

Epitaxial Growth of BSCCO Thin Films Fabricated by Ion Beam Sputtering

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Abstract

BSCCO thin film is fabricated via both processes of co-deposition and layer-by-layer deposition at an ultralow growth rate using ion beam sputtering method. The adsorption of Bi atom and the appearance of Bi-2212 phase shows large difference between both processes. It is found that the resident time of Bi vapor species on the surface of the substrate strongly dominates the film composition and the formation of the structure.

1. Introduction

In previous study, high quality of c-axis oriented Bi-2201 film has been successfully fabricated by layer-by-layer deposition at an ultralow growth rate of 0.13 nm/min using ion beam sputtering(IBS) method[1]. It was found that SrBi_2O_4 structure is easy to precipitate as impurity in layer-by-layer deposition and that this impurity plays a role in alleviating the misfit between Bi-2201 structure and substrate. In this report, we try to ascertain why the impurity phase such as SrBi_2O_4 precipitates in layer-by-layer deposition and to fabricate only Bi-superconductor phase. The comparison between two different processes of co-deposition and layer-by-layer deposition for fabrication of Bi-2212 thin film has been studied using ion beam sputtering method. Notice that clear discrimination between growth rate and deposition rate is expressed in this paper.

2. Experimental

The equipment for layer-by-layer deposition to fabricate Bi-2212 thin film has been reported previously[1]. In order to fabricate Bi-2212 thin film, sputtering time of each target was re-investigated. Sputtering times of SrO and Cu elements were fixed at 84 and 81 sec, respectively. These sputtering times are determined from comparison between total atom numbers adsorbing on the substrate and total ideal atom numbers. Total ideal atom numbers are calculated multiplying total deposition cycles for each element by atom numbers(6.86×10^{14}), which is estimated from dividing substrate area($10 \times 10 \text{ mm}^2$) by the area of ab-plane($0.382 \times 0.382 \text{ nm}^2$) at one unit of c-axis oriented Bi-2212 structure. Sputtering times of Bi and Ca elements were varied between 35 and 565 sec for one (Bi-O) network layer and 120 and 270 sec for Ca layer, respectively. Averaged growth rate for fabrication of Bi-2212 films was

in the range from 0.05 to 0.15 nm/min. SrTiO₃ was used as a substrate and the substrate temperature was held at 780 °C. Ozone gas which highly condensed by the silica gel adsorption method was employed as an oxidation gas and the ozone gas pressure was kept at 5×10^{-5} Torr[2].

A system for co-deposition was newly equipped as shown in Fig. 1. Four sets of cold-cathode type and saddle-field type ion guns were manufactured at handmade, and the respective targets of Bi, Sr, Ca and Cu metals were set by 30 nm apart from the respective guns. The amount of Ar⁺ ion beam generated from the ion gun is so precisely controllable by the ion current that the atom numbers of the sputtered metal are yielded in proportional to ion current as shown Fig. 2.

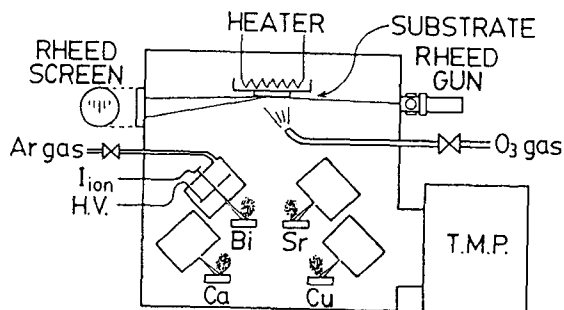


Fig. 1. The apparatus for co-deposition.

The current of each ion beam gun optimized as matching constituent ratio for Bi-2212 films. The growth rates of the films was set in the region from 0.17 to 0.27 nm/min. MgO(100) was used as a substrate. In order to appreciate stable existing region of Bi-2212 phase with temperature and ozone pressure, the substrate temperature was varied between 650 and 820 °C and the highly condensed ozone gas pressure (PO₃) in vacuum chamber was varied between 2

$\times 10^{-6}$ and 5×10^{-5} Torr.

The crystal structure and the composition for the obtained film was checked by X-ray diffractometer(XRD) and energy dispersive X-ray spectrometer(EDX), respectively. The absolute atom numbers of the respective elements were evaluated by inductively coupled plasma (ICP) emission analyzer.

