Analysis of Bi-Superconducting Thin Films Fabricated by Using the Layer by Layer Deposition and Evaporation Deposition Method

Seung-Ho Yang* · Min-Woo Cheon* · Ho-Shik Lee* · Yong-Pil Park*
*Department of Hospital Biomedical Engineering, Dongshin University
E-mail : shyang@dsu.ac.kr

ABSTRACT

The BSCCO thin film fabricated by using the layer by layer deposition method was compared with the BSCCO thin film fabricated by using the evaporation method. Reevaporation in the form of Bi atoms or Bi_2O_3molecules easily bring out the deficiency of Bi atoms in thin film due to the long sputtering time of the layer by layer deposition. On the other hand, the respective atom numbers corresponding to BSCCO phase is concurrently supplied on the film surface in the evaporation deposition process and leads to BSCCO phase formation. Also, it is cofirmed that by optimizing the deposition condition, each single phase of the Bi2201 phase and the Bi2212 phase can be fabricated, the sticking coefficient of Bi element is clearly related to the changing of substrate temperature and the formation of the Bi2212 phase.

Key word

BSCCO Thin Films, Layer by Layer Deposition, Evaporation Deposition Method.

I . Introduction

For various applications to electric devices as well as for fundamental study, it is indispensable to fabricate high quality superconducting thin film with a higher transition temperature(T_c). Nowadays, such techniques as Rf magnetron sputtering, laser ablation and MBE techniques have been employed to prepare superconducting thin films. However, the quality of thin film has not yet reachedthe level needed for the application to electric devices in contrast to that of semiconductors. Recently, it is interesting that Tazoh and Miyazawa[1] reported that the quality of their thin film in YBCO superconductor was improved at the ultra low growthrate by the co deposition. The ultra low growth rate might be an essential factor for obtaining high quality thin film. Accordingly, the BSCCO thin film fabrication is carried out using the ion beam sputtering(IBS) method, noticing that $Bi_2Sr_2Ca_nCu_{n+1}O_y(n \geq 0$; BSCCO) superconductor changes from an insulator to a superconductor with T_c=110 K according to the number of [CuO_2] layer.

Moreover, since BSCCO superconductor has large anisotropy and two dimensionality, it is suitable for fabrication by layer by layer deposition. The IBS method we employed is at an ultra law growth rate of about 0.1 nm/min, so that a similar thin film fabrication as that of Tazoh Miyazawa is expected to occur.

As a first step, we examined the quality difference of BSCCO superconducting thin film fabricated by the two different ion beam sputtering techniques of the evaporation deposition and the layer by layer deposition at an ultra law growth rate.

II Experimental

The BSCCO thin films are fabricated by using the layer by layer deposition[2] and evaporation deposition[3] method at ultra low growth rate. The relation between the sputtering Ar ion current and the flux of each atom species that arrived onto the substrate was estimated beforehand using a quartz

oscillation monitor installed at the substrate position at room temperature. Figure 1 shows a schematic diagram of the layer by layer deposition system. Each of the targets was sputtered in order of Bi→Sr→Cu→(Ca→Cu)→Sr→Bi sequentially. We denote this one cycle as 1 unit hereafter. Compositional analysis and total atom numbers were examined by energy dispersive X ray spectrometer(EDX) and inductively coupled plasma (ICP) photoemission spectroscopy, respectively.

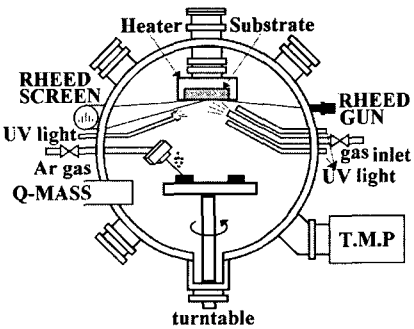

Fig. 1. Schematic diagram of the layer by layer system.

