not an intrinsic but an extrinsic property dependent upon the flux pinning characteristics of the superconducting samples. The flux lines are effectively pinned by defects when their size is comparable to the short coherence length ($\xi \sim 1.5-2$ nm) of YBCO [1]. Therefore, the enhancement of flux pinning by a deliberate generation of defects such as the introduction of nano-sized non-superconducting phase has recently been the subject of renewed interest as CCs approach commercialization. The BaMO$_3$ ($M$: Zr, Ir, and Sn) (BMO) [2-7], cubic rare-earth tantalate $RE_3TaO_7$ [8], and cubic-double-perovskite $Ba_2RETaO_6$ [9, 10] nanorods self-aligned along the $c$-axis of YBCO film prepared by PLD were reported very effective for the enhancement of the flux pinning properties, particularly for the applied field parallel to the $c$-axis of the YBCO film ($B//c$). Among all BMO phases, BZO incorporation has been most extensively studied in YBCO [2, 3] and REBCO films [11-15].

The MOD process is considered to be cost-effective for the fabrication of
long length high-$J_c$ YBCO CCs [16, 17]. As previously mentioned, it is very important to improve the in-field $J_c$ of YBCO films by introducing defects into the YBCO matrix during the MOD process. The MOD-processed YBCO films containing nanoparticles of BZO [18-25], BaHfO$_3$ [26], and cubic-double-perovskite Ba$_2$YTaO$_6$ (BYTO) [27] have been reported to exhibit significantly improved $J_c$ values in magnetic field. Moreover, it is reported that the addition of RE$_2$O$_3$ (RE: Y, Dy, and Ho) can also produce nanoparticles with a size range of 10-50 nm and enhance the flux pinning properties [28-30]. After BaSnO$_3$ (BSO)-doped YBCO films by PLD were reported to show stronger flux pinning properties compared with BZO-doped ones [5, 6], many groups [31-35] have prepared Sn-doped YBCO films by the MOD process and commonly found stronger pinning properties compared with undoped YBCO films.

Recently, our group have successfully fabricated Sn-doped REBCO films ($RE$=Y and Gd) by MOD [36] and PLD [37]. Also, SuNAM Co. have successfully developed a new high-throughput process called RCE-DR for the fabrication of long-length high-$J_c$ GdBCO CCs on LMO-buffered IBAD MgO template [38-40]. In this study, we fully characterized the flux pinning properties of REBCO films fabricated by the PLD, MOD, and RCE-DR process.

### 2.2. Experimental

Each REBCO films were deposited by the MOD, PLD, and RCE-DR process. First, GdBCO films with BaSnO$_3$ addition on CeO$_2$-buffered ion-
beam assisted deposition (IBAD) MgO template by PLD using KrF excimer laser ($\lambda = 248$ nm). For a systematic study, the BSO contents in the PLD targets were controlled to have 2, 3, 4, 5, and 6 vol% relative to GdBCO. The CeO$_2$-buffered IBAD MgO template was composed of CeO$_2$/IBAD-MgO/Y$_2$O$_3$/Al$_2$O$_3$/ Hastelloy, where the in-plane texture $\Delta \phi$ of the CeO$_2$ buffer layer was 4.2$^\circ$. Detailed PLD conditions are reported in our previous paper [41]. Second, undoped and Sn-doped YBCO films on STO (100) substrate by the MOD process. For the coating solution of Sn-doped YBCO, coating solutions were prepared by mixing these precursor solutions to have stoichiometric composition (Y : Ba : Cu = 1 : 2 :3) and the additional amount of Ba acetate corresponding to 10 mol% Sn (II)-acetate addition. The thickness of YBCO films was in the range of 350-400 nm. Further details on the subsequent processing conditions for the preparation of superconducting films are described in our previous reports [16, 36]. Finally, GdBCO CCs were deposited on LMO-buffered IBAD MgO template by the RCE-DR process. Detailed experimental procedures are reported in our previous papers [11, 12]. As-deposited amorphous films were passed through a tube furnace at three different temperature of 840, 860, and 880$^\circ$C with two different oxygen pressure zones.

The REBCO films were characterized by X-ray diffraction (XRD) using Cu-K$\alpha$ radiation (Bruker, D8-Advance). The in-plane texture of REBCO films were analyzed by X-ray $\phi$-scan and $\omega$-scan (PANalytical X’pert Pro) using (103) and (005) plane of REBCO films. Ag protective layers of ~1.5 $\mu$m thickness were sputtered onto REBCO films for the measurement of superconducting properties. Temperature and field dependence of $J_c$ were
measured by commercial SQUID magnetometer (MPMS XL-5, Quantum design) in the magnetic field region of 0-5 T for the field applied parallel to the $c$-axis of the film ($B//c$). The magnetic $J_c$ values were calculated using the equation of $J_c = 20\Delta M/[a(1-(a/3b))]$ derived from a modified critical state model [42], where $a$ and $b$ are width and length of the rectangular film measured in centimeter ($b > a$), respectively, and $\Delta M$ was the magnetization hysteresis loop width measured in emu/cm$^3$. The angular dependence of $J_c$ for the samples was measured using PPMS (Quantum design, model-6000) after patterning a micro-bridge with the width of 40 $\mu$m. TEM specimens were prepared by focused ion beam (FIB) milling technique (SMI3050SE). An analytical TEM (JEOL JEM-3000F, FEI Tecnai F20) was employed to analyze the cross-sectional microstructures of samples. Electron backscatter diffraction (EBSD) analyses of GdBCO CCs were performed within a scanning electron microscope (SEM; Hitach SU70).

2.3. Results and discussion

2.3.1. GdBCO films with BaSnO$_3$ additions by the PLD process

Table 2.1 shows the typical characteristics of the undoped and BSO-doped GdBCO films. The field dependence of magnetic $J_c$ values at 77 and 65 K for $B//c$ is shown in Fig. 2.1 for all samples. As shown in Fig. 2.1 (a) and (b), the magnetic $J_c$ values of 3-6 vol% BSO-doped samples are higher than those of undoped sample in magnetic fields up to 5 T at 65 and 77 K. The $J_c$ values (0-5 T) of BSO-doped samples at 65 K increase with increasing BSO
contents from 2 to 5 vol%, and then decreased with further increasing the BSO content to 6 vol%, indicating that 5 vol% is the optimum content in the GdBCO film. Interestingly, Mele et al. [7] reported that the optimum content of BSO in PLD-YBCO film on STO (100) substrate was 4 wt%, corresponding to 3.48 vol%, while Awaji et al. [43] reported the largest in-field $J_c$ values for the 6 wt% BSO-doped ErBCO film on the STO (100) substrate. Therefore, we can see that the optimum content of BSO is sensitive not only to the PLD deposition conditions as reported by Maiorov et al. [44] but also to the kind of superconducting phase.

The pinning force densities ($F_p$) for all GdBCO films, evaluated by the relationship of $F_p = J_c \times B$, are represented as a function of the magnetic field at 65 and 77 K for $B//c$ in Fig. 2.2. Except 2 vol% doping, the $F_p$ values of 3-6 vol% BSO-doped GdBCO films are larger than those of undoped sample in the whole field region (0-5 T). With increasing the BSO content from 0 to 6 vol%, the peak field of $F_{p,max}$ first decreases at 2 vol%, then continuously increases up to 5 vol%, and finally decreases at 6 vol%. A similar behavior has been reported for BSO-doped YBCO [7] and BSO-doped ErBCO films [43] on the STO by PLD. The largest $F_p$ values are achieved from 5 vol % BSO-doped GdBCO film, implying that the optimum doping content of BSO is 5 vol%, and its maximum $F_p$, $F_{p,max}$ values are 6.5 GN/m$^3$ near 3.2 T at 77 K and 32.5 GN/m$^3$ near 4 T at 65 K, respectively, for $B//c$. At 77 K, the $F_{p,max}$ value of 6.5 GN/m$^3$ is comparable to that of BSO-doped ErBCO [43], but it is much lower than that (28 GN/m$^3$) of BSO-doped YBCO [7]. Recently, Horide et al. [45] reported for 4 wt% BSO-doped YBCO film on IBAD-MgO template that the $F_{p,max}$ of $\sim$12 GN/m$^3$ near 3 T at 77 K and $\sim$60 GN/m$^3$
near 4 T at 65 K, which are twice larger than our $F_{p,max}$ values for BSO-doped GdBCO films. This discrepancy is considered to originate from a significant difference in the biaxial texture of the superconducting matrix. While the $\Delta \phi$ value of our BSO-doped GBCO is 4.1°, their $\Delta \phi$ value of BSO-doped YBCO is 2.55°, which is in turn attributed to a large difference in the in-plane textures of CeO$_2$ buffer layers, where the $\Delta \phi$ values of the CeO$_2$ buffer layers are 2.91° and 4.2° for BSO-doped YBCO and GBCO, respectively.

Fig. 2.3 shows the field-orientation dependence of the transport $J_c$ for undoped and 4, 5, and 6 vol% BSO-doped samples. In this figure, all samples show a sharp $J_c$ peak at $\theta = 90^\circ (B//ab)$ and a broad $J_c$ peak near $\theta = 180^\circ (B//c)$. Civale et al. [46-48] reported that in addition to the intrinsic pinning, the extrinsic pinning due to extended planar defects and extra defects induced by IBAD MgO template can contribute to the $J_c$ peak at $\theta = 0^\circ (B//ab)$ for PLD-YBCO films. A small broad $J_c(\theta)$ peak near $\theta = 180^\circ (B//c)$ for undoped GdBCO film indicates that it has $c$-axis correlated pinning centers. In the previous literature from SRL-ISTEC, Japan [49-52], the small broad $J_c(\theta)$ peak near $B//c$ was also observed for the GdBCO films while it was unobservable for the YBCO films. They suggested that much higher stacking faults and screw dislocations in the undoped GdBCO film compared with those of the undoped YBCO film played a role of $c$-axis correlated pinning centers, responsible for the small broad $J_c(\theta)$ peak for $B//c$. Recently, Kaneko et al. [53] clearly reported the presence of screw dislocations in addition to the stacking faults.

Fig. 2.4 shows the cross-sectional TEM images of undoped GdBCO
specimen. As shown in Fig. 2.4, the selected area diffraction (SAD) patterns of undoped sample along the thickness represent continuous reflection spots, indicating that CeO$_2$ and GdBCO have a cube-on-cube texture with the crystallographic orientation relationships of CeO$_2$ [010] // GdBCO [010] and CeO$_2$ [001] // GdBCO [001], and the GdBCO film is composed of strongly $c$-axis oriented grains.

To identify the defects within the undoped GdBCO matrix, a cross-sectional high resolution (HR)-TEM observation was performed. The results are shown in Fig. 2.5 (a) and (b). A defective structure with numerous stacking faults or wavy (00$l$) planes is observed in GdBCO matrix. The same image was reconstructed in Fig. 2.5 (b) using the obtained FFT mask. It is obvious that a number of stacking faults are distributed in the GdBCO matrix. Yamada et al. [51] also reported a similar TEM image of pure GdBCO film with a high density of stacking faults. They proposed that the substitution of Gd into Ba sites could induce the defects like stacking faults. In good agreement with previous literature [49-51], we also suggest that these stacking faults play a role of $c$-axis correlated pinning centers which are responsible for the small broad $J_c(\theta)$ peak for $B//c$ in undoped GdBCO film.

Another important point to note is that the $c$-axis correlated $J_c$ peak becomes larger with increasing the BSO content up to 5 vol% in Fig. 2.3. In accordance with previous results of magnetic $J_c$ values for $B//c$ in Fig. 2.1, the 5 vol% BSO-doped GdBCO sample represents the highest $J_c$ values in the whole angular region of 60 - 210°, indicating that the most effective pinning can be achieved from 5 vol% BSO-doped GdBCO CC. The
minimum $J_c$ ($J_{c,\text{min}}$) value of 5 vol% BSO-doped GdBCO films were much improved in comparison with that of undoped GdBCO film, for instance, from 0.31 to 0.39 MA/cm$^2$ in 1 T, 0.12 to 0.16 MA/cm$^2$ in 3 T, and 0.004 to 0.067 MA/cm$^2$ in 5 T at 77 K. As the magnetic field increases to 5 T, the $J_c$ peak at $B//c$ becomes lower than the $B//ab$. This behavior might be due to the magnetic field exceeding the matching field $B_\phi \sim 2.8$ T.

To identify $c$-axis correlated pinning of BSO-doped GdBCO films, the cross-sectional HR-TEM observation was also performed for 4-6 vol% BSO-doped GdBCO films. As a representative, the HR-TEM image for the 5 vol% BSO-doped GdBCO film is represented in Fig. 2.6. The columnar defects of BSO, so called “nanorods”, are aligned roughly along the $c$-axis of GdBCO film. The BSO nanorods with ~10 nm diameters are observed as Moiré-fringes which are composed of strips of bright and dark contrast. According to Yamada et al. [54], a lattice mismatch between ErBCO and BZO nanorods is responsible for the Moiré-fringes observed for BZO-doped ErBCO films. Likewise, we believe that the Moiré-fringes in our films are attributed to a lattice mismatch between GdBCO and BSO nanorods. Maiorov et al. [44] clearly showed that the orientation of the Moiré-fringes was changed by changing the diffraction condition, i.e., $\vec{g}$ vector, in the BZO nanorod. Interestingly, although the average diameter of BSO nanorods is almost identical in all BSO-doped films, the optimum BSO content of 5 vol% in GdBCO is slightly larger than 4wt% (~3.48 vol%) in YBCO [7] and ErBCO [43], suggesting that the optimum BSO content is sensitive to the kind of the superconducting phase. Further study must be required to clarify this discrepancy. Though not presented, the diameters of the BSO nanorods for
4-6 vol% BSO-doped GdBCO films were unaltered but their densities were increased with increasing the doping content of BSO. Consequently, not only significantly enhanced $J_c(\theta)$ peaks near $180^\circ$ ($B//c$) but also substantially increased $J_c$ values in the angular region between $90^\circ$ and $180^\circ$ for 4-6 vol% BSO-doped samples in Fig. 2.3 are due to the BSO nanorods incorporated into the GdBCO matrix.

