XRD Patterns and Bismuth Sticking Coefficient in $Bi_2Sr_2Ca_nCu_{n+1}O_y$(n≥0) Thin Films Fabricated by Ion Beam Sputtering Method

Seung-Ho Yang and Yong-Pil Park, *Member, KIMICS*

Abstract—$Bi_2Sr_2Ca_nCu_{n+1}O_y$(n≥0)thin film is fabricatedvia two different processes using an ion beam sputtering method i.e. co-deposition and layer-by-layer deposition. A single phase of Bi2212 can be fabricated via the co-deposition process. While it cannot be obtained by the layer-by-layer process. Ultra-low growth rate in our ion beam sputtering system brings out the difference in Bi element adsorption between the two processes and results in only 30% adsorption against total incident Bi amount by layer-by-layer deposition, in contrast to enough Bi adsorption by co-deposition.

Index Terms—$Bi_2Sr_2Ca_nCu_{n+1}O_y$(n≥0)thin film, ion beam sputtering method, co-deposition, layer-by-layer de-position.

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(Tc). Nowadays, such techniques as rf-magnetron sputtering, laser ablation and molecular beam epitaxy(MBE) techniques have been employed to prepare superconducting thin films. However, the quality of thin film has not yet reached the 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 growth rate 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≥0;) super-conductor 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 co-deposition and the layer-by-layer deposition at an ultra-law growth rate.

II. EXPERIMENTAL

The equipment of the ion beam sputtering system used for the co-deposition and the layer-by-layer deposition has been already reported in detail elsewhere, respectively[2,3]. Thus, each condition for thin film fabrication was summarized in Table 1. First, single crystal MgO(100) was used as a substrate for the co-deposition, but $SrTiO_3$(100) was employed for the layer-by-layer deposition, taking account of the lattice matching with BSCCO structure.

Table 1 Sputtering conditions in the co-deposition and the layer-by-layer deposition.

	Co-deposition	Layer-by-layer deposition
System	Cold-cathode, saddle-field type gun	
	4 sets	1 set
Power of ion gun	6KV,150~30μA	7 KV, 300 μA
Target	Bi, Sr, Ca, Cu metal disk	
Substrate	MgO(100)	$SrTiO_3$(100)
Substrate temperature	700~800 □	600~800 □
Base pressure	2×10^{-8} Torr	
Ar pressure	$2\sim5\times10^{-5}$ Torr	
Ozone pressure	$2\times10^{-6}\sim5\times10^{-5}$ Torr	5×10^{-5} Torr
Distance between target-substrate	70~170 mm	70 mm
Sputtering rate	0.3 nm/min	0.1 nm/min

Crystal structure of the thin film obtained was examined by X-ray diffractometer(XRD) in the Bragg-Brentano geometry using Cu-Kα radiation.

Compositional analysis and total atom numbers were examined by energy dispersive X-ray spectrometer (EDX) and inductively coupled plasma (ICP) photoemission spectroscopy, respectively. Electric

---

Manuscript received November 20, 2006.

Seung-Ho Yang is with the Department of Hospotal BioMedical Engineering, Dongshin Uni-versity, Daeho-dong, Naju, Jeonnam, 520-714, Korea (Tel: +82-61-330-3217,Fax:+82-61-330-2909, Email: shyang@dsu.ac.kr)

Yong-Pil Park is with the Department of Hospotal BioMedical Engineering, Dongshin Uni-versity, Daeho-dong, Naju, Jeonnam, 520-714, Korea (Tel: +82-61-330-3207,Fax:+82-61-330-2909, Email:yppark@dsu.ac.kr)

resistivity was measured using a conventional four-probe method.

III. RESULTS AND DISCUSSION

Fig. 1(a)-(c) show typical XRD patterns of co-deposited (a) and the layer-by-lay deposited (b) and (c) thin film, respectively. Co-deposited thin film in Fig. 1(a) was fabricated at substrate temperature of 795。 C under an ozone pressure of 1×10^{-5} Torr. This thin film with a thickness of 0.4 nm formed a c-axis oriented Bi2212 phase, whose T_c(onset) was about 80 K and T_c(zero) was 45 K. Although a small amount of CuO was mixed as an impurity in several thin films, Bi2212 phase was formed in all of thin films fabricated in temperatures of 755 and 795。 C under ozone pressures of 2×10^{-6} and 2×10^{-5} Torr.