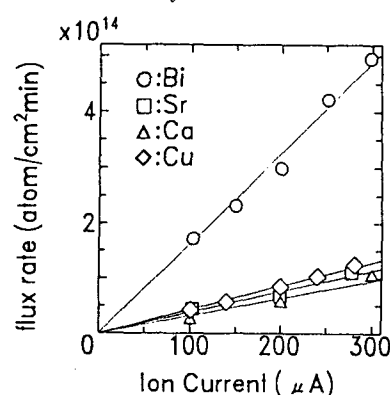


Fig. 2. The relation between the flux rates of the respective elements sputtered by ion gun and the ion current.

3. Results and discussion

3.1. Layer-by-layer deposition

Typical XRD patterns of the films fabricated by layer-by-layer deposition and co-deposition are shown Fig. 3(a) and (b), respectively. Co-deposition is in detail discussed in the following section. In layer-by-layer deposition only a Bi-2201 phase with poor crystallinity was obtained in spite of the sputtering adjusted to Bi-2212 composition, and SrBi₂O₄ frequently coexisted as impurity partly. To make matter worse, only a quite weak and broad XRD pattern was observed in some films owing to inadequate condition. Deposition time for one half unit cell in this sputtering method takes as long as 1200 sec and is much longer than those reported by the other means, which takes from

35 to 60 sec[4-5]. Partial reaction is easy to take place in such an ultralow growth rate and leads to formation of the other phase without a strict fabrication condition. When impurity phase precipitates, remarkable deficiency of Bi atom numbers occurs. Whereas, the atom numbers or compositional ratios of the other elements were correctly included into thin film as expected. This implies that the structural formation is strongly governed by the adsorption of Bi element.

Thus, to realized the Bi-2212 composition, sputtering time of Bi target was examined between 35 and 565 sec. The ratio for Bi element between the adsorbed atom numbers and total ideal atom numbers is plotted against deposition time(t) at one (Bi-O) network layer in Fig. 4. The amount of the adsorbed Bi element increases with t to about 70 sec sputtering, and it decreases over 70 sec. Consequently, only 30 % of the ideal Bi atom numbers reached at maximum.

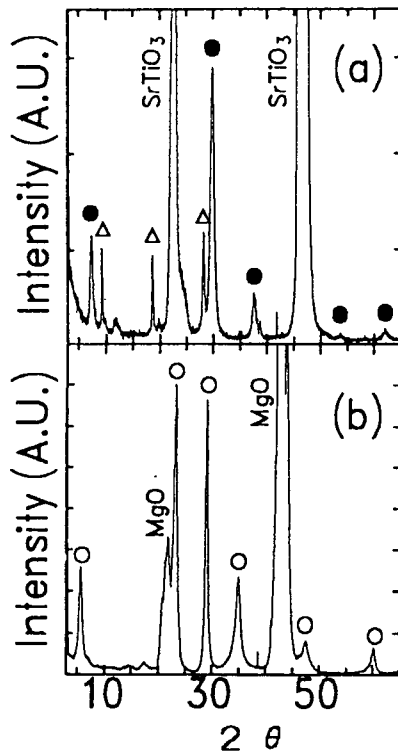


Fig. 3. Typical XRD pattern.
 (a) layer-by-layer deposition
 (b) co-deposition
 ● : Bi-2201
 △ : SrBi₂O₄
 ○ : Bi-2212

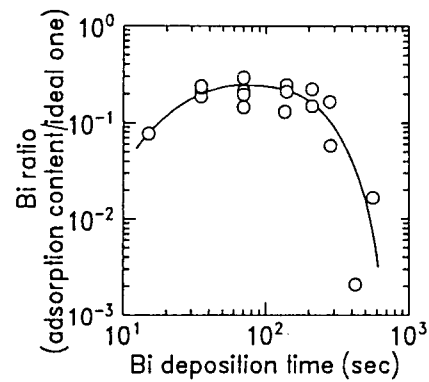


Fig. 4. Deposition time vs. Bi ratio.

It is ascertained that several species of Bi_mO_n molecules are vaporized from Bi₂O₃[3]. This denotes that most of Bi vapor species constantly re-evaporates from substrate even in the course of deposition. Therefore, only 30 % of them at maximum can combine with substrate or the lower Sr-O layer through the formation of Bi-O bonds. However, combination of their Bi-O layer with the lower layer is not stable, so that its adsorbent has a finite resident time. At 70 sec sputtering their re-evaporation rate is in comparable to the deposition one and over 70 sec sputtering the resident time would reach to saturate. Namely, the resident of the adsorbed Bi-O vapor species is inferred to be as long as 70 sec.