On the basis of microstructure observations by TEM in Fig. 2.6, the behavior of $J_c(\theta)$ curves in Fig. 2.3 is understandable. While the $J_c(\theta)$ peaks for $B//ab$ are always observed at $\theta = 90^\circ$ for all samples, the $J_c(\theta)$ peaks for $B//c$ slightly deviate from $\theta = 180^\circ$, which is ascribed to slightly curved BSO nanorods from the $c$-axis of the GdBCO matrix. Similarly, Ozaki et al. [12] have reported the deviation of the $J_c(\theta)$ peaks from $B//c$ for BZO-doped SmBCO films due to BZO nanorods slightly tilted from the $c$-axis of the SmBCO matrix. On the other hand, we may also understand a large difference between our BSO-doped GdBCO CC and BSO-doped YBCO CC by Horide et al. [45]. Since the positions of the peak fields for the $F_{p,max}$ values are similar to each other ($\sim 3$ T at 77 K and $\sim 4$ T at 65 K), the behavior of $J_c(\theta)$ curves is also very close to each other, and further the average diameter of BSO nanorods ($\sim 10$ nm) is almost identical to each other, a difference in the pinning nature and strength related to the BSO nanorods should be insignificant. Therefore, as previously mentioned, we believe that twice larger $F_{p,max}$ values in their BSO-doped YBCO CC compared with those in our BSO-doped GdBCO CC are mainly attributed to enhanced biaxial texturing of the superconducting matrix.
2.3.2. Undoped and Sn-doped YBCO films by the MOD process

The field dependency of $J_c$ at 65 and 77 K for $B//c$ is shown in Fig. 2.7. The $T_{c,\text{zero}}$ values of undoped and Sn-doped YBCO films were 90.1 K with that of 1.2 K and 89.7 K with the transition width of 1.4 K, respectively. No significant reduction in $T_c$ with increasing the amount of Sn doping up to about 10 mol% in MOD-YBCO films has also been reported by Miyanaga et al. [32]. While a significant decrease in $T_{c,\text{zero}}$ was reported with increasing the Sn substituent on the Cu site [55], a slight depression in $T_{c,\text{zero}}$ by Sn-doping in our sample suggests that most of Sn dopants were used to form the YBSO phase and thus Sn doping on the Cu site is very limited. Similarly, insignificant reduction in $T_{c,\text{zero}}$ has been recently reported for MOD-YBCO films with another double perovskite BYTO nanoparticles by Coll et al. [56].

In Fig. 2.7, one can see that an overall increase in $J_c$ occurs in Sn-doped YBCO film, implying that it possesses stronger flux pinning properties compared with undoped YBCO film. As listed in Table 2.2, while the magnetic $J_c$ (77 K, 0 T) value of 3.3 MA/cm$^2$ for Sn-doped YBCO film is only slightly higher than that of undoped YBCO film, much larger $J_c$ (77 K, 1 T) value of 0.29 MA/cm$^2$ was achieved for Sn-doped YBCO film compared with undoped one (0.076 MA/cm$^2$). At 65 K, the field dependency of $J_c$ becomes weaker, and thus magnetic $J_c$ (65 K, 1 T) and $J_c$ (65 K, 3 T) values of undoped YBCO film decrease to 0.24 MA/cm$^2$ (≈ 7% of $J_c$ (65 K, 0 T)) and 0.11 MA/cm$^2$ (≈ 3% of $J_c$ (65 K, 0 T)), respectively, whereas $J_c$ (65 K, 1 T) and $J_c$ (65 K, 3 T) values of Sn-doped YBCO film decrease to 1.2 MA/cm$^2$ (≈ 18 % of $J_c$ (65 K, 0 T)) and 0.46 MA/cm$^2$ (≈ 7 % of $J_c$ (65 K,
0 T), respectively, demonstrating that \( J_c \) depression of undoped sample is more rigorous. The above \( J_c \) values and field dependency are very similar to those recently reported by Ye et al. [35].

Fig. 2.7 (b) shows a log-log plot of \( J_c (B//c, 77\text{K}) \) versus the applied field. Defects like nanoparticle inclusions are known to affect the exponent, \( \alpha \) in the power-law of \( J_c \sim H^\alpha \) calculated by a linear regression of the \( J_c-H \) curve in the field regime of 0.1-1T at 77 K for \( B//c \). The exponent, \( \alpha \) value of \(~0.60\) for undoped YBCO film is similar to the values of \(~0.65\) reported for the undoped MOD-YBCO films [57, 58]. However, this \( \alpha \) value is much larger than the typical value of \(~0.5\) reported for undoped PLD-YBCO films [3, 59, 60], representing that flux pinning is less effective in the case of undoped MOD-YBCO films. On the other hand, the typical regime of the exponent \( \alpha \) is absent for Sn-doped YBCO film since the \( J_c(H) \) data significantly deviate from the power-law in the field regime of 0.1-1T. Instead, the slopes between applied field segments monotonously increase from 0.45 to 1.0 for the fields from 0.1 to 0.5 T, respectively, and then fluctuate between 0.9 and 1.15 in higher fields up to 1 T. This peculiar behavior has also been reported for the MOD-YBCO film with BZO nanoparticles by Pomar et al. [61]. The deviation from the power law in Sn-doped YBCO film might be due to a change in pinning characteristics by high density Sn-containing nanoparticles which will be described later.

The pinning force density, \( F_p = J_c (B) \times B \), at 65 K and 77 K as a function of the magnetic field for \( B//c \) are shown in Fig. 2.8. The 10 mol% Sn-doped YBCO film shows the \( F_{p,\text{max}} \) of 3.0 GN/m\(^3\) (77 K) at \(~0.7\) T and 14.2 GN/m\(^3\) (65 K) at \(~2.5\) T which are about four times higher than those of undoped
YBCO film with $F_{p,\text{max}} = 0.76 \text{ GN/m}^3 (77 \text{ K})$ at $\sim 1 \text{ T}$ and $3.5 \text{ GN/m}^3 (65 \text{ K})$ at $4 \text{ T}$. However, compared with the highest $F_{p,\text{max}}$ values of $\sim 20 \text{ GN/m}^3 (77 \text{ K})$ at $\sim 2 \text{ T}$ and $\sim 78 \text{ GN/m}^3 (65 \text{ K})$ at $\sim 3 \text{ T}$ reported for MOD-YBCO nanocomposite film with 10 mol% BZO [18-19], these values are much smaller, implying that Sn-doping is less effective for flux pinning.

The field-orientation dependence of $J_c$ at $77 \text{ K}$ for $1 \text{ T}$ is shown in Fig. 2.9 for both undoped and Sn-doped YBCO films. Compared with undoped YBCO, Sn-doped YBCO film exhibits nearly isotropic $J_c$ enhancement in the wide $\theta$ region except the field-orientations close to the $ab$-plane of YBCO ($85^\circ < \theta < 95^\circ$). Thus, Sn-doped YBCO film has the minimum $J_c$ value ($J_{c,\text{min}}$) of $0.24 \text{ MA/cm}^2$ which is around three times larger than that of $0.084 \text{ MA/cm}^2$ for undoped YBCO film. The field-orientation dependency of the normalized $J_c(\theta) / J_c(B//ab)$ values at $77 \text{ K}$ similar to the inset in Fig. 2 has been reported for 5 mol% Sn-doped YBCO samples in previous literature [31-34]. However, reported data are slightly different from our data. For instance, in comparison with undoped YBCO, Strickland et al. [31] reported an overall enhancement of $J_c$ for Sn-doped YBCO sample in the whole field-orientation angles, which is commonly observed for the BZO-doped YBCO samples [19, 20, 24, 25]. However, Miyanaga et al. [32] and Teranishi et al. [33, 34] report $J_c$ suppression of Sn-doped YBCO sample in a wide $\theta$ region except $\theta$ values from $\sim 60^\circ$ to $80^\circ$, where Sn-doped sample shows higher $J_c$ values. In our samples, $J_c(B//ab)$ values of undoped YBCO film become larger than those of Sn-doped YBCO for the field-orientations close to the $ab$-plane ($85^\circ < \theta < 95^\circ$). This discrepancy is ascribed to a difference in the density of Sn-containing nanoparticles in the YBCO matrix.
since at least twice higher contents of Sn-containing nanoparticles might be trapped in our Sn-doped YBCO film compared with other reported samples [31-34]. On the other hand, the $J_c(\theta)$ behavior almost identical to our data in Fig. 2.13 was reported for RE (rare earths)-doped YBCO films [25, 29, 30]. Unlike our data of Sn-doped YBCO, however, a small $J_c(\theta)$ peak for $B//c$ (i.e., $\theta = 0^\circ$) is observed for RE-doped YBCO films, suggesting that the pinning nature of RE-doped YBCO is different from Sn-doped YBCO. Consequently, in comparison with undoped YBCO film, while lower $J_c(\theta)$ values for the field-orientations close to the ab-plane are attributed to a decrease in the stacking fault density for RE-doped YBCO films [25, 29, 30], a reduced intrinsic pinning effect along the ab-plane due to high density Sn-containing nanoparticles is most probably responsible for lower $J_c(\theta)$ values for $85^\circ < \theta < 95^\circ$ in our Sn-doped YBCO film.

The XRD $\theta$-2$\theta$ scan of undoped and Sn-doped YBCO films on the STO (100) single crystal substrates are shown in Fig. 2.10. The major peaks in all XRD patterns correspond to the (00$l$) reflections of the YBCO phase, indicating that both films are highly c-axis oriented. While undoped YBCO film shows only (00$l$) peaks of YBCO in Fig. 2.10 (a), Sn-doped YBCO film exhibits two small extra peaks at $2\theta = 30.1^\circ$ and $42.75^\circ$ in Fig. 2.10 (b), which have been indexed as (110) and (200) of the BaSnO$_3$ compound by many groups [32, 33, 35]. However, as suggested by Strickland et al. [31], a peak shift to lower $2\theta$ angle ($\sim 1^\circ$) relative to the (200) peak position of BaSnO$_3$ seems to show the possibility that the Sn-containing phase is not BaSnO$_3$ but the Y-containing Ba-Sn-O compound. We could not identify the phase responsible for a very small peak at around 50$^\circ$. Since this peak is not
always observed in the Sn-doped films, it may be due to a minor second phase solidified from the liquid phase existing in the firing stage.

To identify the Sn-containing phase of the Sn-doped YBCO film, we analyzed it by elemental mapping with STEM-EDS. The results are represented in Fig. 2.11. One particle marked with the dashed circle in Fig. 2.11 (a) has excessive Y and similar Cu components relative to the YBCO matrix while Ba and Sn components are absent in Fig. 2.11 (b), suggesting that this particle is $Y_2Cu_2O_5$. Though not presented, the $Y_2Cu_2O_5$ nanoparticles were also observed in undoped YBCO film. In accordance with this result, the $Y_2Cu_2O_5$ nanoparticles have been observed as the secondary phase of the MOD-processed YBCO films by other researchers [62-64]. On the other hand, many other nanoparticles marked with the arrows in Fig. 2.11 (a) have excessive Sn and similar Y, Ba components relative to the YBCO matrix while Cu component is absent in Fig. 2.11 (b), confirming that Sn-containing nanoparticles are not BaSnO$_3$ but a Y-Ba-Sn-O phase.

To further identify the Y-Ba-Sn-O phase, the STEM-EDS line scans of Y, Ba, Cu, Sn and Sr elements were performed for a Sn-containing particle grown on the STO substrate along the white line shown in Fig. 2.12 (a). In Fig. 2.12 (a), the image of the Sn-containing particle became somewhat unclear due to a damage caused by repeated analyses on this sample. The EDS line profiles of various elements are represented in Fig. 2.12 (b). The peak intensities of Y, Ba and Sn elements are clearly detectable within the Sn-containing particle. In 1992, Paulose et al. [65] first reported a new YBSO compound having a cubic structure which had been formed as the
secondary phase of sintered YBCO ceramics with SnO$_2$ addition. To identify the composition of the Sn-containing particle in Fig. 5a, EDS quantitative analysis was performed and the result is shown in Table 2.3. One can see that the molar ratio of Y : Ba : Sn is 1.25 : 2.0 : 0.95, which is very close to 1 : 2 : 1. This quantitative analysis result and the XRD data in Fig. 2.10 support that the Sn-containing particles are really the double perovskite YBSO compound [65, 66].

Our samples were also analyzed by HR-TEM as shown in Fig. 2.13. Fig. 2.13 (a) shows a cross-sectional TEM image of the Sn-doped YBCO film. The second phase particles are clearly observed. Independent wide-area observation of this specimen revealed that while YBSO particles of a high density were uniformly dispersed and their size was in the range of 20-80 nm with average particle size of 45 nm, Y$_2$Cu$_2$O$_5$ particles of a low density were non-uniformly dispersed and their size was in the range of 10-50 nm with average particle size of 30 nm. The Y$_2$Cu$_2$O$_5$ nanoparticles of both undoped and Sn-doped YBCO films were almost identical in their size and distribution. Due to the relatively lower density of Y$_2$Cu$_2$O$_5$ nanoparticles, their XRD peaks might be undetectable in Fig. 2.10. Consequently, the stronger flux pinning properties of Sn-doped YBCO film in Fig. 2.7 and Fig. 2.8 are attributable to YBSO nanoparticles.

Fig. 2.13 (b) clearly shows the YBSO nanoparticle epitaxially grown on the STO substrate surface. The fast Fourier transform (FFT) converted SAD (selected area diffraction) patterns from YBSO and STO shown in the inset strongly support that YBSO with a cubic structure has a cube-on-cube epitaxial relationship with STO. Two separated SAD patterns along the same
[001] crystallographic direction are due to a small difference in their lattice parameters ($a = 8.434$ and $3.970$ Å for YBSO and STO, respectively). All YBSO nanoparticles on the STO substrate surface were observed to have the cube-on-cube epitaxial relationship with STO, implying that these nanoparticles have epitaxial relationship with the YBCO matrix since YBCO is known to have a cube-on-cube relationship with STO. These epitaxially grown YBSO nanoparticles are considered to have coherent interfaces with YBCO. It can be understood that the XRD peak at $2\theta = 42.75^\circ$ in Fig. 2.10 (b) corresponds to the (004) diffraction peak of epitaxially grown YBSO nanoparticles. On the contrary, most of HR-TEM images of YBSO nanoparticles completely surrounded by the YBCO matrix are similar to Fig. 2.13 (c), representing that those are randomly oriented. Some YBSO particles exhibit the HR-TEM image similar to that of Fig. 2.13 (d), which seems to show an epitaxial relationship between the YBSO nanoparticle and the YBCO matrix. However, detailed analysis with the FFT patterns shown in the inset of Fig. 2.13 (d) reveals that the particle interface in Fig. 2.13 (d) is non-coherent since YBSO has [111] zone axis while the YBCO matrix has [010] zone axis. All YBSO nanoparticles completely surrounded by the YBCO matrix were found randomly oriented in this study. Randomly oriented YBSO nanoparticles have non-coherent interfaces with YBCO since they do not have any specific crystallographic orientation relationship with the surrounding YBCO matrix. One can also see that the YBSO (220) diffraction peak at $2\theta = 30.1^\circ$ in Fig. 2.10 (b) originates from randomly oriented YBSO nanoparticles.