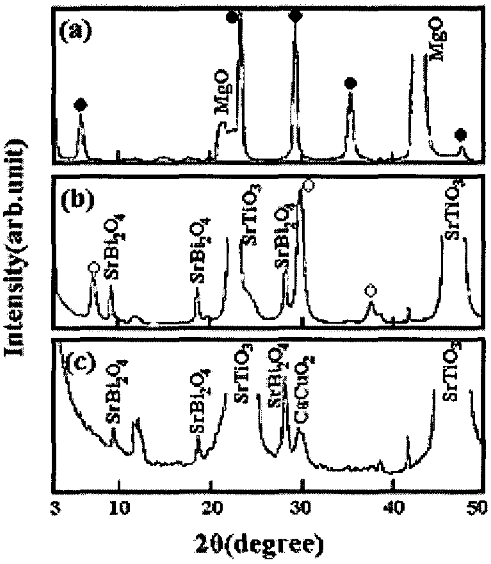


Fig. 1 XRD patterns of (a) co-deposited and (b), (c) layer-by-layer deposited thin film. Marks of ●,○,□ and □ indicate Bi2212, Bi2201, $SrBi_2O_4$ and, $CaCuO_2$ respectively.

On the other hand, Fig. 1(b) shows the XRD pattern of thin film fabricated by the layer-by-layer deposition at 780。 C under 5×10^{-5} Torr. In thin film with a thickness of 40 half unit cells, a Bi2201 phase and a-axis oriented $SrBi_2O_4$ impurity was observed, in contrast to the co-deposition. The sputtering times of the respective targets employed were 136 s for Bi, 84 s for Cu in the repetition order of Bi→Sr→Cu→Ca→Cu→Sr→Bi. In a similar way as Fig. 1(b) only Bi2201 phase with poor crystallinity appeared as a BSCCO compound in thin films ranging from 700 to 800。 C in spite of having sputtered to obtain Bi:Sr:Ca:Cu=2:2:1:2 composition by our ion beam sputtering system, and Bi2212 phase cannot be obtained under any conditions via the layer-by-layer deposition. Fig. 1(c) shows the XRD pattern of thin film fabricated under same conditions as Fig. 1(b) except for Bi-sputtering time of 270 s. BSCCO phase exhausts itself, and only quite weak and broad peaks caused by $SrBi_2O_4$ and $CaCuO_2$ impurities appear in thin film (refer to the height of base line level and the peak of $SrTiO_3$). This $SrBi_2O_4$ impurity tends to coexist with Bi2201 phase as the substrate temperature is lower. In addition, a broad peak around $2\theta=11\sim13°$comes from the periodical defect in a $SrTiO_3$ substrate[2].

In order to clarify the relationship between adsorption of Bi or Ca element and the thin film growth in the layer-by-layer deposition, sputtering times of Bi and Ca targets were varied over 35 to 565 s for a Bi-O layer, and over 120 to 270 s for a Ca layer. Sputtering times of Sr and Cu targets were fixed at 84 and 81 s, respectively. The ratio(R_{Bi}) for Bi elements between the adsorbed atom numbers and total "ideal" atom numbers was plotted against deposition time in Fig. 2. Here, total "ideal" atom numbers represent the one multiplying total deposition cycles for each element by atom numbers(6.86×10^{14}), which is estimated from dividing the substrate area(10×10 nm^2) by the area of ab-plane(0.382×0.382 nm^2) at one unit of c-axis oriented BSCCO structure. R_{Bi} increases with sputtering time to 70 s. And, R_{Bi} keeps approximately a constant value of 30 % from 70 to 140 s, while it decreases again over 200 s. This suggests that the adsorption amount of Bi was largely influenced by Bi-sputtering time in the layer-by-layer deposition by our ion beam sputtering.

