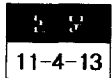


이온 빔 스퍼터법에 의한 BSCCO 박막의 순차 증착



Layer-by-layer Deposition of BSCCO Thin Films Using Ion Beam Sputtering Method

박용필*, 이준웅**

(Yong-Pil Park, Joon-Ung Lee)

Abstract

$\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (Bi-2201) thin films have been fabricated by atomic layer-by-layer deposition using ion beam sputtering (IBS) method. During the deposition, 14 wt%-ozone/oxygen mixture gas of typical pressure of 5.0×10^{-5} Torr is supplied with ultraviolet light irradiation for oxidation. XRD and RHEED investigations reveal that a buffer layer with compositions different from Bi-2201 is formed at the early deposition stage of less than 10 units cell and then Bi-2201 oriented along the *c*-axis is grown.

Key Words(중요용어) : Ion beam sputtering(이온 빔 스퍼터), BSCCO(2201), Ozone(오존), Ultra-violet light(자외선), Superconductor(초전도체), Buffer layer(버퍼층)

1. Introduction

The superconducting mechanism in the oxide superconductor is gradually becoming clear, since highly-oriented single crystals or thin films have been prepared. However, the analysis of the electronic state in each constituent layer is desired for further theoretical investigations and for development as an electronic device, because the high- T_c oxide superconductor is constructed by piling up various layers, which have different roles. For this purpose, atomic layer-by-layer deposition is the most promising method.

Many researches on fabrication of thin films have been reported by various means, such as molecular beam epitaxy(MBE)^{1,2)}, laser ablation³⁾, -

rf-magnetron sputtering and ion beam sputtering(IBS) method⁴⁾, etc. However the well-oriented thin films in these reports are mostly obtained via the co-deposition process. As for the layer-by-layer deposition, Tsukada et al.¹⁾, Kasai and Sakai²⁾, and Kanai et al.³⁾ have reported that thin films of the Bi-type superconductor were obtained using MBE and laser MBE, but few have been reported using other methods. The reason is that the process of this deposition has certain technological difficulties to form metastable states different from $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+6}$ ($n=0,1$ and 2), comparing to the co-deposition process where the electronic neutrality in each unit cell is kept during the deposition.

We report about the layer-by-layer fabrication of $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (abbreviated to Bi-2201 hereafter) thin films by the IBS method, slow deposition rate of which enables us the fine control of the deposition in atomic layer scale under considerably high vacuum.

* : 동신대학교 공대 전기전자공학과

(전남 나주시 대호동 252, Tel: 0613-30-3207

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

** : 광운대학교 공대 전기공학과(신기술연구소)

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2. Experimental

The IBS apparatus used was illustrated in Fig. 1. Pressure of a vacuum chamber is kept usually under 10^{-8} Torr order and the partial pressure of remnant water was checked to be less than 5×10^{-8} Torr by a quadrupole mass spectrometer (Q-mass: ANELVA Co. Ltd., AQA-100 MPX), because it gives a bad influence on the quality of the deposited thin film.

Each disk of metal Cu, Bi and sintered SrO target was set on a step-wise driving stage. 7.0 keV and 0.3 mA of Ar ion beam generated by a saddle-field type ion gun (ION TECH LIMITED, Saddlefield 725) was irradiated to the respective targets. The mirror-polished SrTiO₃ (abbreviated to STO hereafter) (100) was used as a substrate. The surface of this substrate was cleaned before the deposition by keeping at 700 °C for 1 hour under 10^{-7} Torr and followed by exposure to the oxidation gas of 5×10^{-5} Torr for 10 min.

