Fabrication Condition for Single Phase of BSCCO Thin Film

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

Abstract

Phase intergrowth in BSCCO thin films have been investigated. It turned out from XRD analyses of these phases that molar fraction of each constituent phase in the intergrowth thin film can be exhibited as a function of substrate temperature and ozone pressure. Superconducting behavior of the intergrowth thin film is also discussed.

Key Words : $Bi_2Sr_2Ca_{n-1}Cu_nO_x$, BSCCO, superconducting thin films, ion beam sputtering phase intergrowth

1. INTRODUCTION

Bi-superconductor $(Bi_2Sr_2Ca_{n-1}Cu_nO_x < n = 1, 2, 3 \cdots >$; BSCCO) has three stable phases such as $Bi_2Sr_2CuO_x$(Bi2201) with both characters of semiconducting and superconducting behavior($T_c \sim 7$ K), $Bi_2Sr_2CaCu_nO_x$(Bi2212) with $T_c = 80$ K and $Bi_2Sr_2Ca_2Cu_3O_x$(Bi2223) with $T_c \sim 110$ K. Their electric properties corresponding to number of $[CuO_2]$-planes have attracted much attention as a predominant candidate for electric devices. Therefore, a great deal of efforts has been devoted to fabricate high quality thin films and artificial lattice of BSCCO. However, the intergrowth among each phase is occasionally observed in thin film fabrication[1-3] or single crystal growth. Thus. it is an important subject to find out the fabrication conditions for the single phase thin film, depressing the intergrowth.

In this article, we describe the fabrication condition for single phase and the mixed crystal of Bi-superconducting thin films through an

----

* : 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)

analysis of XRD data. The analysis proposed by Hendricks and Teller[4] enables us to estimate molar fraction of each constituent phase in the mixed crystal. We also discuss about the properties of these mixed crystal.

2. EXPERIMENTAL

BSCCO thin films were fabricated via co-deposition process using ion beam sputtering method. The apparatus is almost same as previously reported[5]. Only Bi flux was supplied by an effusion cell because of its low sticking coefficient in fabricating BSCCO phases[5]. MgO(100) used as a substrate was attached on an inconel block using silver paste to heat it uniformly. In order to distinguish the growth condition of single phase from that of the mixed crystal in BSCCO thin films, substrate temperature and the pressure of highly concentrated ozone gas over 90 mol% were systematically varied from 600 to 705 ℃ and from 1.0×10^{-6} to 2.0×10^{-5} Torr, respectively.

The structure and composition ratio of the ilms were examined by XRD and EDX analyzer, respectively. Electric resistivity of the thin films was measured by a standard dc four-probe method.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of BSCCO thin films fabricated under the ozone pressure of 1.0×10^{-5} Torr.
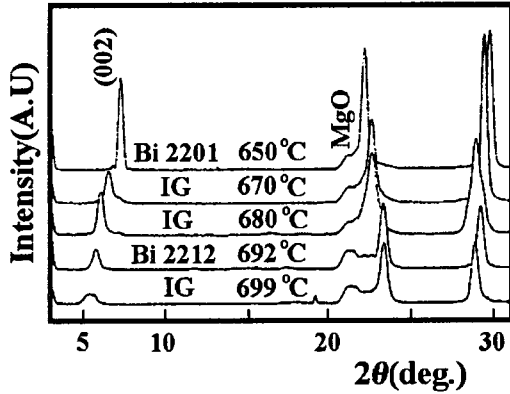

Fig. 1. The XRD patterns of single and intergrowth thin films of BSCCO.

