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Superconducting properties of $\text{Sm}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33}\text{Ba}_2\text{Cu}_3\text{O}_y$ films by metal-organic deposition using metal 2-ethylhexanates.

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Abstract

We have prepared $\text{Sm}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33}\text{Ba}_2\text{Cu}_3\text{O}_y$ (SEGBCO) films on LaAlO_3 single-crystal substrates by metal-organic deposition using 2-ethylhexanate solutions which contain no fluorine. The SEGBCO film fired at 850°C under a low oxygen partial pressure of 2×10^{-6} atm exhibited strong c -axis oriented X-ray diffraction peaks and weak a/b -axis oriented peaks of the SEGBCO phase, and had a granular surface. High resolution cross-sectional transmission electron microscope images indicated the epitaxial growth of the SEGBCO film on the substrate with overgrowth of a/b -axis oriented grains. The critical temperature and critical current density values of the SEGBCO film was 86.5 K and 1.29 MA/cm^2 , respectively, at 77.3 K at the self-field.

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Keywords: metal organic deposition; REBCO films; Sm; Eu; Gd; 2-ethylhexanate

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1. Introduction

$\text{REBa}_2\text{Cu}_3\text{O}_y$ (REBCO: RE = rare earth) superconductors have been intensively researched for high magnetic field applications as second-generation superconducting wires. Advanced REBCO superconductors containing two or three different RE elements (Multi-Rare Earth REBCO: MRE-REBCO) with excellent J_c values even in magnetic fields have been reported [1, 2]. The high J_c - B performance was caused by effective pinning centers in MRE-REBCO, for example, the low critical temperature (T_c) phase formed by RE/Ba substitution or lamella structures [3]. $\text{Sm}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33}\text{Ba}_2\text{Cu}_3\text{O}_y$ (SEGBCO) films with two-dimensional nanostripe pinning centers have been reported to have high J_c - B performance at 77.3 K [4, 5]. To date, many studies have been conducted on deposition techniques for REBCO-coated conductors, including pulsed laser deposition, chemical vapor deposition and metal-organic deposition (MOD). The MOD technique is particularly suited to mass production of REBCO-coated conductors because it is a non-vacuum, cost-effective process. MOD using 2-ethylhexanate (2-EH) solutions has the advantage of involving a simpler pyrolytic process than the technique using metal-naphthenate solutions [6-9]. In addition, it does not require the removal of fluorine from the films. In the present study, we investigated the growth of SEGBCO films by the MOD technique using metal 2-EH

fluorine-free solutions.

2. Experimental

SEGBCO solutions for coating were prepared by mixing stoichiometric amounts (1/3: 1/3: 1/3:2:3) of Sm, Eu, Gd, Ba and Cu 2-EH solutions. The solutions were coated on 10×10 mm LaAlO₃(100) single-crystal substrates by spin coating. The coated films were dried at 120°C for 30 min, and then calcined at 450°C for 20 min in air. In the calcination process, the coated films were quickly inserted into a pre-heated muffle furnace and later quickly removed. The calcined precursor films were fired at a heating rate of 5°C min⁻¹ at 840-860°C for 30 min and then cooled to room temperature in a tube furnace. The firing was performed in a flowing mixture of N₂ and O₂ (flow rate: 0.1 l min⁻¹) with an oxygen partial pressure of 2×10^{-6} atm. Finally, the films were annealed at 500°C for 2 h in O₂ under a flow rate of 0.1 l min⁻¹ and then cooled to 300°C at a cooling rate of -3°C min⁻¹. The phases in the film were identified by X-ray diffractometry (XRD). The electrical resistivity of the samples was measured by the standard four-probe technique to determine the T_c values. The J_c of the 150 nm thick films under a magnetic field was calculated from the B - M curves measured by a superconducting quantum interference device. The surface of the samples was

characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The microstructure, film thickness and the composition of the samples were measured by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX), respectively.

3. Results and discussion

Fig. 1 shows the firing temperature dependence of the XRD patterns for the SEGBCO films. The film fired at 840°C showed very weak peaks associated with the SEGBCO phase and exhibited no superconducting transition. Strong peaks associated with a *c*-axis oriented SEGBCO phase and the highest T_c value of 86.5 K were observed for the film fired at 850°C. According to the result of the EDS analysis of the SEGBCO film, the relatively low T_c values of the film may be due to the decrease in carrier density caused by the RE/Ba substitution and/or residual carbon in the film. Weaker XRD peak intensities for the SEGBCO phase were again found for the film fired at 860°C. A small amount of the *a/b*-axis oriented SEGBCO phase was observed for all firing temperatures, as shown in Fig. 1(b). The firing conditions used in the present work for the growth of a superconducting phase involved higher firing temperatures and lower oxygen partial pressures than for MOD using trifluoroacetates or

metal-naphthenates [2, 9]. These conditions correspond to an unstable region considerably below the stability line of the REBCO phase in the $P(\text{O}_2)$ - $1/T$ thermal equilibrium diagram [10]. This result suggests that the crystallization and decomposition of the SEGBCO phase occurred simultaneously in our firing condition of the present work.

