

Phase Intergrowth in the Syntheses of BSCCO Thin Films

No-Bong Park* and Yong-Pil Park**

Abstract

Phase intergrowth some kinds of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ phases is observed in the thin film fabrication at ultralow co-deposition with multi targets by means of ion beam sputtering. The molar fraction of the Bi2212 phase in the mixed crystal of the grown films is investigated as a function of the applied ozone pressure and the substrate temperature. The activation energy for the phase transformation from the Bi2201 to the Bi2212 is estimated in terms of the Avrami equation. This study reveals that the formation of a liquid phase contributes significantly to the construction of the Bi2212 phase in the thin films, differing from the bulk synthesis.

Key Words : Phase intergrowth, Ion beam sputtering, Activation energy, Avrami equation

1. INTRODUCTION

Development of electronic devices using high T_c superconducting oxides has been recently promoted for the purpose of realizing the superconductor / normal metal / superconductor (S/N/S) junction. Especially, the application of the junctions between the a - and c -axes oriented films in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO)-type structure[1] and of grain boundary junctions to the devices, have been in progress. Meanwhile, much attention has been also devoted to the fabrication of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=1, 2, \text{ and } 3$) thin films, which is hereafter abbreviated generically as BSCCO, because of the two-dimensionality of the

materials and the electronic properties such as the high T_c of the Bi2223 phase and the semi-conducting character of the Bi2201 phase. The Bi2212/Bi2201/Bi2212 trilayer structure would be more appropriate for the S/N/S devices due to its excellent lattice matching along the a - and b -axes, compared to the prevailing YBCO/PrBa₂-Cu₃O₂/YBCO system[2]. Nonetheless, the few applications of this BSCCO thin film system may be due to the difficulty of obtaining high quality films composed of the respective Bi22($n-1$) n pure phases. The phase diagram of the Bi - Sr - Ca - Cu - O system is complicated, and moreover, the three stable phases with $n = 1, 2, \text{ and } 3$ have only slightly different free energies of formation between each other. Accordingly, the main problem that needs to be solved for the realization of the BSCCO thin film application is to establish the thin film fabrication process for each pure phase growth. In this article, we discuss the growing mechanism of the BSCCO thin films with interrelationship among the respective phases.

* : Department of Electrical Engineering,
Chungju National University

** : Department of Electrical & Electronic Eng.,
Dongshin University
(252 Daeho-dong, Naju, Chonnam, 520-714
Fax : 061-330-2909
E-mail : yppark@white.dongshinu.ac.kr)

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2. EXPERIMENTAL

The BSCCO thin films were fabricated using a co-sputtering deposition technique. Fig. 1 shows a schematic diagram of the ion beam sputtering (IBS) apparatus and an effusion cell employed.

Metal targets of Sr, Ca and Cu were simultaneously sputtered by Ar ion or atom beams generated by saddle field type cold cathode guns. The fine regulation of the respective atom fluxes was achieved by independently monitoring each ion beam current using the Faraday cup, which was situated on the opposite side of the Ar ion output from the gun. Only the Bi flux was supplied by an effusion cell because of a far higher yield requirement due to its extremely low sticking coefficient on the substrate[3,4] than the obtainable flux rate (10^{12} atoms/sec \cdot cm 2) by the Ar beam sputtering. This effusion cell was improved by separately heating up the upper and lower parts to realize better control of the Bi flux. A MgO(100) single crystal was used as a substrate and was attached on an inconel block with silver paste so as to produce a homogeneous heating. The substrate temperature was kept at a constant value between 630 and 712 $^{\circ}$ C. Highly condensed ozone gas was obtained by a silica gel adsorption method[5] and was supplied onto the substrate during deposition of the metallic

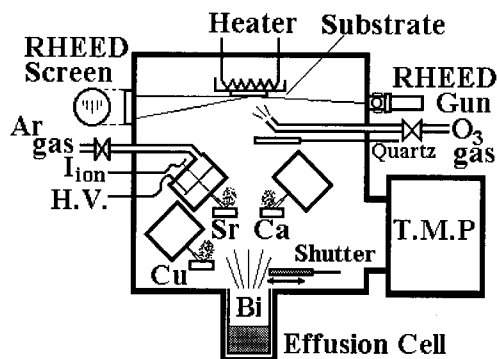


Fig. 1. The schematic diagram of the IBS apparatus.

species to provide an oxidation environment. The ozone gas pressure was regulated between 1.0×10^{-6} and 1.0×10^{-5} Torr, whereby the total one in the deposition chamber was set about 2.0×10^{-5} Torr. The film growth rate during the depositions was kept at about 0.2 m/min.