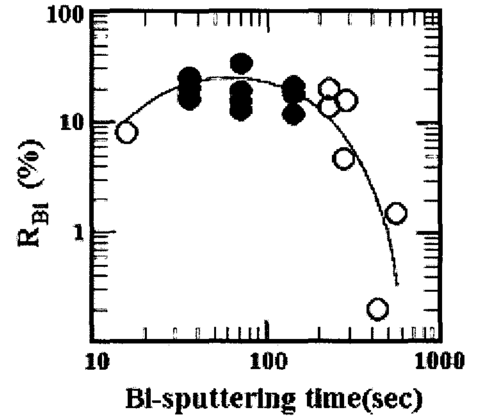


Fig. 2 Sputtering time vs, RBi(see text). The closed andopen circles indicate Bi2201 phase and other phase, respectively.

Fig. 3 represents XRD patterns of different thin film obtained at various at various Bi-sputtering times. In the case of 15 s Bi-sputtering, no remarkable peak was observed except for CuO, while Bi2201 phase was obtained from 70 to 140 s(closed circle in Fig. 2). Bi2201 phase disappears over 2000s again(open circle in Fig. 2). Namely, it turns out that the formation of BSCCO compound has a close relationship with the adsorption amount of Bi element.

We try to elucidate the relationship between the phase appearance and Bi-sputtering time in the layer-by-layer deposition. Overall deposition time for half a unit cell in the layer-by-layer deposition reaches 600-1500 s. This deposition time is much longer in contrast to the other layer-by-layer techniques, whose time takes at most 60 s. Therefore, partial reaction occurs easily and leads to the formation of the other phase. It is interesting that, when such an impurity phase as $SrBi_2O_4$ formed, a remarkable deficiency of only the Bi element in the film was ascertained by ICP analysis, despite the fact that the expected atom numbers or compositional ratios of the other elements were correctly included into thin films. However, only 30 % of the expected Bi atom numbers reached the substrate.

Bi deficiency makes it difficult to form even Bi2201 phase. Accordingly, Bi2212 phase was never formed regardless of containing enough Ca element, whose insertion leads to Bi2212 phase from the Bi2201. In fact, the behaviour of R_{Bi} against Bi-sputtering time is reproducible very well regardless of several different Ca-sputtering times, that is, this implies that Ca-sputtering time give little influence on Bi2212 phase formation, and that the Bi adsorption has a dominant effect on the formation of the BSCCO structure. On the other hand, Bi2212 phase is obtained by the co-deposition in temperatures of 755 and 795。 C under ozone gas pressure of 2×10^{-6} and 2×10^{-5} Torr. Detailed results about the co-deposition presented in a separate paper[5]. A brief explanation is that the Bi vapour forms the Bi_2O_3 liquid phase and that Bi2212 phase is formed through this Bi_2O_3 liquid phase from Bi2201 phase.

The difference between these films obtained by the co-deposition and the layer-by-layer deposition could be explained, taking account of Bi adsorptions as follows: most of Bi vapour which reached on the substrate, re-evaporates constantly from the film surface as molecules of Bi, Bi_2 or $Bi_mO_n(m\geq1,\ n\geq1)$ even in the deposition process. These Bi_mO_n molecules generate as the complex species of Bi_2O_3[6]. Therefore, only 30 % of Bi atoms con combine with the substrate surface or the exposed Sr-O layer on the surface-most layer in the layer-by-layer deposition, as shown in Fig. 2. Accordingly, Bi-O layer attaching to the surface-most layer does not combine stably, since its resident time of adsorption is as long as 70 s, and it is comparable to the re-evaporation rate.

If thin film fabrication obeys a single mechanism in the layer-by-layer deposition, R_{Bi} also ought to be constant over 70 s sputtering. However, the adsorption amount of Bi over 100 s seems to decrease. Thus, R_{Bi} was re-plotted as semi-logarithms and inserted in Fig. 2. The data except for 420 s agree well with an equation of R_{Bi}=-Aexp(-t/τ). This suggests that another mechanism as well as that of Bi adsorption gives some influence on the film formation in the case of the longer sputtering. The retention time τ caused by another mechanism resulted in 120 s from this fitting.

