



27th International Symposium on Superconductivity, ISS 2014

Preparation of (11*n*) Oriented Bi₂Sr₂CaCu₂O_{8+x} thin films by the metal-organic decomposition method

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Abstract

We report on the preparation of (11*n*) oriented thin films of Bi₂Sr₂CaCu₂O_{8+x} (Bi2212), which were fabricated by the metal-organic decomposition method on SrTiO₃ (110) and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. By controlling the post-deposition annealing condition (temperature 640 °C ≤ *T*_a ≤ 780 °C and time 30 min ≤ *t*_a ≤ 120 min), films with only the Bi2212 (117) XRD peak were obtained under the condition *T*_a = 780 °C and *t*_a = 30 min. Furthermore, by forming films with a double-layer structure, films are found to have better crystallinity. Film properties are discussed on basis of SEM and resistivity measurements.

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Peer-review under responsibility of the ISS 2014 Program Committee

Keywords: Bi2212; (11*n*) oriented; in-plane anisotropy; MOD method; thin films

1. Introduction

The oscillator using intrinsic Josephson junctions of Bi₂Sr₂CaCu₂O_{8+x} (Bi2212) is considered to be a promising device that fills the frequency domain called the "terahertz gap". It has already been proved that the μW class continuous coherent terahertz wave can be oscillated [1]. The major preparation methods thus far reported on the Bi2212 intrinsic Josephson junction device require complicated procedures, such as the etching process of *c*-axis oriented Bi2212 thin films in the depth direction. However, if non-*c*-axis oriented thin films are used, it would be possible to prepare the planar type device without the etching in the depth direction.

The metal-organic decomposition (MOD) method is attractive as one of the useful preparation techniques. It has been reported that, using this method, high quality *c*-axis oriented Bi2212 thin films on SrTiO₃ (STO) (100) substrates have been prepared by controlling only the post-depositing conditions [2, 3]. It is also expected that the crystal orientation is controllable by selecting a suitable substrate [4, 5]. In this study, we report on the preparation of MOD Bi2212 thin films with the (11*n*) orientation using STO (110) substrates, and characterization by measurements of the X-ray diffraction (XRD), scanning electron microscopy (SEM) and resistivity measurements.

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2. Experimental

Bi2212 thin films under study were prepared by the MOD method using a stoichiometric Bi-Sr-Ca-Cu-O metal organic (MO) solution purchased from Kojundo Chemical Lab. Co., Ltd.. Substrates used are STO (110), the size of which is 10 mm × 10 mm × 0.5 mm t. Preparation procedures are as follows [3]:

- (1) 6 μ l Bi-Sr-Ca-Cu-O 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 in a thermostat chamber at 120 °C for 40 min.
- (4) The films were annealed in a box furnace at a fixed temperature T_a for an annealing time t_a in O₂ atmosphere.

The annealing started at T_a directly and cooling was carried out naturally. When depositing the second layer of the thin film, the above steps are repeated. The crystal structures of the annealed thin films were investigated by XRD measurements. The surface morphologies were observed by SEM. The resistive transition (RT) curves were measured using the dc four-terminal method in a cryostat. Summary of sample labels and their annealing conditions is shown in Table 1. Sample S780c2 only has a double-layer structure, while the others have single-layer structures.

Table 1. Summary of sample labels and their annealing conditions. *1 and *2 represent conditions in the bottom layer and the top layer, respectively.

Sample label	Annealing temperature T_a [°C]	Annealing time t_a [min]
S640a	640	120
S690a	690	120
S720a	720	120
S750a	750	120
S780a	780	120
S780b	780	60
S780c	780	30
S780c2	780 *1	30 *1
	810 *2	120 *2

3. Results and discussion

3.1. XRD patterns

Figures 1 (a) and (b) show a comparison of the XRD patterns in our samples with different annealing temperatures $T_a = 690$ °C and 780 °C for a fixed annealing time $t_a = 120$ min. The diffraction peak of Bi₂Sr₂CuO_{6+x} (Bi2201) (115) is observed at $2\theta = 29.8^\circ$ as indicated by asterisk (*), which is commonly observed in samples with 640 °C $\leq T_a \leq 750$ °C. On the other hand, when the annealing was carried out at $T_a = 780$ °C, the diffraction peak of Bi2212 (117) appears at $2\theta = 31.0^\circ$ as indicated by open circle (○), no such peak being observed in samples prepared under the annealing conditions 640 °C $\leq T_a \leq 750$ °C and $t_a = 120$ min. It is found that the intensity of Bi2201 (115) peak tends to vanish with decreasing t_a as displayed in Fig. 1 (c) for the sample S780c. Therefore, the condition $T_a = 780$ °C for $t_a = 30$ min is most preferable among the annealing processes listed in Table 1. By adopting the double-layer structure, we have eventually obtained samples showing no evidence of the Bi2201 (115) XRD peak, a typical data of which are displayed in Fig. 1 (d).