IG : intergrowth thin film

The compositional deviation from the stoichiometry in thin films obtained in Bi2212 composition is approximately 2.0 ± 0.4 : 2.0 ± 0.2 : 1.0 ± 0.3 : 2.0 ± 0.4. A gradual peak shift of Bi2201 phase to Bi2212 one was observed with the increase of the substrate temperature, suggests that the mixed crystal consisting of Bi2212 and Bi2201 phases forms as a function of substrate temperature. According to Hendricks and Teller[4] and Ranno et al. [2], the molar fraction of Bi2212 phase in the mixed crystal, p and intensity of XRD, $I(\theta, p)$ is related to,

$$I(\theta, p) = |F(\theta)| [2p(1-p)\{1-\cos[k(d_2-d_1)]\}]/X$$
$$X = 1+p^2+(1-p)^2+2p(1-p)\cos[k(d_2-d_1)] -$$
$$2p\cos(kd_1)-2(1-p)\cos(kd_2) \qquad (1).$$

Here, θ is the Bragg angle, $k = 4\pi \sin\theta / \lambda$ the scattering vector and $F(\theta)$ the structure factor. The value of X indicates the shift of 2θ with the formation of the mixed crystal. Assuming that the unit cell of BSCCO is consisted by $Bi_2Sr_2O_x$ and $Ca_{n-1}Cu_nO_x$ subunits, the dominant parts scattering the incident X-ray are $Bi_2Sr_2O_x$

subunits. And the periodicity of this subunit is a half of c-axis in length, therefore d_1 and d_2 are respectively given 1.535 nm and 1.219 nm for the analysis of the intergrowth between Bi2212 and Bi2201. It is enough only to change d_2 to 1.850 nm in case of analyzing the mixed crystal with Bi2212 and Bi2223 phases. Utilizing eq. (1), the variation of each constituent phase was calculated in these intergrowth samples using (002) peaks of BSCCO phase in similar way to Ref.[2]. The results calculated in terms of eq. (1) under 5.0×10^{-6} Torr and 1.0×10^{-5} Torr are depicted in Fig.2.
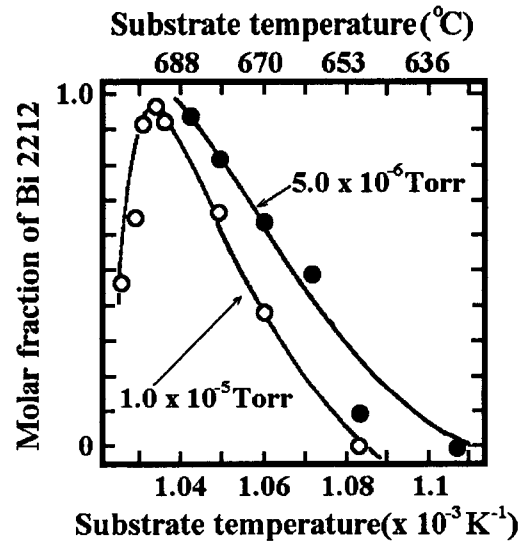

Fig. 2. The substrare temperature and the ozone pressure dependence of the molar fraction of Bi2212 in the mixed crystals.

This graph clearly reveals that the formation temperature of single phase shifts toward the higher one with the increase of ozone pressure. Moreover, comparing the formation temperatures of the mixed crystals with same molar fraction of Bi2212 phase, it becomes lower in the case of the lower oxygen pressure. The reduction of Bi2212 phase in the thin films fabricated under 1.0×10^{-5} Torr is observed in higher temperature than 695 ℃. This is brought about by progressing from Bi2212 phase to Bi2223 one,

and suggests that the mixed crystal with Bi2212 and Bi2223 phases must be considered in spite of Bi2212 composition. Furthermore, this analysis clarifies that single phase Bi2212 can be obtained under only narrow substrate temperature, but that its formation ratio reaches to 97 % at maximum.

In the case of 1.0×10^{-5} Torr, it is permitted only 5 ℃ as temperature fluctuation to obtain the maximal Bi2212-formation. We cannot refer to applicable extent of eq. 1, but it is naturally difficult to form complete Bi2212 single phase taking the difference of formation free energy between Bi2212 and Bi2201 phases into consideration[6-7]. Although we tried to fit the data in Fig. 2 using Avrami's equation, and obtained reproducibly about 450 kJ/mol as an activation energy, we cannot strictly elucidate the origin of this value for the sake of deficiency of time dependence measurement.

