

GROWTH OF $\text{GdBa}_2\text{Cu}_3\text{O}_y$ FILMS PREPARED BY BaF_2 PROCESS WITHOUT WATER VAPOR

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We have investigated the influences of the heating rate and film thickness on the growth of $\text{GdBa}_2\text{Cu}_3\text{O}_y$ (GBCO) thin films prepared by the BaF_2 ex-situ process without water vapor. Critical current density (J_c) and surface morphology of the GBCO films were improved by increasing the heating rate during growth from $30^\circ\text{C}/\text{min}$ to $50^\circ\text{C}/\text{min}$. The GBCO films prepared by the heating rate of $50^\circ\text{C}/\text{min}$ had the maximum J_c of $2.1 \text{ MA}/\text{cm}^2$. The J_c value of the GBCO films was about $2 \text{ MA}/\text{cm}^2$ up to 200 nm, and decreased to $0.92 \text{ MA}/\text{cm}^2$ at 400 nm.

Keywords: BaF_2 process; ex-situ annealing; Gd123 films

1. Introduction

The superconducting wires have been studied energetically for the application in electric-power transmission and high magnetic-field generation. $\text{REBa}_2\text{Cu}_3\text{O}_y$ (RE = Y and Rare Earth: REBCO) superconductors are promising materials for the second-generation superconducting wires because they have higher critical current densities (J_c) in high magnetic field than Bi-Sr-Ca-Cu-O superconductors. It has been reported that several film growth techniques such as a pulsed-laser deposition, a metal-organic deposition and the post annealing of the precursor films include BaF_2 , so-called a BaF_2 ex-situ process are suitable for the fabrication of high- J_c REBCO coated conductors.¹⁻⁵ Generally, the fabrication of the RE123 films by the BaF_2 ex-situ process requires the introduction of water vapor to remove fluorine in the films and crystallize RE123 phases. Therefore, it is essential to control partial pressures of the water vapor and the distribution of the flow of water vapor in a growth chamber. On the other hand, YBCO films with J_c over $1 \text{ MA}/\text{cm}^2$ have been successfully fabricated by the in-situ annealing of Y- BaF_2 -Cu precursor films for very short time without water vapor.⁶ The film fabrication process without water vapor has advantages of fewer control parameters and apparatuses for mass production of the coated conductors. Recently we have demonstrated GBCO films with J_c of $1.5 \text{ MA}/\text{cm}^2$ were prepared by the ex-situ annealing of co-evaporated Gd- BaF_2 -Cu precursor films without water vapor.⁵

In this study, we have investigated the heating rate and thickness dependence on the growth of the GBCO films by the ex-situ post annealing of Gd- BaF_2 -Cu precursor films without water vapor.

2. Experimental

Precursor films were deposited on SrTiO_3 (100) single crystals at room temperature by a co-evaporation technique using Gd, BaF_2 and Cu as evaporation sources. The precursor films were taken out from the deposition chamber and fired at 800°C for 30-130 min in a gas mixture of nitrogen and oxygen. Total gas pressure and oxygen partial pressure ($p\text{O}_2$) during firing was 1 atm and 10^{-5} atm, respectively. The heating rate during growth was varied from $30^\circ\text{C}/\text{min}$ to $50^\circ\text{C}/\text{min}$. The films were finally annealed at 500°C for 2 hr in oxygen. Thickness of the GBCO films was varied from 100nm to 400nm. Crystalline phases and grain orientation of the films were measured by X-ray diffraction (XRD) using CuK_α radiation. The critical temperature (T_c) of the films was measured by a standard DC four-probe method. The magnetization J_c was measured by a superconducting quantum

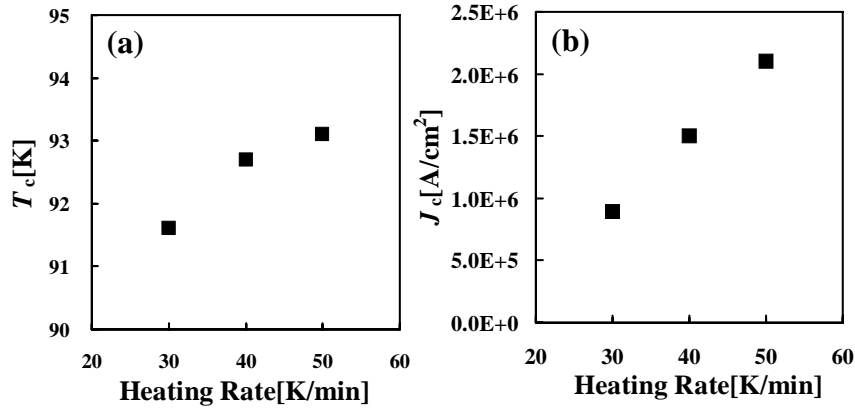


Fig. 1 Heating rate dependence of T_c and J_c for 200-nm-thick GBCO films.

interference device. Surface morphology was observed by using a scanning electron microscope (SEM). The cross-sectional views of the film were studied by using a high resolution transmission electron microscope (TEM). Quantitative analysis for the surface and cross section of the films was performed with an energy-dispersive X-ray spectrometer (EDS).