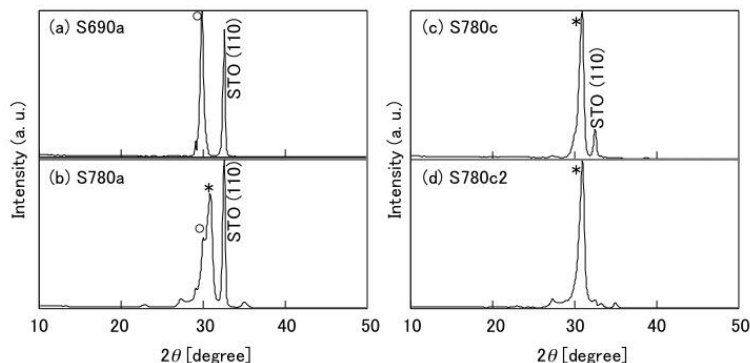


Fig. 1. XRD patterns of samples (a) S690a, (b) S780a, (c) S780c and (d) S780c2. The open circles (○) and asterisks (*) indicate the diffraction peaks of Bi2201 (115) and Bi2212 (117), respectively.

3.2. SEM images

Figure 2 shows SEM images (x15000) of samples (a) S780c and (b) S780c2. The arrows in Figs. 2 (a) and (b) represent the Bi2212 $[1\bar{1}0]$ direction. Crystal grains with stripe-like structures can be observed in both of the samples. The grains with such structures exist only partially in Fig. 2 (a), whereas those are grown over the entire region of Fig. 2 (b). Judging from the results for XRD patterns, these crystal grain structures are regarded as being the Bi2212 (117) orientation. According to Refs. [4] and [5], Bi2212 $[1\bar{1}0]$ direction is assumed to be the direction of the stripe-like structure. A top view of the lattice matching for Bi2212 (117) and STO (110) substrate planes is illustrated in Fig. 2 (c). The lattice constants of Bi2212 are assumed to be $a = b = 5.4 \text{ \AA}$, $c = 30.8 \text{ \AA}$, and those of STO are assumed to be $a = b = c = 3.9 \text{ \AA}$, respectively. Therefore, mismatch in the lattice constant of Bi2212 (117) with respect to the substrate is -2.2% for the STO $[001]$ direction of the substrate and that for the STO $[\bar{1}10]$ direction is $+5.6\%$. In Fig. 2 (d) we show a side view of Bi2212 crystals from the Bi2212 $[1\bar{1}0]$ direction, from which the c -axis of Bi2212 is regarded to be inclined by approximately 49° from the normal direction of substrate. The c -axis of Bi2212 is perpendicular to the STO $[001]$ direction, and this structure is considered to form a random twin structure.

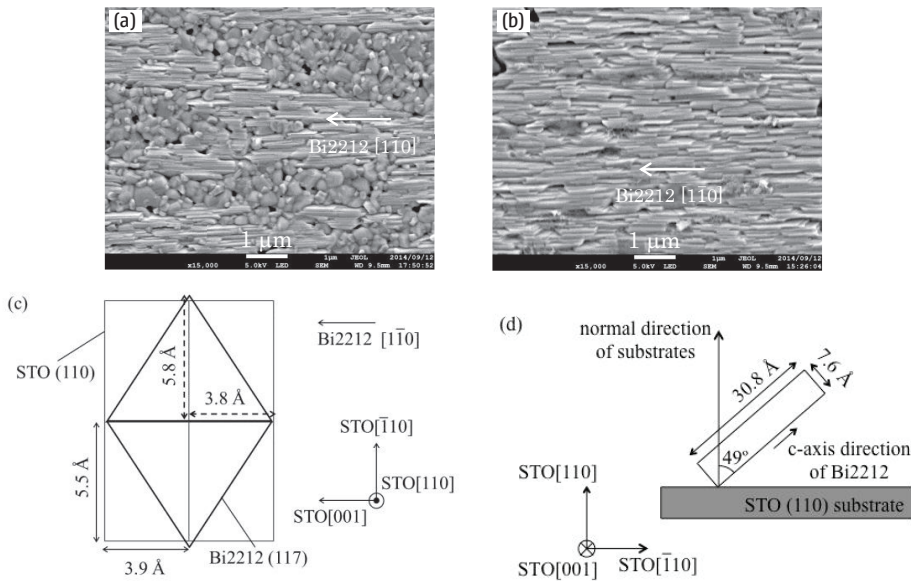


Fig. 2. SEM images (x15000) of surface morphology of samples (a) S780c and (b) S780c2. The arrows along the stripe-like structures indicate the direction of Bi2212 $[1\bar{1}0]$, which is along STO $[001]$. (c) Schematic drawing of a top view of the lattice matching for Bi2212 (117) and STO (110) substrate planes. (d) Schematic drawing of a side view of the Bi2212 unit cell from the $[1\bar{1}0]$ direction.