The crystal structure and atomic compositional ratio of the deposited films were examined by x-ray diffractometry(XRD) using Cu-K α radiation, and by energy dispersive x-ray spectrometer(EDX), respectively. Each atom flux from the respective targets was regulated so as to get the films with an atomic ratio of Bi:Sr:Ca:Cu = 2:2:1:2. By EDX inspection, the compositional ratio of the thin films really obtained was determined to be Bi:Sr:Ca:Cu = $.21 \pm 0.2:2.0 \pm 0.1:0.9 \pm 0.1:2.0 \pm 0.2$.

3. RESULTS AND DISCUSSION

The XRD patterns of the films prepared under an ozone pressure of 1.0×10^{-5} Torr are presented in Fig. 2.

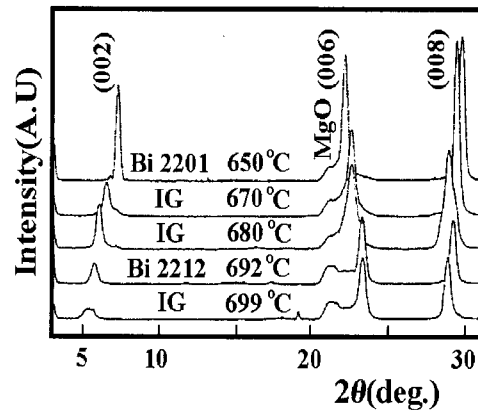


Fig. 2. XRD patterns of the thin films fabricated at various substrate temperatures under the ozone pressure of 1.0×10^{-5} Torr. Substrate temperatures are indicated in the figure. IG represents a thin film with intergrowth.

In the macroscopical domain where the individual Bi2201 and Bi2212 phases are mixed separately, the intensity ratio of the (00*l*) peaks comes from both phases and should be observed in proportion to the molar fraction. Only a single peak actually appears at the midpoint between the individual Bi2201 and Bi2212 peaks or the Bi2212 and Bi2223 peaks. This means that the two phases are not separated in macroscopical domains larger than the x-ray penetration range of 1 μm , but the intergrowth takes place in the domain due to the stacking modulation of Ca and CuO₂ layers between the Bi2201 and Bi2212 phases. Namely, this successive peak shift with the substrate temperature as indicated by the dashed lines in Fig. 2 suggests that such a mixed crystal as proposed by Hendricks and Teller[6] is constructed.

Ranno *et al.*[7] have also observed similar XRD peak shift in the BSCCO thin films fabricated by the pulsed laser deposition(PLD) method using a single target. The theoretical relationship between the (00*l*) peak position at 2θ and the molar fraction (p) of Bi2212 in the BSCCO(Bi2212 + Bi2201) thin film can be estimated in terms of the equation given by Hendricks and Teller and Ranno *et al.* Here, we noticed the behavior of the (002) peak instead of the main (008) peak of the Bi2212 phase owing to avoiding the overlapping with the MgO peak and the result is presented in Fig. 3. The full and dashed lines show the results corresponding to the intergrowth of the Bi2212/Bi2201 and the Bi2212/Bi2223, respectively. Applying the real 2θ observed in each film to the relation in Fig. 3, the molar fraction p was estimated for each film fabricated at the growth temperature and it was plotted in Fig. 4, where the open circle shows the data for $P_{\text{O}_3} = 1.0 \times 10^{-5}$ Torr and the full circle for $P_{\text{O}_3} = 5.0 \times 10^{-6}$ Torr.