Ranno et al.[2] reported that the increase of oxygen pressure during the deposition gives rise to a phase evolution from a mixed crystal consisting of Bi2201 and Bi 2212 phases to that of Bi2212 and Bi2223 ones. Their results for oxygen pressure are inconsistent to our result, as shown in Fig. 2. Thus, let us consider about the effect of the oxygen pressure on the gradual transformation of Bi2201(Bi2212) phase to Bi2212 (Bi2223) one. Recently, Park et al.[5] reported that a liquid phase of Bi_2O_3 plays an important role in the growth of Bi2212 phase from the study of temperature dependence of sticking coefficient of Bi. And, Luo et al.[8] denoted that a liquid phase formation reduced considerably activation energy for phase transition of $(Bi_{2-x}Pb_x)Sr_2CaCu_2O_z$ to $(Bi_{2-x}Pb_x)Sr_2Ca_2Cu_3O_x$ or Bi2212 to Bi2223 from 3,100 kJ/mol to 460 kJ/mol. These results suggest that a liquid phase reaction is profitable for the phase reaction is profitable for the phase evolution to Bi2212(Bi2223) phase from Bi2201(Bi2212) one. In other words, Bi-superconductor is incline to grow at higher temperature under lower oxidation pressure in comparison with the insertion of $CaCuO_2$ layers.
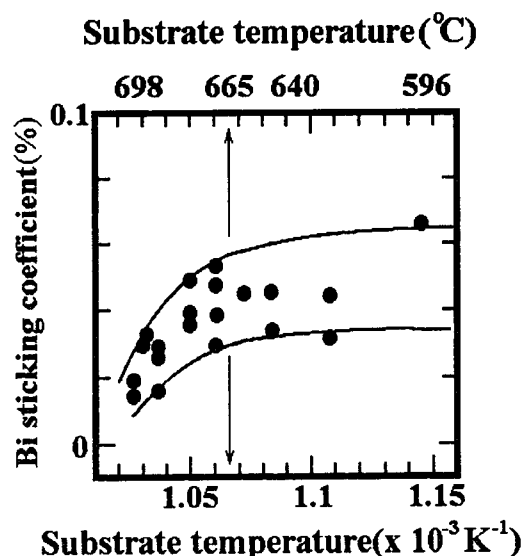

Substrate temperature(℃)

Fig. 3. The temperature dependence of the sticking coefficient of Bi.

To clarify the existence of a liquid phase during the deposition, we investigated the sticking coefficient of Bi in the similar manner to Park et al.[5]. Fig. 3 shows the sticking coefficient of Bi for the BSCCO thin films. An obvious decrease of the sticking coefficient was observed about 1.067×10^{-3} K^{-1}(approx. 665 ℃).

This temperature corresponds to the beginning one of intergrowth shown Fig. 2. And the activation energy estimated by our trial fitting of Avrami's equation agree well with that of a liquid phase proposed by Luo et al[8]. These results supports existence of a liquid phase reaction. Namely according to Clausius-Clapeyron rule, both conditions of high temperature and low oxygen pressure help the formation of the liquid phase(maybe partially). Therefore, it can be ascertained that temperature and ozone pressure dependence of the molar fraction of Bi2212 phase shown in Fig. 2 are quite reasonable. The discrepancy between the results of Ranno et al. and ours may come form the difference of growth mechanism due to the different fabrication method. We also investigated phase intergrowth in fabricating Bi2223 phase by adjusting the compositional

ratio, Bi : Sr : Ca : Cu = 2.0±0.4 : 2.0±0.3 : 2.0±0.4 : 3.0±0.5.

