Crystal grains alignment of SmBCO film by advanced TFA-MOD method

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Abstract. We grew SmBa2Cu3O7-y (SmBCO) films on LaAlO3 (LAO) single crystalline substrates by an advanced TFA-MOD method and discussed the effects of process conditions such as oxygen partial pressure in the crystallization step on the crystal grains alignment of SmBCO film. Oxygen partial pressure affected strongly on the orientation of SmBCO film. Formation of a-axis crystal grains of the SmBCO was suppressed, and, at the same time, c-axis crystal grains of the SmBCO increased with decreasing the oxygen concentration.

1. Introduction

Superconducting films for tape and wire applications require a high critical temperature ($T_c$) and current density ($J_c$). REBa2Cu3O7-y (REBCO, RE = rare earth elements) system superconducting materials show $T_c$s higher than the boiling point of liquid nitrogen, and the research of YBCO films with high performance has been proceeded[1,2]. SmBCO is one of the attractive REBCO materials since it has higher $T_c$s than that of YBCO as well as stronger vortex-flux pinning, which results in the high $J_c$[3]. In order to apply SmBCO films for tape and wire applications, high $J_c$ films with high crystal grain alignment of the SmBCO are required in a low-cost fabrication technique. Metal organic deposition (MOD) method using tri-fluoroacetates (TFA) precursor is a promising process for YBCO films because of its high $J_c$ property by a non-vacuum low-cost processing[4,5]. However, there are few reports for SmBCO films grown by the TFA-MOD method[6].

In this study, we have grown SmBCO films on LaAlO3 substrates by an advanced TFA-MOD method. Process parameters which affect the crystal grains alignment of SmBCO were investigated. Crystallization conditions such as oxygen partial pressure in the crystallization step in this method were optimized for obtaining high crystal grain alignments in the SmBCO films.

2. Experimental

The precursor solution for growth of the SmBCO films was prepared by dissolving the TFA salts for Sm and Ba elements and a fluorine-free naphthenic salt for Cu with the 1:2:3 cation ratio into an appropriate solvent. The solution was controlled to have a total metal ion concentration of 1.2 mol/L, and was coated on a LaAlO3 (LAO) single crystalline substrate by a spin-coating method. Then, a two-step heat treatment was applied to the coated film[7]. In the first step, the coated film was calcined to
form a homogeneous amorphous precursor by increasing the temperature to 400-500°C at the heating rate with 2°C/min in a humid (P_{H2O} = 2%) oxygen atmosphere. In the second step, the precursor film was crystallized at a high temperature for an appropriate time at the heating rate with 25°C/min in a mixed gas atmosphere of humid (P_{H2O} = 10-13%) argon and oxygen with low oxygen partial pressure. The total gas flow volume was fixed to be 1 L/min and was humidified by bubbling in a heated water reservoir.

In this study, we optimized the calcination conditions, firstly, in order to obtain homogeneous precursor films. Influences of water vapour inlet-start temperature, $T_{H2O}$, and calcinations temperature in the calcination step on microstructures were investigated. And then, heating temperature in the crystallization step was optimized. Finally, effects of oxygen partial pressure, $P_{O2}$, in the crystallization step on the crystal grain alignments of SmBCO film were studied. Crystal structure and the reaction phase in the SmBCO film were identified by X-ray diffraction analysis (XRD). Microstructures of the obtained films were observed by scanning electron microscopy (SEM), Optical Microscopy (OM) and Atomic Force Microscopy (AFM).

3. Results and discussion

3.1. Optimization of $T_{H2O}$ conditions in calcinations step

In order to investigate the influence of $T_{H2O}$ in the calcinations step on the crystallinity and microstructure of the SmBCO film, calcined films were prepared under the $T_{H2O}$ of 200, 300 and 350°C. Figure 1 shows OM images of the calcined films which were prepared with $T_{H2O}$ of 200°C and 350°C, respectively. As seen in fig. 1(a), a large pore and rough surface morphologies were recognized in the film which prepared with $T_{H2O}$ of 200°C. Electron Probe Micro Analyser (EPMA) analysis indicated segregations of Ba and Cu around large pore in the calcined film prepared with $T_{H2O}$ of 200°C. On the other hand very flat surface and no large pore were observed in the film calcined by introducing the H_{2}O gas from 350°C as seen in fig.1(b). Then, these 3 calcined films were crystallized under a constant crystallization condition and influences of $T_{H2O}$ in the calcinations step on the crystallinity of final SmBCO film were investigated by XRD analysis. Figure 2 shows the dependences of crystallinity of SmBCO films on $T_{H2O}$ in the calcinations step. Intensities of 001 peaks ($l = 3$ and 6) for c-axis oriented SmBCO films changed drastically as a function of $T_{H2O}$. High intensities were recognized in the films which were prepared at the higher $T_{H2O}$ than 300°C. On the other hand, in the case of the SmBCO film which was prepared at $T_{H2O}$ of 200°C, the peak intensity

![Figure 1](image1.png)
became lower, indicating poor orientation of the SmBCO film. From the results of OM and EPMA analysis, it was suggested that the main reason for the lower orientation of SmBCO film under $T_{H2O}$ of 200°C is segregations of Ba and Cu around large pores. Consequently, $T_{H2O}$ in the calcinations step was fixed to be 350°C as an optimized $T_{H2O}$ condition. Calcination temperatures were discussed in the next sentence.

