Effects of vicinal substrates on the orientation of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ thin films when the metal-organic decomposition method is used

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Abstract. We have prepared (010) (or (100)) oriented Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212) thin films by metal-organic decomposition (MOD) method which is one kind of solution method. The flat and vicinal (100) substrate (the miscut angle $\phi = 5^\circ$ toward the direction [001]) of NdGaO$_3$ (NGO) was used. When using vicinal substrates, the Bi2212 (020) (or (200)) peak appeared clearly in the XRD patterns. 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 Bi2212 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 fabricated 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.

We are attempting to prepare (010) (or (100)) oriented Bi2212 thin films [7-9] for planar type intrinsic Josephson oscillator devices that are not required etching processes. These new type devices can be prepared by a combination of orientation control technique of Bi2212 thin film by metal-organic decomposition (MOD) method and application of raw material solution by printing method. In order to prepare planar type devices, it is necessary to form a current path parallel to the substrate, so that the c-axis of Bi2212 is required to be parallel or incline to the substrate. In addition, if the c-axis is parallel to...
the substrate, no c-twinning structure is formed (c-twinning structure is not preferable for preparing IJJ devices).

Bi2212 is an orthorhombic crystal having a lattice constant of \(a = 5.414 \, \text{Å}, b = 5.418 \, \text{Å}, c = 30.6 \sim 30.9 \, \text{Å}\) [10,11]. NdGaO\(_3\) (NGO) is also orthorhombic with lattice constants \(a = 5.427 \, \text{Å}, b = 5.497 \, \text{Å}, c = 7.707 \, \text{Å}\) [12]. The length of the \(a\)-axis of Bi2212 is approximately equal to the length of the \(a\)-axis of NGO, and that of \(c\)-axis of Bi2212 is approximately equal to four times that of \(c\)-axis of NGO. Since these values are very close, it is expected that lattice matching occurs well and Bi2212 will be epitaxially grown. Actually, we succeeded in growing (010) (or (100)) oriented Bi2212 crystal grains [9]. However, (11\(n\)) oriented crystal grains are also formed, which is a problem to be solved.

In this study, we report fabrication Bi2212 thin films by the MOD method using vicinal NGO (100) substrates with the size of 10 × 10 × 0.5 mm and the miscut angle \(\phi = 5^\circ\) toward the direction \([001]\). 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 MOD method using a stoichiometric BSCCO metal organic (MO) solution (supplied by Kojundo Chemical Lab. Co., Ltd. SK-BSCCO008). Substrates used were flat and vicinal NGO (100) substrates with the size of 10 × 10 × 0.5 mm and the miscut angle \(\phi = 5^\circ\) toward the direction \([001]\). In the following, the flat substrates were expressed as \(\phi = 0^\circ\). Preparation procedures were as follows [8]:

1. An amount of 6μℓ BSCCO MO solution was dropped onto substrates using a digital micropipette.
2. The dropped solution was spin-coated by a 2-step process with 500 rpm for 5 sec and 3000 rpm for 1 min.
3. The spin-coated films were dried at 120 °C for 40 min.
4. The dried films were annealed at temperature \(T_a\) for time \(t_a\) in \(O_2\) or Air atmosphere.
5. Furnace cooling were carried out.

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) shows the temperature profile of a box furnace corresponding to the above steps (3) ~ (5). In this paper, annealing time \(t_a\) is 60 min. When setting the \(O_2\) atmosphere, 100% \(O_2\) gas was kept flowing to the box furnace from the start of annealing. The preparation condition of the samples is shown in Table 1. The crystal structures of the samples were investigated by \(\theta\)-2\(\theta\) XRD patterns with CuK\(\alpha\) radiation (\(\lambda = 1.54 \, \text{Å}\)). In addition, the XRD pattern of the flat and vicinal NGO (100) substrates were also measured for reference.

The coordinate system was defined as shown in the figure 1(b). The \(x\)- and \(z\)-axis were parallel to the NGO [010] direction and the normal direction of the NGO substrate, respectively. X-rays were irradiated along with the \(x\)-axis, which was within the \(xz\) plane. The surface morphologies were observed by SEM.

