단결정 형성을 위한 열역학 분석

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Analysis of Thermodynamics for Single Crystal Formation

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Abstract

High quality $Bi_2Sr_2Ca_nCu_{n+1}O_x$ superconducting thin films fabricated by using the evaporation method at various substrate temperatures, T_{sub}, and ozone gas pressures, pO_3. The correlation diagrams of the $Bi_2Sr_2Ca_nCu_{n+1}O_x$ phases with T_{sub} and pO_3 are established in the 2212 and 2223 compositional films.

In spite of 2212 compositional sputtering, Bi2201 and Bi2223 as well as Bi2212 phases come out as stable phases depending on T_{sub} and pO_3. From these results, the thermodynamic evaluation of ΔH and ΔS, which are related with Gibbs' free energy change for single Bi2212 or Bi2223 phase, was performed.

Key Words : Thermodynamics, BSCCO phases, ΔH, ΔS, Gibbs' phase rule

1. 서 론

Superconducting thin films have come into the spotlight for ultramodern devices. Development of electronic devices using high-T_c superconducting oxides has recently been promoted for the purpose of realizing superconductor/normal-metal/superconductor junctions [1]. Superconducting $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ system has many stable phases such as $Bi_2Sr_2Cu_1O_x$ (2201), $Bi_2Sr_2Ca_1Cu_2O_x$ (2212), $Bi_2Sr_2Ca_2Cu_3O_x$ (2223), $Bi_2Sr_2Ca_3Cu_4O_x$ (2234), etc. It is known that the superconducting transition temperature (T_c) of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ increases from 8 K for the n=1 phase to 110 K for the n=3 phase, and above n=4, Tc decreases with the number of n. 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 $Bi_2Sr_2Ca_{n-1}Cu_nO_x$. However, it is difficult to obtain high quality n=4 samples in comparison with those of n=2 or n=3 phase because of its complicated crystalline structure. These stable phases have only slightly different activation energies for formation. However, the intergrowth among each phase is occasionally observed in thin film fabrication[2,3] 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.

And than, 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. Navertheless, to our knowledge we can find no report concering thermodynamic consideration for the phase 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 paper, we establish the stably existing regions of Bi2201, Bi2212 and Bi2223 phases as functions of the substrate temperature and ozone pressure by taking the enthalpy of and entropy of reaction in BSCCO system into consideration.

2. 실 험

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.

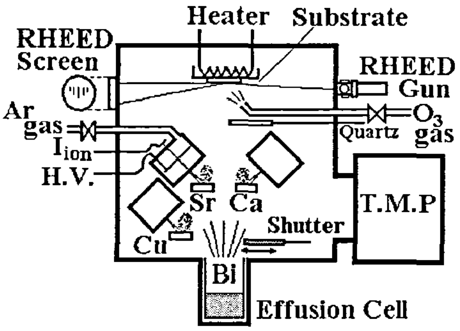

Fig. 1. The schematic diagram of the IBS apparatus.

Metal targets of Sr, Ca and Cu were simultaneously sputtered by Ar ion or atom beans 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 than the obtainable flux rate(10^{12} atoms/sec 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 650 and 710 ℃. Highly condensed ozone gas was obtained by a silica gel adsorption method and was supplied onto the substrate during deposition of the metallic species to provide an oxidation environment. The ozone gas pressure was regulated between 2.0×10^{-6} and 2.0×10^{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 nm/min.

The crystal structure and atomic compositional ratio of the deposited films were examined by x-ray diffractometer(XRD) using Cu-Kα 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 = 2.1±0.2 : 2.0±0.1 : 0.9±0.1 : 2.0±0.2.

3. 결과 및 고찰

The phases presented in the thin films fabricated with Bi2212 composition were plotted in Fig. 2 as functions of inverse temperature and logarithm of ozone gas pressure.

