# Epitaxial Growth of BSCCO Type Structure in Atomic Layer by Layer Deposition by Ion Beam Sputtering

Hee-Kab Lee and Yong-Pil Park*

*Department of Electrical and Electronic Engineering, Dongshin University, Naju, Chonnam 520-714, Korea*

Jeong-Ho Kim

*Department of Mechatronics Engineering, Changwon National University, Changwon, Kyongnam 641-773, Korea*

E-mail : yppark@white.dongshinu.ac.kr

$Bi_2Sr_2CuO_x(Bi(2201))$ thin films are fabricated by atomic layer by layer deposition using ion beam sputtering(IBS) method. During the deposition, 10 %-ozone/oxygen mixture gas of typical $5.0 \times 10^{-5}$ Torr is applied with ultraviolet light irradiation for oxidation. XRD and RHEED investigations reveal out that a buffer layer with some different compositions is formed at the early deposition stage of less than 10 units cell and then $c$-axis oriented $Bi(2201)$ is grown.

## 1. INTRODUCTION

Not only for fundamental research but also application to electronic devices, fabrication of high quality thin films of the oxide superconductors have been required. In general the less-defect surface and the highly-oriented crystalline of the films are essential conditions for the surface analysis and the spectroscopies, e.g., scanning tunneling microscopy/scanning tunneling spectroscopy(STM/STS), ultra-violet photoelectron spectroscopy(UPS) etc. which are exceedingly sensitive to the surface cleanness. Analysis of the electronic state in each constituent layer is desired for investigation and development of the new oxide superconductors. For this purpose, atomic layer by layer deposition is the most promising method. This deposition process, however, has certain technological difficulties in forming each metastable layer stage of Bi(2201) as compared to the co-deposition process where the electronic neutrality every unit cell is kept during the deposition. In this work, we investigate the layer by layer fabrication condition of Bi(2201) thin films by the IBS, of which slow deposition rate enables us fine deposition in atomic layer scale under considerably high vacuum.

For fabrication of such excellent cuprate oxide films, introducing oxidation gas is particularly an important factor. According to the reference[1], the Gibbs' free energy gains in formation of the following oxides at 1000 K are calculated at; $2Bi \rightarrow Bi_2O_3$ : -295.702 kJ/mol, $Sr \rightarrow SrO$ -: -491.231 kJ/mol, $Cu \rightarrow CuO$ : -66.385 kJ/mol. These values indicate that it is the most difficult to oxidize Cu element which plays an essential role in high Tc superconductivity realization. The significant difference(424.846 kJ/mol = 4.4 eV/atom) between Cu and Sr will cause some different phase formations by partial reactions under insufficient oxidizing gas condition during the preparation of cuprate oxides.

Many investigations on fabrication of the thin films have been reported by various means; such as molecular beam epitaxy(MBE), laser ablation, ion beam sputtering[2-4], rf-magnetron sputtering. However, these successful reports on deposition of well-oriented films are mostly by the process of the co-depostion. As for the layer by layer deposition, Tsukada et al.[5] and Kanai et al.[6] reported that the oriented BSCCO thin films were obtained using MBE and laser MBE respectively. Using the other method, few have been reported.

We describe here the atomic layer by layer deposition of Bi(2201) thin films by using the IBS method.