In order to evaluate the internal strain of our films, we performed the
strain analysis for the XRD data in Fig. 2.10 by using the Williamson-Hall method [67]. Williamson-Hall plot for undoped and Sn-doped YBCO films is shown in Fig. 2.14. From the slopes of the linear fits in Fig. 2.14, we could obtain the values of $\varepsilon = 0.276 \pm 0.004\%$ for Sn-doped YBCO film and $\varepsilon = 0.091 \pm 0.019\%$ for undoped YBCO film. The higher nanostrain generated in the Sn-doped YBCO film is mainly attributed to the incorporation of YBSO nanoparticles within the YBCO matrix. The nanostrain value of $\varepsilon \approx 0.28\%$ our YBCO film with 10 mol\% YBSO nanoparticles is slightly larger than $\varepsilon \approx 0.25\%$ for MOD-YBCO film with 10 mol\% BZO nanoparticles reported by Llordes et al. [27]. This difference seems to be in agreement with the prediction by the in-plane lattice mismatch since the in-plane lattice mismatch value of 9.2\% between YBCO and YBSO is larger than that of 8.7\% between YBCO and BZO in a cube-on-cube epitaxy and thus the internal strain value of the YBCO film induced by YBSO nanoparticles is expected to be larger than that by BZO nanoparticles. However, as previously mentioned, the flux pinning effect of BZO nanoparticles is stronger compared with that of YBSO nanoparticles with the same 10 mol\% inclusion in the MOD-YBCO films. If we take into account of the difference in the average particle sizes between YBSO (~ 45 nm) and BZO (~ 15 nm) for the same doping content of 10 mol\%, the total interface area of YBCO/BZO is around 9 times larger than that of YBCO/YBSO. Consequently, in comparison with BZO nanoparticles, less effective pinning by YBSO nanoparticles is attributable to much lower density of the pinning sites although the pinning strength per each pinning site related to YBSO is considered to be slightly stronger due to its higher nanostrain value.
2.3.3. GdBCO films by the RCE-DR process

The field dependency of \( J_c \) at 65 and 77 K for \( B//c \) is shown in Fig. 2.15. In Fig. 2.15 (a), the self-field \( J_c \) values (77 K) of GdBCO CCs grown at 840, 860, and 880°C are 3.2, 2.9, and 1.9 MA/cm\(^2\), respectively. The properties of the sample grown at 860°C sample have already been published in our previous paper [38]. This sample exhibited higher magnetic \( J_c \) values at the field above 3 T at 77 K compared with those of 840 and 880°C samples. Although higher magnetic \( J_c \) values of this sample are not observed at 65 K up to 5 T, we believe that this behavior occurs at much higher magnetic fields. This behavior might be due to enhanced in-plane texture as it will be shown below in Fig. 2.19.

Fig. 2.15 (b) shows a log-log plot of \( J_c (B//c) \) versus applied field. At low fields, vortices are far apart, and thus their mutual interactions are negligibly weak. In this single vortex pinning regime, \( J_c \) is independent of \( H \). As \( H \) increases, vortex-vortex interactions increase and \( J_c \) decreases. It is shown that several common features, including a region of a nearly constant \( J_c \) up to a characteristic crossover field, the accommodation field, \( H_{acc} \), followed by a transition to a power-law regime at intermediate fields, \( J_c \propto H^\alpha \). In Fig. 2.15 (c), the exponent \( \alpha \) in the power-law relationship \( J \sim H^\alpha \) of GdBCO CCs grown at 840, 860, and 880°C are ~ 1.02, 1.03, and 1.05 at 77K, respectively, which are larger than MOD-[68, 69] and PLD-REBCO films [70, 71]. This result indicates that flux pinning of GdBCO CCs by RCE-DR is less effective than that of in the case of MOD- and PLD-GdBCO films.

The pinning force densities \( (F_p) \) for GdBCO CCs, evaluated by the
relationship of $F_p = J_c \times B$, are represented as a function of the magnetic field at 65 and 77 K for $B//c$ in Fig. 2.16. The GdBCO film grown at 840°C exhibits the highest pinning force densities in the entire fields of 0-5 T ($B//c$) at 77 and 65 K. It shows the $F_{p,max}$ of 2.8 GN/m$^3$ (77 K, $B//c$) near at 0.4 T and 8.8 GN/m$^3$ (65 K, $B//c$) near at 1.8 T, which is similar to PLD-GdBCO films on CeO$_2$-buffered IBAD MgO template [37].

The field-orientation dependence of $J_c$ for GdBCO CCs is shown in Fig. 2.17. All samples show a typical behavior of a sharp $J_c$ peak at $\theta = 90^\circ$ ($B//ab$). A small broad peak of $J_c$ near $\theta = 180^\circ$ ($B//c$) is also observed. In the GdBCO films by PLD, a small peak has also been detected at $B//c$ as well as at $B//ab$ [37], [49], [50]. The small $J_c$ peak for $B//c$ is ascribed to the defective structure with stacking faults [37, 49]. As shown in Fig. 2.17, field-orientation dependence of $J_c$ shows rather large anisotropy behavior, representing that Gd$_2$O$_3$ particles are less effective for flux pinning compared with MOD-processed GdBCO films with Gd$_2$O$_3$, and thus refinement of Gd$_2$O$_3$ particles in the GdBCO matrix seems to be required for stronger flux pinning.

Fig. 2.18 shows XRD patterns of GdBCO CCs grown at three different temperatures with 840, 860, and 880°C. The GdBCO (00$l$) reflections are observed for all samples, implying that the GdBCO film is highly $c$-axis oriented. The second phase peaks such as Gd$_2$O$_3$ and CuO are also observed in addition to IBAD template peaks. Interestingly, one can see that a small GdBCO (103) peak was observed for the film prepared at 840°C, suggesting that small randomly oriented GdBCO grains exist in the film. With increasing growth temperature, BaCuO$_2$ peak was observed in 880°C sample.
while GdBCO (103) poly peak disappeared. It can be estimated that the crystal growth for GdBCO phase is seriously affected by conversion temperature.

Fig. 2.19 shows the $\phi$–scan value of GdBCO (103) reflection and $\omega$–scan of GdBCO (005) reflection of GdBCO CCs. The full-width at half–maximum (FWHM) values of $\phi$–scan for 840, 860, and 880°C are 4.3°, 3.4°, and 2.6°, and also FWHM values of $\omega$–scan are 2.5°, 1.5° and 1°, respectively. The in-plane texture and out-of-plane texture of GdBCO CCs are gradually enhanced with increasing growth temperature of GdBCO films.

To identify the origin of GdBCO (103) peak of sample grown at 840°C, its surface morphology was observed by polarized light microscopy. The sample was mechanically polished from top surface to bottom of substrate using 0.02μm blue colloidal silica (ALLIED). In Fig. 2.20 (a) and (b), a lot of small grains were observed at the surface. However, the small grains disappear at the bottom of film.

To further identify the small grains within the GdBCO matrix, we performed the EBSD analysis. The analysis results are shown in Fig. 2.21. The first map shown in Fig. 2.21 (a) is the so-called image quality map, which resembles the standard SEM-BSE image. The second map in Fig. 2.21 (b) is the phase map, where the c-axis oriented GdBCO phase is indicated as red-colored region, the 45°-rotated GdBCO phase as pink or yellow and the Gd$_2$O$_3$ particles as green. The third map in Fig. 2.21 (c) is the inverse pole figure in the [001] direction, which gives the crystallographic orientations of each grain according to the stereographic triangles on the right, indicating that a lot of small grains are rotated 45°.
Cross-sectional TEM images of GdBCO CCs are shown in Fig. 2.22. A lot of second phases such as Gd$_2$O$_3$ particles and a small amount of CuO phase are observed in the matrix, which has already been confirmed by STEM-EDS [38]. The Gd$_2$O$_3$ particles were uniformly dispersed in the GdBCO matrix. The CuO phase is also found on the top surface of the GdBCO film, which might be solidified from a liquid phase exected from the GdBCO film after its expitaxial growth from the LMO layer. Fig. 2.22 (a) shows GdBCO CCs with growth temperature at 840°C, indicating that the average particle size of Gd$_2$O$_3$ is 126.5 ± 42.6 nm in the 840 °C sample which is smaller than that of 171.4 ± 53.1 nm in the 860 °C sample and 217.8 ± 49.4 nm in the 880°C sample. In Fig. 2.22 (a), Gd$_2$O$_3$ particles show slight in-plane alignment. In contrast, Gd$_2$O$_3$ particles in 860 and 880°C samples (Fig. 2.22 (b) and Fig. 2.22 (c)) are strongly elongated along the film plane. From the cross-sectional TEM images, Gd$_2$O$_3$ particles size becomes smaller in the matrix with decreasing growth temperature. The reason for refined Gd$_2$O$_3$ at lower growth temperature is that as-grown Gd$_2$O$_3$ particles in PO$_2$ of $10^{-5}$ Torr are smaller.

To further identify the second phase particles within the GdBCO matrix, we performed the scanning transmission electron microscopy (STEM)-energy dispersive X-ray spectroscopy (EDS) elemental mapping. The results are shown in Fig. 2.23. It is evident that the second phase particles are Gd$_2$O$_3$. The Gd$_2$O$_3$ particles are uniformly dispersed in the GdBCO matrix and their size is in the range of 70-150nm. A small amount of the Cu-O phase also observed within the GdBCO matrix. The microstructural features of GdBCO CCs by RCE-DR are somewhat similar to those by MOD. In the case of MOD-processed YBCO films, the second phases such as Y$_2$O$_3$, Y$_2$Cu$_2$O$_5$, and
Ba-Cu-O are observed within the film [72]. However their sizes are much smaller than those of Gd$_2$O$_3$ particles in GdBCO films by RCE-DR. The Cu-O phases are also found on the top surface of the GdBCO film, which might be solidified from a liquid phase exacted from the GdBCO film after its exsoriphic growth on the LMO layer.

Fig. 2.24 shows high resolution (HR)-TEM images and the orientation relationship among LMO layer, Gd$_2$O$_3$ particles, and the GdBCO film. The HR-TEM image of a Gd$_2$O$_3$ particle grown on the LMO buffer layer but trapped in the GdBCO matrix is shown in Fig. 2.24 (a). The inset shows fast Fourier transformation (FFT) patterns of Fig. 2.24 (a). From the FFT analysis data, it is obvious that this Gd$_2$O$_3$ particle is biaxially textured with the following crystallographic orientation relationship: LMO [010] // GdBCO [010] // Gd$_2$O$_3$ [110]; LMO [001] // GdBCO [001] // Gd$_2$O$_3$ [001]. Fig. 2.24 (b), (c), and (d) show Gd$_2$O$_3$ particles fully trapped in the GdBCO matrix. As can be seen in FFT patterns, these particles are randomly oriented.

To obtain additional information of orientation of Gd$_2$O$_3$ particles in the GdBCO matrix, high-resolution (HR)-TEM analysis was performed. In our previous report [38], Gd$_2$O$_3$ particles fully trapped GdBCO matrix were randomly oriented while Gd$_2$O$_3$ grown on the LMO buffer layer were biaxially textured. Fig. 2.25 (a) shows Gd$_2$O$_3$ particles fully trapped GdBCO matrix. In Fig. 2.25 (b)-(1) and (2), Gd$_2$O$_3$ (220) plane was rotated with the angles of ~30° and ~40° from GdBCO (00l) plane, respectively, implying that Gd$_2$O$_3$ particle has noncoherent interfaces with the GdBCO matrix. In Fig. 2.25 (b)-(3), the GdBCO matrix were rotated ~ 15° from each other, representing that the high angle boundaries of GdBCO locally exist although
in-plane alignment analyzed by X-ray $\phi$–scan is less than $5^\circ$ in Fig. 2.19.

The Gd$_2$O$_3$ particle rotated by $\sim 30^\circ$ have non-coherent interfaces with GdBCO matrix, which is confirmed by fast Fourier transformation (FFT) patterns in Fig. 2.25 (b)-whole area. As can be seen in Fig. 2.25 (b)-(2) and (3), the Gd$_2$O$_3$ particle induces GdBCO matrix rotations around it of $\sim 12^\circ$ and $15^\circ$. It means that strain is generated around Gd$_2$O$_3$ particles which is reflected in the associated disorder of the GdBCO matrix.

2.4. Summary

In this study, we characterized the pinning properties of REBCO films by the PLD, MOD, and RCE-DR processes. First, GdBCO films with BSO additions up to 6 vol% were prepared on the CeO$_2$-buffered IBAD MgO template by PLD. Compared with undoped GdBCO film, all BSO-doped GdBCO films showed significantly improved magnetic $J_c(B)$ and $F_{p,max}$ for $B//c$, and also transport $J_c(\theta)$ values in magnetic fields up to 5 T at 65 and 77 K, implying that BSO doping is very effective for improving the pinning properties of GdBCO films. The optimum BSO doping content for GdBCO films by PLD was turned out to be 5 vol%. From the optimally doped GdBCO film, we could obtain high $J_{c,min}$ values of 0.39 and 0.68 MA/cm$^2$ at $\theta = 120^\circ$ for 1 T at 77 K and for 3 T at 65 K, respectively. From the cross-sectional TEM analysis results, it is obvious that the BSO nanorods with the diameter of $\sim 10$ nm, grown roughly parallel to the $c$-axis of the GdBCO film, are responsible for such a significant in-field $J_c$ improvement. Second, both undoped-YBCO and 10 mol% Sn-doped YBCO films on STO (001)
single crystal substrates were prepared by the MOD process for the investigation of the flux pinning characteristics of Sn-doped YBCO film. Compared with undoped YBCO film, 10 mol% Sn-doped YBCO film exhibited significantly improved $J_c$ values in magnetic fields up to 5 T at 65 and 77 K for $B//c$, and also much enhanced angular dependency of $J_c$ at 77 K for 1 T except the field-orientations close to the $ab$-plane of YBCO ($85^\circ < \theta < 95^\circ$). Lower $J_c(\theta)$ values for $85^\circ < \theta < 95^\circ$ in Sn-doped YBCO film may be due to a reduced intrinsic pinning effect along the $ab$-plane because of high density Sn-containing nanoparticles trapped in the YBCO matrix. Sn-containing nanoparticles could be indentified as the double perovskite YBSO compound. Consequently, the stronger pinning effect in Sn-doped YBCO film is attributable to YBSO nanoparticles trapped in the YBCO matrix. In addition, the YBSO nanoparticles completely surrounded by the YBCO matrix have random orientation with YBCO while those located at the interface of YBCO/STO substrate have epitaxial relationship with YBCO. Finally, high-$J_c$ GdBCO CCs were successfully fabricated by the RCE-DR process in the $PO_2$ of 150 mTorr with three different growth temperatures of 840, 860, and 880°C. With increasing the growth temperature, while the formation of (103)-oriented GdBCO grains can be avoided, biaxial textures can be (both in-plane and out-of-plane) improved. The sample grown at 840°C exhibited the highest $F_{p,max}$ value of 2.8 GN/m$^3$ (77 K, $H//c$) near at 0.4 T, and also the highest minimum transport critical current density ($J_{c,min}$) value of 0.6 (77 K, 1 T) and 0.63 MA/cm$^2$ (65 K, 3 T) for $\theta = 130^\circ$, respectively. These results represent that the positive pinning effect of Gd$_2$O$_3$ refinement outweighs the negative effect of degraded in-plane texture. It is
related to microstructure, indicating Gd₂O₃ particles become larger in the matrix as increasing growth temperature by TEM analysis. In conclusion, it is important to control of Gd₂O₃ particles size for the improvement of superconducting properties. Further improvement of pinning properties will be possible by refining Gd₂O₃ without forming (103) grains and degrading in-plane textures of GdBCO.
References


Table 2.1. Typical characteristics of the undoped and BSO-additions GdBCO films.