Fig. 4 shows the temperature dependence of resistivity for the intergrowth thin films with both phases of Bi2201 and Bi2212. For the intergrowth thin film including to Bi2212 phase of 92 mol%(sample (a)), T_c^{onset} and T_c^{zero} are 82 K and 55 K, respectively. It's broadening may be brought about a strong anisotropic behavior of Bi-superconductor and thickness of our films ($\simeq$40 nm). T_c^{onset} of all the samples was unchanged at 82 K with molar fraction of Bi2201 phase. But resistivity profiles below T_c^{onset} were changed from superconducting behavior to semiconducting one with reduction of the fraction of Bi2212 phase. For the samples (b) and (c), the profiles were somewhat metallic behavior in normal state and T_c^{zero} was about 5 K. Samples (d) and (e) show semiconducting behavior. Sample (e), which molar function of Bi2212 phase reached to 38 %, seems to display semiconducting transition no longer. The variation of carrier density in [CuO$_2$]-layers by transference between Bi2201 and Bi2212 phase is one of the possible reason for these behaviors. Detail investigation on the electric properties of the inter growth thin films will be described elsewhere.
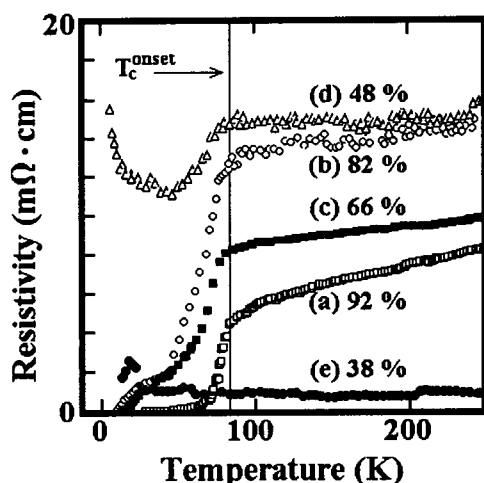

Fig. 4. The resistivity vs the temperature for the mixed crystals of Bi2212 and Bi2201 phase.

4. CONCLUSIONS

Among the optimum for the single phase fabrication of Bi2201, Bi2212 and Bi2223 thin films, phase intergrowth inevitably occurred. According to the XRD analysis proposed by Ref. [4], The molar fraction of each constituent phase in the mixed crystal was varied by ozone pressure and substrate temperature. If the single phase of Bi-superconductor thin film were obtained, very strict fabrication conditions would be required, even from view point of XRD observation. Therefore, it was noted that liquid phase formation plays an important role as the reference to the temperature dependence on the sticking coefficient of Bi. The resistivity of the intergrowth thin films with both phases of Bi2212 and Bi2201 phase were systematically changed by molar fraction of Bi2212 phase.

REFERENCES

[1] D. G. Schlom, A. F. Marshall, J. T. Sizemore, Z. J. Chen, J. N. Eckstein, I. Bozovic, K. E. Von Dessonneck, J. S. Haris Jr and J. C. Bravman, J. Cryst. Growth, 102, 361-375 (1990)

[2] L. Ranno, D. Martinez-Garcia, J. Perriere and P. Barboux, Phys. Rev. B 48, 13945-13948(1993)

[3] K. Nakamura and T. Hatano, J. Appl. Phys. 77, 6402-6409(1995)

[4] S. Hendricks and E. Teller, J. Chem. Phys. 10, 147-167(1942)

[5] Y. P. Park, H. K. Lee, K. W. Lee and J. U. Lee, Journal of KIEEME, 13, 1, 80-84(2000)

[6] Y. P. Park, H. K. Lee and J. H. Kim, Proceeding of the KIEEME Autumn Annual Conference 2000, 13, 1, - (2000)

[7] Y. Idemoto, K. Shizuka, Y. Yasuda and K. Fueki, Physica C, 211, 36-44(1993)

[8] J. S. Luo, N. Merchant, E. Escorcia-Aparicio, V. A. Maroni, D. M. Gruen, B. S. Tani, G. N. Riley Jr. and W. L. Carter, IEEE Trans. Appl. Supercond. 3, 972-975(1993)