## 2. EXPERIMENTAL

Fig. 1 shows the high vacuum deposition chamber with the ion beam sputtering gun. Each disk of metal Cu, Bi and sintered SrO target was set on a step-wise driving stage. A saddle-field type ion gun was accelerated by voltage of 7.0 kV and Ar ion beam of 0.3 mA current was emitted and irradiated to the targets. Each of the targets was sputtered in order of [Bi → SrO → Cu → SrO → Bi] sequentially. We denote this one cycle as 1 unit hereafter. The atomic layer by layer deposition was carried out on polished $SrTiO_3(100)$ substrate at 700 °C. The deposition rate of each target was observed, so that 0.544 nm/min and 0.673 nm/min for Bi and Cu, respectively. For the real deposition process of the layer by layer sequentially, it differs and the optimum sputtering time rates were determined at 68 sec for Bi, 180 sec for SrO, 23 sec for Cu from the X-ray diffraction pattern(XRD) analysis of the deposited film structure. The average layer deposition speed was estimated at 0.13 nm/min. This speed is much slower than other techniques, and will be suitable for fine regulation of the atomic layer deposition.
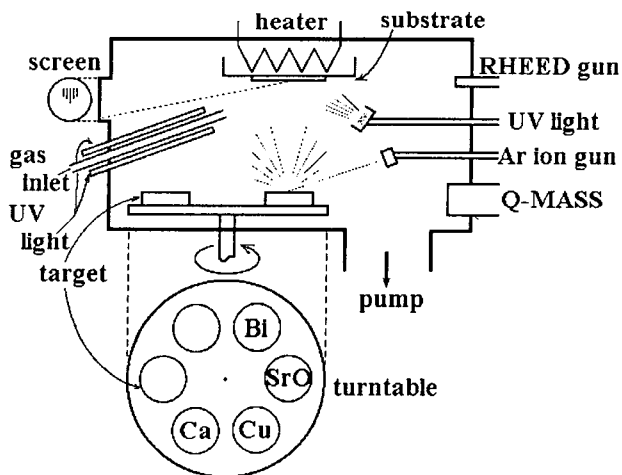


Fig. 1. Schematic illustration of the ion beam sputtering apparatus.

For the oxidation, 10 %-ozone/oxygen mixture gas (abbreviated to 10 %-ozone hereafter) was introduced to the deposition chamber. Photodecomposition of ozone by ultraviolet light yields excited atomic oxygen[7] as ; $O_3 \rightarrow O_2 + O(^1D)$. This activated oxygen can react effectively with deposited metal

elements to form the oxide, the irradiation of ultraviolet light also promote the oxidation[8]. Then, we installed two mercury-argon lamps(UV-lamps) in the vessel as shown in Fig. 1. During the deposition process, atomic arrangement on the film surface was monitored by reflection high energy electron diffraction(RHEED) pattern.

## 3. RESULTS AND DISCUSSION

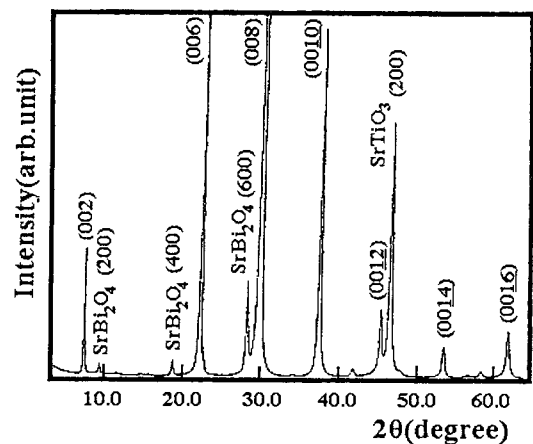Fig. 2 shows the XRD of Bi(2201) thin film after 120 units deposition.



Fig. 2. XRD patterns .of a thin film(120 units) after annealing

The ambient gas pressure in the chamber was kept at $5.0 \times 10^{-5}$ Torr by regulating the 10 %-ozone gas flow during the deposition, and then it was followed by an annealing process of one hour heating at 700 °C. Then cooled down in the rate of 3 °C/min. From this spectrum characteristics, it is found that Bi(2201) epitaxial film highly oriented along c-axis could be obtained, and its lattice parameter was estimated to be 2.40 nm. The (002) peak of Bi(2201) corresponds to the elementary reflection of the c-axis half unit cell and reflects the essential formation of the Bi(2201) structure. The full width at half maximum(FWHM) of the (002) peak was 0.16 ° and was nearly equal to that of the $SrTiO_3$ single crystal substrate. This indicates that the high quality of Bi(2201) was achieved by the IBS method. But some peaks which do not correspond to those of Bi(2201) are also found in Fig. 2. All of these peaks can be ascertained to a spinel compound $SrBi_2O_4$ oriented along a-axis with lattice parameter is $a = 1.90$ nm(according to ASTM data, $a = 1.92882$ nm). The fractional ratio of spinel/(spinel + Bi(2201)) was estimated from the each (002) peak height and it turned out about 11 % spinel containing in this film. The

chemical composition analyzed by the inductively coupled plasma emission spectroscopy (ICP) was Bi : SrO : Cu = 1.99 : 3.25 : 1.00. This excess Sr component from the Bi(2201) stoichiometry may be attributed to the partial extraction from the substrate surface at the acid dissolving process. Since 11 % $SrBi_2O_4$ containing makes little influence to the total composition, the chemically analyzed ratio of Bi/Cu = 1.99 is considered in reasonable agreement with the Bi(2201) stoichiometry.