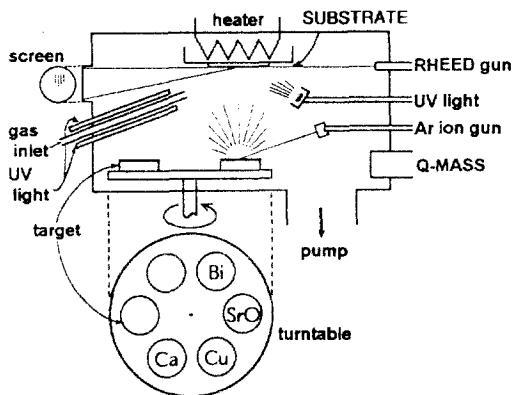


그림 1. IBS 장치의 개략도

Fig. 1. Schematic diagram of IBS apparatus

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 optimum sputtering times were determined as 68 sec for Bi 180 sec for SrO, 23 sec for Cu by the composition analyses using the inductively coupled plasma(ICP) emission spectroscopy and X-ray diffraction(XRD) patterns of the obtained films, and the average growth rate was estimated at 0.13 nm/min. This speed is much slower than other techniques, and

therefore, IBS method will be suitable for a fine control of the atomic layer-by-layer deposition.

The oxidation gas is particularly an important factor for fabrication of the high quality thin films. According to the reference⁵⁾, each gain of Gibb's free energy ΔG is calculated at 1000 K in formations of the following oxides; $2\text{Bi} \rightarrow \text{Bi}_2\text{O}_3$: -295.702 kJ/mol, $\text{Sr} \rightarrow \text{SrO}$: -491.231 kJ/mol, $\text{Cu} \rightarrow \text{CuO}$: -66.385 kJ/mol.

The difference of the formation energies among these oxides indicates that it is the most difficult to oxidize Cu element, which plays an essential role in the occurrence of high- T_c superconductivity. The significant difference (424.846 kJ/mol = 4.4 eV/atom) between Cu and Sr will cause the formations of some different phases via partial reactions in the condition of the insufficient oxidizing gas during preparation of cupric oxides. Thus, ozone, atomic oxygen, NO₂ and N₂O gases were tried as candidates of the oxidation gases⁵⁾, and we adopted the 14 wt%-ozone/oxygen mixture gas (abbreviated to 14 wt%-ozone hereafter; Sumitomo Precision Products Co. Ltd. Ozonizer SG-01A) for oxidation.

Photo-decomposition of ozone by ultraviolet light (UV light) facilitates to produce the excited atomic oxygen⁷⁾ through the reaction such as $\text{O}_3 \rightarrow \text{O}_2 + \text{O}(^1\text{D})$. This activated atomic oxygen can react effectively with the deposited metal elements to form the oxide under high vacuum condition. We installed two mercury-argon lamps in the vessel as shown in Fig. 1. It was ascertained by Siegrist et al.⁸⁾ that the irradiation of UV light to the substrates promotes the oxidation in the fabrication of Y-superconducting thin film. Moreover, the UV light for irradiating the inlet gas was also set to increase the amount of the excited atomic oxygen O(¹D).

Atomic arrangement on the surface of the growing film was monitored by an in-situ reflection high energy electron diffraction (RHEED; Japan Physitac Co. Ltd., RH 1000 15 kV) equipment. The structure and surface morphology of the thin film fabricated were examined by XRD and scanning electron microscope (SEM) instruments, respectively. The composition of the thin

film was also evaluated by ICP emission spectroscopy.

3. Results and Discussion

Figure 2 shows the XRD pattern of Bi-2201 thin film after 120 units deposition. The ambient gas pressure in the chamber was kept at 5.0×10^{-5} Torr by regulating the flow rate of 14 wt%-ozone gas with two UV lights irradiation during the deposition. After it was followed by an annealing process of one hour heating at 700 °C, the deposited film was cooled down at the rate of 3 °C/min. The XRD pattern of this film indicates

