Low Temperature Fabrication of REBa$_2$Cu$_3$O$_y$ Epitaxial Films on SrTiO$_3$ (100) Substrate Prepared by Molten Hydroxide Method in 1-atm Air

S. Funaki*, Y. Yamada, Y. Miyachi, R. Okunishi

Abstract

In order to establish the fabrication method of high-$T_c$ REBa$_2$Cu$_3$O$_y$ (RE123) films by feasible simple system, we fabricated the RE123 films on SrTiO$_3$ substrate by molten hydroxide method in low temperature and 1-atm air. Obtain films of RE-123 (RE = Gd, Eu, Sm) fabricated at low temperature of 525°C show a c-axis orientation of RE123 and REBa$_2$Cu$_4$O$_8$ phases. Moreover, the Nd-123 films show a bi-axial orientation of Nd123 single phase completely above 425°C. The $T_c$ onset of Nd123 film fabricated at 525°C denotes 67.1 K which was drastically lower compared with previous study of Nd123 single crystalline film, and $T_c$ onset of Nd123 films degrade with decreasing fabrication temperature. We can consider that the Nd/Ba substitution was caused by lowering the fabrication temperature.

Keywords: Superconducting film; Critical temperature; Molten hydroxide method; REBa$_2$Cu$_3$O$_y$; Liquid phase epitaxy

1. Introduction

It is well known that the critical temperature ($T_c$) of REBa$_2$Cu$_3$O$_y$ (RE123; RE: rare earth elements) improve with increasing RE ionic radius [1, 2]. Recently, many groups have investigated the coated conductors (CC) for various applications such as superconducting cable, transformer and magnet, however, RE123-CC fabrication needs a high growth temperature during film deposition and multi-layered buffer structure in restraint of impurity diffusion from metallic tape substrate. In result, fabrication rate of the RE123-CC is not enough to produce in economically fast rate. Yoshida et al. reported that possibility of lower temperature fabrication in Sm123 film by LTG technique, and they succeeded the fabrication of high-performance Sm123 films at low temperature of 740°C [3]. However, this technique based on vapor phase deposition (low growth rate) process and needs a high temperature for RE123-CC fabrication. From these report, in order to establish the RE123 fabrication method with lower temperature and high growth rate to develop a RE123-CC by simple and reasonable system.

As example of high growth rate fabrication methods, it is well known the Liquid phase growth process such as top-seeded solution growth (TSSG) and liquid phase epitaxy (LPE). For single crystalline bulk crystals and LPE films of
RE123, BaO-CuO flux (so-called self-flux) was used as a growth flux. Although the BaO-CuO flux provides a high growth rate more than 10 μm/min, the growth temperature needs approximately 900°C. Recently, the preparation methods of single crystalline REBa₂Cu₄O₈ (RE124) compound by LPE process are reported by using molten alkali hydroxide in ambient atmosphere. Song et al. described synthesis of Y124 single crystal using molten potassium hydroxide (KOH) with growth temperature of 700°C [4]. In previous work, we achieved the synthesis of bi-axial oriented RE124 epitaxial films on NdGaO₃ (001) single crystalline substrate fabricated by molten hydroxide method with low growth temperature of ~650°C [5]. Furthermore, we succeeded the fabrication of bi-axial oriented Y123 epitaxial films by controlling oxygen partial pressure, and the Y123 film fabricated at 650°C in low oxygen partial pressure indicates high-\(T_c\) of ~90 K comparable to conventional Y123 films. In this investigation, in order to establish the fabrication method of more high-\(T_c\) RE123 film by feasible simple system, we fabricated the RE123 films on SrTiO₃ (STO) substrate by molten hydroxide method in 1-atm air using various RE elements, and also discussed the grown phases, orientation and superconducting properties.

2. Experimental procedure

Rare earth (RE = Yb, Er, Ho, Y, Dy, Gd, Eu, Sm, La) oxide, barium carbonate and copper oxide powders were used as starting materials, and KOH was used as a solvent. The RE-123 powder and film were prepared via three steps: first step is the heat-treated at 700°C of KOH flux with a weight of 5.0 g to remove water, and then second step is the falling temperature rapidly for growth temperature such as 400~525°C and put a STO (100) substrate and mixed starting materials with a total weight of 2.5 g with a molar ratio of RE : Ba : Cu = 1 : 2 : 3 into a molten KOH, and last step is heat-treated for 12 hours to grow the RE123. In addition, all steps were performed in 1-atm air. After cooling to room temperature, film and powder samples was extracted from the flux, and Obtained samples were washed by distilled water and ethanol using ultrasonic cleaning to eliminate the KOH, K₂CO₃, and then performed oxygenation anneal at from 400°C (or 450°C) to 300°C with slow cooling.

The grown phase identification, orientation and lattice constant were measured by X-ray diffraction (XRD) pattern with a CuKα source. Surface morphology was obtained by scanning electron microscope (SEM).