<table>
<thead>
<tr>
<th>BSO content (vol %)</th>
<th>In-plane texture $\Delta \phi (^{\circ})$</th>
<th>$T_{c,zero}$ (K)</th>
<th>$T_{c,onset}$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>$c$-axis lattice parameter (Å)</th>
<th>$F_{p,max}$ at 77 K (GN/m$^3$)</th>
<th>$F_{p,max}$ at 65 K (GN/m$^3$)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>3.4</td>
<td>91.2</td>
<td>91.9</td>
<td>0.7</td>
<td>11.7436</td>
<td>2.7 (~ 1.4 T)</td>
<td>1.7 (~ 2.6 T)</td>
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<tr>
<td>2</td>
<td>3.4</td>
<td>91</td>
<td>91.7</td>
<td>0.7</td>
<td>11.7553</td>
<td>2.9 (~ 1.2 T)</td>
<td>14.2 (~ 2 T)</td>
</tr>
<tr>
<td>3</td>
<td>3.6</td>
<td>90.8</td>
<td>91.6</td>
<td>0.8</td>
<td>11.7585</td>
<td>4.4 (~ 2 T)</td>
<td>19.5 (~ 4 T)</td>
</tr>
<tr>
<td>4</td>
<td>3.9</td>
<td>90.7</td>
<td>91.5</td>
<td>0.8</td>
<td>11.7615</td>
<td>6.3 (~ 2.2 T)</td>
<td>30.4 (~ 3.2 T)</td>
</tr>
<tr>
<td>5</td>
<td>4.1</td>
<td>90.5</td>
<td>91.4</td>
<td>0.9</td>
<td>11.7670</td>
<td>6.5 (~ 3.2 T)</td>
<td>32.5 (~ 4 T)</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>89.9</td>
<td>90.9</td>
<td>1.0</td>
<td>11.7635</td>
<td>5.7 (~ 2.2 T)</td>
<td>26.3 (~ 3.4 T)</td>
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Table 2.2. Magnetic $J_c$ values of samples at 77 K and 65 K in 0–5 T.

<table>
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<tr>
<th>Samples</th>
<th>Temp.</th>
<th>Magnetic $J_c$ (MA/cm²)</th>
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<tr>
<td></td>
<td></td>
<td>0 T</td>
</tr>
<tr>
<td>undoped YBCO</td>
<td>77 K</td>
<td>2</td>
</tr>
<tr>
<td>Sn-doped YBCO</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>undoped YBCO</td>
<td>66 K</td>
<td>3.5</td>
</tr>
<tr>
<td>Sn-doped YBCO</td>
<td></td>
<td>6.7</td>
</tr>
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</table>
Table 2.3. EDS quantitative analysis data for the chemical composition of the Sn-containing particle in Fig. 12 (a).

<table>
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<tr>
<th>Elements</th>
<th>Weight fraction (%)</th>
<th>Atomic fraction (%)</th>
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</thead>
<tbody>
<tr>
<td>O(K)</td>
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<td>78.63</td>
</tr>
<tr>
<td>Y(K)</td>
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</tr>
<tr>
<td>Sn(K)</td>
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</tr>
<tr>
<td>Ba(K)</td>
<td>36.74</td>
<td>10.15</td>
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</table>
Fig. 2.1. $J_c$–$B$ characteristic of undoped and 2-6 vol% BSO-doped GdBCO films at (a) 77 and (b) 65 K for $B//c$. 
Fig. 2.2. The pinning force density ($F_p = J_c \times B$) values at (a) 77 and (b) 65 K for $B//c$ as a function of the magnetic field for undoped and 2-5 vol% BSO-doped GdBCO films.
Fig. 2.3. Field-orientation dependence of the transport $J_c$ values for undoped and 4, 5, and 6 vol% BSO-doped GdBCO samples measured at (a) 77 K, 1 T (b) 77 K, 3 T (c) 77 K, 5 T, (d) 65 K, 1 T (e) 65 K, 3 T and (f) 65 K, 5 T.
Fig. 2.4. Cross-sectional TEM images of undoped GdBCO film (~ 300 nm thickness).
Fig. 2.5. Cross-sectional HR-TEM image (a), and reconstructed masked inverse FFT image (b) of (c) (white arrows indicate a number of stacking faults) for undoped GdBCO film.
Fig. 2.6. Cross-sectional TEM image of the GdBCO film with 5 vol% BSO addition.
Fig. 2.7. (a) Field dependency of $J_c$ at 65 and 77 K for $B//c$. Data for undoped YBCO film are also represented for a comparison with those for Sn-doped YBCO film. (b) Log-log plot of $J_c$ values in the magnetic field region of 0.1 ~ 1 T for undoped and Sn-doped YBCO films.
Fig. 2.8. Pinning force, $F_p(H)$, curves of the undoped and Sn-doped YBCO film at 65 and 77 K.
Fig. 2.9. Field-orientation dependence of $J_c$ at 77K, 1T for Sn-doped YBCO film compared with undoped YBCO. The inset shows normalized to $J_c(\theta) / J_c(\mathbf{B}||\mathbf{ab})$. 
Fig. 2.10. XRD patterns of (a) undoped and (b) Sn-doped YBCO films. Two additional small peaks at $2\theta \approx 30^\circ$ and $43^\circ$, denoted by red dots in (b), are originated from Sn-related phase.
Fig. 2.11. Cross-sectional Z-contrast STEM image (a) of Sn-doped YBCO film, and the Y, Ba, Cu, and Sn spectral images (b) analyzed for the square area related by a dashed line in (a). The YBSO and the $\text{Y}_2\text{Cu}_2\text{O}_5$ nanoparticle are marked with the arrows and dashed circle, respectively.
Fig. 2.12. Z-contrast STEM image (a) of a Sn-containing particle at the interface between YBCO and STO substrate, and the EDS line scans by STEM (b) for various elements including Y, Ba, Sn, and Sr. EDS quantitative analysis in Table 3 was performed on the rectangular area related by a dashed line in (a).
Fig. 2.13. The cross-sectional TEM bright-field images of the Sn-doped YBCO film (a) and the epitaxially grown YBSO nanoparticle at the interface between YBCO and STO substrate (b). Inset in (b) represents the Fast Fourier Transformation (FFT) pattern of the image (b). High-resolution TEM images (c) and (d) of randomly oriented YBSO nanoparticles within the YBCO matrix, and inset in (d) represents its FFT pattern of the image (d).
Fig. 2.14. Williamson–Hall plot for undoped and Sn-doped YBCO films.
Fig. 2.15. For GdBCO CCs grown at 840, 860, and 880°C, (a) field dependence of $J_c$ at 65 and 77 K for $B//c$, (b) log-log plot of $J_c$, and (c) log-log plot of $J_c$ values in the magnetic field region of 0.1 ~ 1 T.
Fig. 2.16. The pinning force density \( F_p = J_c \times B \) values at 77 and 65 K for \( \text{B/} \text{c} \) as a function of the magnetic field for GdBCO CCs grown at three different temperatures of 840, 860, and 880°C.
Fig. 2.9. Field-orientation dependence of $J_c$ at (a) 77 K in 1 T, (b) 77 K in 3 T, (c) 65 K in 1 T, and (d) 65 K in 3 T for GdBCO CCs.
Fig. 2.18. XRD $\theta$-2$\theta$ diffraction patterns of GdBCO films for three different growth temperatures.
Fig. 2.19. In-plane texture ($\Delta \phi$) and out-of-plane texture ($\Delta \omega$) of GdBCO CCs.
Fig. 2.20. Polarized light microscope images of 840°C GdBCO CCs for the different depth from the surface. The images after polishing (a) ~100 nm, (b) ~200 nm, (c) ~400 nm from the top of film surface, and (d) metal substrate surface.
Fig. 2.10. EBSD analysis of GdBCO CCs. (a) image quality maps, (b) phase maps, and (c) inverse pole figure maps.
Fig. 2.22. Cross-sectional TEM images of three different GdBCO CCs grown at (a) 840, (b) 860, and (c) 880°C.
Fig. 2.23. (a) Z-contrast STEM image of GdBCO CCs, (b) and (c) the Gd, Ba, Cu, and O spectral images analyzed for the square area related by dashed line in (a).
Fig. 2.24. (a) HR-TEM images of Gd$_2$O$_3$ particles between GdBCO matrix and LMO layer, (b), (c) and (c) HR-TEM images of Gd$_2$O$_3$ particles fully trapped in the GdBCO matrix. (Inset: FFT patterns of the corresponding images).
Fig. 2.25. TEM images of local microstructure in GdBCO film grown at 880°C in the region near an incoherent Gd$_2$O$_3$ particle. (a) HR-TEM images of Gd$_2$O$_3$ particles trapped in the GdBCO matrix and (b) FFT patterns of the corresponding images of each area.
Chapter 3. Improvement of pinning properties of Gd$_2$O$_3$-doped GdBCO films on CeO$_2$-buffered MgO (100) substrate by PLD

3.1. Introduction

PLD-GdBCO CCs have recently drawn great attention since they are known to possess stronger pinning properties compared with PLD-YBCO CCs [1-4]. The $J_c$ is one of the most important factors for a real application of superconductors. Recently, GdBCO CCs with high $J_c$ have been successfully fabricated on metallic substrates with textured buffer layers by the PLD process [1-4]. However, GdBCO films still have problems that the $J_c$ decreases rapidly as magnetic field increases. To improve flux pinning properties in high magnetic field, the introduction of strong flux pinning is required. Many researchers have tried to improve pinning properties of GdBCO films by introducing defects or nano-sized second phases into the superconducting matrix. Up to date, various doping materials, including yttria-stabilized zirconium (YSZ) [3, 4], Au [5, 6], BaZrO$_3$ (BZO) [7-11], BSO [12-15], and BaHfO$_3$ (BHO) [16, 17], have been incorporated into the GdBCO films by PLD. These materials act c-axis correlated pinning centers in GdBCO matrix such as columnar defects or nanorods. To introduce randomly dispersed pinning centers, Mele et al. [18] reported Y$_2$O$_3$-doped YBCO films using ‘surface modified target’ method, recently. However, the
$J_c(B, \theta, T)$ properties of Gd$_2$O$_3$-doped GdBCO films by PLD have never been reported yet in the literature.

Recently, SuNAM Co. and our group has successfully developed long-length high-$J_c$ GdBCO CCs on LMO-buffered IBAD MgO template by the RCE-DR process [19-20]. According to our preliminary study on GdBCO CCs by RCE-DR [21], the post-annealing process at low $PO_2$ of 300 mTorr could be used for improving the flux pinning properties of GdBCO films. Since the average particle size of Gd$_2$O$_3$ trapped in the GdBCO matrix of GdBCO CC by RCE-DR is much larger than those by PLD, it must be very interesting to study the effect of the post annealing process on the GdBCO films with Gd$_2$O$_3$ nanoparticles on a robust substrate.

In this study, therefore, we tried to improve flux pinning properties of Gd$_2$O$_3$-doped GdBCO films by PLD and post-annealing. First, we used Gd$_2$O$_3$ sectors on GdBCO target for systemic study. On the basis of the results from systemic study, 2 mol% Gd$_2$O$_3$-doped GdBCO films by PLD were post-annealed in various temperatures and $PO_2$ in order to enhance their pinning properties. Details of superconducting properties and microstructural features of as-deposited and post-annealed Gd$_2$O$_3$-doped GdBCO films were discussed in this chapter.

### 3.2. Experimental

The undoped and Gd$_2$O$_3$-doped GdBCO films were deposited on CeO$_2$-buffered MgO (100) substrate. For the deposition of GdBCO on MgO (100) substrate, it is necessary to deposit buffer layer. The biaxial textured CeO$_2$
buffer layers on MgO (100) substrate by an annealing heat treatment prior to
CeO$_2$ deposition by RF-magnetron sputtering. The annealing process was
performed in a tube furnace (ex-situ annealing) or in a sputter chamber (in-
situ annealing). The CeO$_2$ films were grown at mixed oxygen and argon
partial pressure of 5 mTorr, substrate temperature ($T_s$) of 800°C, and power
of 150 W.

For a systematic study, the GdBCO targets with a Gd$_2$O$_3$ second phase
targets were controlled to have 2, 4, 6, and 10 mol%. The GdBCO and Gd$_2$O$_3$
targets were prepared by the solid-state reaction employing
precursors of Gd$_2$O$_3$ (High Purity Co., 99.9%), BaCO$_3$ (Cerac., 99.9%), and
CuO (High Purity Co., 99.9%). Detailed PLD conditions are reported in our
previous paper [15]. A Lambda Physik KrF excimer laser ($\lambda$= 248 nm) was
used to deposit GdBCO films at the energy density of 2 J/cm$^2$ and the laser
frequency of 8 Hz. The substrate temperature of 800°C and the PO$_2$ of 300
mTorr were used to deposit undoped and Gd$_2$O$_3$-doped GdBCO films. After
deposition, samples were annealed at 500°C for 1 h in a pure oxygen
atmosphere.

