Preparation of (11n) oriented Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ thin films by solution methods using NdGaO$_3$ (100) substrates

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Abstract. We have prepared (11$n$) oriented Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212) thin films by KCl flux method which is one kind of solution method. The (100) substrate of NdGaO$_3$ (NGO) was used. Heat treatment was performed with four different temperature profiles. Only the (11$n$) peak appeared in the $\theta$-2$\theta$ X-ray diffraction pattern. From the SEM image, it was found that elongated plate-like crystal grains of Bi2212 were grown. From the viewpoint of lattice matching, this elongated crystal grain is considered to be (010) (or (100)) oriented crystal grains.

1. Introduction

Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212) has a layered perovskite structure and forms an intrinsic Josephson junction (IJJ). When a voltage is applied in the c-axis direction, an alternating current with a frequency proportional to the voltage is generated. A vibration mode excited by matching the frequency of the alternating current with a cavity resonance frequency can be used for a terahertz oscillator, which is considered to be a promising device that fills a frequency domain called the "terahertz gap". It has already been proved that a $\mu$W class continuous coherent terahertz wave can be oscillated [1-4].

The major preparation methods thus far have been reported on c-axis oriented Bi2212 that requires complicated procedures and dry etching, such as a precisely controlled etching process in depth direction in order to form the c-axis current paths. If a non-c-axis oriented thin film of which the c-axis parallel or incline to the substrate surface can be prepared, planar type IJJ devices can be fabricate simply by forming current paths parallel to the substrate [5,6]. In preparing such non-c-axis oriented thin films, it is important that selection of substrates focusing on lattice matching. If such substrates are selected and solution or powder material is coated on that substrate by a printing method, it is considered that an IJJ devices can be fabricated only by performing a heat treatment.

In the case of preparing Bi2212 thin films, c-axis oriented thin films were formed by using SrTiO$_3$ (STO) (100) substrates [7,8], and (117) oriented thin film with c-axis twin structure ("c-twinning") are formed by using STO (110) substrates [9]. In order to fabricate Bi2212 IJJ devices, it is necessary to prepare thin films having no c-twinning in order to form c-axis current paths. The c-axis lattice constant of Bi2212 is $c = 30.6 \sim 30.9$ Å [10,11], which is relatively close to 8 times the lattice constant of STO (3.095 $\times$ 8 = 31.24 Å). However, as mentioned above, actually (117) oriented thin film is formed. NdGaO$_3$ (NGO) has a lattice constant of $a = 5.427$ Å, $b = 5.497$ Å, $c = 7.707$ Å [12]. Four times the c-axis length of NGO is 7.707 $\times$ 4 = 30.82 Å, which is almost equal to that of Bi2212. This
value is closer than 8 times the c-axis length of STO. If an NGO (100) substrate is used, it is expected that the c-axis of Bi2212 grows lattice-matched to the c-axis of the NGO (100) substrate.

In this study, we report fabrication of (11n) oriented Bi2212 thin films using NGO (100) substrate by KCl flux method which is one kind of solution method. A typical flux method requires a large amount of solution and mechanical motion. On the other hand, in this report, a prototype was made by a simple method of simply coating the substrate and heat treating it in order to apply it to the printing method. Evaluation of the thin film was carried out through X-ray diffraction (XRD) pattern, observation of surface morphology by scanning electron microscope (SEM) image.

2. Experimental Procedure
Bi2212 thin films under study were prepared by the KCl flux method. Substrates used were NGO (100) substrates with the size of 10 × 10 × 0.5 mm. Preparation procedures were as follows:

1. The raw material powder is weighed so that the molar ratio is Bi2O3 : SrCO3 : CaCO3 : CuO : KCl = 1:2:1:2:94.
2. The weighed powder is mixed using an agate mortar and pestle in 2-propanol for 2 h.
3. The mixed powder is dried using an IR lamp.
4. Approximately 30 mg of the dried mixed powder is coated on the NGO (100) substrate.
5. The dried mixed powder is coated on an NGO (100) substrate. The amount of powder is about 30 mg.
6. Heat treatment is carried out using a box furnace with four temperature profiles.
7. KCl flux is dissolved and removed using purified water.

The samples were taken into the box furnace at room temperature. Then, the samples were taken out after being cooled to room temperature. Figure 1(a) ~ (d) shows the temperature profile of a box furnace. The crystal structures of the samples were investigated by θ-2θ XRD patterns with CuKα radiation (λ = 1.54 Å). The surface morphologies were observed by SEM.

3. Result and Discussion
Figure 2 shows comparison of XRD patterns of samples with different temperature profiles. (a) ~ (d) of figure 2 correspond to (a) ~ (d) of figure 1, respectively. Only peaks of Bi2212 phase and NGO substrates appeared in these XRD patterns. As the time maintained at (or close to) 810 °C is longer, the (11n) peak of Bi2212 tends to become larger.
Figure 2. $\theta$-$2\theta$ XRD patterns of samples with different temperature profiles using NGO (100) substrates.

Figure 3 shows a comparison of the observed surface morphologies by SEM with different temperature profiles. (a)~(d) of figure 3 correspond to (a)~(d) of figure 1, respectively. From the viewpoint of lattice matching, elongated plate-like crystal grains along the white broken arrow in the figure are considered to be (010) (or (100)) oriented crystal grains. The (010) (or (100)) oriented crystal grains should appear as (020) (or (200)) peaks on $2\theta = 33.16^\circ$ on the XRD pattern. However, it is considered that it can not be observed in figure 2 because it is located at the position overlapping the peak of the NGO substrate.

Figure 3. The observed surface morphologies by SEM. The white solid arrow in the figure indicates the $c$-axis direction of the Bi2212, and the white broken line arrow indicates the $a$-axis (or $b$-axis) direction.
Figure 4 show a top schematic view (imaginary view) of lattice matching. The lengths of the $a$-axis and the $b$-axis of Bi2212 were set to the same average length (= 5.41 Å) in the figure. Since the crystal grains of Bi2212 grow to extend in the $ab$ plane direction, it is considered that the crystal grains oriented in the (010) (or (100)) orientation become elongated in the $a$-axis (or $b$-axis) direction.

4. Conclusion
In order to realize fabrication of non-$c$-axis oriented thin film that can be used for Bi2212 IJJ device by printing method, we attempted to fabricate non-$c$-axis oriented thin film by KCl flux method. For that purpose, focusing on lattice matching, NGO (100) substrates was used. The crystallinity and orientation were evaluated by the $\theta$-2$\theta$ pattern of XRD. As a result, the followings were clarified.

1. In comparison of XRD patterns of samples with different temperature profiles, as the time maintained at (or close to) 810 °C is longer, the (11$n$) peak of Bi2212 tends to become larger.

2. From the viewpoint of lattice matching, elongated plate-like crystal grains in SEM images are considered to be (010) (or (100)) oriented crystal grains.

In this report, we succeeded in growing (010) (or (100)) oriented Bi2212 crystal grains. However, (11$n$) oriented crystal grains with $c$-twinning are also formed, which is a problem to be solved in the future.

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