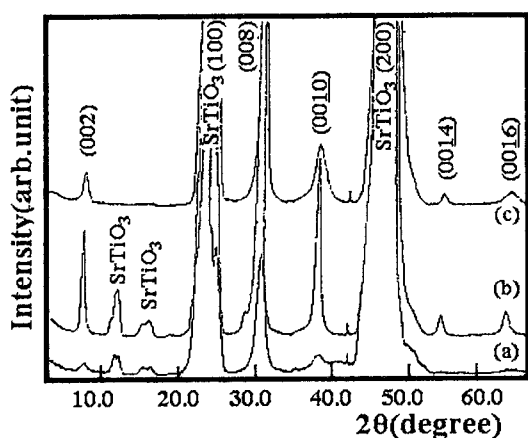Fig. 3 shows XRD patterns of the films which prepared at different gas pressures.



Fig. 3. XRD patterns of 30 units' films prepared under various gas pressures. (a) $1.0 \times 10^{-5}$ Torr (b) $5.0 \times 10^{-5}$ Torr (c) $9.0 \times 10^{-5}$ Torr.

The pressure of 10%-ozone gas was kept at $1.0 \times 10^{-5}$ Torr for the film (a), $5.0 \times 10^{-5}$ Torr for the (b), $9.0 \times 10^{-5}$ Torr for the (c) during the each deposition of 30 units. Neither *in-situ* anneal nor slow cooling was carried out in these film preparations. At $1.0 \times 10^{-5}$ Torr, only a trace of the primary (002) peak is observed (Fig. 3(a)). This means that the oxygen deficiency resulted in poor quality of the Bi(2201) component as compared to (b) where sharp(001) lines are observed significantly. The surface morphology of the film (b) was observed by scanning electron microscope(SEM) image as shown in Fig. 4. The SEM image reveals that lots of spherical objects in diameter of submicrons exist on the film surface as precipitates. These bright precipitates are presumed as containing heavy atoms like Bi or Sr. Nevertheless, in Fig. 3 no any peaks are observed other than those of Bi(2201) and the substrate $SrTiO_3$. This may suggest that these precipitates are in amorphous-like structure. On these SEM images, we found that these precipitates decreased in numbers with increment of ambient gas pressure to $10^{-4}$ Torr. On the other hand, The XRD peaks show in Fig. 3 that the growing and

sharp (002) peak of Bi(002) became again wider to 0.50 ° of the FWHM at $9.0 \times 10^{-5}$ Torr. This implies that the pressure $5.0 \times 10^{-5}$ Torr of 10 %-ozone gas will be almost in optimum.
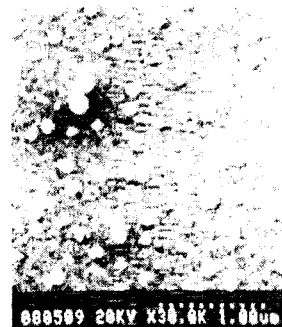


Fig. 4. SEM image of the film (b) in Fig. 3.

By refering to Fig. 3, we consider that the appearance of $SrBi_2O_4$ peaks in Fig. 2 is due to the *in-situ* anneal. Accordingly, investigation on early stage of the layer by layer deposition was undertaken after 30 units deposition and followed by the annealing. The XRD pattern of this film is shown in Fig. 5, where the peaks corresponding both to the spinel compound $SrBi_2O_4$ oriented along *a*-axis and Bi(2201) oriented along *c*-axis can be seen. Moreover, in contrast to the appearance of $SrBi_2O_4$, the bright precipitates in the SEM image had disappeared. The content of $SrBi_2O_4$ estimated at 45 % from the corresponding peaks ratio in Fig. 5. Since this 45 % content of $SrBi_2O_4$ is considerably large as compared with the 11 % in the case of 120 units in Fig. 2, it is supposed that a large amount of the precipitate phase which is changed to $SrBi_2O_4$ by *in-situ* anneal will be formed at the early stages of the deposition.
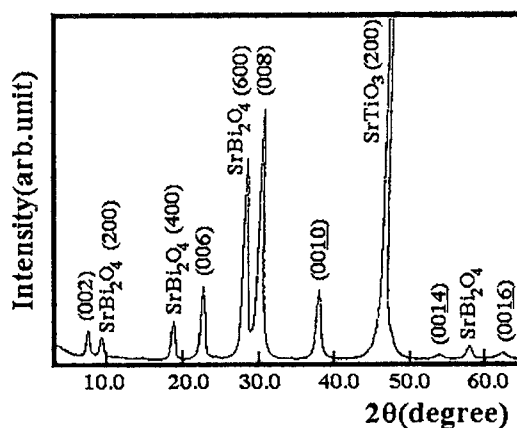


