Doping of Tin-oxides pinning centers into YBCO films by MOD method

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Abstract. Tin-oxides were doped into YBCO films as pinning centers to improve Jc properties in a magnetic field. YBCO films were grown by a metal organic deposition process using trifluoroacetates starting solutions which contains tin compounds such as SnO2 particles or tin-acetylacetone salts for pinning centers. Jc of the YBCO films were enhanced by introducing pinning centers both SnO2 and tin-acetylacetone in the wide range of the magnetic angle. Especially, Jc of YBCO film grown by the solution with tin-acetylacetone increased in all magnetic field angles. XRD analysis and TEM observation revealed the existence of BaSnO3 particles with the size of about 30 nm in the YBCO film grown by the solution with tin-acetylacetone. The BaSnO3 nano particles were distributed randomly in the film and were considered to act as 3-dimensional pinning centers.

1. Introduction

REBa2Cu3O7-δ (REBCO, RE: rare earth elements) superconductors have been expected to use in many electric power applications since they have high critical current densities (Jc) at a liquid nitrogen temperature (77.3K) under self-field. A metal organic deposition (MOD) process using trifluoroacetates (TFA) is expected as a promising method for REBCO films since this technique can provide the films in a cost-effective process with non-vacuum system [1-4]. In order to apply REBCO for electric power applications, Jc should be enhanced in a magnetic field (B). Recently, researches of Jc enhancement for REBCO films have been proceeded by introducing artificial pinning centers into the films. It has been reported that Jc properties in magnetic fields were well improved for REBCO films with pinning centers such as RE2O3 and BaZrO3 nano compounds or Ce-Gd-O nanowalls by the MOD process using TFA salts [5-9]. On the other hand, we have been reported that BaSnO3 nano rods acted stronger than BaZrO3 as pinning centers in REBCO film grown by a pulsed laser deposition method [10]. In this paper, we grow YBCO films by a MOD process using TFA starting solutions. Tin compounds such as SnO2 nano particles and soluble organic salts of tin were added into the TFA starting solutions as pinning centers. The effects of tin-compounds as pinning centers for YBCO films were discussed.
2. Experimental

The starting solutions for growth of the YBCO films were prepared by dissolving the TFA salts for Y and Ba elements and a fluorine-free naphthenic salt for Cu with the 1:2:3 cation ratio into an appropriate solvent. Two kinds of TFA starting solution were prepared. One starting solution contains dispersion liquid solutions of SnO₂ nano particle (particle size of about 10-30nm) with a concentration range of from 1 to 5 mol% to the total concentration of cation in TFA solutions. Tin-acetylacetonates with a concentration range of from 1 to 2 mol% to the total concentration of cation in TFA solutions were added to another starting solution. Each starting solution was coated on LaAlO₃ (LAO) single crystalline substrates by a spin-coating method. Then, a two-step heat treatment was applied to the coated film. In the first step, the coated film was calcined to form a homogeneous amorphous precursor by increasing the temperature to 400°C at the heating rate of 2°C/min in an oxygen atmosphere with a water vapour partial pressure, \( P_{\text{H}_2\text{O}} \), of 2 vol%. In the second step, the precursor film was crystallized at a temperature of 760°C for an appropriate time at the heating rate of 25°C/min in a mixed gas atmosphere of humid (\( P_{\text{H}_2\text{O}} = 13\% \)) argon and oxygen with low oxygen partial pressure. The total gas flow volume was fixed to be 1 L/min and the gas was humidified by bubbling in a heated water reservoir. Consequently, YBCO films with thickness of about 150 nm were obtained.

Crystal structure and the reaction phase in the YBCO film were identified by X-ray diffraction analysis (XRD). Electron microscopes of transmission electron microscopy (TEM) and TEM-EDS (Energy Dispersive X-ray Spectroscopy) were used to analyze the microstructure and composition of the films in detail. \( T_c \) value was measured by a DC four-probe method. \( J_c \) value was measured by both DC four-probe method and inductive method at 77.3 K.

3. Results and discussion

3.1. YBCO films by TFA solution with SnO₂ nano particles

The XRD \( \theta-2\theta \) scan was performed to evaluate crystallinity of the obtained YBCO films. Figure 1 shows dependences of YBCO peak intensity on SnO₂ concentration in starting solution. The YBCO 005 peak intensities were divided by the LaAlO₃ 200 peak intensities on each film in figure 1. Peak intensity of YBCO decreased with increasing the concentration of SnO₂ addition, it is indicating that the YBCO crystallinity decreases with the SnO₂ addition. From the result of XRD \( \theta-2\theta \) scan, no new peaks were detected without YBCO and LaAlO₃ phases in this experimental condition.

![Figure 1. Dependences of YBCO peak intensity on SnO₂ concentration in starting solution.](image-url)
In order to discuss the microstructure of the YBCO films with SnO$_2$ addition, we observed the cross sections of the YBCO films by TEM. The film was thinned by the focused ion beam (FIB) method for the preparation of cross-sectional view TEM specimens. Firstly, carbon, platinum and tungsten were deposited on the thin plate to protect the surface of the film, then microsampling and FIB polishing were performed. Figure 2 shows a bright field image of the YBCO film crystallized by the starting solution with SnO$_2$ 2 mol% addition. As seen in figure 2, the second phase particles about 30 nm in diameter signed by the white arrow were observed in the film. Many second phase particles segregated near substrate in the YBCO film. A selected area electron diffraction pattern (SAEDP) of YBCO with particles surrounded by the white circle in the cross-sectional image was shown in figure 2. This image was taken in the YBCO[010] zone axis. We can observe reflections only for YBCO, no reflections appeared for particles. The compositional element of these second phase particles were clarified by TEM-EDS measurement for element mapping. Figure 3 is an element mapping of YBCO film with SnO$_2$ 2 mol% addition. In the figure, existences of Sn element were observed where particles existed, it is indicating that the second phase particles were tin containing compounds.