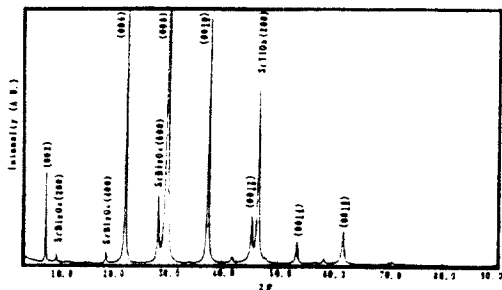


그림 2. 열 처리 후 120 유닛 박막의 XRD 패턴

Fig. 2. XRD pattern of the 120 units film after annealing

Bi=68 s, SrO=180 s and Cu=23 s; 2.0×10^{-5} Torr

that Bi-2201 epitaxial film oriented highly along the *c*-axis could be obtained, and its lattice parameter of the *c*-axis is estimated to be 2.40 nm. The full width at half maximum(FWHM) of the (002) peak was 0.16 °, which is nearly equal to that of the SrTiO₃ single crystal substrate. This indicates that the high quality of Bi-2201 was fabricated by the IBS method. Some peaks which do not correspond to those of Bi-2201, however, are also found in Fig. 2. All of these peaks can be identified as a pseudo-spinel compound SrBi₂O₃ oriented along the *a*-axis with the lattice parameter of 1.90 nm(*a*=1.92882 nm according to ASTM data; space group: C2/m). About 11 % content of SrBi₂O₄ was estimated to

be contained in this films from the peak height ratio between (002) of Bi (2201) and (200) of SrBi₂O₄, that is, SrBi₂O₄/(SrBi₂O₄+ Bi-2201).

It is important to find an optimum condition of the layer-by-layer deposition for obtaining the high quality thin film and getting rid of the impurity phase. First we investigate the ambient pressure effect of 14 wt% ozone gas. Thus thin films of 30 units were fabricated at 1.0, 5.0 and 9.0×10^{-5} Torr with two UV lights irradiation. Neither in-situ annealing nor slow cooling processes were carried out in these film preparations. Only a trace of the primary (002) peak is observed in XRD pattern of the thin film obtained under 1.0×10^{-5} Torr. This means that the oxygen deficiency led to poor quality of the Bi-2201 component as compared to under 5.0×10^{-5} Torr, where sharp (001) lines are observed significantly. The surface morphologies of these films observed by SEM image are shown in Fig. 3(a)-(c), corresponding to the respective pressures. These SEM images reveal that lots of spherical objects with diameter of microns exists on the film surface as precipitates. These bright precipitates are presumed as containing heavy atoms like Bi or Sr. Nevertheless, no other peaks except for Bi-2201 and the substrate SrTiO₃ are seen in XRD patterns of the obtained thin films. This suggests that these precipitates are in amorphous-like structure. We found that the numbers of these precipitates decreased by increasing ambient gas pressure to 9×10^{-5} Torr. However, the XRD denotes that the FWHM of (002) peak from the Bi-2201 fabricated at 9.0×10^{-5} Torr became wider to 0.50 °. This implies that the pressure of 5.0×10^{-5} Torr would be almost an optimum one for the fabrication of Bi-2201 in the layer-by-layer deposition used the 14 wt%-ozone gas.

Next, the Bi-2201 thin film with 30 units deposition was fabricated under 5.0×10^{-5} Torr of 14 wt%-ozone with or without the mercury-argon lamps to investigate the effect of UV light irradiation in the following conditions; (a) without UV lights irradiation, (b) with the UV light irradiating the surface of the substrate, (c) with