3.3. RT curves

For the representation of RT data, we use the sheet resistance rather than the resistivity since the dimensions of the sample area where the measuring current flows is not exactly known. Figure 3 shows RT curves measured (a) along the Bi2212 $[1\bar{1}0]$ direction shown in Fig. 2 (b) for which the sheet resistance is referred to as R_s^a and (b) along its perpendicular direction as R_s^b . Room-temperature values of the sheet resistance in sample S780c2 are $R_s^a = 0.27 \text{ \Omega/sq.}$, and $R_s^b = 910 \text{ \Omega/sq.}$. The large difference in these resistance values is originated from the stripe-like structure of the film. The RT data in Fig. 3 (a) show a double transition behavior with the resistance drops at about $T = 80 \text{ K}$ and 40 K , between which the RT exhibits a semiconducting feature. The reason of this strange variation would be deduced that the film is composed of metallic grains with semiconducting grain boundaries. On the other hand, the RT data in Fig. 3 (b) shows a monotonous transition, which is considered that ab -plane of adjacent crystal grains are connected by grain boundaries, because it forms the twin structure. Furthermore, since the lattice mismatch is large, it is considered that the crystal grains with each other are connected only partially, and as a result resistance is much larger.

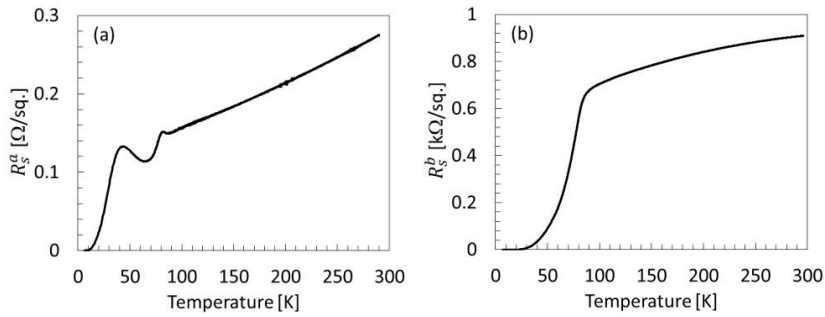


Fig. 3. RT curves of (a) along the Bi2212 $[1\bar{1}0]$ direction and (b) along perpendicular direction of Bi2212 $[1\bar{1}0]$.

4. Conclusion

A trial study has been presented for fabricating Bi2212 films with $(11n)$ orientation, using the conventional MOD method. By changing annealing conditions, films with Bi2212 (117) orientation have been obtained under the conditions $T_a = 780$ °C and $t_a = 30$ min. The crystalline properties are found to be improved by the deposition of another MOD layer forming a double-structure. The SEM study has been used to characterize the film morphology, demonstrating a stripe-like structure. The resistive data may lend support to the existence of the stripe-like structure.

Acknowledgements

This study was partly supported by Grant-in-Aid for Cooperative Education and Research among Nagaoka University of Technology and National Institute of Technology, Oyama College.

References

- [1] L. Ozyuzer, A. E. Koshelev, C. Kurter, N. Gopalsami, Q. Li, M. Tachiki, K. Kadowaki, T. Yamamoto, H. Minami, H. Yamaguchi, T. Tachiki, K. E. Gray, W.-K. Kwok, U. Welp, *Science* 318 (2007) 1291-1293
- [2] H. Iwasaki, S. Machikawa, S. Yufune, T. Ishibashi, K. Sato, *IEEE Trans. Appl. Supercond.* 15 (2005) 3058-3061
- [3] Y. Deguchi, H. Kikuchi, N. Mori, Y. Yamada, T. Atsumi, K. Yoshida, T. Ishibashi, *Physics Procedia* 45 (2013) 193-196
- [4] K. Kuroda, K. Kojima, O. Wada, M. Tanioku, K. Yokoyama, K. Hamanaka, *Jpn. J. Appl. Phys.* 29 (1990) L1816-L1818
- [5] K. Kuroda, O. Wada, K. Kojima, J. Tanimura, M. Kataoka, T. Takami, K. Yokoyama, T. Ogawa, K. Hamanaka, *Jpn. J. Appl. Phys.* 30 (1991) L475-L477