

## Phase Stability of Bi-2212 and Bi-2223 Thin Films Prepared by IBS Technique

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Bi-2212 and Bi-2223 thin films are prepared by IBS(ion beam sputtering) technique. Three phases of Bi-2201, Bi-2212 and Bi-2223 appear as stable ones in spite of the conditions for thin film fabrication of Bi-2212 and Bi-2223 compositions, depending on substrate temperature ( $T_{sub}$ ) and ozone pressure( $PO_3$ ). It is found out that these phases show similar  $T_{sub}$  and  $PO_3$  dependence, and that the stable regions of these phases are limited within very narrow temperature.

*Keywords* : phase stability, Bi-superconductor, thin film, ion beam sputtering, free energy

### 1. INTRODUCTION

Thermodynamic study of multi-constituent compounds such as  $Bi_2Sr_2Ca_nCu_{n+1}O_x$ (BSCCO;  $Bi22n(n+1)$ ,  $n \geq 0$ ) system is very difficult because of polymorphism. Most of thermodynamical studies have been carried out about the phase stabilities in bulk BSCCO samples under the equilibrium state of 1 atmosphere. To our knowledge, however, we can find no report concerning thermodynamic consideration for thin film fabrication because it suffers a large influence not only on thermodynamic factor but also on growth kinetic one due to non-equilibrium process. Thus, we attempted to determine the stably existing regions of Bi-2201, Bi-2212 and Bi-2223 phases as functions of the substrate temperature( $T_{sub}$ ) and ozone pressure ( $PO_3$ ).

### 2. EXPERIMENTAL

The equipment of ion beam sputtering system used for the co-deposition method has already reported in detail elsewhere[1-3], thus in brief, only essential points would be described. Only Bi element was vaporized from an effusion cell due to its little sticking coefficient, differing from the others sputtered by ion

beam source. The outputs of each ion gun and flux rate of effusion cell were controlled for adjusting the constituent ratio of Bi-2212 or Bi-2223 composition. Single crystal of MgO(100) was used as a substrate, and the substrate temperature was varied between 670 and 710 °C.

Highly condensed ozone gas over 90 mol% was employed as an oxidation gas, and introduced into vacuum chamber, keeping a constant pressure between  $2 \times 10^{-6}$  and  $2 \times 10^{-5}$  Torr. The thickness of thin film obtained is about 45 nm, corresponding to 30 half unit cells of Bi-2212 phase.

Crystal structure and compositional analysis of the thin film obtained were examined by X-ray diffractometer(XRD) in the Bragg-Brentano geometry using Cu-K $\alpha$  radiation and energy dispersive X-ray spectrometer(EDX), respectively.

### 3. RESULTS AND DISCUSSION

Each phase that appeared in the thin films with Bi-2212 composition was plotted in Fig. 1 as functions of inverse temperature( $1000/T$ ) and logarithm of ozone gas pressure( $\ln PO_3$ ). The open, close and hatched

circles represent single phases of Bi-2201( $2\theta = 7.24^\circ$  for (002) peak in bulk), Bi-2212( $2\theta = 5.76^\circ$ ) and Bi-2223( $2\theta = 4.77^\circ$ ), respectively, which were judged from peak positions by XRD. Although some doubt may take place that Bi-2201 and Bi-2223 phases was found as stable ones in spite of having been set in Bi-2212 composition, it was verified by EDX that the ratio of the constituent elements in the thin film coincides nearly with Bi-2212 composition within the error of  $\pm 2\%$ . Bi-2201 single phase are formed in wide temperature region near  $660^\circ\text{C}$ , while Bi-2212 one is limited in very narrow temperature ranging of about  $5^\circ\text{C}$ , and this Bi-2212 phase stability region shifts to the higher temperature in proportional to the increase of  $\text{PO}_3$ . In farther high temperature region, Bi-2223 phase come out instead of Bi-2212 one. The peak positions in some samples locate in their intermediate angle according to the substrate temperature, were closely connected with the formation of the mixed crystal by Hendricks and Teller[4]. The mixed crystal is represented as the superimposing of each mark in Fig. 1. Accordingly, these thin films obtained can be clarified into two groups of Bi-2201, Bi-2212 of Bi-2223 single phase and the mixed crystal consisting of the intergrowth among the respective phases. This temperature effect on the formation of the mixed crystal between these phases would be interpreted in a separate paper.