To identify the effect of the post-annealing process on the pinning
properties Gd$_2$O$_3$-doped GdBCO films, we performed post-annealing in
various temperature and oxygen pressure. The schematic of post-annealing
conditions using GdBCO phase diagram are simply shown in Fig. 3.1. The
highest $F_{p,max}$ of 2mol% Gd$_2$O$_3$-doped GdBCO films were post-annealing at
750-850°C at 3-100 mTorr of PO$_2$ for 15min, and then quenched using a reel
to reel tube furnace as shown in Fig. 3.2. After annealing, samples were
annealed at 500°C for oxygenation.
The XRD $\theta$-2$\theta$ patterns were obtained from all samples using an X-ray diffractometer (Bruker D8-Advance, Cu K\(\alpha\) radiation). The in-plane texture ($\Delta\phi$) and out-of-texture ($\Delta\omega$) of CeO\(_2\) and GdBCO films were analyzed by X-ray $\phi$- and $\omega$-scan (PANalytical X’pert Pro). Field emission-scanning electron microscopy (FE-SEM, MERLIN Compact) and transmission electron microscopy (TEM, JEOL JEM-2100F) were employed to characterize the microstructures of samples. A standard four-point probe technique was used to measure the superconducting properties of samples. The transport $J_c$ values were evaluated by measuring the $I$-$V$ curves with the 1 $\mu$V/cm criterion. Magnetic field dependence of $J_c$ was evaluated from the magnetic hysteresis curve measured by Quantum design SQUID magnetometer (MPMS XL-5) for the field applied parallel to the $c$-axis of GdBCO films ($B//c$) in the field region of 0-5 T. The angular dependence of transport $J_c$ for the samples was measured using the PPMS (Quantum design model-6000) after patterning a micro-bridge. For the measurement of field-orientation dependence of the transport $J_c$, the samples were rotated from 0 to 210° at 77 K in the magnetic fields of 1 T, where $\theta = 90^\circ$ corresponds to $B//ab$, and $\theta = 180^\circ$ to $B//c$.

3.3. Results and discussion

3.3.1. CeO\(_2\) buffer layer on MgO (100) substrate by RF sputtering

GdBCO films are difficult to grow directly on MgO (100) single crystal substrate due to a large lattice mismatch between substrate and GdBCO film.
Various buffer layer such as CeO$_2$[22-29], STO [30, 31] and LMO [32-34] have been studied for HTS buffer layer. CeO$_2$ has been mostly used as buffer layer for the growth GdBCO film. It has simple structure, chemical stability and relatively good lattice mismatch between GdBCO and MgO.

Fig. 3.3 shows the XRD $\theta$-$2\theta$ patterns of the CeO$_2$ buffer layers deposited on MgO (100) substrate. As shown in Fig. 3.3 (a), CeO$_2$ layer deposited on non-annealed MgO (100) substrate always shows (111) random orientations. In our previous study [35], we confirmed from X-ray photoelectron spectroscopy (XPS) that Mg(OH)$_2$ which is induced random oriented CeO$_2$ grains on the MgO surface was fully decomposed at >700$^\circ$C by in-situ annealing. To obtain biaxial textured CeO$_2$ grains, we also performed ex-situ annealing for 5h at 1000$^\circ$C. After ex-situ annealing of CeO$_2$ film, we obtained only $c$-axis oriented CeO$_2$ layer on MgO substrate in Fig. 3.3 (b). The lattice parameter of CeO$_2$ film on in-situ annealed MgO was larger than ex-situ annealing. It means deficiency of oxygen during sputtering results in substoichiometric phases such as CeO$_{2-x}$ with larger lattice parameters.

Fig. 3.4 shows in-plane ($\Delta\phi$) and out-of plane ($\Delta\omega$) texture of CeO$_2$ films. The $\Delta\phi$ and $\Delta\omega$ values of CeO$_2$ layer on in-situ annealed MgO (100) substrate are 4.9$^\circ$ and 3.2$^\circ$, respectively, while those of CeO$_2$ film after ex-situ annealing are 2.3 and 1.2$^\circ$, respectively. Although (111) random orientations of CeO$_2$ exist from XRD peak in Fig. 3.3, we could not obtain 45$^\circ$-rotated CeO$_2$ grains from $\phi$ and $\omega$ scans. However, the texture of CeO$_2$ film after ex-situ annealing is improved than those of CeO$_2$ film on in-situ annealed MgO.

Fig. 3.5 shows SEM surface morphology of CeO$_2$ film. It is clear that the
grain size becomes larger after *ex-situ* annealing. It means that CeO$_2$ gains grow by recrystallization. The small grain size leads to considerable peak broadening from texture analysis in Fig. 3.4.

### 3.3.2. Pinning improvement of Gd$_2$O$_3$-doped GdBCO films via optimum doping of Gd$_2$O$_3$

Fig. 3.6 shows the XRD $\theta$-2$\theta$ scans of all GdBCO films deposited on CeO$_2$-buffered MgO (100) substrate. As shown in Fig. 3.6, the major peaks are from the GdBCO (00$l$) reflections, indicating that all GdBCO films are strongly $c$-axis oriented. We can also observe the minor peak of CeO$_2$ (l00) reflection in addition to MgO (100) substrate peak. Only small Gd$_2$O$_3$ (222) reflection is observed in 10 mol% Gd$_2$O$_3$-doped GdBCO film.

The typical characteristics of the undoped and Gd$_2$O$_3$-doped GdBCO films are shown in Table 3.1. The $\phi$-scan of (103) reflection and $\omega$-scan of (005) reflection results for all films are shown in Fig. 3.7. The $\Delta\phi$ and $\Delta\omega$ values are plotted as a function of the Gd$_2$O$_3$ doping concentration in Fig. 3.7. It is obvious that in-plane textures of the GdBCO films are gradually deteriorated with further increase in Gd$_2$O$_3$ doping up to 10 mol%. The gradual degradation in the in-plane and out-of-plane texture of GdBCO films with increasing the Gd$_2$O$_3$ content probably originates from a gradual increase in the lattice strain induced by the in-plane lattice mismatch (~ - 6.8%, GdBCO : Gd$_2$O$_3$= 3 :1) between the GdBCO matrix and trapped Gd$_2$O$_3$ particles. In previous reports, including BSO-doped GdBCO films [15, 36] and BZO-doped SmBCO films [37], the degradation of in-plane
texture with increasing the doping contents has also been attributed to the lattice strain induced by doping.

Fig. 3.8 shows the $T_{c,\text{zero}}$ and $\Delta T$ variation as a function of the nominal concentration of Gd$_2$O$_3$ in the GdBCO matrix. The $T_{c,\text{zero}}$ values are gradually decreased and $\Delta T$ values are slightly increased with increasing the Gd$_2$O$_3$ content. Though not presented, the resistivity ($\rho$)-temperature ($T$) curves have a linear metallic behavior and the normal $\rho$ of GdBCO films is increased with increasing the Gd$_2$O$_3$ content. As suggested by many authors [38-41], a gradual increase in the GdBCO lattice strain with increasing the doping content is regarded as the origin for the gradual degradation in $T_c$ values.

The typical SEM plan-view micrographs of undoped and Gd$_2$O$_3$-doped GdBCO films are shown in Fig. 3.9. As increasing doping concentration of Gd$_2$O$_3$, white particles are observed on the film surfaces. However, the large particles were observed on surface of 2 mol% which is might be contaminations.

The field dependency of $J_c$ at 65 and 77 K for $B//c$ is shown in Fig. 3.10 (a). As listed below in Table 3.1, the magnetic $J_c$ values (at 77 K and 65 K in 0 T) are slightly decreased with increasing Gd$_2$O$_3$ content. As increasing magnetic fields up to 5 T at 77 and 65 K, however, $J_c$ values of 2 and 4 mol% Gd$_2$O$_3$-doped GdBCO films are higher than those of undoped sample. Fig. 3.10 (b) shows a log-log plot of $J_c$ ($B//c$, 77K) versus the applied field. The exponent $\alpha$ value, which is calculated by a linear regression of the $J_c$-$H^\alpha$ curve, of undoped GdBCO film is ~0.52. This value is similar to the values of ~ 0.5 reported for the undoped PLD-GdBCO films [42]. The $\alpha$ value of
~0.36 for 2 mol% Gd$_2$O$_3$-doped GdBCO film exhibited the stronger pinning performance than other Gd$_2$O$_3$-doped GdBCO films.

The pinning force density, $F_p = J_c (B) \times B$, at 65 K and 77 K as a function of the magnetic field for $B//c$ are shown in Fig. 3.11. The 2 mol% Gd$_2$O$_3$-doped GdBCO film shows the $F_{p,\text{max}}$ of 11.3 GN/m$^3$ near 1.8 T at 77 K and 37.3 GN/m$^3$ near 2.8 T at 65 K which are higher than those of undoped GdBCO film with $F_{p,\text{max}}$ of 6.5 GN/m$^3$ near 1 T at 77 K and 30.4 GN/m$^3$ near 2.4 T at 65K. The largest $F_{p,\text{max}}$ values are achieved from the 2 mol% Gd$_2$O$_3$-doped GdBCO film, implying that the optimum doping content of Gd$_2$O$_3$ is 2 mol%. Recently, Mele et al. [18] have reported for Y$_2$O$_3$-doped YBCO films on STO-buffered MgO (100) substrate that the $F_{p,\text{max}}$ of 7.78 GN/m$^3$ at 77 K which is smaller than our value, but the $F_{p,\text{max}}$ of 54.5 GN/m$^3$ at 65 K which is higher than our value. It means that Y$_2$O$_3$-doped YBCO films more effective lower temperatures in this result.

Fig. 3.12 shows field orientation dependence of $J_c$ for undoped and 2 mol% Gd$_2$O$_3$-doped GdBCO films. Compared with undoped GdBCO, 2 mol% Gd$_2$O$_3$-doped GdBCO film exhibits nearly isotropic $J_c$ enhancement. In this data, all films show a sharp $J_c$ peak at $\theta = 90^\circ$ ($B//ab$) from intrinsic pinning such as planar defects due to the well-known tendency of epitaxial REBCO film [43-45]. A small broad $J_c$ peak near $\theta = 180^\circ$ ($B//c$) was also observed for GdBCO films while it was unobservable for the YBCO films. SRL-ISTEC group, Japan [1-4], suggested that much higher stacking faults and screw dislocations in the undoped GdBCO film compared with those of the undoped YBCO film played a role of c-axis-correlated pinning centers, which are responsible for the small broad $J_c(\theta)$ peak for $B//c$. 

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Fig. 3.13 shows the cross-sectional TEM images of undoped GdBCO film. The thickness of undoped GdBCO film is 500nm. This GdBCO layer is mainly composed of c-axis oriented GdBCO grains. As shown in Fig. 3.13 (b), the selected area diffraction (SAD) patterns of undoped sample along the thickness represent continuous reflection spots, indicating that crystal orientation relationships between the CeO$_2$ and GdBCO have a cube-on-cube texture. This result is similar to our previous report, deposited on PLD-CeO$_2$-buffered IBAD MgO template [15].

To investigate microstructure of 2 mol% Gd$_2$O$_3$-doped film, we also performed TEM analysis. The low magnification TEM image is shown in Fig. 3.14 (a). The round-shaped Gd$_2$O$_3$ nanoparticles are clearly visible in Fig. 3.14 (b). The nanoparticles are randomly distributed. The diameter of Gd$_2$O$_3$ nanoparticles is estimated to be of the order of 6-7 nm, which is similar to Y$_2$O$_3$ particles in YBCO with 6-8 nm [18].

### 3.3.3. Pinning improvement of Gd$_2$O$_3$-doped GdBCO films via post-annealing

Fig. 3.15 shows the XRD $\theta$-2$\theta$ scans of post-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO films by various temperatures and $PO_2$. As shown in Fig. 3.15, there is no significant difference between a non-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO films and the sample annealed at 750 °C in the $PO_2$ of 3 mTorr. However, the BaCuO$_2$ phase was observed as increasing temperature and $PO_2$. Unidentified peaks at $2\theta \approx 26.6$, 28.7, 32.1, and 35.1 ° were also observed after annealing over 825°C. Though not presented, EDS
quantitative analysis from SEM indicated that Mo was detected surface of film for 850°C in 100 mTorr. It means that the surface of GdBCO film reacted with Mo metal because we used metal tape for post-annealing in reel-to-reel furnace. Therefore, unidentified peaks come from the reaction between the GdBCO film and substrate.

The SEM surface micrographs of undoped and Gd$_2$O$_3$-doped GdBCO films are shown in Fig. 3.16. The surface of post-annealed GdBCO films in lower temperatures and $PO_2$ exhibit no significant difference in their surface morphologies. However, post-annealed GdBCO films in higher temperatures and $PO_2$ exhibit out-growth phases in their surface morphologies. The out-growth phase might be a BaCuO$_2$ phase.

The $\rho$-$T$ curves of the 2 mol% Gd$_2$O$_3$-doped GdBCO film and annealed 2 mol% Gd$_2$O$_3$-doped GdBCO in various temperature and $PO_2$ are shown in Fig. 3.17. The $T_{c,\text{zero}}$ and $\Delta T$ values of all annealed samples are listed in Table 3.2. The $T_{c,\text{zero}}$ values of GdBCO films annealed at 800 °C in the $PO_2$ of 10 mTorr are increased up to ~91.4 K. The enhancement of $T_{c,\text{zero}}$ comes from the rearrangement of Gd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_{7+d}$ matrix toward decreasing the $x$ value after annealing at the high temperature of 800°C in the low $PO_2$ of 10 mTorr. However, $T_{c,\text{zero}}$ values of the GdBCO films annealed at high temperature in high $PO_2$ is decreased. The GdBCO film annealed at 850 °C in the $PO_2$ of 100 mTorr does not shows the typical $\rho$-$T$ curves of superconductor, which is due to reaction between GdBCO film and metal tape in tube furnace. It is good agreement with XRD data in Fig. 3.15.

Fig. 3.18 shows field orientation dependence of $J_c$ for non-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO, GdBCO film annealed at 800°C in 30 mTorr,
and annealed at 800°C in 10 mTorr. Compared with non-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO, the flux pinning properties of GdBCO film annealed at 800°C in 10 mTorr are slightly improved along the direction parallel to the $c$-axis, indicates that it has $c$-axis correlated pinning centers, while those of GdBCO film annealed at 800°C in 30 mTorr are much degraded.