3. Results and Discussion

Figure 1 shows the heating rate dependence of T_c and J_c for the GBCO thin films of 200nm thickness. The T_c values of the GBCO thin films slightly increased with the increase in heating rate as shown in Fig. 1(a): 91.6 K for 30°C /min, 92.7 K for 40K/min and 93.1K for 50°C /min. On the other hand, GBCO thin films showed the distinct increase in J_c with the heating rate (Fig. 1(b)). The J_c values of the GBCO thin films prepared by the heating rate of 30°C/min, 40°C/min and 50°C /min were 0.89 MA/cm², 1.5MA/cm² and 2.1MA/cm², respectively. It was reported for YBCO films prepared by TFA-MOD process that the decrease in J_c with the hearing rate was caused by abrupt HF

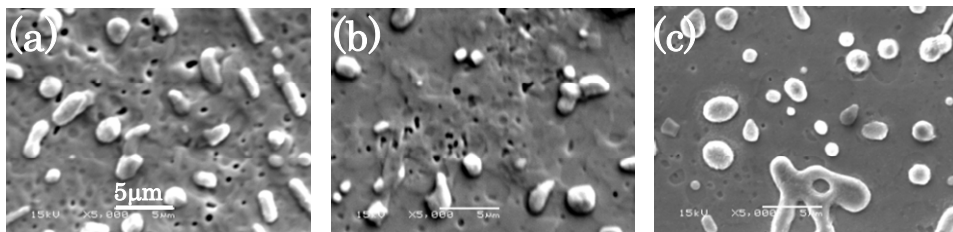


Fig. 2 SEM surface images of the 200-nm-thick GBCO films prepared by the heating rates of (a) 30 °C/min, (b) 40°C/min and (c) 50°C/min.

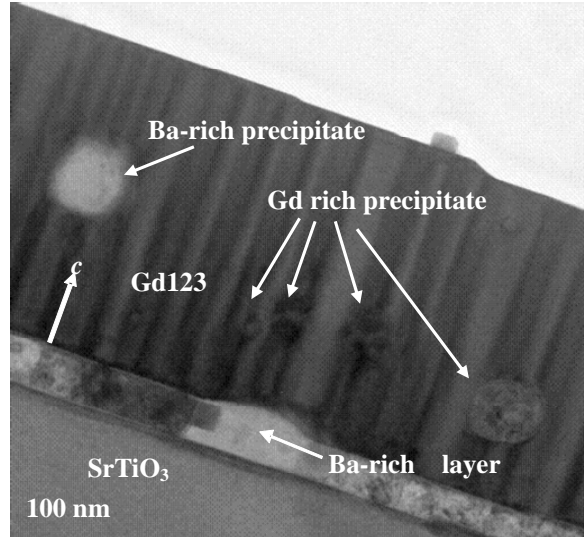


Fig.3 Cross-sectional TEM image of the 200-nm-thick GBCO film.

gas generation⁷.

The heating rate dependence of the surface morphology for the 200-nm-thick GBCO films was represented in Fig. 2. The density of the pores observed in the matrix surface decreased with the increase in the heating rate. The flatness of the superconducting matrix was improved with the heating rate. The XRD results indicate that the crystallinity of the GBCO films was improved as the heating rate increased. These results indicate that