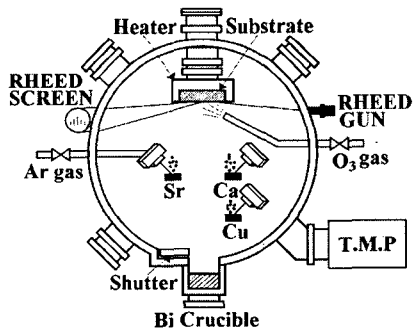

Fig. 2. Schematic diagram of the evaporation system.

Figure 2 shows a schematic diagram of the evaporation system and an effusion cell employed. Metal targets of Sr, Ca and Cu were simultaneously sputtered by Ar ion or atom beans generated by saddle field type cold cathode guns. The substrate temperature was kept at a constant value between 600 and 705 ℃. Highly condensed ozone gas was obtained by a silica gel adsorption method[4]and was supplied onto the substrate during deposition of the metallic species to provide an oxidation environment.

Each condition for thin film fabrication was summarized in Table 1.

Table 1. Deposition conditions in the layer by layer deposition and the evaporation deposition.

	Layer by Layer Deposition	Evaporation Deposition
Substrate	$SrTiO_3$(100)	MgO(100)
Substrate temperature	780 ℃	660~720 ℃
Ozone pressure	5×10^{-5} Torr.	$1\sim20\times10^{-6}$Torr
Target	Bi, SrO Ca, Cu	Sr, Ca, Cu

III. Results and Discussion

1. Layer-by-Layer Depositiont

Typical XRD patterns of the films fabricated by layer by layer deposition is shown Figure 3. In the 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 $SrBi_2O_4$ frequently coexisted as impurity partly. To make matters 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 1,200 sec and was much longer than those reported by the other means, which takes from 35 to 60 sec[5-7]. Partial reaction is easy to take place in such an ultra low growth rate and leads to formation of the other phase without a strict fabrication condition. When impurity phase precipitates, considerable 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.

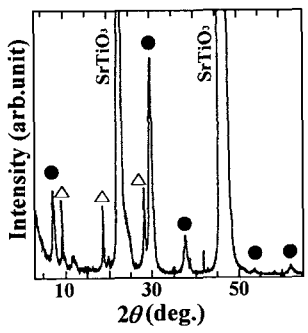

Fig. 3. Typical XRD patterns of the films fabricated by layer by layer deposition.

Thus, to realize 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 up to about 70 sec sputtering, and it decreases over 70 sec. Consequently, only 30% of the ideal Bi atom numbers reached at maximum.

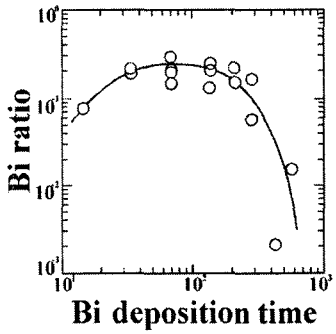

Fig. 4. Bi deposition time vs. Bi ratio.

It is ascertained that several species of Bi_mO_n molecules are vaporized from Bi_2O_3. This implies that most of Bi vapor species constantly re-evaporates from substrate even in the process of deposition. Therefore, at most 30 % of them 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 was comparable to the deposition one and over 70 sec sputtering the resident time would reach a saturation. Hence, the resident time of the adsorbed Bi-O vapor species can be inferred to be as long as 70 sec.

2. Evaporation Depositiont

Even in the high substrate temperature re evaporating Bi element alot, to get a stable element molecular, Bi element was supplied by the evaporation method using the faraday cup. Figure 6 represented the characteristics of the faraday cup. The vapor atoms spouted in the chamber can be regarded as molecular flow, the distribution is determined by the distribution of the plain evaporation source. In this case, the intensity of the molecular beam from the faraday cup becomes only the function of the temperature and does not rely on the quantity of the material in the faraday cup[8]. Therefore, by the fine temperature control, the stable supply of Bi element is always possible, and the excellent control equal to Ar ion bean gun can be realized. The quantity of evaporation By using the faraday cup could be 10~100 times as much as that by using the sputtering method.