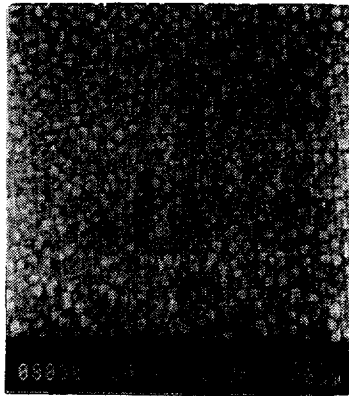
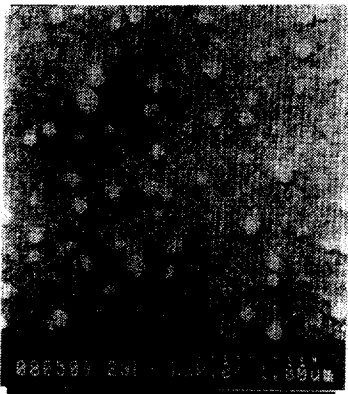
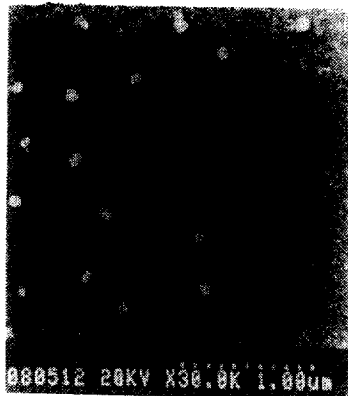
(a) 1.0×10^{-5} Torr(b) 5.0×10^{-5} Torr(c) 9.0×10^{-5} Torr

그림 3. 14 wt% - 오존가스압에 대한 SEM 상
 Fig. 3. SEM images for 14 wt%-ozone gas pressure

the one irradiating the gas inlet, and (d) with both UV lights irradiation. Judging from FWHM of (001) peaks, the qualities of thin films in cases of (c) and (d) are considerably improved as compared to that fabricated without UV light irradiation in case of (a). There is little difference between the qualities of thin films in cases of (c) and (d). This suggests that the reaction of $O_3 \rightarrow O_2 + O(^1D)$ is promoted by irradiating UV light to the inlet gas and that the effective amount of the activated atomic oxygen increases. On the other hand, the quality of thin film obtained by the UV irradiation on only the surface of the substrate (case (b)) becomes worse than that without UV light irradiation. This denotes that the UV light irradiation on the surface of the substrate would work not for the formation of the Bi-2201 but for the dissociation, in contrast to the fabrication of Y-superconducting thin film by Siegrist et al.[8].

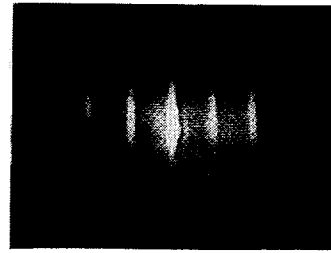
The appearance of $SrBi_2O_4$ observed in Fig.2 would disturb the fabrication of high quality Bi-2201 thin film by the layer-by-layer deposition. In order to find the origin of $SrBi_2O_4$, the investigation on the early stage of layer-by-layer deposition was undertaken in 30 units deposition with the annealing process. Both compounds of Bi-2201 and $SrBi_2O_4$ were formed in the obtained thin film, in similar to that after 120 units deposition (see Fig.2). The amorphous-like bright precipitates, which were observed by the SEM image in the thin film without the annealing process, have disappeared after the annealing and then that $SrBi_2O_4$ has appeared. The content of $SrBi_2O_4$ was estimated to be 45 % from the ratio of $SrBi_2O_4 / (SrBi_2O_4 + Bi-2201)$. This 45 % content of $SrBi_2O_4$ in 30 units is about four times as large as the 11 % content in the case of 120 units in Fig. 2. The same amount of $SrBi_2O_4$ are produced in spite of film thickness, taking the number of the deposited layer into consideration. Consequently, it is supposed that a large amount of the amorphous-like precipitate, which are changed to $SrBi_2O_4$ via in-situ annealing process,

will be formed at the early stage of the deposition.

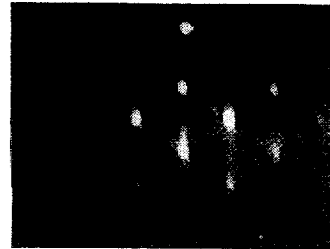
By means of RHEED observation we study the two-dimensional atomic arrangement on the film surface in the process of crystal growth under the conditions of the optimum deposition described above. Figures 4(a) to (d) show the RHEED patterns at initial stages of the deposition.