Figure 2. Bright field image of the YBCO film crystallized by the starting solution with SnO$_2$ 2 mol% addition and selected area electron diffraction pattern (SAEDP) of YBCO with particles surrounded by the white circle in the cross-sectional image.

Figure 3. Element mapping of YBCO film grown by the solution with SnO$_2$ 2 mol% addition.
3.2. YBCO films by TFA solution with Tin-acetylacetonate salts

Results of XRD θ-2θ scan for the YBCO films with tin-acetylacetonates were shown in figure 4. The peak intensities of YBCO decreased with increasing concentration of tin-acetylacetonates. Especially, crystallinity was decreased for YBCO film with tin-acetylacetonates of 5 mol% addition. A peak was newly seen at near 43 ° in YBCO films with 1, 2 and 5 mol% tin-acetylacetonates addition, respectively. This peak was considered to be a peak corresponding to BaSnO3 (200) since the lattice constant is calculated to be about 0.419 nm, which is similar to that of BaSnO3 of 0.412 nm[11].

![Figure 4. XRD θ-2θ scans for the YBCO films with tin-acetylacetonates.](image)

Figure 5 shows a bright field image of the YBCO film crystallized by the starting solution with tin-acetylacetonates 2 mol% addition. As seen in figure 5, the second phase particles about 30 nm in diameter signed by the white arrow were observed in the film. These particles were dispersed randomly in the YBCO film. TEM-EDS mapping revealed that the second phase particles contained tin element. As seen in the SAEDP of YBCO film with particles shown in figure 5, the spots signed by the white arrow were similar to that of LaAlO3 (LAO). This suggests that these particles have a cubic perovskite structure.

![Figure 5. Bright field image and SAEDP of YBCO film with particles crystallized by starting solution with tin-acetylacetonates 2 mol% addition.](image)
Then, we assumed that these second phase particles were cubic structure and estimated the lattice constant by using camera constant, lattice constant of LaAlO$_3$, direct spot–to-diffraction spot spacing. As a result, the lattice constant of the particles can be estimated as 0.429 nm. This is in good agreement with the results of XRD measurement and the lattice constant of BaSnO$_3$, 0.412 nm.

3.3. Angular dependences of $J_c$ for YBCO films with pinning centers

The angular dependences of $J_c$ at 77.3 K in 1 T are shown in Figure 6. In order to discuss pinning effects of Sn-compounds, each $J_c$ value was divided by the $J_c$ at $B$//c-axis to be normalized ($J_c/J_c$ ($B$//c-axis)). Here, $T_c$ values of the pure YBCO film, YBCO film with SnO$_2$ of 5 mol%, and YBCO film with tin-acetylacetone of 1 mol% were 91.5 K, 90.0K, and 91.0K, respectively. $J_c$ of the pure YBCO film, YBCO film with SnO$_2$ of 5 mol%, and YBCO film with tin-acetylacetone of 1 mol% were 2.5 MA/cm$^2$, 1.0 MA/cm$^2$, and 2.7 MA/cm$^2$, respectively. Also, $J_c$ at $B$//a-axis ($B$ = 1T) of the pure YBCO film, YBCO film with SnO$_2$ of 5 mol%, and YBCO film with tin-acetylacetone of 1 mol% were 0.92 MA/cm$^2$, 0.7 MA/cm$^2$, and 2.2 MA/cm$^2$, respectively. From the results of figure 6, $J_c$ of the YBCO films were enhanced by introducing pinning centers both SnO$_2$ and tin-acetylacetone in the wide range of the angle. These results show that the second phase nanoparticles of SnO$_2$ and BaSnO$_3$ are effective as three dimensional pinning centers. Especially, higher $J_c$ was obtained for YBCO film with tin-acetylacetone since the second phase particles of BaSnO$_3$ were dispersed randomly in the YBCO film.

![Figure 6. Angular dependences of $J_c$ for YBCO films at 77.3 K in 1 T.](image)

Conclusions

YBCO films were grown by a MOD process using TFA starting solution containing SnO$_2$ nano particles or tin-acetylacetone salts as pinning centers. XRD analysis and TEM observation indicated that SnO$_2$ particles existed with the size of about 30 nm in diameter and were segregated near substrate in the YBCO films crystallized by the solution with SnO$_2$ particles. On the other hand, BaSnO$_3$ particles were dispersed randomly in the YBCO films crystallized by the solution with tin-
acetylacetonates. $J_c$ of the YBCO films were enhanced by introducing pinning centers both SnO$_2$ or tin-acetylacetonates in the wide range of the magnetic angle. Especially, $J_c$ of YBCO film grown by the solution with tin-acetylacetnates increased in all magnetic field angles. The BaSnO$_3$ nano particles distributed randomly in the films were considered to act as 3-dimentional pinning centers.

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