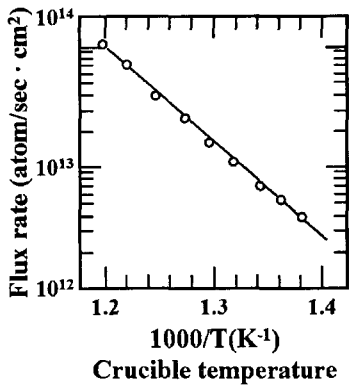

Fig. 5. Characteristics of faraday cup.

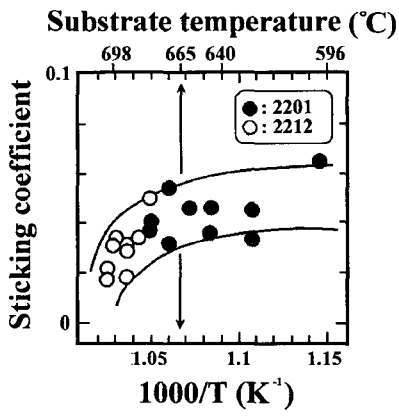

Fig. 6. Sticking characteristics of Bi element in the $Bi_2Sr_2Ca_nCu_{n+1}O$ thin films fabricated by using the evaporation method.

Thus, in this case, the review on the dependence on the substrate temperature of the sticking coefficient of the Bi element and the result of that are represented in Figure 6. In Figure 6, ○ indicates the formed thin film of Bi2212 phase and ● indicates that of Bi2201.

Figure 7 represents the XRDpattern of formed thin film. Figure 7 (a) is the pattern comparing the Bi2201 phase with the mixing phase of Bi2212 and both of them are orientational to the C axis, and as

a impurity phase, a little bit CuO can be shown. The peak intensity of this impurity phase (CuO) is increasing as much as the deposition environment transfer to the axes of the low temperature and the low pressure. This is thought that because the composition of the thin film is Bi2212, in case that Bi2201 is formed, the excess Ca and Cu in the thin film form and depose the compound. Figure 7 (b) is the XRD pattern of the formed thin film of the Bi2212 phase. In either case, it can be known that each one is the the Bi2212 single crystal film orientational to c axis and this case is also that a little bit CuO peak grow in the deposed thin film on the condition of the low temperature and the low pressure.

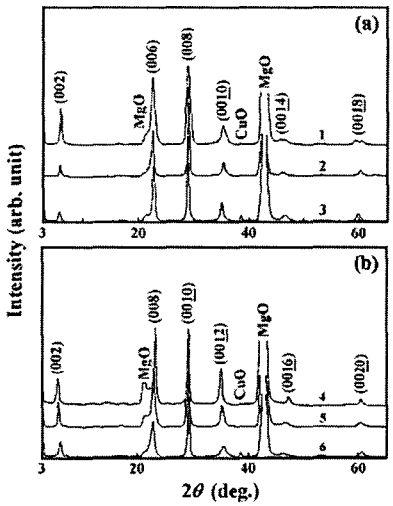

Fig. 7. XRD patterns of the obtained thin films. (a) Bi2201/Bi2212 formation (b) Bi2212 formation.

IV. Conclusions

The BSCCO thin film fabricated by using the layer by layer deposition method was compared with the BSCCO thin film fabricated by using the evaporation method. Reevaporation in the form of Bi atoms or Bi_2O_3molecules easily bring out the deficiency of Bi atoms in thin film due to the long sputtering time of the layer by layer deposition. Bi deficiency leads to compositional deviation on the substrate surface,and to the formation of impurity compounds.

On the other hand, the respective atom numbers corresponding to BSCCO phase is concurrently supplied on the film surface in the evaporation deposition process and leads to BSCCO phase formation. Also, it is cofirmed that by optimizing the deposition condition, each single phase of the Bi2201 phase and the Bi2212 phase can be fabricated, the sticking coefficient of Bi element is clearly related to the changing of substrate temperature and the formation of the Bi2212 phase. It was found out that evaporation deposition process is more favorable to fabricate BSCCO thin films than layer by layer deposition.

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