3.2. Optimization of calcinations and crystallization temperatures

Calcined films were prepared under the temperature of 400-500°C with the $T_{H2O}$ of 350°C, and then the films were crystallized under the temperature of 780-860°C. Figure 3 shows the dependence of 003 peak intensity of SmBCO films on the crystallization temperature under various calcination temperatures. Similar peak intensities were observed in the SmBCO film calcined at 400 and 500°C. Highest peak intensity was recognized for the SmBCO film calcined at 400°C and crystallized at 840°C. OM observations of the film surface for each SmBCO film showed no remarkable difference. Consequently, calcination temperature and crystallization temperature were fixed to be 400°C and 840°C, respectively, as the optimized heating temperature.
3.3. Effects of $P_{O_2}$ on the in-plane crystal grain alignments of SmBCO film

Effects of oxygen partial pressure, $P_{O_2}$, in the crystallization step on the crystal grain alignments of SmBCO film were studied in order to obtain high crystal grain alignment to both out of plane and in-plane for the SmBCO films. We made a quantitative estimation of the a-axis/c-axis volume fraction by using the following equation;

$$a - axis \ \text{volume fraction} \ (%) = \frac{I_{100}}{I_{100} + I_{003}} \times 100$$

(1)

where $I_{100}$ and $I_{003}$ are the intensities of 100 peak and 003 peak intensities of the XRD θ-2θ scan for

![Figure 4. The relationship between a-axis volume ratio and $P_{O_2}$ during SmBCO crystallization.](image)

![Figure 5. SEM images of surface morphology for the SmBCO films which were crystallized under the $P_{O_2}$ conditions of 10 ppm (a) and 1000 ppm (b).](image)
the SmBCO films. The plots of a-axis grains volume versus $P_{O_2}$ during SmBCO crystallization are shown in Figure 4. The a-axis grains volume was depended strongly on the $P_{O_2}$, and the a-axis grains decreased with decreasing the $P_{O_2}$. Figure 5 shows SEM images of surface morphology for the SmBCO films which were crystallized under the $P_{O_2}$ conditions of 10 ppm(a) and 1000 ppm (b). As seen in Fig. 5(a), c-axis crystal grains of SmBCO were observed in the SmBCO film crystallized under lower $P_{O_2}$ condition. On the other hand, many a-axis crystal grains were confirmed in the SmBCO film crystallized under higher $P_{O_2}$ condition as shown in Fig.5(b). These results were corresponding with the results of Figure 4. The reason for the difference in the in-plane crystal grains alignment due to the $P_{O_2}$ was discussed by the relation of the nucleation rate. The basic reaction for the formation of the YBCO phase from the precursor film in the TFA-MOD method is recognized as [8]:

$$\frac{1}{2} Y_2Cu_3O_5 (s) + 2 BaF_2 (s) + 2CuO (s) + 2H_2O (g) + \frac{x}{2} O_2 (g) \rightarrow YBa_2Cu_3O_{6.5+x} (s) + 4HF (g) \quad (2)$$

The overall reaction of SmBCO is assumed to be Equation (2). The free energy change of this phase transformation, $\Delta G$, can be described on the assumption that the activities of the solid phases are unity;

$$\Delta G = \Delta G^0 + 2RT \ln \left( \frac{P_{HF}^2}{P_{H_2O}^2 \cdot P_{O_2}^2} \right) \quad (3)$$

$$K = \frac{P_{HF}^2}{P_{H_2O}^2 \cdot P_{O_2}^2} \quad (4)$$

where $\Delta G^0$, $R$, $T$, $P_{HF}$, $P_{H_2O}$, $K$ are the standard free energy change for the reaction, gas constant, temperature, partial pressure of HF gas, partial pressure of H$_2$O gas and the reaction product, respectively. When the reaction (2) is achieved equilibrium condition, which means $\Delta G = 0$, the $K$ value should be defined as to be the equilibrium constant, $K_e$, which resulted in $\Delta G^0 = -2RT \ln(K_e)$. As a result, $\Delta G$ can be rewritten as;

$$\Delta G = 2RT \ln \left( \frac{K}{K_e} \right) \quad (5)$$

According to equations (3) - (5), the absolute value of $\Delta G$ depends on the $P_{O_2}$. On the other hand, the nucleation rate, $N$, can be expressed by using the free energy change as;

$$N = A \exp\left(-\frac{1}{\Delta G^2}\right) \quad (6)$$

where $A$ is a constant. According to the equation (6), $N$ is raised with increasing the absolute value of $\Delta G$ which is derived from the increasing of $P_{O_2}$. Consequently, the nucleation rate ratio of a-axis crystal grain to a-axis crystal grain, $N_a/N_c$, increases with increasing the $P_{O_2}$.

**Conclusion**

SmBCO films were grown on LaAlO$_3$ (LAO) single crystalline substrates by an advanced TFA-MOD method and discussed the effects of process conditions such as oxygen partial pressure, $P_{O_2}$, in the crystallization step on an in-plane crystal grain alignment of SmBCO film. In-plane crystal grains alignment of SmBCO film was affected strongly on the $P_{O_2}$. Formation of a-axis crystal grains of the
SmBCO was suppressed with decreasing the $P_{O_2}$. The reason for the difference in the in-plane crystal grains alignment due to the $P_{O_2}$ was explained by the deference of nucleation rate for a-axis crystal grain and c-axis crystal grain.

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