![Figure 1](image-url)

**Figure 1.** (a) Temperature profile of a box furnace. (b) Schematic drawing of NGO substrate and X-ray irradiate direction. \(\phi\) is the miscut angle toward the direction [001].
### Table 1. Summary of sample labels and their annealing conditions.

| Sample label | Miscut angle $\varphi$ (°) | Annealing temperature $T_a$ (°C) | Atmosphere |
|--------------|-----------------------------|----------------------------------|-------------|
| N0-780-60    | 0                           | 780                              | O$_2$       |
| N5-780-60    | 5                           | 780                              | O$_2$       |
| N0-810-60    | 0                           | 810                              | O$_2$       |
| N5-810-60    | 5                           | 810                              | O$_2$       |
| N0-810-60-a  | 0                           | 810                              | Air         |
| N5-810-60-a  | 5                           | 810                              | Air         |

### 3. Result and Discussion

Figure 2 shows a comparison of the observed surface morphologies by SEM with different conditions ((a) N0-780-60, (b) N5-780-60, (c) N0-810-60, (d) N5-810-60, (e) N0-810-60-a, (f) N5-810-60-a). From the viewpoint of lattice matching, elongated plate-like crystal grains (as surrounded by broken line in the figure (a)) are considered to be (010) (or (100)) oriented crystal grains. From these figures, it can be seen that the (010) (or (100)) oriented crystal grains are most abundant when annealed at 780 °C using the vicinal substrate.
Figure 2. The observed surface morphologies by SEM of samples with different conditions ((a) N0-780-60, (b) N5-780-60, (c) N0-810-60, (d) N5-810-60, (e) N0-810-60-a, (f) N5-810-60-a). In figure (a), elongated crystal grains in the lateral direction in the part surrounded by the white broken line is considered to be the Bi2212 (010) (or (100)) oriented grain. The white solid arrow indicates the c-axis direction of the grain.

Figure 3 shows comparison of XRD patterns of samples with different conditions. (a) ~ (f) of figure 3 correspond to (a) ~ (f) of figure 2, respectively. Only peaks of Bi2212 phase and NGO substrates appeared in these XRD patterns. In comparison of XRD patterns of samples with different substrates types, the (11n) peak of Bi2212 tends to become smaller in the case of using vicinal NGO (100) substrates. In the XRD patterns of flat NGO (100) substrates, NGO (200) peaks appeared on 2θ = 33° whereas no peak appeared on the XRD pattern of the vicinal NGO (100) substrates.

In the figure (a), (c) and (e), the peaks appeared on 2θ = 33°. They are considered to overlap NGO (200) and Bi2212 (020) (or (200)) peaks. In contrast, the peaks appeared on 2θ = 33° in the figure (b), (d) and (f), are considered to be Bi2212 (020) (or (200)) peaks. Because in the XRD pattern of the vicinal NGO (100) substrates no peaks appeared. From these figures, it can be seen that the (010) (or (100)) oriented crystal grains are most abundant when annealed at 810 °C in O2 atmosphere using the vicinal substrate.

Figure 3. θ-2θ XRD patterns of samples with different conditions ((a) N0-780-60, (b) N5-780-60, (c) N0-810-60, (d) N5-810-60, (e) N0-810-60-a, (f) N5-810-60-a).

Figure 4 show schematic views (imaginary views) of lattice matching for Bi2212 and NGO substrate. 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. (b) is a view from NGO [010] direction of a thin film prepared on a vicinal substrate. Since the crystal grains of Bi2212 grow to extend in the ab plane direction, it is considered that the (010) (or (100)) oriented grains become elongated in the a-axis (or b-axis) direction along step edges of vicinal substrate.
4. Conclusion

In order to realize fabrication of (010) (or (100)) oriented thin film that can be used for Bi2212 IJJ device by printing method, we attempted to fabricate (010) (or (100)) oriented thin film by MOD 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 substrates types, when using vicinal substrates, the \((11n)\) peak of Bi2212 tends to become smaller, and the \((020)\) (or \((200)\)) peak of that appeared clearly.

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 have succeeded in growing Bi2212 \((010)\) (or \((100)\)) crystal grains occupying larger proportion by using vicinal NGO (100) substrates. However, the conditions under which the \((010)\) (or \((100)\)) oriented crystal grains became the most abundant were different from those suggested from the SEM images and the XRD patterns. Furthermore, the SEM images show that \((11n)\) oriented crystal grains still occupy a large proportion. They are problems to be clarified in the future.

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