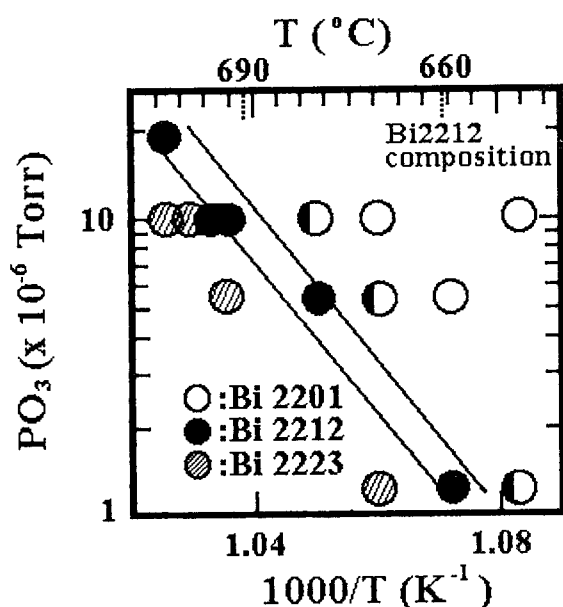


Fig. 1. Phase diagram against inverse temperature and  $\text{PO}_3$ . The thin film composition was fixed in ratio of Bi-2212

It was well known that thermodynamical phase stability increases in the order of Bi-2223 < Bi-2212 < Bi-2201 phases[6]. Generally speaking, phase transition from the more stable phase to the less stable one is recognized to be brought by the increase of entropy. Thus, phase transition in BSCCO compounds would be mainly dominated by three entropy changes due to the conformation, the mixture and the evaporation. It is considered that phase transition in the bulk sample would be governed by the mixing entropy because each phase is successively synthesized through the diffusion process of the constituent element[7]. In the case of the compound with volatile character, however, Kim *et al.*[8] have reported that entropy change due to evaporation becomes important rather than the mixing entropy. In thin film fabrication the similar situation can take place, considering that the adsorption of each element is determined by the equilibrium between the intake and re-evaporation. Fig. 2 shows temperature dependence of sticking coefficient of Bi element, which is given as the ratio of atom numbers in the thin film against the incident ones onto the substrate. Sticking coefficient of Bi element decreases lineally with temperature above  $650^\circ\text{C}$ , at which Bi-2212 structure approximately begins to form. This decrease of Bi-sticking coefficient implies that the larger amount of Bi atoms would come to vaporize from thin film surface with the increase of substrate temperature.

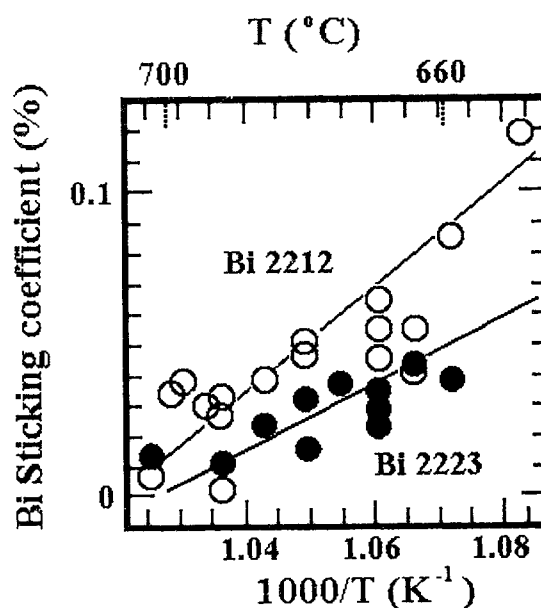


Fig. 2. Sticking coefficient of Bi element as the function of temperature.

