Thermodynamics for Formation of Each Stable Single Phase in BSCCO Thin Films

Sung-Ho Yang*, Yong-Pil Park* and Gwi-Yeol Kim**

Abstract

High quality BSCCO thin films have been fabricated by means of an ion beam sputtering at various substrate temperatures, T_{sub}, and ozone gas pressures, PO_3. The correlation diagrams of the BSCCO phases appeared against T_{sub} and PO_3 are established in the 2212 and 2223 compositional films. In spite of 2212 compositional sputtering, Bi2201 and Bi2223 phases as well as Bi2212 one come out as stable phases depending on T_{sub} and PO_3. From these results, the thermodynamic evaluations of ΔH and ΔS which are related with Gibbs' free energy change for single Bi2212 or Bi2223 phase are performed.

Key Words : thermodynamics, BSCCO phases, ion beam sputtering, Gibbs' free energy

1. INTRODUCTION

The Bi-superconductor $Bi_2Sr_2Ca_nCu_{n+1}O_y$(hereafter denoted by BSCCO or Bi22n(n+1);≥0) is a multi-constituent compound in which each component is allotted a different role. It is difficult to construct a single BSCCO phase from each component without the basic knowledge concerning the complex reactions among components each other. The generation of the impurity phases and the phase intergrowth of BSCCO structure would be easily brought about. Nevertheless, to our knowledge we can find no report concerning thermodynamic consideration for the phases appearing in the thin film fabrication. The participation not only of thermodynamic factors but also of growth kinetics due to non-equilibrium processes enhance the difficulty to understand the process of the thin film fabrication. In this article, we establish the stably existing regions of Bi2201, Bi2212 and Bi2223 phases as functions of the substrate temperature (T_{sub}) and ozone pressure(PO_3) by taking the enthalpy of (ΔH) and entropy (ΔS) of reaction in BSCCO system into consideration.

2. EXPERIMENT

Equipment of the ion beam sputtering system used for the co-deposition of BSCCO thin film has already reported in detail elsewhere[1-2], thus only essential points are described in brief. A single crystal of MgO(100) was used as a substrate, and its temperature was varied between 650 and 710 ℃. Highly condensed ozone

* : 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)
** : School of Information and Technology Eng.,
　　Korea University of Technology and Education

gas over 90 mol% was employed as an oxidation gas. And the thickness of thin film obtained was about 45 nm, corresponding to 30 half unit cells of the Bi2212 phase.

3. RESULTS AND DISCUSSION

The phases presented in the thin films fabricated with Bi2212 composition were plotted in Fig. 1. The marks of the triangular, circle and square in Fig. 1 indicate the phases of Bi2201(2θ = 7.24 ° for (002) peak in the bulk), Bi2212(2θ = 5.76 °) and Bi2223(2θ = 4.77 °), respectively. Although one seems it to come from the compositional fluctuation that Bi2201 and Bi2223 phases were found as stable ones in spite of having been set in Bi2212 composition. In the thin film fabrication the Bi2201 single phase are formed in the wide temperature region below 660 ℃, while the Bi2212 one is limited to very narrow temperature range of about 5 ℃ and the stable region of this Bi2212 phase shifts to the higher temperature in proportion to the increase of PO_3. In higher temperature region, the Bi2223 phase comes out instead of Bi2212 one and the peak positions in some samples locate at the intermediate angles between Bi2201 and Bi2212 phases, depending on the substrate temperature. These peak shifts have a close relationship to the formation of the mixed crystal as having been discussed by Hendricks and Teller[3]. This mixed crystal are depicted in Fig. 1 as the superimposing of each mark. Accordingly, these thin films obtained can be classified into the two groups of the single phase, i.e. Bi2201, Bi2212 or Bi2223, and the mixed crystal consisting of the intergrowth among the respective phases. T_{sub}-and PO_3-dependence similar to Fig. 1 was also established in the case of the Bi2223 compositional sputtering and it turned out that the stable region of Bi2223 phase was almost overlapped with that of Bi2212 in Fig. 1. This suggests a similarity in the processes of the phase formation between Bi2212 and Bi2223 phases.
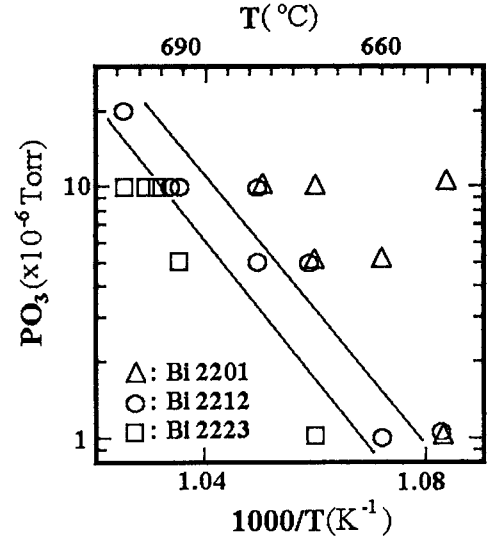

Fig. 1. Phase diagram for th thin films by 2212 compositional sputtering against the inverse T_{sub} and $lnPO_3$.