3.2. Co-deposition

XRD pattern of thin film fabricated at 795 °C under 1×10^{-5} Torr by the co-deposition is shown Fig. 3(b). High quality of c-axis oriented Bi-2212 thin film with $T_c(\text{onset})$ of about 80 K and $T_c(\text{offset})$ of about 45 K is obtained. Only a small amount of CuO in some films was observed as impurity, and no impurity phase such as SrBi_2O_4 was observed in all of the obtained films. Dependence of phase diagram on PO_3 and temperature is arranged in Fig. 5. The distinguished variation in structural formation is observed with temperature. Bi-2212 phase appeared in the temperature range of 755 and 795 °C and single phase of Bi-2201 existed in the lower region than 785 °C. Only amorphous-like phase was observed over 810 °C. Whereas, PO_3 dependence on structural formation was scarcely observed regardless of the pressure variation between 2×10^{-6} and 2×10^{-5} Torr. This would be due to ample supply of ozone gas with strong oxidation power even under 2×10^{-6} Torr. It is noticeable that the quality of the thin film was inclined to be improved as PO_3 decreases.

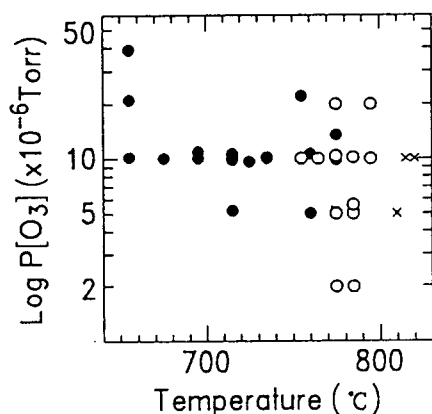


Fig. 5. Phase diagram against temperature and $\log \text{PO}_3$.
 (○:Bi-2212 (+Bi-2201), ●:Bi-2201 and
 ×:amorphous-like phase)

3.3. Comparison between co-deposition and layer-by-layer deposition

The growth rate of co-deposition is a little faster than that of layer-by-layer deposition, but their growth rates are slower than those of other physical vapor depositions[4-5]. Comparing to both processes, clear difference of phase existing range in the obtained films is observed against PO_3 and temperature. In the ultralow growing layer-by-layer deposition, partial reaction to form the impurity phase such as SrBi_2O_4 is easy to occur, since (Bi-O) layer is sandwiched between the upper and the lower (Sr-O) layers. This SrBi_2O_4 is more stable energetically than BSCCO structure, therefore less stable BSCCO structure is difficult to construct on account of deficiency of Bi and Sr contents.

Moreover, the melting point of Bi metal is as low as 271 °C, while the bismuth oxide Bi_2O_3 have melting point at 824 °C, which is slight higher than substrate temperature. The re-evaporation amount as Bi atom or oxide Bi_mO_n increase, so that deficiency of Bi atom in the film easily takes place owing to long deposition time. Insufficient adsorption of Bi atom brings about the composition variation at the growing surface. Therefore, in the ultralow growing layer-by-layer deposition, surface composition changes gradually every deposition time. On the other hand, in co-deposition process the respective atom numbers corresponding to Bi-2212 is constantly supplied at the surface, so that Bi-2212 structure is formed. When the Bi atom with the other elements coalesces into island of Bi-2212 crystal structure, it would be stabilized and protected from the desorption. However, re-evaporation of Bi vapor species comes to be inevitable in higher temperature than 810 °C and the increase of PO_3 . This supports that structure formation would be determined by the adsorption power or the resident time of Bi vapor species. Nevertheless,

even in the film fabricated by co-deposition the Bi atom numbers was included less than half of the incident atom numbers expected from the ion current and deposition time. This would come from only a little amount of stable Bi vapor species with long resident time as described before.

Tazoh and Miyazawa reported about the improvement of film quality at the ultralow growth rate in the fabrication of Y-superconductor thin film using reactive co-deposition[6]. Accordingly, in the fabrication of Bi-superconductor at an ultralow growth rate, compensation of re-evaporation of Bi vapor species is indispensable, taking into the sticking coefficient of Bi vapor species consideration.

4. Conclusions

In ultralow growth rate the re-evaporation of Bi atom is easy to take place. When the re-evaporation rate is higher than the deposition rate, Bi deficiency easily occurs and leads to deviation of the surface composition in the layer-by-layer deposition. Consequently, it would become the cause of formation of the other stable phase.

Co-deposition process is more favorable to fabricate BSCCO thin film than layer-by-layer deposition. The sticking coefficient of Bi is less than half, so that the Bi-2212 structure would be promoted only by the constant supply at compensated compositional ratio.

References

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