Phase Intergrowth in the Synthesesof Bi-superconducting Thin Films

Min-Woo Chun, In-Soon An, Yong-Pil Park

Abstract

Phase intergrowth some kinds of the $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ 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 junction. Especially, the application of the junctions between the $a-$ and $c-$axes oriented films in the $YBa_2Cu_3O_x$ type structure[1,2] and of grain boundary junctions to the devices, have been in progress. Meanwhile, much attention has been also devoted to the fabrication of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$(n=1, 2, and 3) thin films. 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/PrBa_2-Cu_3O_2/YBCO system[3]. In this article, we discuss the growing mechanism of the

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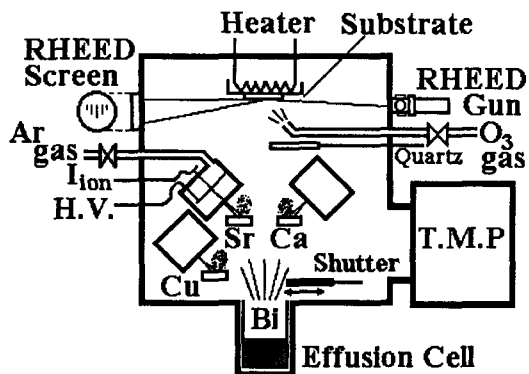Fax : 061-330-2909
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BSCCO thin films with interrelationship among the respective phases.

2. EXPERIMENTAL

The BSCCO thin films were fabricated using a co-sputtering deposition technique. Figure 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 beans generated by saddle field type cold cathode guns.

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 ℃. Highly condensed ozone gas was obtained by a silica gel adsorption method[6] and was supplied onto the substrate during deposition of the metallic species to provide an oxidation environment.

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

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. 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 = 2.1 ± 0.2 : 2.0 ± 0.1 : 0.9 ± 0.1 : 2.0 ± 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. In the macroscopical domain where the individual Bi2201 and Bi2212 phases are mixed separately, the intensity ratio of the $(00l)$ 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 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[7] is constructed. Ranno et al.[8] have also observed similar XRD peak shift in the BSCCO thin films fabricated by PLD method using a single target.
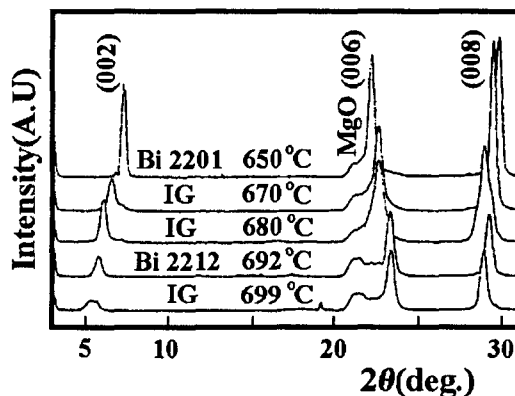

Fig. 2. XRD patterns of the thin films fabricated at various substrate temperatures under the ozone pressure of 1.0×10^{5} Torr.

The theoretical relationship between the $(00l)$ 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.

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 $PO_3 = 1.0 \times 10^{-5}$ Torr and the full circle for $PO_3 = 5.0 \times 10^{6}$ 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.

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 Bi22n(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.
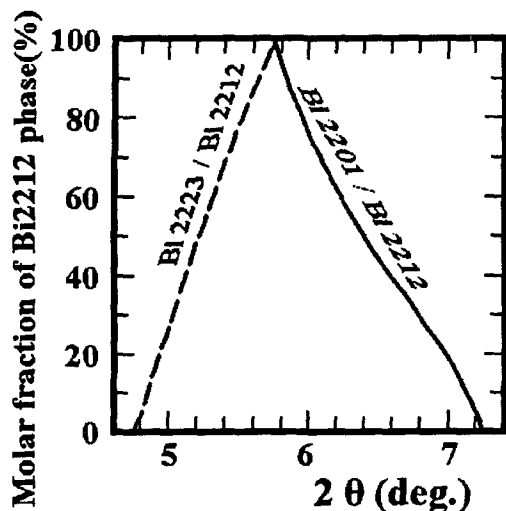
Fig. 3. The relationship between the molar fraction p of the Bi2212 phase and the (002) peak position of the mixed crystal of the BSCCO compounds is estimated ideally in terms of an equation given by Ranno et al.

Ohkubo et al.[9] obtained a similar result for the de-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 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 $\Delta T = \pm 5$ °C at $T = 690$ °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[10,11].
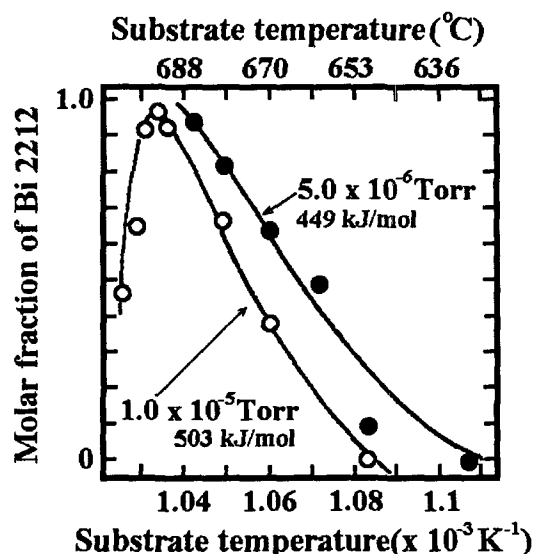

Fig. 4. The molar fraction of the Bi2212 phase in the mixed crystals as a function of the substrate temperature.

The results of Ranno et al. and Ohkubo et al., however, are opposite to ours. The Bi sticking coefficients differ by a factor of about one order of magnitude depending on whether they ore supplied by an effusion cell or ion beam sputtering in our experiments.[5] It is largely influenced even by the procedural difference between co-sputtering and layer-by-layer sputtering under the same fabrication system conditions[12].

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[13] and expressed as follows:

$$p = 1 - \exp(-k\,t^{n})$$

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 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 ol 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[14]. On the other hand, it was found that the activation energy ranging from 1500 to 3000 kJ/mol is required by the solid state reaction process without the aid of the liquid state[15].

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. 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 superconduc- ting 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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