In order to identify the origin for improvement of flux pinning, cross-sectional TEM analyses were performed for GdBCO film post-annealed at 800°C in the $PO_2$ of 10 mTorr. As shown in Fig. 3.19 (b), some defects along the $c$-axis of GdBCO are observed in the post-annealed sample. The FFT patterns of area in (2) are distorted from exact GdBCO matrix, indicating that GdBa$_2$Cu$_4$O$_8$ (Gd124) type of stacking faults existed very local area. A $RE$124 occurs due to the insertion of an extra CuO plane in the $REBCO$ structure. From the angular dependence of $J_c$, it can be deduced that flux pinning along $c$-axis ($B//c$) in the post-annealed sample might be improved by the stacking faults filed up along the $c$-axis of GdBCO matrix.

2.4. Summary

In this study, $c$-axis oriented CeO$_2$ buffer layer was successfully fabricated by RF-sputtering on MgO (100) substrate. Prior to the deposition of CeO$_2$ films, the high temperature treatment was carried out to the MgO substrate. After $ex$-$situ$ annealing (1000°C, 5 h) of CeO$_2$ film, we obtained cube-on-cube oriented CeO$_2$ film, implying CeO$_2$[100] // MgO [100] growth. From SEM surface morphology, grain size becomes larger after $ex$-$situ$ annealing. This result suggests that CeO$_2$ gains grow by recrystallization.
Second, we tried to optimize the Gd$_2$O$_3$ additions in GdBCO films on CeO$_2$-buffered MgO (100) substrate. The Gd$_2$O$_3$-doped GdBCO films with Gd$_2$O$_3$ contents up to 10 mol% were successfully fabricated by PLD. Compared with undoped GdBCO film, 2 mol% Gd$_2$O$_3$-doped GdBCO film shows significantly improved $J_c$ ($B$) and $F_{p,max}$ at 65 and 77 K, implying that Gd$_2$O$_3$ doping is effective for improving the pinning properties of GdBCO films. The optimum Gd$_2$O$_3$ content for GdBCO films by PLD is 2 mol% in this study. From angular dependence $J_c$, we could obtain nearly isotropic $J_c$ enhancement. The $J_{c,min}$ values of 2 mol% Gd$_2$O$_3$-doped GdBCO film with 0.96 MA/cm$^2$ at $\theta = 135^\circ$ for 1 T at 77 K which is twice larger than that of undoped GdBCO film with 0.55 MA/cm$^2$. From the cross-sectional TEM analysis results, it is obvious that the Gd$_2$O$_3$ nanoparticles with the diameter of $\sim$10-20 nm, which are grown roughly parallel to the $ab$-axis of the GdBCO film, are responsible for such a significant in-field $J_c$ improvement.

Third, we investigated the effect of post-annealing on the pinning properties of Gd$_2$O$_3$-doped GdBCO film. The BaCuO$_2$ phase was detected as increasing temperature and $P$O$_2$, which is correspond to out-growth phases in surface. The $T_{c,zero}$ values of GdBCO films annealed at 800 °C in the $P$O$_2$ of 10 mTorr are increased up to $\sim$91.4 K. Compared with non-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO film, the angular dependence $J_c$ of GdBCO film annealed at 800°C in 10 mTorr are slightly improved along the direction parallel to the $c$-axis, indicates that it has $c$-axis correlated pinning centers. From TEM analysis, some defects along the $c$-axis of GdBCO are observed in the post-annealed sample. It suggested that flux pinning along $c$-axis ($B//c$) in the post-annealed sample might be improved by the stacking faults.
filed up along the $c$-axis of GdBCO matrix.
References


Table 3.1. Typical characteristics of the undoped and Gd$_2$O$_3$-doped GdBCO films.

<table>
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<tr>
<th>Gd$_2$O$_3$ content (vol %)</th>
<th>In-plane texture $\Delta \phi$ (°)</th>
<th>Out-of-plane texture $\Delta \theta$ (°)</th>
<th>$T_{c,ave}$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>Magnetic $J_{c}'$ at 77 K (MA/cm$^2$)</th>
<th>Magnetic $J_{c}'$ at 65 K (MA/cm$^2$)</th>
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<td>(- 1 T)</td>
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<td>2</td>
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<td>(- 2.4 T)</td>
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Table 3.2. The $T_{c\text{,zero}}$ and $\Delta T$ values of 2 mol% Gd$_2$O$_3$-doped GdBCO films by various temperatures and $PO_2$.

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<th>$\Delta T$ (K)</th>
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<td>-</td>
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<td>800°C, 100mTorr</td>
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<td>825°C, 30mTorr</td>
<td>90.0</td>
<td>1.7</td>
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<tr>
<td>800°C, 30mTorr</td>
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<td>2.1</td>
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<td>750°C, 30mTorr</td>
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<td>750°C, 3mTorr</td>
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Fig. 3.1. The schematic phase diagram of GdBCO and representing of post-annealing conditions.
Fig. 3.2 The schematic of reel-to-reel furnace used for post-annealing.
Fig. 3.3. XRD $\theta$-2$\theta$ patterns of the CeO$_2$ buffer layers deposited on MgO (100) substrate. Comparisons of CeO$_2$ layer on (a) before annealed and after \textit{in-situ} annealed MgO and (b) \textit{in-situ} annealed and after \textit{ex-situ} annealing of CeO$_2$ film.
Fig. 3.4. The $\phi$–scans and $\omega$-scans of CeO$_2$ buffer layers on (a) *in-situ* annealed MgO and (b) after *ex-situ* annealed MgO.
Fig. 3.5. SEM surface morphologies of (a) CeO$_2$ film on \textit{ex-situ}+\textit{in-situ} annealed MgO (100) substrate and (b) after oxygen annealing of sample (a).
Fig. 3.6. XRD $\theta$-2$\theta$ patterns of 0, 2, 4, 6, and 10 mol\% Gd$_2$O$_3$-doped GdBCO films deposited on CeO$_2$-buffered MgO (100) substrate.
Fig. 3.7. The $\phi$-scans and $\omega$-scan of the undoped and 2-10 mol% Gd$_2$O$_3$-doped GdBCO films.
Fig. 3.8. The $T_{c,\text{zero}}$ and $\Delta T$ values of GdBCO films with Gd$_2$O$_3$ doping contents.
Fig. 3.9. Surface morphologies of (a) undoped, (b) 2 mol%, (c) 4 mol%, (d) 6 mol%, and (e) 10 mol% Gd$_2$O$_3$-doped GdBCO films deposited on CeO$_2$-buffered MgO (100) substrate.
Fig. 3.10. $J_c$–$B$ characteristic of undoped and 2-10 mol% Gd$_2$O$_3$-doped GdBCO films at (a) 77 and (b) 65 K for $B//c$. 
Fig. 3.11. The pinning force density \( (F_p = J_c \times B) \) values at 77 and 65 K for \( B//c \) as a function of the magnetic field for undoped and 2-10 mol\% Gd\(_2\)O\(_3\)-doped GdBCO films.
Fig. 3.12. Field-orientation dependence of the transport $J_c$ values for undoped and 2 mol% Gd$_2$O$_3$-doped GdBCO samples measured at 77 K, 1 T.
Fig. 3.13. Cross-sectional TEM image of undoped GdBCO film (~ 500 nm thickness). (a) Low magnification image and (b) SAD patterns of each area in (1)-(3).
Fig. 3.14. (a) Low magnification TEM image and (b) HR-TEM image of 2 mol% Gd$_2$O$_3$-doped GdBCO film.
Fig. 3.15. XRD $\theta$-2$\theta$ patterns of post-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO films in various temperatures and $PO_2$. 
Fig. 3.16. SEM surface morphologies of post-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO films by various temperatures and $P_{O_2}$. 
Fig. 3.17. The $\rho$-$T$ curves of the 2 mol% Gd$_2$O$_3$-doped GdBCO film and annealed 2 mol% Gd$_2$O$_3$-doped GdBCO in various temperature and $PO_2$. 
Fig. 3.18. (a) Field-orientation dependence of the transport $J_c$ values and (b) normalized $J_c$ values for 2 mol% Gd$_2$O$_3$-doped GdBCO film and post-annealed film.
Fig. 3.19. Cross-sectional TEM image of GdBCO film annealed 800°C in 10mTorr. (a) Low magnification image, (b) HR-TEM image, and (c) FFT patterns of (1) and (3) in (b).
Chapter 4. Comparison of pinning properties between \( \text{REBCO} \) films prepared by PLD, MOD, MOCVD, and RCE-DR processes

4.1. Introduction

To improve the \( J_c \) properties of HTS films in high magnetic, the introduction of pinning centers to superconducting films was attempted in many research groups [1-9]. The control of the structure of pinning centers, such as shape, density or distribution depends on deposition method. As mentioned before in chapter 1, there are three kinds of APCs. 1D-APCs are line like defects such as a dislocation or a columnar defect. 2D-APCs are plane like defects such as a grain boundary and an anti-phase boundary. 3D-APCs are fine particle like defects such as an impurity nanoparticle and a composition fluctuation in a nanoscale region. In the case of PLD process, nanorods such as \( \text{BMO}_3 \) and nanoparticles such as \( \text{Y}_2\text{O}_3 \) was found in the superconducting matrix. The length or dimension and the density could easily be controlled by using a modified target in PLD. On the other hands, in the case of MOD and RCE-DR, only nanoparticles was found in the superconducting matrix.

Up to now, we also tried to fabricate \( \text{REBCO} \) films prepared by the MOD, PLD, and RCE-DR process for improvement pinning properties, which described above chapter 2 and 3. The flux pinning properties of
REBCO films depend on various deposition method. To fully understand flux pinning mechanism, discussion of comparisons with the microstructure and pinning properties is needed. In this study, we discuss comparisons of flux pinning properties and microstructures between REBCO films prepared by the MOD, PLD, and RCE-DR process.

4.2. Results and discussion

4.2.1. Comparison of exponent $\alpha$ ($J_c \propto H^\alpha$)

Fig. 4.1 shows typical log-log plot of $J_c$-$H$ curve [10]. This log-log plot clearly reveals the important aspects of field dependence. First is the low-field plateau region. This region exhibits that the $J_c$ remains relatively constant, where the field independence corresponds to a single-vortex pinning regime, since the pinning energy is much larger than the vortex-vortex interaction. As $H$ increases, vortex-vortex interactions increase and $J_c$ decreases, which is power law region ($J_c \propto H^\alpha$). Therefore, we could obtain $\alpha$ from power law region. The exponent $\alpha$ value suggests several pinning mechanisms, which are dependent on materials and processing parameters [11].

We summarized exponent $\alpha$ value of REBCO films fabricated by various deposition method such as PLD, MOD, MOCVD, and RCE-DR in Table 4.1 and Fig. 4.2. The average exponent $\alpha$ values for undoped REBCO fabricated by PLD, MOD, MOCVD, and RCE-DR are ~ 0.5, 0.6, 0.5 and 1.03, respectively. The exponent $\alpha$ values of RCE-DR processed GdBCO film [31]
is higher than PLD-, MOD-, and MOCVD-REBCO films [12-30], implying that flux pinning of GdBCO films by RCE-DR is less effective compared with that of REBCO films by PLD, MOD, and MOCVD.

4.2.2. Comparison of maximum pinning force density ($F_{p,\text{max}}$)

Applying an external current density $J$ to the vortex system, the flux lines start to move under the Lorentz force ($F_L = J \times B$) as described in chapter 1.3. If pinning force ($F_p$) is larger than $F_L$, there is no flux motion. However, the flux will move if $F_p$ is smaller than the $F_L$. When the superconductor is in the state in which the $F_L$ is equal to the $F_p$, that is, $F_L = F_p$, then the flux does not move. This state is known as the critical state called $J_c$. Therefore, we could obtain that $F_p$ evaluated by the relation, $F_p = J_c \times B$.

We also summarized $F_{p,\text{max}}$ of REBCO films fabricated by various deposition method such as PLD, MOD, MOCVD, and RCE-DR in Table 4.2 and Fig. 4.3. As can be seen in Fig. 4.3, $F_{p,\text{max}}$ of REBCO films by PLD is much higher than MOD-, MOCVD-, RCE-DR and REBCO films. Recently, Feldmann et al. [34] have reported the highest $F_{p,\text{max}}$ values of 32.3 GN/m$^3$ near 2.5 T at 75.5 K and 122 GN/m$^3$ near 5 T at 65 K, for YBCO films with Ba$_2$YNbO$_6$ nanorods, implying that flux pinning properties of REBCO films by PLD is much effective compared with that of REBCO films by MOD, MOCVD, RCE-DR.

4.2.3. Comparison of minimum $J_c$ ($J_{c,\text{min}}$)
The minimum \( J_c(J_{c,\text{min}}) \) value was extracted from angular dependence of \( J_c \), which is located at an intermediate angle between 0° \((B//c)\) and 90° \((B//ab)\). The \( J_{c,\text{min}} \) value is important for application.

We summarized \( J_{c,\text{min}} \) value of \( REBCO \) films fabricated by various deposition method such as PLD, MOD, MOCVD, and RCE-DR in Table 4.3 and Fig. 4.4. The \( J_{c,\text{min}} \) values of 2 mol % Gd\(_2\)O\(_3\)-doped GdBCO film by PLD is 0.96 MA/cm\(^2\) at 77 K in 1 T, which is higher than other \( REBCO \) films by PLD [2, 15, 18, 19, 23, 33, 34, 38]. The highest value is \(~2.5\) MA/cm\(^2\) at 77 K in 1 T for MOD-processed YBCO+BZO film up to now [9]. Although GdBCO films by RCE-DR is less effective in high magnetic fields as mentioned above, the \( J_{c,\text{min}} \) values of GdBCO films by RCE-DR [31] is comparable with other \( REBCO \) films by PLD, MOD, and MOCVD, implying that flux pinning of GdBCO films by RCE-DR is still effective in low magnetic fields.