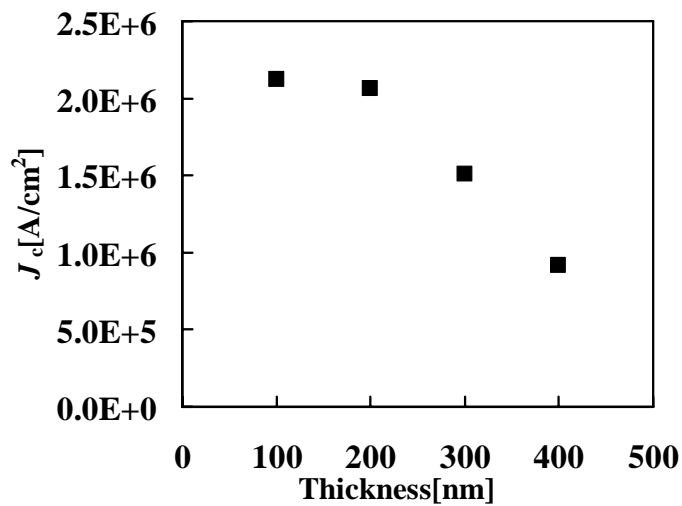


Fig. 4 Thickness dependence of J_c for the GBCO films at 77 K at self-field.

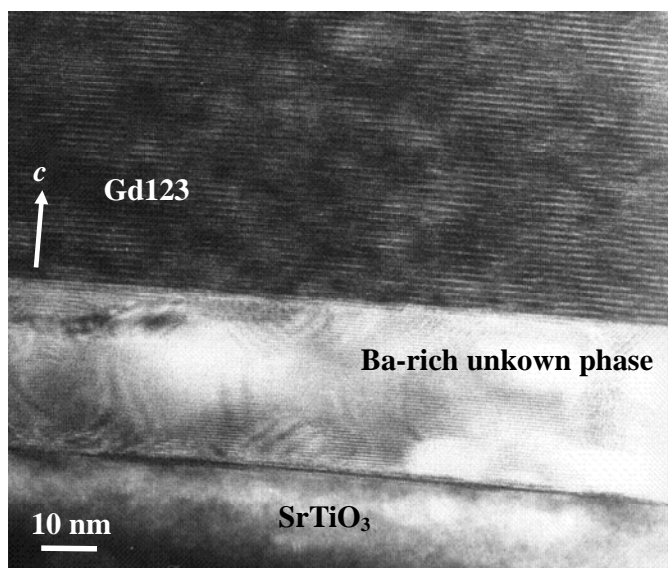


Fig. 5 Cross-sectional TEM image of the 400-nm-thick GBCO film.

the increase in J_c shown in Fig. 1 was attributed to both the improvement of the connection between the crystal grains in the GBCO films and the crystallinity of the films. The formation of the pores was frequently observed for the REBCO thin films fabricated by the TFA-MOD process.⁸⁻⁹ The precipitates observed in the film surfaces had the Ba and Cu-rich composition from EDS analysis. The precipitates were probably due to the deviation of the precursor film composition from the stoichiometric composition.

Figure 3 shows the high-resolution cross-sectional view of the 200-nm thick GBCO film with J_c of 2.1 MA/cm². The TEM image shows that a 30-nm-thick unknown layer with a Ba-rich composition exists between the GBCO film and the substrate. The c -axis oriented GBCO film epitaxially grows on the unknown layer. The results indicate that high-quality GBCO thin films can be grown by the BaF₂ process without water vapor as in the case of the process with water vapor.¹⁰ The thickness dependence of J_c at 77K at self-field is shown in Fig. 4. The J_c values of the films were about 2MA/cm² up to 200 nm, and decreased to 0.92 MA/cm² at 400 nm. The thickness dependence of J_c has been generally studied for the REBCO films grown by various methods. One of the reasons for the decrease in J_c with the film thickness was reported to be attributed to degradation in the superconducting layer structure.¹⁰⁻¹¹

Figure 5 represents the cross-sectional view of the 400-nm-thick GBCO film. The TEM image shows some precipitates which were confirmed to be Gd-rich or Ba-rich phases by EDS. The decrease in J_c observed for the thick GBCO films was probably caused by these impurity phases. In the pervious paper, we reported that the growth of the superconducting phase was strongly influenced by the fluorine content in films.⁶ We speculate the formation of the impurity phases depends on desorption of fluorine from the films. It is necessary for high-quality thick GBCO films by the BaF₂ process without

water vapor to optimize the heat treatment condition.

4. Conclusion

The heating rate and film thickness dependence on the growth of GBCO films by the BaF₂ ex-situ process without water vapor has been studied. J_c and surface morphology of the GBCO films were improved with the increase in the heating rate during the growth. The 200-nm-Gd123 films with J_c of 2.1 MA/cm² were successfully grown at the heating rate of 50°C/min. J_c of the GBCO films was about 2MA/cm² up to 200 nm and decreased to 0.92 MA/cm² at 400 nm. The impurity phases with Gd or Ba-rich compositions were observed for the 400 nm films.

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