A comparative study on the flux pinning properties of Zr-doped YBCO film with those of Sn-doped one prepared by metal-organic deposition

S. M. Choi, G. M. Shin, Y. S. Joo, and S. I. Yoo*

Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIAM), Seoul National University, Seoul, Korea

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Abstract

We investigated the flux pinning properties of both 10 mol% Zr- and Sn-doped YBa2Cu3O7-δ (YBCO) films with the same thickness of ~350 nm for a comparative purpose. The films were prepared on the SrTiO3 (STO) single crystal substrate by the metal-organic deposition (MOD) process. Compared with Sn-doped YBCO film, Zr-doped one exhibited a significant enhancement in the critical current density ($J_c$) and pinning force density ($F_p$). The anisotropic $J_c$ values were obtained from MOD-processed Zr-doped YBCO film. The stronger pinning effect in Zr-doped YBCO film is attributable to smaller BaZrO3 (BZO) nanoparticles (the average size ≈ 28.4 nm) incorporated in Sn-doped YBCO film since smaller nanoparticles can generate more defects acting as effective flux pinning sites due to larger incoherent interfacial area for the same doping concentration.

Keywords: Metal-organic deposition, YBCO film, YBa2SnO5.5 and BaZrO3 nanoparticles, Flux pinning

1. INTRODUCTION

Coated conductors (CCs) based on YBCO or REBCO (REBa2Cu3O7, RE = rare earth elements) superconductors are approaching a commercialization threshold. For practical applications, however, $J_c$ improvement in high magnetic field over all field-orientation angles is still required. The field and field-orientation dependency of $J_c$ are directly dependent upon the types of defects and their densities within the superconducting matrix, and thus higher $J_c$ values are achievable from stronger flux pinning centers. In order to improve the flux pinning property, it is considered to be the most effective approach to incorporate an optimal amount of non-superconducting phases with a dimension similar to the short coherence length ($\xi$~1.5-2 nm) of YBCO into the superconducting YBCO matrix.

As the pinning centers, various non-superconducting phases like Y2O3 [1, 2], perovskite BaMO3 (M: Zr, Ir, Sn, Ti, Nb, and Hf) (BMO) [3-10], cubic rare-earth tantalate RE2TaO7 [11], and cubic-double-perovskite Ba2YTaO6 [12, 13] compounds have been widely incorporated into the YBCO matrix by pulsed laser deposition (PLD). While RE2O3 single oxides are reported to form point-like nanoparticles in the YBCO matrix, other oxide compounds are reported to form nano-structured columnar defects. The columnar defects are known to be very effective particularly for the field applied parallel to the c-axis of the YBCO film ($H//c$). Among all BMO phases, incorporation of BZO columnar defects into the YBCO and REBCO (RE: Nd, Sm, Gd, and Er) films has been most extensively studied [14-18].

On the other hand, many oxides, including RE2O3 (RE: Y, Dy, and Ho) [19-21], perovskite BZO [22-30], BSO [31-35], BaHfO3 [36], cubic-double-perovskite Ba2YTaO6 [37] and YBa2SnO5.5 [38], have also been incorporated into the YBCO and REBCO (RE: Sm, and Gd) matrix by the MOD process. Unlike nano-structured columnar defects in PLD-processed YBCO or REBCO films except RE2O3, all the above oxides formed point-like nanoparticles in MOD-processed YBCO films. These nanoparticles were found to be effective for nearly isotropic $J_c$ enhancement in magnetic field.

As previously mentioned, there are many papers reporting the vortex pinning improvement by various non-superconducting nanoparticles in MOD-processed YBCO films, a comparative study between their flux pinning characteristics is very limited. Within the best of our knowledge, only one paper from Strickland et al. [31] is available at the moment, reporting that 5 mol% Zr-doped YBCO film possesses stronger flux pinning properties compared with 5 mol% Sn-doped YBCO film. As such an effort, in this study, we tried to compare the flux pinning properties of 10 mol% Zr-doped YBCO film with those of 10 mol% Sn-doped one prepared by the MOD process.

* Corresponding author: siyoo@snu.ac.kr
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2. EXPERIMENTAL PROCEDURE

At first, the precursors of fluorine-free Y-acetylacetone, Cu-acetylacetone, and Zr-acetylacetone were weighed and put into the solvent of a propionic acid. Then, the solutions were stirred until precursor materials were completely dissolved, and dried at 80°C to form a dark green gel. This gel was dissolved again in methyl alcohol to produce the precursor solution including Y, Cu, and Zr components. Next, the Ba acetate was dissolved in a trifluoroacetic acid for the preparation of the Ba precursor solution, dried to form the Ba-trifluoroacetate (TFA) gel, and then completely dissolved into methyl alcohol. Finally, the 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% Zr addition. The coating solutions were deposited on STO (100) single crystal substrates by the dip-coating method. Further details on the subsequent processing conditions for the preparation of superconducting films are described in our previous reports [38, 39].