Fig. 5. XRD pattern of 30 units' film after annealing.

At early stages of the deposition, the RHEED observation revealed out that a spot pattern appeared at the first Bi deposition stage in the beginning of the second unit. This pattern gradually turned into a mosaic pattern due to an occurrence of the mixing of different directional microcrystals growth. After 10th unit deposition, dim streak lines gradually superposed on this pattern. The XRD spectrum for these stages of ultra thin films are shown in Fig. 6, where (a) to (c) are corresponding to the deposition of 2, 5 and 8 units, respectively. For these films, the *in-situ* annealing procedure was not carried out. Neither peak coming from Bi(2201) nor precipitates is observed in both cases of (a) and (b). In the (c), for the first time, broad and slight peaks of the Bi(2201) structure appeared. Surface images of these samples obtained by SEM were similar to those with the spherical precipitates as shown in Fig. 4.
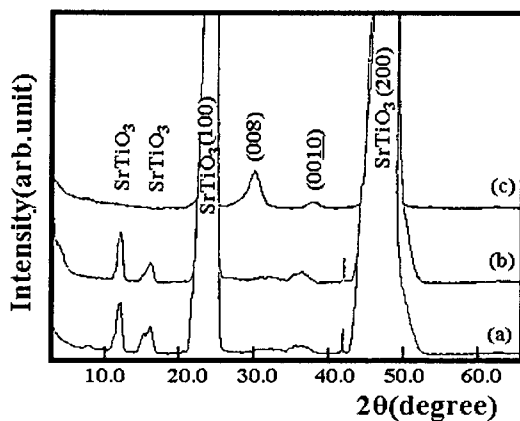


Fig. 6. XRD patterns of the films by 2(a), 5(b) and 8 units(c) depositions.

## 4. CONCLUSIONS

These results are summarized as follow; At early stages of the atomic layer by layer deposition, two dimensional epitaxial growth which covers the substrate surface would be suppressed by the stress and strain caused by the lattice misfit, then three dimensional growth takes place.

Since Cu element is the most difficult to oxidize, only Sr and Bi react with each other predominantly, and forms a buffer layer on the substrate in an amorphous-like structure, which is changed to $SrBi_2O_4$ by *in-situ* anneal. The Bi(2201) phase is grown partially in the buffer layer and predominates at about the 10th unit deposition and goes into the two dimensional growth.

The 120 units deposited sample specimen was undertaken to the electric resistivity R measurement. It showed typical semiconductor's temperature dependence of $R \propto \exp[-E/2k_BT]$, with E = 37.1 meV, below 300 K. This simple excitation process with certain activation energy E suggests that our Bi(2201) films are considered in a unified electronic system.

## REFERENCES

[1] I. Bavin, *Thermochemical Data of Pure Substance*, VHC Co., pp. 202, 484 and 1427, 1989.

[2] Y. P. Park and J. U. Lee, *Journal of KIEEME*, Vol. 10, No. 5, pp. 425-433, 1997.

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

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

[5] I. Tsukada, K. Uchinokura, *Jpn. J. Appl. Phys.* Vol. 30, L1114, 1991.

[6] M. Kanai, T. Kawai, S. Kawai and H. Tabata, *Appl. Phys. Lett.* Vol. 54, p. 1802, 1989.

[7] H. Okabe, *Photochemistry of Small Molecules*, Wiley-Interscience Pub., New York, pp. 149-183, 1978.

[8] T. Siegrist, D. A. Mixon, E. Coleman and T. H. Tiefel, *Appl. Phys. Lett.* Vol. 60, p. 2489, 1992.