**4.2.4. Comparison of angular dependence of \( J_c \) & microstructures**

The \( REBCO \) films fabricated by PLD, MOD, MOCVD, and RCE-DR process contained different type of pinning centers. In the case of PLD and MOCVD, the \( REBCO \) films with BZO [2] or Zr [30] additions revealed that the self-aligned BZO nanorods of 5-10 nm in the diameter were formed in the epitaxial \( REBCO \) films, as represented in Fig. 4.5 (a) and (b). The nanorods are grown parallel to the \( c \)-axis of the films and they act as \( c \)-axis correlated pinning centers. These methods provide a broad \( J_c \) peak near of \( \theta = 0^\circ \) \((B//c)\) in the magnetic field angular dependence of \( J_c(\theta) \), as shown in
Fig. 4.5 (c) and (d). However, there are different type of the second phases in superconducting matrix fabricated by MOD, as shown in Fig. 4.6 (a). High-density of BZO nanoparticles could be introduced in the YBCO films [9] by mixing Zr in the proper quantity with a starting solution including Y, Ba, and Cu. The diameter of BZO nanoparticles is about 15-30 nm. Compared with undoped YBCO, BZO+YBCO film exhibits nearly isotropic $J_c$ enhancement in the wide region. Although the typical formation of BMO nanorods is confirmed in the PLD process, the introduction of nanoparticle is also possible by PLD using the target surface modification. In this method, a small piece of the sintered $Y_2O_3$ material is put on the YBCO target surface [7]. Fig. 4.7 (a) shows cross-sectional TEM image of the $Y_2O_3$ nanoparticles in the YBCO film. The diameter of $Y_2O_3$ nanoparticles is about 10 nm, and they distribute in a high density in the film. Although comparison of angular dependence of $J_c$ between undoped YBCO and $Y_2O_3$+YBCO films does not show in the paper, our previous results of Gd$_2$O$_3$ doped GdBCO film in chapter 3.3.2 show nearly isotropic $J_c$ enhancement in field angular dependence of $J_c$ ($\theta$). In the case of GdBCO film by RCE-DR shown in Fig. 4.8 (a), a lot of Gd$_2$O$_3$ particles with over 100 nm was observed in the GdBCO matrix [31]. From angular dependence $J_c$ in Fig. 4.8 (b), the $J_c(\theta)$ is improved nearly isotropic as decreasing growth temperature. It is difficult to suggest that the Gd$_2$O$_3$ particles are pinning centers, because the average size is much larger than other pinning centers such as BZO, $Y_2O_3$, Gd$_2$O$_3$ by PLD. However, if Gd$_2$O$_3$ particles are refined by modification of processing, improvement of pinning properties will be possible, as mentioned before in chapter 2.3.3.
4.3. Summary

In this study, we summarized comparison of flux pinning properties and microstructures for REBCO films by PLD, MOD, MOCVD, and RCE-DR. The comparison between REBCO films with different materials, processing parameters, substrate, and thickness is somewhat misleading. As a result of comparison, the flux pinning properties of REBCO films by PLD exhibit much higher than other deposition method until now. However, since the laser source is very expensive and deposition rate and area is restricted, the fabrication of REBCO film by the PLD process is known to be inappropriate for a commercialization. Although the GdBCO films by the RCE-DR process still exhibit lower flux pinning properties, we proved that enhancement of flux pinning properties will be possible by Gd$_2$O$_3$ refinement and post-annealing process through Gd$_2$O$_3$-doped GdBCO film. Therefore, the GdBCO CCs by RCE-DR should become commercially competitive in the future.
References


Table 4.1. The exponent $\alpha$ value of REBCO film by PLD, MOD, MOCVD, and REC-DR.

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<th>Deposition method</th>
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<td></td>
<td>YBCO+BZO</td>
<td>CeO$_2$ buffered RABiTS tape</td>
<td>0.5</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>GdBCO</td>
<td>STO (100)</td>
<td>0.48</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>GdBCO</td>
<td>CeO$_2$/BAD-MgO templates</td>
<td>0.46</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>YBCO+5 vol% BZO</td>
<td></td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td><strong>MOD</strong></td>
<td>YBCO</td>
<td>CeO$_2$/YSZ/Y$_2$O$_3$/NiW</td>
<td>-</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>Dy–add (0.5Dy/1Dy)</td>
<td></td>
<td>0.8/0.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11-A-YBCO</td>
<td>(Ce, Zr)O$_2$ buffered YSZ single crystals and YSZ stainless steel</td>
<td>0.5</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td>YSZ stainless steel</td>
<td>undefined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>RABiTS tape</td>
<td>0.55–0.65</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Grain size</td>
<td>Size: -at</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11-A-YBCO</td>
<td>LAO (100)</td>
<td>0.6/</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>Ba-poor YBCO/TSnBCO stoichionic YBCO film</td>
<td>CeO$_2$ buffered IBAD-Gd$_2$Zr$_2$O$_7$/Hastelloy</td>
<td>0.62</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+YB$<em>{2}$SnO$</em>{3.5}$</td>
<td></td>
<td>0.6</td>
<td>[29]</td>
</tr>
<tr>
<td><strong>MOCVD</strong></td>
<td>YBCO</td>
<td>LMO/IBAD-MgO templates</td>
<td>0.5</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td>LMO/IBAD-MgO templates</td>
<td>0.35–0.39</td>
<td></td>
</tr>
<tr>
<td><strong>REC-DR</strong></td>
<td>GdBCO</td>
<td>LMO/IBAD-MgO templates</td>
<td>1.02–1.05</td>
<td>[31]</td>
</tr>
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Table 4.2. The $F_{p,\text{max}}$ value of REBCO film by PLD, MOD, MOCVD, and REC-DR.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Materials</th>
<th>substrate</th>
<th>$F_{p,\text{max}}$ (G/N/cm$^2$) at 77 K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PLD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO buffered MgO (100)</td>
<td>5.69 (~2T)</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td>STO (100)</td>
<td>-</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>NdBCO (RABiTS)</td>
<td>RABiTS</td>
<td>-</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>NdBCO+BZO</td>
<td></td>
<td>9.5 (~4T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NdBCO (IBAD-MgO)</td>
<td>LMO/IBAD-MgO templates</td>
<td>4 (~2.5T)</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>NdBCO+BZO</td>
<td></td>
<td>14 (~3T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GdBCO</td>
<td>CeO$_2$ buffered IBAD MgO</td>
<td>2.7 (~1.4T)</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>GdBCO+BSO (5vol%)</td>
<td></td>
<td>6.5 (~3.2T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ErBCO</td>
<td>STO (100)</td>
<td>1.2 (~2T)</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>ErBCO+BZO (3.5vol%)</td>
<td></td>
<td>4 (~2.5T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>6.5 (~2T)</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BSO (4vol%)</td>
<td></td>
<td>28.3 (~3T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (4vol%)</td>
<td></td>
<td>16.3 (~4T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>CeO$_2$ buffered STO or YSZ</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>YBCO+Ba$_2$Yb$_2$O$_3$</td>
<td></td>
<td>32.3 (~2.5T)</td>
<td></td>
</tr>
<tr>
<td><strong>MOD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TFA-YBCO</td>
<td>STO (100)</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td></td>
<td>21 (~2T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ba-poor YBCO</td>
<td></td>
<td>3.2 (~1.5T)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Ba-poor YSmBCO</td>
<td></td>
<td>4 (~2T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>stoichiometric YBCO film</td>
<td></td>
<td>2.5 (~1T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>0.76 (~1T)</td>
<td>[29, 35]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BSO (10mol%)</td>
<td></td>
<td>3 (~0.7T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (10mol%)</td>
<td></td>
<td>5 (~0.5T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TFA-YBCO</td>
<td>CeO$_2$ buffered YSZ/RABiTS tape</td>
<td>3 (~1T)</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BSO</td>
<td></td>
<td>5 (~1.5T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ba-poor YSmBCO+BZO</td>
<td>CeO$_2$/IBAD-GZO/Hasstelloy</td>
<td>6.74 (~2T)</td>
<td>[37]</td>
</tr>
<tr>
<td><strong>MOCVD</strong></td>
<td>YBCO</td>
<td>LMO/IBAD-MgO templates</td>
<td>-</td>
<td>[30]</td>
</tr>
<tr>
<td><strong>REC-DR</strong></td>
<td>GdBCO</td>
<td>LMO/IBAD-MgO templates</td>
<td>2.8 (~0.4T)</td>
<td>[31]</td>
</tr>
</tbody>
</table>
Table 4.3. The $J_{c, \text{min}}$ value of REBCO film by PLD, MOD, MOCVD, and REC-DR.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Materials</th>
<th>substrate</th>
<th>$J_{c, \text{min}}$ (MA/cm$^2$) at 77 K in 1 T</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PLD</strong></td>
<td>YBCO</td>
<td>CeO$_2$/YSZ/Y$_2$O$_3$/Ni-5 at.%W</td>
<td>~0.18</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (2 vol%)</td>
<td></td>
<td>~0.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>-</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>NdBCO (RABiTS)</td>
<td></td>
<td>~0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NdBCO+BZO</td>
<td>RABiTS</td>
<td>~0.24</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>NdBCO (IBAD-MgO)</td>
<td>LMO/IBAD-MgO templates</td>
<td>~0.15</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>NdBCO+BZO</td>
<td>CeO$_2$ buffered IBAD MgO</td>
<td>~0.39</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>~0.5</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (4wt%)</td>
<td></td>
<td>~0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (4wt%)</td>
<td></td>
<td>~0.15</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>CeO$_2$ buffered STO or YSZ</td>
<td>~0.85</td>
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</tr>
<tr>
<td></td>
<td>YBCO+Ba$_2$YNbO$_8$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SmBCO</td>
<td>MgO (100)</td>
<td>0.15</td>
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</tr>
<tr>
<td></td>
<td>SmBCO+BZO (2 vol%)</td>
<td></td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td><strong>MOD</strong></td>
<td>TFA-YBCO</td>
<td>STO (100)</td>
<td>~0.4</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td></td>
<td>~2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO</td>
<td>RABiTS</td>
<td>~0.45</td>
<td>[39]</td>
</tr>
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<td></td>
<td>Y(Dy)$_2$BCO</td>
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<td>~0.75</td>
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</tr>
<tr>
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<td>YBCO/Y(Dy)$_2$BCO</td>
<td></td>
<td>~0.6</td>
<td></td>
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<tr>
<td></td>
<td>YBCO</td>
<td>STO (100)</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (10mol%)</td>
<td></td>
<td>0.084</td>
<td>[29, 35]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (10mol%)</td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TFA-YBCO</td>
<td>CeO$_2$ buffered YSZ/ RABiTS tape</td>
<td>~0.3</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO</td>
<td></td>
<td>~0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ba-poor YSmBCO+BZO</td>
<td></td>
<td>~0.52</td>
<td>[37]</td>
</tr>
<tr>
<td><strong>MOCVD</strong></td>
<td>YBCO</td>
<td>CeO$_2$/ IBAD-GZO/Hastelloy</td>
<td>~0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YBCO+BZO (2.5 mol%)</td>
<td>LMO/IBAD-MgO templates</td>
<td>~0.17</td>
<td>[30]</td>
</tr>
<tr>
<td><strong>RCE-DR</strong></td>
<td>GdBBCO (840–880°C)</td>
<td>LMO/IBAD-MgO templates</td>
<td>0.6, 0.36, 0.2</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Post-annealing</td>
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<td>0.5</td>
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</tr>
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</table>
Fig 4.1. The typical log-log plot of $J_c$-$H$ curve [10].
Fig. 4.2. Re-plot of the exponent $\alpha$ value in table 4.1.
Fig. 4.3. Re-plot of $F_{p,max}$ value in table 4.2.
Fig. 4.4. Re-plot of $J_{c, \text{min}}$ value in table 4.3.
Fig. 4.5. Cross-sectional TEM images of (a) BZO-doped YBCO film and (b) YBCO film with Zr additions. Angular dependence of $J_c$ at 77 K, 1 T for (c) an undoped YBCO film and 2 vol% BZO-doped YBCO film on RABiTS and (d) 5 mol% Zr-added MOCVD-YBCO films at various deposition rates. ((a) and (c) is fabricated by PLD [2], and (b) and (d) is fabricated by MOCVD [30]).
Fig. 4.6. (a) Cross-sectional TEM images and (b) angular dependence of $J_c$ for BZO+YBCO film by MOD [9].
Fig. 4.7. (a) Cross-sectional TEM images and (b) angular dependence of $J_c$ for $\text{Y}_2\text{O}_3+\text{YBCO}$ film by PLD [6].
Fig. 4.8. (a) Cross-sectional TEM images and (b) angular dependence of $J_c$ for GdBCO film by RCE-DR [31].
Chapter 5. Summary

In this thesis, we characterized the flux pinning properties of $REBCO$ superconducting films by the PLD, MOD, and RCE-DR processes. We also successfully grown pure and Gd$_2$O$_3$-added GdBCO films on CeO$_2$-buffered MgO (100) substrate by PLD for systemic study. On the basis of the results from systemic study, 2 mol % Gd$_2$O$_3$-doped GdBCO films by PLD were post-annealed in various temperatures and $PO_2$ for enhancement of their pinning properties. Finally, we summarized comparison of pinning properties and microstructures of $REBCO$ films prepared by various methods. The major results are as the following.