The slope of PO_3 against the inverse T_{sub} for these respective phases have a close relationship with the variation of Gibbs' free energy(ΔG) between before and after BSCCO phase formation. In an equilibrium state a chemical potential of oxygen dissolved into the solid phase, $\mu o(s)$, is equal to that of O_2 gas one, $\mu o_2(g)$. Taking O_2 gas state of 1 atmosphere as a standard, $\mu^0 o_2(g)$,

$$2\mu o(s) = \mu o_2(g) = \mu^0 o_2(g) - RTlnpO_2 \qquad (1)$$

Accordingly, $\Delta \overline{G}o_2$ is related with chemical potential in solid and gas phases as follows

$$Go_2 - G^0 o_2 = \Delta \overline{G}o_2 = \mu o_2(g) - \mu^0 o_2(g)$$
$$= 2\mu o(s) - \mu^0 o_2(g) = -RTlnpO_2$$
$$= \Delta \overline{H}o_2 - T\Delta \overline{S}o_2 \qquad (2)$$

The variation of the enthalpy, $\Delta \overline{H}o_2$ and the entropy, $\Delta \overline{S}o_2$ are given in terms of

Gibbs-Helmholtz equations as

$$\Delta \overline{Ho}_2 = \frac{\partial(\Delta \overline{Go}_2/T)}{\partial(1/T)} = \frac{\partial Rln pO_2}{\partial(1/T)} \qquad (3)$$

$$\Delta \overline{So}_2 = -\frac{\partial(\Delta \overline{Go}_2)}{\partial T} = -\frac{\partial RTln pO_2}{\partial T} \qquad (4)$$

These values can be hardly estimated directly in the thin film fabrication used the ozone gas under our experimental condition of 10^{-6} - 10^{-5} Torr as known from eqs. 1 and 2. This mortal fault comes from the deficiency of the knowledge for the oxidation or decomposition process of O_3 gas under introduced O_3 gas on BSCCO structural formation.

The phase stability boundary between Bi2212 and Bi2223 phases obtained in the 2212 compositional sputtering(Fig. 1) under the ozone gas introduction (line(a)) was illustrated in Fig. 2, in contrast to those under the equilibrium state with 1 atmosphere O_2 gas by Rubin et al.(line(b))[4].

It is found from the bulk syntheses in line(b) that the PO_2- and T- dependence on the phase stability lines for Bi2212 and Bi2223 phases agree well with that for CuO= Cu_2O shown by a dotted line[4]. The standard formation energies of CuO from $Cu_2O(\Delta H_f^0)$ are evaluated to be -450 and -266 kJ/mol in the reaction with O_3 and O_2 from JANAF's[5] and Schlom et al.'s data[6], respectively. The difference of this thermodynamical evaluation between O_2 and O_3 gases exhibits clearly that phase equilibrium line between $3Cu_2O + O_3 \rightarrow 6CuO$ shifts toward the pressure region lower than that of $2Cu_2O + O_2 \rightarrow 4CuO$ reflecting difference of the oxidation power between O_2 and O_3. The $lnPO_3$ in line(a) under low ozone pressure can be virtually replaced by $lnPO_2$ in line(c) under O_2 atmosphere of 1 atm, utilizing this pressure ratios among the equilibrium lines of $CuO-Cu_2O$ under O_3 and O_2 atmosphere at each temperature given by Schlom et al.[6] The virtual line (c) lies in the stable region of Bi2212 or Bi2223 phase with a similar slope to line (b).
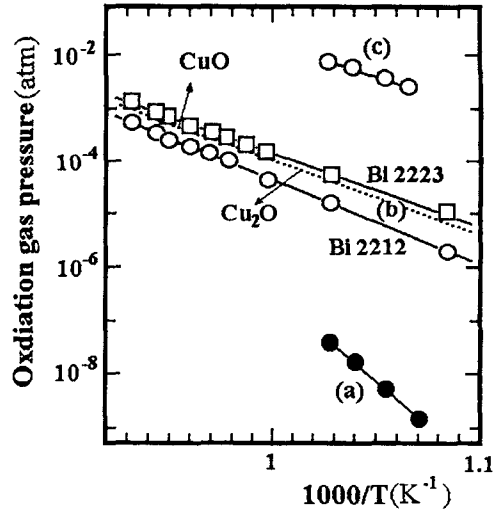

Fig. 2. Phase stability boundaries of obtained by 2212 compositional sputtering BSCCO in different oxidation conditions. The line(b) represents every phase boundary line of Bi2212. Bi2223 and CuO-Cu₂O.