X-ray diffraction (XRD) (Bruker, D8-Advance) was performed for phase and orientation analyses of films. Surface morphology and thickness of samples were observed using a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6330F). An analytical transmission electron microscope (TEM) (JEOL JEM-3000F, FEI Tecnai F20) was employed to examine the cross-sectional microstructure. The critical temperature ($T_c$) was measured by the four-point probe method. The hysteretic magnetization curves were measured with the magnetic field applied parallel to the c-axis of YBCO films in a SQUID magnetometer (Quantum design, MPMS XL-5). The angular dependence of $J_c$ was measured using the PPMS (Quantum design, model-6000) after patterning the micro-bridge for samples. The transport $J_c$ values were evaluated from the current versus voltage curves with the 0.3 $\mu$V/cm criterion. For the measurements of field-orientation dependence of $J_c$, the samples were rotated from 0 to 230° (0° for H//c and 90° for H//ab) at 77 and 65 K in the magnetic fields of 1 and 3 T.

3. RESULTS AND DISCUSSION

Fig. 1. XRD patterns of YBCO films: (a) undoped, (b) Sn-doped, and (c) Zr-doped YBCO films. The XRD data in Fig. 1 (a) and (b) are from ref. [38] for a comparison.

The XRD patterns of all MOD-processed YBCO films are represented in Fig. 1. The major peaks in all XRD patterns correspond to the (00l) reflections of the YBCO phase, indicating that all YBCO films are highly c-axis oriented. Unlike the undoped YBCO film exhibiting only (00l) peaks, Sn- and Zr-doped YBCO films show small extra peaks at 2θ ≈ 30° and 43° due to the second phase, respectively. In accordance with previous reports [22, 28 30, 31], the second phase in Zr-doped YBCO film must be BZO. In the case of Sn-doped YBCO film, however, the second phase is not BaSnO$_3$ but YBa$_2$SnO$_{5.5}$ (YBSO) according to our previous study [38]. Relatively larger BZO (200) and YBSO (004) peaks compared with BZO (110) and YBSO (220) major peaks in their JCPDS cards imply that a portion of these non-superconducting particles might have preferential orientation along their c-axis. The difference between Zr- and Sn-doped YBCO films is that the peak intensity of YBSO (004) is much higher than that of BZO (002) although their doping level is identical.

The in-plane texture analysis results of samples by the XRD phi scan ($\phi$) for YBCO (102) plane, though not presented here, revealed that the $\Delta \phi$ values of Zr- and Sn-doped YBCO films were 1.9 and 1.63, respectively. Compared with undoped YBCO film having $\Delta \phi = 1.39$, the degradation in the in-plane textures of Zr- and Sn-doped samples is ascribed to the incorporation of the second phase particles into the YBCO matrix.

SEM micrographs of YBCO films are shown in Fig. 2. All samples have the film thickness of ~350 nm. One can see that surface morphologies of Zr- and Sn-doped YBCO films are significantly different from that of undoped YBCO film. Unlike undoped YBCO film in Fig. 2 (a), numerous small particles, most probably due to BZO and YBSO nano-sized particles, can be observed on the film surfaces in Fig. 2 (b) and (c), respectively. From Fig. 2 (b) and (c), however, it is difficult to observe an apparent difference between Zr- and Sn-doped YBCO films.

Fig. 2. SEM micrographs showing the surface morphologies of YBCO films: (a) undoped, (b) Zr-doped, and (c) Sn-doped YBCO films. Insets are the cross-sectional images of the films.
Fig. 3 (a) and (b) show the cross-sectional TEM images of undoped and 10 mol% Zr-doped YBCO films, respectively. The cross-sectional TEM images of Sn-doped YBCO film by MOD have already been published in our previous paper [38]. The secondary phase particles of a low density within the undoped YBCO film observed in Fig. 3 (a), which also existed in Zr- and Sn-doped YBCO films, were identified as the Y₂Cu₂O₅ phase [38]. The average particle size of BZO in Fig. 3 (b) was 28.4 nm, which is much smaller than that of YBSO (45.0 nm) [38]. These average particle sizes are considerably larger than the coherence length of YBCO required for the most effective flux pinning. The high-resolution (HR)-TEM image in Fig. 3 (c) clearly shows an epitaxially grown BZO nanoparticle at the interface between STO and YBCO. The fast Fourier transform (FFT) patterns from the nanoparticle and STO shown in the inset strongly support that the nanoparticle of a cubic-structure has a cube-on-cube epitaxial relationship with STO. On the other hand, most of HR-TEM images of nanoparticles were completely surrounded by the YBCO matrix as shown in Fig. 3 (d), representing that their FFT patterns are in coherent with the YBCO matrix. All BZO and YBSO nanoparticles [38] on the STO substrate surface were observed to have the cube-on-cube epitaxial relationship with STO, implying that these nanoparticles have an epitaxial relationship with the YBCO matrix. From this result, it is obvious that relatively larger BZO (002) and YBSO (004) peaks observed in Fig. 1 (b) and (c), respectively, are due to BZO and YBSO nanoparticles epitaxially grown on the STO substrate surface. This result is in good agreement with previous studies from Gutierrez et al. [22] and Puig et al. [23] in that the BZO nanoparticles formed in the MOD-processed YBCO film are mostly random-oriented except a small amount of nanoparticles epitaxially grown on the substrate surface.