3. Results and discussion

3.1. Grown phases and orientation

From XRD 2θ-θ observation of powder samples heat-treated at 525°C, it is revealed that the RE-123 powders with smaller ionic radius elements of Yb, Er, Ho, Y, Dy showed weak diffraction patterns of the raw materials and Ba-Cu-O related phases. On the other hands, the powder with larger ionic radius elements of Gd, Eu, Sm, Nd showed sharp and intense peak of RE123 and RE124 phases in addition to raw materials and Ba-Cu-O. From these results, we can consider that the XRD pattern varied by solubility between light RE elements and heavy RE elements. Furthermore, the peak intensity originated RE124 phase decreased with increasing of ionic radius, and the Nd-123 powder showed peaks of Nd123 single phase completely. In contrast, the La-123 powder which is largest ionic radius element of RE showed sharp LaCuO₄ peaks as well known an obtainable phase reproducibility at low temperature by KOH/NaOH eutectic flux [6].

The RE123 superconducting material has anisotropic physical properties owing to layered crystal structure with alternating two-dimensional CuO₂ planes, and the critical current density (\(J_c\)) along the CuO₂ planes (/// ab-plane) is superior to that of along c-axis direction. Furthermore, in the case of RE123, the increase of in-plane misorientation angle between two grains causes serious degradation of \(J_c\), even for the c-axis oriented film [7]. The samples of obtaining the RE123 and RE124 powder (RE = Gd, Eu, Sm, Nd) as mentioned above, we can find the crystal growth on STO (100) substrate with favorable coverage. Fig. 1(a) shows XRD 2θ-θ patterns of films grown with Gd, Eu, Sm, Nd-123 synthesized at 525°C. It is found that the c-axis oriented RE123 and RE124 phase grew on STO (100) substrate and the Nd-123 film indicates c-axis oriented Nd123 single phase completely. Fig. 1(b) shows in-plane orientation of RE123 phase in Gd, Eu, Sm, Nd-123 films. It is revealed that the RE123 phase grew with in-plane alignment such as RE123 [100] // STO [100]. From these results, we succeed fabrication of bi-axial oriented Gd, Eu, Sm, Nd123 films by KOH flux with low temperature of 525°C.
3.2. Lower temperature fabrication of Nd123 films

We discussed the possibility of fabrication of Nd123 film at lower temperature in terms of orientation and $T_c$. Fig. 2 shows XRD 2$\theta$-$\theta$ patterns of Nd-123 films fabricated at 400–500°C. We can found that the Nd123 phase grew with complete $c$-axis orientation above 425°C ($c$-axis length calculated by XRD patterns were inserted in Fig. 2). Moreover, we confirmed that the Nd123 film fabricated at 425°C has an in-plane orientation completely from XRD measurement.

$R$-$T$ curves of Nd123 films fabricated at 425–525°C are shown in Fig. 3. $T_c^{\text{onset}}$ of film fabricated at 525°C is 67.1 K, which is much lower than that of single crystalline Nd123 film ($T_c \sim 94$ K) fabricated by tri-phase epitaxy method using BaO-CuO flux [8], and $T_c^{\text{onset}}$ degraded with decreasing fabrication temperature. Takita et al. reported that the Nd123...
single crystalline bulk prepared by conventional solid state reaction denotes $c$-axis length shrinkage and $T_c$ degradation due to increasing of amount of Nd substitution for Ba site [9]. Hence, $c$-axis length of Nd123 film fabricated at 525°C (11.717 Å) was shorter than that of stoichiometric Nd123 single crystal of 11.764 Å [9], and $c$-axis length of Nd123 films shrunk with decreasing fabrication temperature. Furthermore, the amount of Na/Ba substitution observed by SEM-EDS was increase with decreasing fabrication temperature in qualitatively. It is considered that $T_c$ degradation of lower temperature fabricated Nd123 films caused by Nd/Ba substitution. From these considerations, we suggest that a suppression of the Nd/Ba substitution by preparing of starting material’s ratio, oxygen-controlled melt growth (OCMG) process [10] enables to achieve higher $T_c$ in lower temperature fabricated Nd123 films.

4. Conclusion

We fabricated the RE123 films on STO (100) substrate at lower temperature by molten hydroxide method in 1-atm air using various RE elements and investigated the grown phases, orientation and superconducting properties. Obtained films of Gd, Eu, Sm-123 fabricated at 525°C showed a $c$-axis orientation of RE123 and RE124 phases. Moreover, we succeeded fabrication of bi-axial oriented Nd123 films by KOH flux at lower temperature of 425°C. The $T_{c\text{onset}}$ of Nd123 film fabricated at 525°C was 67.1 K which was drastically lower compared with single crystalline Nd123 film fabricated by BaO-CuO flux. It is speculated that the $T_c$ degradation of Nd123 films were caused by increasing amount of Nd substitution for Ba site with lowering the fabrication temperature.

References