Fig. 2 shows SEM images of the SEGBCO films fired at various temperatures. The film fired at 840°C had a surface with a reticulated structure that is typical of films prepared by 2-EH solutions (Fig. 2(a)). A rough and porous surface consisting of many fine crystal grains was observed for the film fired at 850°C, as shown in Fig. 2(b). The SEGBCO films fired at 860°C showed a surface with larger grains in addition to needle-shaped grains that are typical of a/b -axis oriented grains (Fig. 2(c)). These results agree with the XRD analysis shown in Fig. 1. An AFM image of the SEGBCO film fired at 850°C is shown in Fig. 3. A collection of crystalline grains with various diameters of at most 1 μm and thicknesses of 100-200 nm is seen in the image. The grains had relatively flat surfaces with roughnesses of 2-3 nm, whereas the root mean square roughness (R_{rms}) of the film was 74 nm.

Fig. 4 shows the magnetic field dependence of J_c measured at 77.3 K for SEGBCO and GdBCO films prepared by 2-EH. The J_c value of the SEGBCO film was 1.29

MA/cm² at the self-field, which was higher than that of the GdBCO film [9]. However, the J_c of the SEGBCO film decreased rapidly with increasing magnetic field and no improvement of the J_c - B properties was observed. The sudden decrease in J_c in the presence of a magnetic field was possibly caused by poor connectivity between the superconducting grains due to weak links, and also to the presence of the a/b -axis oriented superconducting phase in the film.

Fig. 5 shows cross-sectional TEM images and electron diffraction (ED) patterns of the SEGBCO film fired at 850°C. In Fig. 5(a), a large barium oxide precipitate is seen to partially exist on the surface of the 150-nm-thick epilayer. Although the epilayer is predominantly c -axis oriented, some grains have an a/b -axis orientation. As seen in the high resolution TEM image shown in Fig. 5(b), both the c -axis and a/b -axis oriented grains grow epitaxially on the substrate. The orientation of these grains is confirmed by the ED patterns shown in Figs. 5(c) and 5(d). In addition, the a/b -axis oriented grains, which suppress superconducting currents parallel to the substrate, were in some cases observed to overgrow the c -axis oriented grains. To improve the J_c - B properties of the MOD-SEGBCO films, it is necessary to decrease the occurrence of such a/b -axis oriented grains and to reduce the amount of impurities in the film by optimizing the film preparation

process.

4. Conclusions

SEGBCO films were prepared on LaAlO₃ single-crystal substrates by MOD using 2-EH solutions containing no fluorine. Strong XRD peaks due to the *c*-axis oriented superconducting phase were observed for the SEGBCO film calcined at 450°C and fired at 850°C in a flowing mixture of N₂ and O₂ with an oxygen partial pressure of 2×10^{-6} atm. In addition, a small amount of an *a/b*-axis oriented superconducting phase was observed for firing temperatures ranging from 840 to 860°C. The SEGBCO film fired at 850°C was polycrystalline with various diameters of at most 1 μm and thicknesses of 100-200 nm. The film had a porous surface with a R_{rms} of 74 nm and contained large barium oxide precipitates. In addition, it was found that *a/b*-axis oriented grains sometimes overgrew neighboring *c*-axis oriented grains. The T_c and J_c values of the film were 86.5 K and 1.29 MA/cm², respectively, at 77.3 K at the self-field.

Acknowledgements

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Figure captions

Fig. 1 (a) Firing temperature dependence of XRD patterns for SEGBCO films. (b) Expanded XRD patterns near the (200) diffraction peak. The squares indicate a *c*-axis oriented SEGBCO phase. (b) The triangles indicate an *a/b*-axis oriented SEGBCO phase.

Fig. 2 SEM images of SEGBCO films fired at (a) 840°C, (b) 850°C and (c) 860°C, respectively. The white circles indicate needle-shaped precipitates.

Fig. 3 AFM image of the SEGBCO film fired at 850°C for 30 min after calcining at 450°C for 20 min.

Fig. 4 Magnetic field dependence of J_c values measured at 77.3 K for SEGBCO and GdBCO films prepared using 2-EH.

Fig. 5 (a) Cross-sectional TEM images of the SEGBCO film. (b) High resolution image near interface between the film and substrate. (c), (d) ED patterns obtained from regions 1 and 2, respectively, indicated in Fig. 5(a).

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Fig. 5 WTP-57 / ISS2009