The marks of the triangular, circle and square in Fig. 2 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, it was confirmed by EDX that the ratio of the total constituent elements in the thin films obtained coincided nearly with Bi2212 composition with in the error of 2 %. In the thin film fabrication the Bi2201 single phase are formed in the wide temperature region blow 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. This mixed crystal are depicted in Fig. 2 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. 2 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. 2. This suggests a similarity in the processes of the phase formation between Bi2212 and Bi2223 phases.

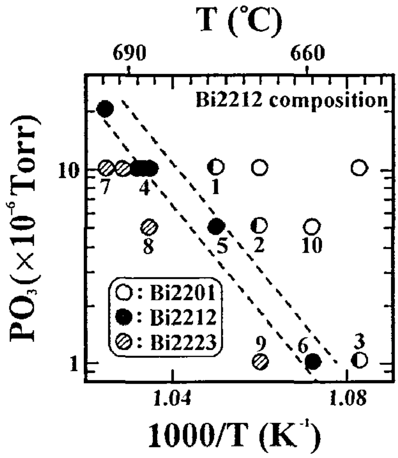

Fig. 2. Phase diagram for the thin films obtained by 2212 compositional sputtering against the inverse T_{sub} and $\ln Po_3$

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, $\mu^0 o_2(g)$,

$$2\mu o(s) = \mu o_2(g) = \mu^0 o_2(g) - RT\ln pO_2 \quad (1)$$

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

$$\begin{aligned} G_{O_2} - G^0_{O_2} &= \Delta\bar{G}_{O_2} = \mu_{O_2}(g) - \mu^0_{O_2}(g) \\ &= 2\mu_O(s) - \mu 0o2(g) = -RTlnpO2 \\ &= \Delta\bar{H}_{O_2} - T\Delta\bar{S}_{O_2} \end{aligned} \quad (2)$$

Here, the suffix 0 represents a thermodynamical standard state. Then, the variation of the enthalpy, $\Delta\bar{H}_{O_2}$ and the entropy, $\Delta\bar{S}_{O_2}$ are given in terms of Gibbs-Helmholtz equations as

$$\Delta\bar{H}_{O_2} = \frac{\partial(\Delta\bar{G}_{O_2})}{\partial(1/T)} = \frac{\partial R\ln pO_2}{\partial(1/T)} \quad (3)$$

$$\Delta\bar{S}_{O_2} = -\frac{\partial(\Delta\bar{G}_{O_2})}{\partial T} = -\frac{\partial RT\ln pO_2}{\partial T} \quad (4)$$

These values can be hardly estimated directly in the thin film fabrication used the ozone gas under our experimental condition 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 the reduced pressure and for the effects of partial pressure of O_2 or the introduced O_3 gas on BSCCO structural formation.

4. 결 론

In the deposition using co-sputtering method, the single phase of Bi 2201 was fabricated in the low temperature of substrate and the phase of Bi 2212 in above 750℃. In both cases, the c axis-oriented phases were acquired. Despite setting the composition of thin film Bi2212 or Bi2223, in both cases, Bi2201, Bi2212 and Bi2223 phase were appeared. It was confirmed the obtained field of stabilizing phase was represented in the diagonal direction of the right below end in the Arrhenius plot of temperature of the substrate and PO_3, and it was distributed in the rezone. Through the thermodynamical calculation of $\Delta\bar{H}O_2$ and $\Delta\bar{S}O_2$, in the case of fabricating the single phase of Bi2212, the values of -260 kJ/mol and -225 J/mol · K were acquired respectively. In the compounds of the plural system such as oxide superconducting thin films, a lot of stable phases and semi-stable phases exist. Therefore, it is important that the reaction process without occurring the formation of strange phase is established for gaining the intended phase. But establishing it is very complicated, so we cannot help finding the reaction process overburdened thermodynamically. It can be thought that this is the one of the causes the superconductivity of thin film is inferior to the bulk superconductor.

감사의 글

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