Thermodynamic evaluations of the partial molar enthalpy of reaction, $\Delta \overline{Ho}_2$, and entropy, $\Delta \overline{So}_2$, for the dissolved oxygen can be performed in terms of eqs.(3) and (4) from the relations of $Rln pO_2$ vs. $1/T$ in Fig. 3(a) and $RTln pO_2$ vs. T in Fig. 3(b), and resulted in -225 kJ/mol and -260 J/mol $\cdot$ K for the Bi2212 single phase formation under 2212 compositional sputtering, respectively. In the similar procedure $\Delta \overline{Ho}_2$ and $\Delta \overline{So}_2$ for Bi2223 single phase with 2223 compositional sputtering were estimated to be -248 kJ/mol and -260 kJ/mol $\cdot$ K, respectively. These results coincided reasonably with that presented by Tetenbaum et al.[5] who investigated the phase stability for the bulk Bi2212 and Bi2223 under an equilibrium condition These coincidence support that the validity of the replacement from the BSCCO system to the simple CuO one which is an important constituent in the BSCCO structure.
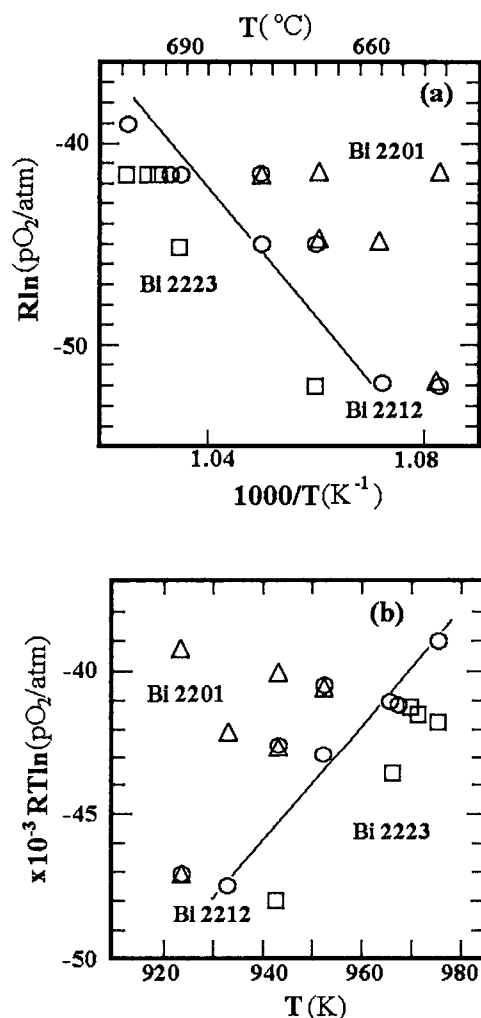
T(°C)

690   660

(a)

-40

BI 2201

Rln(pO₂/atm)

□□□□   △   △

□   △   △

BI 2223

-50

□   BI 2212

1.04   1.08

1000/T(K⁻¹)

(b)

△

-40   △   ⚹

BI 2201

△

⚹   ⚹□□   □

x10⁻³ RTln(pO₂/atm)

-45   BI 2223

⚹   □

BI 2212

-50

920   940   960   980

T (K)

Fig. 3. (a)RlnpO₂ vs. 1/T plot and (b)RTlnpO₂ vs. T plot.

The solid state reaction for the Bi2212 or Bi2223 phase takes place reversibly between the upper and lower sides of line (b) according to the intake or release of the oxygen, while the reaction across the line (c) for thin film fabrication is irreversible. It gives large influence on thin film fabrication that any liquid phase is required to construct Bi2212 or Bi2223 phase[7]. Namely, only an irreversible reaction from right to left side in Fig. 1 successively takes place with temperature, that is, Bi2201- Bi2212-Bi2223-decomposed phases. The Bi2223 phase constructed

at 700 ° C never took place reconstruction to Bi2212 one with the reduction of temperature at same lnPO₃ in Fig.1 in spite of Bi2212 composition. In the similar way, the Bi2212 composition was never improved to the Bi2212 one.

4. CONCLUSIONS

It was found out that Bi2201, Bi2212 and Bi2223 phases were formed in spite of adjusting the film composition, and that Bi2212 or Bi2223 single phase existed in very narrow temperature region. The phase stability regions for the Bi2212 and Bi2223 thin film fabrication were determined, and tehrmodynamic evaluations of $\Delta \overline{Ho}_2$ and $\Delta \overline{So}_2$ for the dissolved oxygen were successfully performed as -225 kJ/mol and -260 kJ/mol · K for Bi2212 single phase formation and as -248 kJ/mol and -260 kJ/mol · K for Bi2223 one. respectively. It is confirmed that our attempt is effective to evaluate thermodynamical parameters in the thin film fabrication under the reduced atmosphere.

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