Thereby, the increase of the entropy due to evaporation would be induced. On the other hand, notice that the liquid phase formation may be brought simultaneously. In bulk sample, phase transitions from Bi-2201 or Bi-2212 to Bi-2212 or Bi-2223 are known to be promoted through the partial melt state. And, the liquid phase formation in thin film fabrication has been also reported in BSCCO system[2] and Pb-superconductor by Ikegawa et al.[5]. This liquefaction accompanies with adsorption of the large energy caused by the latent heat, that is, the large enthalpy change. This enthalpy change would work as a more important driving force of phase transition. Accordingly, in thin film fabrication BSCCO-phase transition would be influenced not only by entropy change but also by enthalpy one.

Next, we investigated the stable region of phases which appeared in the thin film fabricated in Bi-2223 composition. Its phase diagram was shown in Fig. 3. In similar to Fig. 1., three phases of Bi-2201, Bi-2212 and Bi-2223 come out and similar dependence is displayed on  $T_{sub}$  and  $PO_3$  for each phase generation. However, the slopes of  $T_{sub}$  vs.  $PO_3$  for the respective phases in Fig. 3 are largely different from those for the phases corresponding in Fig. 1.

The slope of  $PO_3$  against the inverse  $T_{sub}$  for these respective phases can have a close relationship with the change of Gibbs free energy( $\Delta G$ ) between before and after BSCCO phase formation. Generally speaking,  $\Delta G^\circ$  is evaluated only in equilibrium state between solid and gas phases under the oxidation condition with gas circumstance of 1 atmosphere. Then,  $\Delta G^\circ$  is calculated as  $RT \ln p_{O_2}$  as functions of temperature( $T$ ) and partial oxygen pressure( $p_{O_2}$ ). However, it is impossible to estimate directly even quantitative  $\Delta G$  from  $PO_3$  under our experimental condition of  $10^{-6} \sim 10^{-5}$  Torr. This mortal fault comes from the deficiency of the knowledge for the oxidation of decomposition process of  $O_3$  gas under the reduced pressure and for the effects of partial pressure of  $O_2$  or the introduced  $O_3$  gas on BSCCO structural formation. Although we tried to estimate  $\Delta G$  from these slopes for phase transition of BSCCO, we failed to estimate  $\Delta G$  nowadays.

Here, let us consider the reason why the respective phases in thin film exist stably. Fig. 4 shows the boundary of phase stability between Bi-2212 and Bi-2223 phases of Fig. 1 under the ozone injected into the reduced pressure (a), in comparison with those under the equilibrium state of 1 atmosphere (b)[9]. Under 1 atmosphere the  $p_{O_2}$ - and  $T$ -dependence on the phase stability region between  $CuO$  and  $Cu_2O$  has been reported to agree well with those between Bi-2212 and Bi-2223 phases[9].

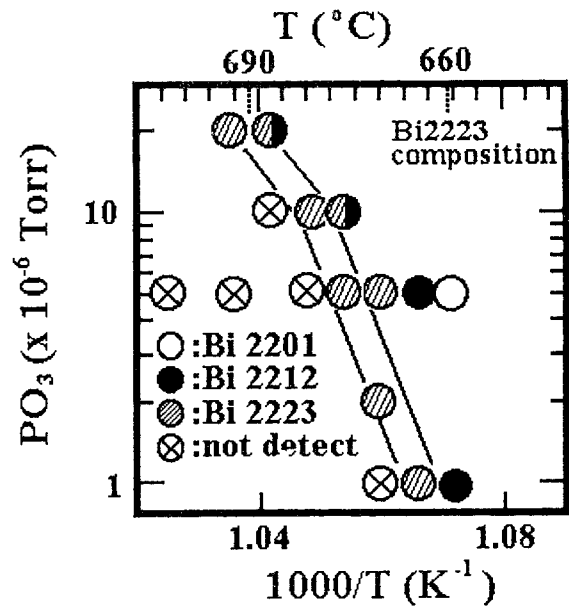


Fig. 3. Phase diagram of thin film fabricated as matching the ratio of Bi-2223.