For temperatures above 690 °C, the Bi2212/Bi2223 mixed crystals take place in Fig. 4 and the molar fraction of the Bi2223 phase is enhanced when the substrate temperature is increased up to 700 °C, while the Bi2212 fraction

decreases as indicated by a dashed line in Fig. 4. This implied that the structural formation evolves smoothly toward the next step, the construction of Bi2223 phase. Beyond $T_{\text{sub}}=700$ °C, however, any BSCCO phase cannot be constituted.

In relation to the BSCCO film fabrication by means of the PLD method, Ranno *et al.* have pointed out that the essential factors for the selective growth of each phase of the Bi22*n*(*n*-1) are influenced not only on the beam supply of proper atom compositions and the substrate temperatures T_{sub} , but also on the regulation of the oxidizing atmosphere during the deposition. Ohkubo *et al.*[8] obtained a similar result for the dc-sputtering method using a cylindrical sputtering gun(CSS). Referring to the results described above, our data shown in Fig. 4 have the following characters; (i) elevation of the substrate temperature T_{sub} is favorable to the formation of the Bi2212 phase up to 690 °C and then the

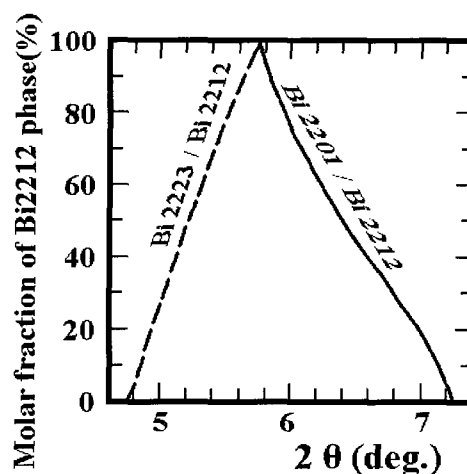


Fig. 3. The relationship between the molar fraction p of the Bi2212 phase and the (002) peak position of the mixed crystal of the BSCCO compounds, is estimated ideally in terms of an equation given by Ranno *et al.* The full and dashed lines are for the Bi2201/Bi2223 mixed crystals, respectively.

formation of the Bi2223 phase, (ii) lower ozone pressure promotes the formation of the Bi2212 phase at the same substrate temperature, and (iii) the Bi2212 single phase can be obtained only in the narrow substrate temperature range of $\Delta T = \pm 5^\circ\text{C}$ at $T = 690^\circ\text{C}$. Strictly denoting, the Bi2212 really single phase cannot be attained because of the participation of several additional reactions in the partially melting process.

The tendency of the larger Bi2212 fraction is inversely proportional to the lower oxygen pressure in Fig. 4 and agrees with the pressure dependence observed for the solid state reaction in the bulk sintering process[9, 10]. The results of Ranno *et al.* and Ohkubo *et al.*, however, are opposite to ours. These contradictory results would be caused by the fact that the factors

playing dominantly due to the Bi2212 thin film formation differs among the film deposition procedures such as the IBS, PLD, or CSS methods. The following factors are considered to give a large influence on the thin film fabrication; species of the oxidant, vacuum pressure and types of the target, and growth rate and energy of the sputtering particle. The sticking coefficient of the Bi element, for instance, can be considered as evidence of a close relationship between the growth processes and/or the particle energy. The Bi sticking coefficients differ by a factor of about one order of magnitude depending on whether they are supplied by an effusion cell or ion beam sputtering in our experiments[4]. It is largely influenced even by the procedural difference between co-sputtering and layer-by-layer sputtering under the same fabrication system conditions[11].

