한국전기전자재료학회
'99 추계학술대회 논문집

Fabrication of Bi-superconducting Thin Films by Layer-by-layer Sputtering Method

Jin-In Jung, Hee-Kab Lee and Yong-Pil Park

Department of Electrical & Electronic Engineering Dongshin University

Abstract

$Bi_2Sr_2CuO_x$ thin films have been fabricated by atomic layer-by-layer deposition using ion beam sputtering(IBS) method.

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 : layer-by-layer deposition, IBS, buffer layer, Bi-2201

1. Introduction

Many researches on fabrication of thin films have been reported by various means, such as molecular beam epitaxy(MBE)[1,2], laser ablation[3], rf-magnetron sputtering and ion beam sputtering(IBS) methods[4], etc. However, the well-oriented thin films in these reports are mostly obiained via the co-deposition process. As for the layer-by-layer deposition, Tsukada et al.[1], Kasai and Sakai[2], 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 $Bi_2Sr_2Ca_nCu_{n+1}O_{2n+6}$(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 $Bi_2Sr_2CuO_x$(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.

2. Experimental

The IBS apparatus used was illustrated in Fig. 1. Pressure of a vacuum chamber is kept usually under 10^{-8} Torr order

Each disk of metal Cu, Bi and sintered SrO target was set on a step-wise driving stage. $SrTiO_3$ (100) was used as a substrate. The surface of this substrate was cleaned before the deposition by keeping at 700℃ for 1 hour under 10^{-7} Torr and followed by exposure to the oxidation gas of 5×10^{-5} Torr for 10 min.

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 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.

According to the reference[5], each gain of Gibb's free energy ΔG is calculated at 1000 K in formations of the following oxides; $2Bi \rightarrow Bi_2O_3$: -295.702 kJ/mol, $Sr \rightarrow SrO$: -491.231 kJ/mol, $Cu \rightarrow CuO$: -66.385 kJ/mol.

Atomic arrangement on the surface of the growing film was monitored by an in-situ reflection high energy electron diffraction(RHEED) 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.

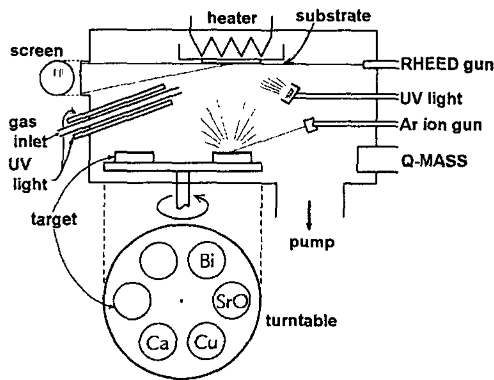


Fig. 1. Schematic diagram of IBS apparatus

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 durring the deposition. After it was followed by an annealing process of one hour heating at 700 ℃, the deposited film was cooled down at the rate of 3 ℃/min. The XRD pattern of this film indicates 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 maximun(FWHM) of the (002) peak was 0.16 °, which is nearly equal to that of the $SrTiO_3$ single crystal substrate. 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 $SrBi_2O_3$ 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 $SrBi_2O_4$ was estimated to be contained in this films from the peak height ratio between (002) of Bi (2201) and (200) of $SrBi_2O_4$, that is, $SrBi_2O_4$/($SrBi_2O_4$+ Bi-2201).

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. 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, 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 $SrTiO_3$ 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.

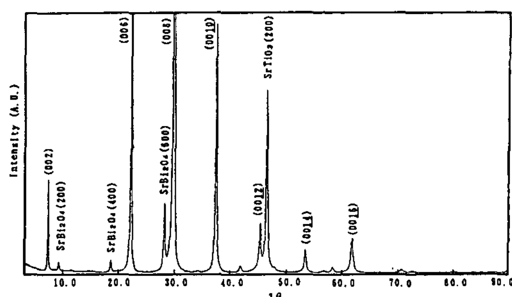
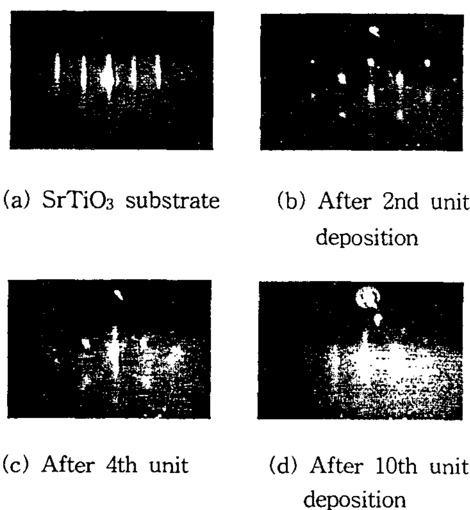


Fig. 2. XRD pattern of the 120 units film after annealing

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 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.[6]

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 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.

Figures 3(a) to (d) show the RHEED patterns at initial stages of the deposition.



(a) $SrTiO_3$ substrate
(b) After 2nd unit deposition
(c) After 4th unit
(d) After 10th unit deposition

Fig. 3. RHEED patterns

The streak patttern coming from the STO substrate is clearly observed before the deposition as shown in Fig. 3(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. 3(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. 3(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. 3(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. 4(a) to (c). Here, two broad peaks appearing between 10 ° and 20 ° in Fig. 4 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 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. 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.

4. 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 diffcult 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.

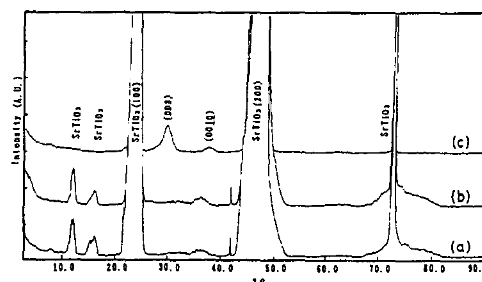


Fig. 4. XRD patterns taken after depositions of (a) 2, (b) 5 and (c) 8 units

References

[1] Tsukada. I. and Uchinokura, K., Jpn. J. Appl. Phys. vol. 30. p. L 1114, 1991.

[2] Kasai, Y. and Sakai, S., J. Cryst. Growth, vol. 115 p. 758, 1991.

[3] Kanai. M., Kawai, T., and Kawai, S., Appl Phys. Lett, vol. 58 P. 771, 1991.

[4] Fujita, J., Yoshitake, T., and Satoh, T., Appl. Phys. Lett., vol. 56, p. 295, 1990

[5] Bavin, I., "Thermochemical Data of Pure Substance," VCH 1989.

[6] Siegrist, T., Mixon, D., Coleman, E. and Tiefl, T. H., Appl. Phys. Lett., vol. 60, p. 2489, 1992.