The streak pattern coming from the STO substrate is clearly observed before the deposition as shown in Fig. 4(a). The additional streaks were frequently observed at the central parts of each original streak of the STO substrate before flushing the oxygen. These streaks may be attributed to the periodic defect, the spacing of which corresponds to twice of the lattice parameter. As shown in Fig. 4(b), these streaks drastically turned into a spot pattern at the first Bi deposition stage in the beginning of the second unit cell, and this denotes the beginning of three-dimensional growth. These spots gradually become obscure, and then a circular mosaic pattern appears after 4th unit deposition as shown in Fig. 4(c). It implies the growth of the microcrystal, a- and b-axes of which are placed in random directions on a two-dimensional layer. Though this pattern continued until about 10th unit deposition, a weak streak pattern gradually comes to superpose on this pattern. Resultantly it turns into a clear streak pattern after about 10th unit deposition as shown in Fig. 4(d), and this indicates that two-dimensional layer structure was gradually formed. This initial process of the film growth was also investigated by the XRD patterns after the depositions of 2, 5, and 8 units as shown in Figs. 5(a) to (c). Here, two broad peaks appearing between 10° and 20° in Fig. 5 were occasionally observed even for the STO (100) substrates.

These peaks correspond to 2 or $\sqrt{2}$ times of the lattice parameter, 0.30905 nm, and are considered to come from the periodic defects on the STO surface, which might correspond to the additional streaks in the RHEED observation. Neither a peak coming from Bi-2201 nor



(a) SrTiO₃ substrate



(b) After the Bi element deposition of the 2nd unit



(c) After 4th unit deposition



(d) After 10th unit deposition

그림 4. RHEED 패턴

Fig. 4. RHEED patterns

precipitates is observed in either case of (a) or (b), and then the broad (008) and (0010) peaks for the Bi-2201 structure slightly appeared in the 8 units deposition (case (c)). The SEM observation revealed that surface images of these samples are similar to those with the spherical precipitates as

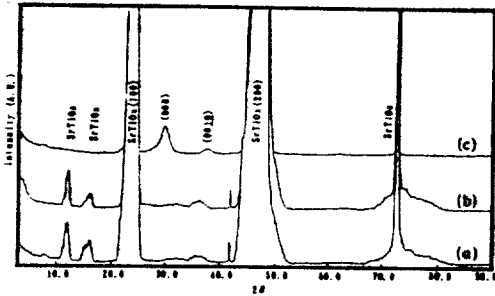


그림 5. (a) 2, (b) 5 및 (c) 8 유니트 증착 후 XRD 패턴

Fig. 5. XRD patterns taken after depositions of (a) 2, (b) 5 and (c) 8 units

shown in Fig. 3. This SEM observation seems to provide a reasonable correspondence with the result of RHEED observation. In the case of the atomic layer-by-layer deposition process, this precipitate layer plays an important role of the buffer for the misfit of Bi-2201 layer with the substrate.

3. Conclusions

These results are summarized as follows: at the early stages of atomic layer-by-layer deposition, the two dimensional epitaxial growth which covers the substrate surface would be suppressed by the stress and strain caused thermally as well as by the lattice misfit, then three-dimensional growth takes place. Since Cu element is the most difficult to oxidize, Sr and Bi predominantly react each other and form an amorphous-like precipitate, which is changed to SrBi_2O_4 via the in-situ annealing process. This precipitate seems to act as a buffer layer, which relaxes the stress and strain between Bi-2201 and the STO substrate. The Bi-2201 phase is grown partially in the buffer layer at the early stage, and then gradually predominates upto about 10th unit deposition, and finally goes into the two-dimensional growth.

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