Next, we consider the growth process in the BSCCO thin film fabrication, and estimate the activation energy for the Bi2212 phase formation from Fig. 4 in terms of the Avrami equation, which has been successfully applied to analyze kinetics of the phase transformation for the bulk oxide superconductors[12] and expressed as follows:

$$p = 1 - \exp(-k t^n) \quad (1)$$

Here, p is the Bi2212 molar fraction as described above, k the reaction rate, t the reaction time, and n the Avrami exponent which depends on the reaction mechanism and geometry of nuclei and so on. The reaction rate k is related with the activation energy of the reaction E in terms of the following Arrhenius-type equation:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (2)$$

Here, R is the universal gas constant, T is the absolute temperature, and k_0 is constant. Substituting Eq. (2) into Eq. (1), we can obtain

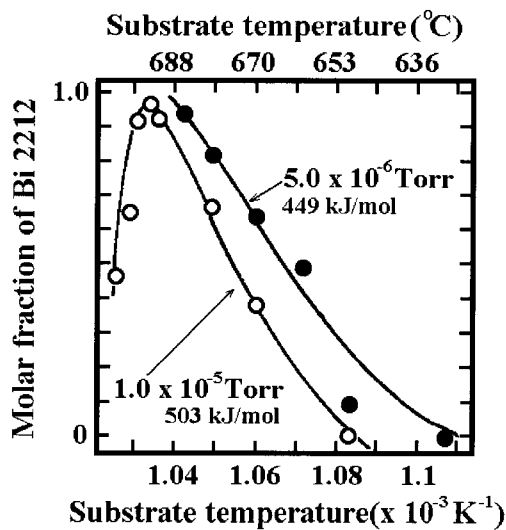


Fig. 4. The molar fraction of the Bi2212 phase in the mixed crystals as a function of the substrate temperature. The full and dashed lines indicate the behavior of the phase transformation in the Bi2201/Bi2212 and Bi2212/Bi2223 mixed crystals, respectively. The closed and open circles exhibit at 5.0×10^{-6} and 1.0×10^{-5} Torr, respectively.

$$p = 1 - \exp\left[-\alpha(t) \exp\left(\frac{-E}{RT}\right)\right] \quad (3)$$

Although $\alpha(t)=k_0t^n$ is a function depending strongly on t , here it can be regarded as a constant since the deposition time t is kept constant in our successive experiments. Equation (3) represents the temperature dependence of the molar fraction $p(T)$ of the Bi2212 phase. Consequently, the activation energy E for the phase transformation from the Bi2201 to the Bi2212 can be determined from the experimental data in Fig. 4 by least-squares fitting method. The fitting curves are expressed by full lines for the both ozone pressures in Fig. 4.

The activation energy E for the phase transformation from the Bi2201 to the Bi2212 phase were given as 449 and 503 kJ/mol for the co-deposition under the ozone pressure of 5.0×10^{-6} and 1.0×10^{-5} Torr, respectively. These values are found in approximate agreement with those estimated for the solid state reaction with a partial melting process. The activation energy E in the case of the bulk synthesis of the Bi2223 from the Bi2212 has been summarized as ranging from 250 to 400 kJ/mol on the basis of the other's reports. On the other hand, it was found that the activation energy ranging from 1,500 to 3,000 kJ/mol is required by the solid state reaction process without the aid of the liquid state[13].

Our group has already reported that the liquid state of Bi_2O_3 exists partially on the substrate from temperature dependence on Bi sticking coefficient[3] and that the liquid phase plays an important role in the phase formation of Bi2212 thin films. The coincidence of the activation energy with the bulk synthesis supports the validity of our insistence that the liquid state largely contributes to the phase transformation. Moreover, this lower activation energy displays that the diffusion process of each element or any clusters would be a rate determined one. To be interesting, it is well known in the bulk synthesis that the partial melting state plays an important

role in the phase transformation process from Bi2212 to Bi2223, but that it does not function between the Bi2201 and Bi2212 phases. It was found out that the liquid state participates significantly in every stage of the superconducting phase formation in the thin film fabrication, differing from the bulk synthesis.

4. CONCLUSIONS

In this paper, we have investigated the phase intergrowth of the BSCCO thin films. The substrate temperature and ozone pressure dependence on the molar fraction of the Bi2212 phase in the mixed crystals of the BSCCO thin films clarified that a liquid phase plays an important role in the Bi2212 as well as Bi2223 phase formations.

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