Fig. 4 shows the ρ-T curves of Zr- and Sn-doped YBCO films. The ρ-T curve of undoped film is also presented for a comparison. The $T_{c,zero}$ values of the Zr- and Sn-doped YBCO films are 88.1 K with the transition width of 2.1 K and 89.7 K with that of 1.4 K, respectively. It is slightly reduced compared with that of undoped YBCO film which has $T_{c,zero}$ values of 90.1 K with the transition width of 1.2 K. A slight $T_c$ suppression of ~ 4 vol% doping of Zr and Sn has already been reported for REBCO polycrystalline samples [40]. The Zr- and Sn-doped YBCO films [3, 8, 41] by the PLD process, which have self-aligned nano-structured columnar defects, are also reported to exhibit a little more reduced $T_c$ values. For PLD-processed YBCO films, Goyal et al. [42] insisted that a microstrain generated around BZO columnar defects was responsible for the depression in $T_c$. Likewise, we also believe the microstrains generated around BZO and YBSO nanoparticles are responsible for reduced $T_c$ values.

Fig. 5 (a) shows the field dependency of $J_c$ at 65 and 77 K for $H//c$. From Fig. 5 (a), one can see that an overall increase in $J_c(B)$ curves occurs in Zr-doped YBCO film compared with Sn-doped one. The magnetic $J_c$ values were 2.9 and 3.3 MA/cm² for Zr- and Sn-doped YBCO films at 77 K (self-field), respectively. At 65 K, the $J_c$ values of Zr-doped YBCO film are 1.6 and 1.5 times higher than those of Sn-doped YBCO film for 3 T and 5 T, respectively. While self-field $J_c$ retentions of Zr- and Sn-doped YBCO films were ~13% and ~9% in 1 T at 77 K, those of Zr- and Sn-doped YBCO films were ~22% and ~18% in 1 T at 65 K. The greatest fractional enhancement in Zr-doped YBCO film occurs at around 0.1 T. While Strickland et al. [31] reported that $J_c(B)$ curves for 5 mol% Zr- and 5 mol% Sn-doped YBCO films at 77 K were overlapped, our $J_c(B)$ curves for 10 mol% doped films are definitely separated and the separation becomes larger at 65 K, revealing that BZO is more effective than YBSO for flux pinning. Therefore, it is obvious that the flux pinning of BZO nanoparticles is more effective than that of YBSO particles.
Fig. 5 (b) shows a log-log plot of $J_c$ ($H//c$, 77 K) versus applied field. The previous research of our result, the exponent in the power-law relationship $J_c \sim H^\alpha$ is ~0.60 for undoped YBCO [38], which is a typical value reported in the literature [44, 45]. The typical regime of the exponent $\alpha$ does not exist in Sn- and Zr-doped YBCO films. This peculiar behavior has also been reported by Pomar et al. [28] for the MOD-YBCO film with BaZrO$_3$ nanoparticles. The deviation from the power law in Zr- and Sn-doped YBCO film might be due to a change in the vortex pinning characteristics by BZO and YBSO nanoparticles, respectively.

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 $H//c$ are shown in Fig. 6. While Zr-doped YBCO film possesses $F_{p,\text{max}} = 5$ GN/m$^3$ (77 K) at ~0.5 T and $F_{p,\text{max}} = 19$ GN/m$^3$ (65 K) at ~2 T, Sn-doped YBCO film has $F_{p,\text{max}} = 3$ GN/m$^3$ (77 K) at ~0.7 T and $F_{p,\text{max}} = 14.2$ GN/m$^3$ (65 K) at ~2.5 T. It means that Zr-doped YBCO film includes more effective flux pinning centers. Since 4.3 vol% BZO and YBSO nanoparticles have the average particle diameters of 28.4 and 45.0 nm, respectively, and a film thickness of 350 nm, calculated areal densities of nanoparticles are 1250 $\mu$m$^{-2}$ and 450 $\mu$m$^{-2}$ for BZO and YBSO, respectively. If each vortex is pinned by a single nanoparticle, this gives a matching field of 2.5 T and 0.9 T, respectively. However, the measured magnetic field of $F_{p,\text{max}}$ is much lower than calculated values at 77 K, implying that the above assumption is so much simplified.