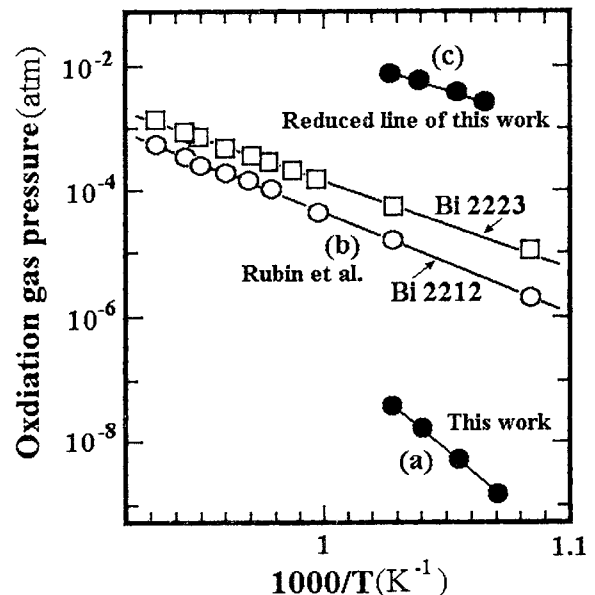


Fig. 4. Phase stability boundaries of BSCCO phase in different oxidation condition.

And, the boundary of phase stability of CuO-Cu<sub>2</sub>O under O<sub>2</sub> or O<sub>3</sub> gas can be evaluated from JANAF's data[8], exhibits that phase equilibrium line between  $3\text{Cu}_2\text{O} + \text{O}_3 \rightarrow 6\text{CuO}$  shifts toward the lower pressure region than that of  $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$ , reflecting difference of the oxidation power between O<sub>2</sub> and O<sub>3</sub>. The  $\text{InPO}_3$  under low pressure can be virtually replaced to  $\text{InPO}_2$  under partial pressure, utilizing the pressure ratio of O<sub>3</sub>/O<sub>2</sub> in each phase equilibrium line at each temperature, and line (a) under ozone pressure is regarded as line (c) under oxygen partial pressure of 1 atmosphere. The virtual line (c) locates within the stable region of Bi-2212 or Bi-2223 phase and slope of this line agrees approximately with that of line (b). This denotes that our fabrication condition for Bi-superconducting thin film is enough to form all phases of BSCCO. The virtual boundary of phase stability between Bi-2212 and Bi-2223 phases in Fig. 3 also stays in stable region of Bi-2223 phase.

These may guess from these virtual boundary lines that only the phase corresponding to the deposited elemental ratio should be considered to come out, and that the transference from Bi-2201 or Bi-2212 phase to Bi-2212 or Bi-2223 one would occur with time, respectively. However, clear difference between bulk synthesis and thin film fabrication would come out in the formation processes of these phases. The solid state reaction for the Bi-2212 or Bi-2223 phase is performed reversibly between the upper and lower sides of line (b) according to intake or release of the oxygen, while the reaction across the line (c) in thin film is irreversible, considering that Bi<sub>2</sub>O<sub>3</sub> liquid phase is required to construct Bi-2212 or Bi-2223 phase[2]. Namely, only a directional reaction from right to left side successively takes place with temperature, that is, Bi-2201 → Bi-2212 → Bi-2223 → decomposed phases examining the reaction in Fig. 1 or 3 with the increase of temperature at same  $\text{InPO}_3$

#### 4. CONCLUSIONS

We have examined the phase stability of Bi-superconductor as functions of the substrate temperature and ozone pressure, fixing the constituent ratio of Bi-2212 or Bi-2223 composition. As the result, it was found out that Bi-2201, Bi-2212 and Bi-2223 phase were formed in spite of the film composition, and that Bi-2212 or Bi-2223 single phase existed in very narrow temperature region. The stable region of Bi-2212 phase in the thin film with Bi-2212 composition almost overlaps with that of Bi-2223 phase in the thin film with Bi-2223 composition. These stability line

of the reaction under the ozone pressure injected in the vacuum chamber were converted to that in oxygen partial pressure at 1 atmosphere, using the phase stability relationship between Cu<sub>2</sub>O and CuO.

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