First, our group have successfully fabricated Sn-doped $REBCO$ films by MOD and PLD. Also, SuNAM Co. have successfully developed long-length high-$J_c$ GdBCO CCs on LMO-buffered IBAD MgO template by RCE-DR. In this study, we fully investigated the characteristics of the flux pinning properties for $REBCO$ films deposited by the PLD, MOD, and RCE-DR process. In the case of Sn-doped GdBCO films by PLD, 5 vol% Sn-doped GdBCO film exhibited the $F_{p,max}$ values of 32.5 GN/m$^3$ near 4 T at 65 K and 6.5 GN/m$^3$ near 3.2 T at 77 K for $B//c$ ($\theta = 180^\circ$) and also the highest $J_{c,min}$ of 0.39 MA/cm$^2$ at 77 K in 1 T and 0.68 MA/cm$^2$ at 65 K in 3 T for $\theta = 120^\circ$, representing that 5 vol% is the optimum content. Observation of Sn-doped GdBCO films by TEM revealed that the effective flux pinning of Sn-doped GdBCO film was attributed to the BSO nanorods of ~ 10 nm diameters roughly aligned along the $c$-axis of the GdBCO matrix. In the case of Sn-
doped YBCO films MOD process, the Sn-doped YBCO film on STO (100) substrate exhibited significantly enhanced $J_c$ and $F_{p,max}$ in magnetic fields up to 5 T at 65 and 77 K for $H//c$, indicating that the Sn-doped YBCO film possesses more effective flux pinning centers. Larger $J_c$ (77 K, 1 T) values of Sn-doped YBCO film are observed over a wide field-orientation angle ($\theta$) except the field-orientations close to the $ab$-plane of YBCO ($85^\circ < \theta < 95^\circ$). Smaller $J_c$ values for $85^\circ < \theta < 95^\circ$ in Sn-doped YBCO film are most probably caused by a reduced intrinsic pinning effect along the $ab$-plane due to high density Sn-containing nanoparticles trapped in the YBCO matrix. The effective pinning centers in Sn-doped YBCO film are attributable to Sn-containing nanoparticles trapped in the YBCO matrix which could be first identified as the YBSO phase by TEM. We also investigated high-$J_c$ GdBCO CCs by the RCE-DR process in the oxygen pressure of 150 mTorr with three different growth temperatures of 840, 860, and 880°C. With decreasing the growth temperature, the $J_c$ and $F_{p,max}$ at 65 and 77 K were improved due to enhanced pinning properties, which are attributable to refined Gd$_2$O$_3$ particles trapped in the GdBCO matrix. Analyses by TEM revealed that the average particle size of Gd$_2$O$_3$ for 840°C sample is much smaller than that of 860 and 880°C samples. While the formation of (103)-oriented GdBCO grains can be avoided, biaxial textures can be improved with increasing the growth temperature. While (103) misoriented GdBCO grains existed in the film grown at 840°C, it exhibited higher $J_c$ values compared with other films. This result suggested that the increase in $J_c$ due to pinning by refined Gd$_2$O$_3$ particles surpasses the degradation of $J_c$ by (103)-oriented grains present at the film surface.
Second, the pinning properties for the Gd$_2$O$_3$ additions in GdBCO films on CeO$_2$-buffered MgO (100) substrate were systematically studied. The 2 mol% Gd$_2$O$_3$-doped GdBCO film exhibited the highest self-field $J_c$ value of 2.88 MA/cm$^2$ at 77 K and 4.72 MA/cm$^2$ at 65 K, and also shows the $F_{p,max}$ values of 37.3 GN/m$^3$ near 2.8 T at 65 K and 11.3 GN/m$^3$ near 1.8 T at 77 K, evidencing that 2 mol% is the optimum Gd$_2$O$_3$ content. According to our preliminary study on GdBCO CCs by RCE-DR, the flux pinning properties of GdBCO CCs were improved by post-annealing. Therefore, we also tried to enhance flux pinning properties of Gd$_2$O$_3$-doped GdBCO film by post-annealing process in various temperature and PO$_2$. The GdBCO films annealed at 800°C in the PO$_2$ of 10 mTorr exhibited enhancement of $T_{c,zero}$ values with ~91.4 K and $J_{c,min}$ with 0.98 MA/cm$^2$ at 77 K in 1 T ($\theta = 60^\circ$). The angular dependence of $J_c$ of GdBCO film annealed at 800°C in 10 mTorr also showed slightly improvement of $J_c$ along the $c$-axis ($B//c$) compared with non-annealed 2 mol% Gd$_2$O$_3$-doped GdBCO film, representing that it has $c$-axis correlated pinning centers. From TEM analysis, some defects along the $c$-axis of GdBCO matrix were observed in the post-annealed sample. It suggested that flux pinning along $c$-axis in the post-annealed sample might be improved by the stacking faults filed up along the $c$-axis of GdBCO matrix.

Third, we summarized significant amount of research in pinning properties and microstructures for REBCO films prepared by PLD, MOD, MOCVD, and RCE-DR. There are many reports of REBCO films by introduction of second phases such as BMO, $RE_2$O$_3$, and double perovskite Ba$_2$YNbO$_6$. Although superconductor/insulator interfaces have been widely studied, the fundamental mechanism of flux pinning centers have not been confirmed yet precisely.
Nevertheless, the flux pinning properties of REBCO films by PLD still exhibit much higher than other deposition method so far. Although the GdBCO films by the RCE-DR process still exhibit lower flux pinning properties, we suggest that improvement of pinning properties will be feasible by Gd$_2$O$_3$ refinement and post-annealing process through Gd$_2$O$_3$-doped GdBCO film.
Publications

Papers (SCI journals)


2. Soon-Mi Choi, Won-Jae Oh, Jung-Woo Lee, and Sang-Im Yoo, “Improvement of flux pinning properties of GdBa$_2$Cu$_3$O$_{7-δ}$ films with 2 mol% Gd$_2$O$_3$ additions by post-annealing process”, to be submitted.


Contributed papers (SCI journals)


7. Geo-Myung Shin, Jung-Woo Lee, Soon-Mi Choi, Seung-Hyun Moon, and Sang-Im Yoo, “The improved critical currents of MOD-processed YBCO thick films with BaMO$_3$ ($M$: Ce, Zr) or YBa$_2$SnO$_{5.5}$ particles”, IEEE Transactions on Applied Superconductivity, (accepted)


9. Hyo-Jin Kim, Jae-Hyung Yoo, Soon-Mi Choi, and Sang-Im Yoo, “Magneto-transport properties of La$_{0.7}$Sr$_{0.3}$Mn$_{1+d}$O$_3$-manganese oxide composites prepared by liquid phase sintering”, Journal of Magnetics, (accepted)


15. Seunghoon Nam, Sungsoo Kim, Sungun Wi, Hongsik Choi, Sujin Byun, Soon-Mi Choi, Sang-Im Yoo, Kyu Tae Lee, and Byungwoo Park, “The role of carbon incorporation in SnO$_2$ nanoparticles for Li rechargeable batteries”, *Journal of Power Sources*, vol. 211 (2012) 154


17. Sung-Yun Lee, Soon-Mi Choi, Mi-Young Kim, Sang-Im Yoo, Ji Hye Lee, William Jo, Young-Hwan Kim, and Kyoung Jin Choi,

**Papers (proceeding and domestic journals)**


**Patents**

1. 유상임, 이정우, 최순미, 문승환, 이현주, 이재훈, “초전도체 및 초전도체 형성방법”, 제 10-1456152호, 2014년 10월 23일
초 록

고온초전도체 선재 (HTS CCs)의 응용을 위해서는 높은 자기장 하에서 높은 임계전류밀도($J_c$)를 가지는 것이 바람직하다. 높은 자기장 하에서 고온초전도 선재의 전류 용량을 향상시키기 위해 나노 크기의 입자들을 고온초전도 모체내에 포함시키는 것이 요구된다. 본 연구에서는 펄스레이저 증착법(pulsed laser deposition: PLD), 유기금속증착법(metal-organic deposition: MOD), 그리고 반응성 동시증발 증착(reactive co-evaporation by deposition & reaction: RCE-DR)에 의해 증착한 $REBa_2Cu_3O_{7-δ}$ ($REBCO, RE$는 Y 그리고 Gd) 박막의 자속 고정 특성(flux pinning property)을 분석하였다. 또한 조직적인 연구를 위해 $CeO_2$-완충층이 증착되어 있는 MgO (100) 단결정 기판 위에 PLD법을 이용하여 Gd$_2$O$_3$를 첨가한 GdBCO박막을 성공적으로 제조하였다. 이러한 조직적인 연구를 통한 결과를 도대로 피닝 특성을 향상시키기 위해 여러가지 온도와 산소 분압 ($PO_2$)에서 Gd$_2$O$_3$가 첨가된 GdBCO박막을 후열처리공정을 진행하였다. 마지막으로 여러가지 방법으로 증착된 $REBCO$ 박막의 피닝특성과 미세구조를 비교하여 요약하였다. 각 세부 내용에 대한 주요 결과들은 다음과 같다.

첫째, 우리 그룹에서 MOD 그리고 PLD법을 이용하여 Sn을 첨가한 $REBCO$ 박막을 성공적으로 제조하였다. 또한, 서남에서 LaMnO$_3$ (LMO)완충층이 증착되어 있는 IBAD MgO 기판 위에 높은 $J_c$ 를 가지는 GdBCO 장선재를 RCE-DR법으로 불리는 높은 처리율을 가지는 새로운 방법을 이용하여 성공적으로 개발하였다.
하지만 이렇게 제조된 REBCO 박막의 자속 고정 특성은 아직 충분히 규명되지 않았다. 본 연구에서는 PLD, MOD, 그리고 RCE-DR법으로 제조된 REBCO 박막의 자속 고정 특성을 충분히 규명하고자 하였다. 결과적으로, CeO₂-완충층이 증착되어 있는 IBAD MgO 기판 위에 PLD법을 이용하여 증착한 5 vol% Sn이 첨가된 GdBCO 박막은 가장 높은 최대 자속 고정 힘 밀도 (maximum pinning force density, $F_{p,max}$) 와 $J_c$를 나타내었다. 이는 5 vol% Sn 이 최적화된 양이라는 증거이기도 하다. MOD 공정의 경우, SrTiO₃(STO) (100) 단결정 기판 위에 Sn이 첨가된 YBCO 박막이 순수한 YBCO 박막보다 더 향상된 $J_c$와 $F_{p,max}$를 나타내었다. 고분해능 투과전자현미경(high resolution-transmission electron microscope: HR-TEM) 이미지를 통해 고속푸리에변환 (fast Fourier transform: FFT) 패턴과 주사형 투과전자 현미경-에너지 분산 X선 분광분석기 (scanning transmission electron microscope-energy dispersive X-ray spectroscopy: STEM-EDS)를 통하여, Sn이 포함된 나노입자들이 BaSnO₃가 아닌 YBa₂SnO₅.₅ 라는 것을 처음으로 규명하고 보고하였다. 또한 LMO 완충층이 증착되어 있는 IBAD MgO 기판 위에 RCE-DR법으로 증착한 GdBCO 전체의 미세구조와 피닝 특성을 성장 온도에 따른 효과를 조사하였다. 840, 860, 그리고 880°C의 각기 다른 세 가지 온도를 사용하였다. 성장 온도가 낮아질수록 65 그리고 77 K에서 $J_c$가 향상되는데 이는 GdBCO 모재 내에 포함된 Gd₂O₃ 입자의 미립화에 기인한다. 투과전자현미경(transmission electron microscopy: TEM) 분석을 통하여 840°C 시편의 Gd₂O₃ 평균 입자는 126.5 nm로 860°C 시편에서의 171.4 nm와 880도 시편에서의 217.8 nm보다 더 작다는 것을
확인할 수 있었다. 홍미롭게도, 비록 840°C 시편에서 이축배향된 GdBCO 결정립과 함께 (103) 배향성을 가지는 GdBCO 결정립이 존재하지라도 이축배향된 결정립만 존재하는 다른 선재와 비교하여 자장하에 높은 $J_c$를 나타내는데 이는 미세화된 Gd$_2$O$_3$ 입자에 의한 피닝이 표면에서만 존재하는 (103) 배향된 결정립에 의한 $J_c$ 감소를 뚫어 넘기 때문이다.

둘째, CeO$_2$-완충층이 증착된 MgO (100) 단결정 기판 위에 Gd$_2$O$_3$를 첨가한 GdBCO박막의 최적화 실험을 진행하였다. GdBCO에 대한 다양한 $x$ mol% ($x = 0, 2, 4, 6$, 그리고 10)인 Gd$_2$O$_3$가 첨가된 GdBCO 박막을 PLD법을 이용하여 300 mTorr의 PO$_2$ 하에 800°C 에서 준비하였다. 제조된 모든 박막들 중에 2 mol% Gd$_2$O$_3$를 첨가한 GdBCO박막이 77 K에서 2.88 MA/cm$^2$, 그리고 65 K에서 4.72 MA/cm$^2$의 가장 높은 $J_c$ 값을 나타내었다. 또한 65 K, 2.8 T 근처에서 37.3 GN/m$^3$, 그리고 77 K, 1.8 T 근처에서 11.3 GN/m$^3$ 의 $F_{p,max}$를 나타내었는데 이는 2 mol%가 최적화된 Gd$_2$O$_3$양임을 증명한다. 다음으로 자속 고정 특성을 향상시키기 위하여 Gd$_2$O$_3$가 첨가된 GdBCO박막의 후열처리 공정(post-annealing process)을 진행하였다. RCE-DR법으로 제조된 GdBCO 선재에 대한 우리의 선행 연구 결과에 따르면, 후열처리 공정을 통해 GdBCO 선재의 자속 고정 특성이 향상되었다. PLD법에 의해 GdBCO 박막 내부에 Gd$_2$O$_3$ 평균 입자 사이즈를 미세화시킬 수 있다면, 단단한 기판 위에 증착된 Gd2O3 나노입자들이 포획된 GdBCO박막의 후열처리 공정의 효과를 더 크게 기대할 수 있을 것이라 예상되었다. Gd$_2$O$_3$가 첨가된 GdBCO 박막의 피닝 특성의 후열처리 효과를 규명하기 위해 다양한 온도와 PO$_2$에서 후열처리 공정을
진행하였다. 10 mTorr의 PO₂ 하에 800°C 에서 열처리를 한 GdBCO 박막의 임계 온도 (T_{c, zero})가 ~91.4 K 으로 상승하였다. 10 mTorr의 PO₂ 하에 800°C 에서 열처리를 한 GdBCO 박막의 자장하 각도 의존성 Jc 결과 후열처리를 하지 않은 2 mol% Gd₂O₃를 첨가한 GdBCO 박막과 비교하여 c-축에 평행하게 자장을 걸어주었을 때 조금 상승하였다. 이는 c-축으로 연관된 자속 고정점(pinning center)이 있다는 것이다. TEM 분석 결과 후열처리를 진행한 GdBCO 박막의 경우 c-축을 따라 약간의 결함들이 관찰되었다. 이것은 후열처리를 한 시편에서 c-축을 따라 자속 고정 특성이 GdBCO 박막의 c-축을 따라 겹쳐진 GdBa₂Cu₄O₈ (Gd124) 적층 결합에 의해 향상됨을 제안할 수 있었다.

마지막으로, PLD, MOD, 금속유기화학기상증착법 (metal-organic chemical vapor deposition: MOCVD), 그리고 RCE-DR법으로 제조된 REBCO박막의 자속 고정 특성 및 미세구조를 비교 논의하였다. REBCO 박막들의 α 지수 값, F_{p,max}, 최저 Jc(J_{c, min}), 자장하 각도 의존성 Jc, 그리고 자속고정점의 형태와 크기에 대해 비교하였다. 그 결과, 현재까지 PLD법에 의해 제조된 REBCO박막의 자속 고정 특성이 다른 방법에 의해 증착된 박막보다 더 우수하였다. 비록 RCE-DR법에 의해 제조된 GdBCO 선재의 경우 높은 자장하에서 자속 고정 특성이 낮지만, 앞선 연구 결과를 토대로 GdBCO 모체 내의 Gd₂O₃ 입자 사이즈의 미세화와 후열처리 공정을 통하여 더 높은 자속고정 특성을 이루어 낼 수 있을 것이라 기대한다.

주요어: REBa₂Cu₃O₇₋δ (REBCO, RE는 Y 그리고 Gd) 박막, Gd₂O₃가 첨가된 GdBCO 박막, 펄스레이저 증착법 (PLD), 후열처리 공정,
임계전류밀도 \((J_c)\), 최대 자속 고정 힘 밀도 \((F_{p,\text{max}})\)

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