The field-orientation dependence of $J_c$ for undoped, Zr- and Sn-doped YBCO films are shown in Fig. 7. The Zr- and Sn-doped YBCO films exhibit nearly isotropic $J_c$ enhancement in a wide angular region except the field-orientations close to the $ab$-plane ($H//ab$) of YBCO. In Fig. 7 (a), the anisotropy ratios of $J_{c,\text{min}}/J_{c,\text{max}}$ at 77 K in 1 T for Zr- and Sn-doped YBCO films are 0.39 and 0.23, respectively, which are much higher than undoped YBCO with 0.053. The Zr-doped YBCO film shows higher field-orientation dependence of $J_c$ than Sn-doped YBCO film in Fig. 7 (a), indicating that uniformly dispersed BZO nanoparticles in Zr-doped YBCO film act as more effective flux pinning centers. On the other hand, while Zr-doped YBCO film exhibits a slight suppression in $J_c$ values for $H//ab$ in Fig. 7 (b) compared with undoped YBCO, Sn-doped YBCO film exhibits a significant $J_c$ decrease for $H//ab$ as shown in Fig. 7 (a) and (b), which is considered to be caused by a reduced intrinsic pinning effect along the $ab$ plane of YBCO due to larger YBSO nanoparticles.

To identify the internal microstrain of Zr- and Sn-doped YBCO films, we performed the strain analysis for the XRD data in Fig.1 by using the Williamson-Hall method [46], Williamson-Hall plots for Zr- and Sn-doped YBCO films are shown in Fig. 8. From the slopes of the linear fits, we could obtain the values of $\varepsilon = 0.299 \pm 0.017\%$ for Zr-doped YBCO film and $\varepsilon = 0.276 \pm 0.004\%$ for Sn-doped YBCO film [38], respectively. The microstrain value of Zr-doped YBCO film is relatively larger than Sn-doped YBCO film, which is probably responsible for effective flux pinning according to the recent proposal by Llordés et al. [37] that nanoscale strain-induced Cooper pair suppression is a new vortex pinning mechanism.

The variation of flux pinning effect in the Zr- and Sn-doped YBCO films can be caused by the defects, including microstrain and stacking fault, generated at the interface between the nanoparticles and the YBCO matrix.
The defects associated with randomly oriented BZO and YBSO nanoparticles, which have an incoherent interface with the YBCO matrix, can make major contribution to the improvement of the flux pinning properties as suggested by Takahashi et al. [16] since the particle sizes of BZO and YBSO are still considerably larger than the coherence length of YBCO. Smaller particles can provide higher density of nanoparticles for the same doping concentration, and thus more defects can be generated due to larger interfacial area. Since the calculated net surface area of BZO nanoparticles (3.5 cm²) is 1.5 times higher than that of YBSO nanoparticles (2.3 cm²), Zr-doped YBCO film can exhibit stronger flux pinning effect due to more defects generated at the BZO/YBCO interface.

4. CONCLUSION

The YBSO and BZO nanoparticles were incorporated in the Zr- and Sn-doped YBCO films by the MOD process. Compared with undoped YBCO film, 10 mol% Zr- and Sn-doped YBCO films containing BZO and YBSO nanoparticles, respectively, exhibited significantly enhanced \( J_c \) in magnetic fields up to 5 T at 65 and 77 K for \( H//c \). Zr-doped YBCO film has much improved \( J_c \) in magnetic fields and angular dependency of \( J_c \) at 65 K for 1 T than Sn-doped YBCO film, indicating that Zr-doped YBCO film possesses more effective flux pinning centers. TEM analyses revealed that while both BZO and YBSO nanoparticles on the STO substrate surface were epitaxially grown and thus form coherent interface with YBCO, those completely trapped by the YBCO matrix are randomly oriented and thus form incoherent interface with YBCO. Stronger flux pinning effect in Zr-doped YBCO film is attributable to BaZrO₃ (BZO) nanoparticles (the average size \( \approx 28.4 \) nm) incorporated in the Zr-doped YBCO film, which are smaller than YBa₂SnO₅.₅ (YBSO) nanoparticles (the average size \( \approx 45.0 \) nm) incorporated in Sn-doped YBCO film, since relatively smaller nanoparticles can provide more defects acting as effective pinning sites at the nanoparticle/YBCO interface due to larger interfacial area for the same doping concentration.

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