Once Bi coalesces into an island with Bi2201 structure, it would be stabilized and protected from the desorption. However, we cannot give any rigorous explanation for the exhaustion of Bi2201 phase and the decrease of R_{Bi} over about 200 s without the gradual disintegration process of Bi2201 phase in the layer-by-layer deposition. Namely, this τ would correspond to the disintegrating time of Bi2201 phase, Accordingly, the disintegration mechanism brings out the compositional variation and the formation of different compounds from BSCCO structure on the thin film surface. therefore, at a too ultra-low growth rate in the layer-by-layer deposition R_{Bi} changes gradually with Bi-sputtering time. Bi-O network layer reacts partially with the nearest-neighbouring Sr-O layers in the upper and lower sides and form more energetically stable $SrBi_2O_4$ than Bi2201 structure, and the next step partial reaction in $[Cu\text{-}O_2]\rightarrow Ca\rightarrow[Cu\text{-}O_2]$ layers leads to the formation of $CaCuO_2$[7]. At ultra-low growing rate via the layer-by-layer process, partial reactions to form such impurity phases as $SrBi_2O_4$ or $CaCuO_2$ occur easily.

On the other hand, when each element simultaneously reaches the surface in the co-deposition, high quality thin film would be formed. We also obtain a similar result[5] as that presented by Tazoh and Miyazawa[1].

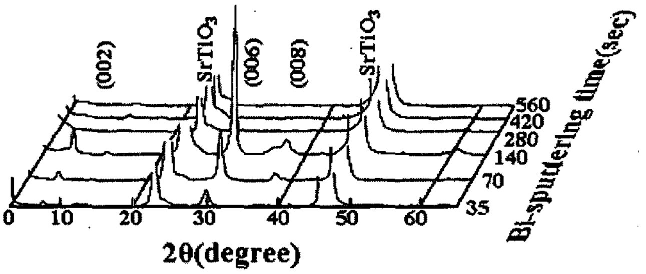


Fig. 3 XRD patterns of the layer-by-layer deposited thin films vs. Bi-sputtering time.

IV. SUMMARY

We examined the difference of the co- deposition and the layer-by-layer deposition processes on the BSCCO structure formation at ultra-low growth rate. Re-evaporation in the form of Bi atoms or Bi_2O_3 molecules 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 Bi2212 phase is concurrently supplied on the film surface in the co-deposition process and leads to Bi2212 phase formation. It was found out that the Bi2212 structure is difficult to construct at such a low growth rate in the layer-by-layer deposition.

REFERENCES

[1] Y. Tazoh and S. Miyazawa, *Appl. phys. Lett.*, 62, p. 408, 1993.

[2] Y. P. Park, J. U. Lee, *Journal of KIEEME,* vol. 11, No. 4, pp. 334-339, 1998.

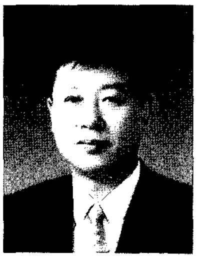
[3] Y. P. Park, *Journal of EEIS,* vol. 3, No. 4, pp. 491-494, 1998.

[4] Y. Kasai, S. Sakai, *J. Crystal Growth,* 115, p. 758, 1991.

[5] Y. P. Park, H. K. Lee, K. W. Lee and J. U. Lee, *Journal of KIEEME,* vol. 13, No. 1, pp. 80-84, 2000.
[6] S. C. Marschman and D. C. Lynch, *Canadian J. Chem, Eng.,* p.875, 1984.
[7] K. Nakamura and T. Hatano, *J. Appl. Phys., 77,* p. 6462, 1995.

Seung-Ho Yang

Member of KIMICS. Reveived B.S. degree in Electrical & Electronic Engineering, Dongshin University, Korea, in 1998. M.S. degree in Electrical & Electronic Engineering from Dongshin University, Korea in 2000. Ph.D. degree in Electrical & Electronic Engineering from Dongshin University, Korea in 2003. Since 2003, he has been with the Department of Hospital Biomedical Engineering at Dongshin University as Plural Professor. His current research interests are in the superconducting materials and Biomaterials.



Yong-Pil Park

Member of KIMICS. Reveived the B.S., M.S., and Ph.D. degree in Electrical Engineering from Kwangwoon University in 1981, 1983 and 1992, respectively. He performed a post-doctoral course as a visiting researcher in the Osaka University, Japan, form 1995 to 1996. Since 1992, he has been with the Department of Electronic Engineering at Dongshin University as Professor. His current research interests are in the high-Tc superconducting materials and Biomaterials.