동시 스퍼터법으로 제작한 Bi 초전도 박막의 성장 모델

천민우 · 박용필
동신대학교 전기전자정보통신공학부

Growth Model of Bi-Superconducting Thin Film Fabricated by Co-sputtering Method

Min-Woo Chun, Yong-Pil Park
Dept. of Electrical, Electronic, Info. & Commun. Eng., Dongshin Univ.
E-mail : ccuccu7@hanmail.net

ABSTRACT

BSCCO thin films are fabricated via a co-deposition process at an ultra-low growth rate using ion beam sputtering. The sticking coefficient of Bi element exhibits a characteristic temperature dependence. This temperature dependence of the sticking coefficient was explained consistently on the basis of the evaporation and sublimation processes of Bi_2O_3.

키워드
Bi-Superconducting Thin Film, co-deposition, sticking coefficient, Bi2212 phase, growth process

Ⅰ. Introduction

Not only for fundamental research but also application to electronic devices, fabrication of high quality thin films of the oxide supercon- ductors have been required.

For applications, a high quality thin film fabrication is required and the growth mechanism at atomic scales must be investigated. As a first approach, we pay attention to the sticking coefficients of constituent elements.

In our experiment, the sticking coefficient of Bi element showed a distinctive temperature dependence. This result reveals an essential condition for the growth of $Bi_2Sr_2CaCu_2O_y$ (Bi2212) thin film using a co-deposition technique

Ⅱ. Experimental

BSCCO thin films were fabricated via a co-deposition process by an ion beam sputtering (IBS) method[1-2] at an ultra-low growth rate of 0.17-0.27 nm/min. Saddle-field and cold-cathode type ion guns were set in a vacuum chamber, and the respective targets of Bi, Sr, Ca and Cu metals were simultaneously sputtered. MgO(100) was used as a substrate, and highly condensed ozone gas was applied as an oxidant[3]. Thin films were grown in the substrate temperature from 650 to 820℃ under ozone gas pressures of 2×10^{-6} to 4×10^{-5} Torr.

The relation between the sputtering Ar ion current and the flux of each atom species that arrived onto the substrate was estimated beforehand using a quartz oscillation monitor installed at the substrate position at room temperature. Therefore, the total incident atom number of each element could be calculated from the Ar ion current and the deposition period. On the other hand, real atom numbers of Cu element in the films were analyzed by the inductively coupled plasma(ICP) photoemission spectroscopy for several reference samples. From the comparisons among these results, the sticking coefficient of Cu element turns out to be almost unity and shows little dependence on the substrate temperature.

Accordingly, the atom number of Cu element was used as a reference for the number estimation of other elements from the relative compositional data by the energy dispersive X-ray(EDX) spectrometer.

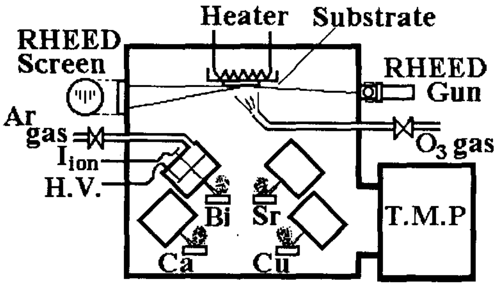

Fig.1. Schematic diagram of the IBS system.

III. Results and discussion

The phase diagram of BSCCO is shown in Fig. 2 as both functions of the ozone gas pressure and the inverse temperature.

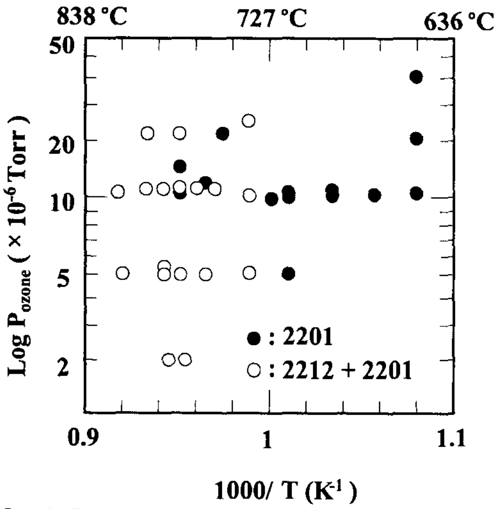

Fig. 2. Phase diagram against substrate temperature and ozone gas pressure.

Here, it is found separated into two phase domains; Bi(2201) phase and Bi(2212) (+Bi(2201)) one, which means partial mixture of the Bi(2201) phase in the Bi(2212) host phase. The Bi(2201) phase grows in a wide temperature range, while the Bi(2212)(+Bi(2201)) phase grows in temperatures higher than 730℃. Especially, a single Bi(2212) phase can be grown at sufficiently higher temperatures than 730℃.

XRD pattern of thin film fabricated at 795 ℃ under 1×10^{-5} Torr by the co-deposition is shown in Fig. 3.

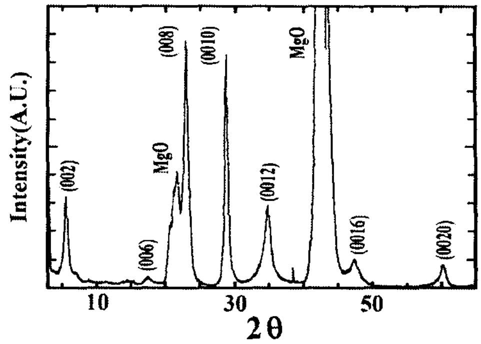

Fig. 3. Typical XRD pattern.

High quality of c-axis oriented Bi-2212 thin film with Tc(onset) of about 80 K and Tc(offset) of about 45 K was obtained. Only a small amount of CuO in some films was observed as impurity, and no impuity phase such as $SrBi_2O_4$ was observed in all of the obtained films. Dependence of phase diagram on PO_3 and temperature is arranged in Fig. 2.

The distinguished variation in structural formation is observed with temperature.

Sr and Ca, displayed no such remarkable temperature dependence under the present experimental conditions. Accordingly, it is considered that the sticking of Sr and Ca elements have less influence on the Bi(2212) formation. The sticking coefficient of Bi element can be distinguished into two regions in terms of temperature; the region with a nearly constant value of 0.49 on average below about 730℃ and that with a linearly decreasing value for temperatures over 730℃.

The liquid phase of Bi_2O_3 is formed on the substrate over 730℃, and this liquid phase plays an important role for the Bi(2212) phase formation[4-5].

In the thin film fabrication via the co- deposition process, the Bi(2212) phase appears above about 730℃, while the single Bi(2201) phase exists below about 730℃ as shown in Fig. 2.

This corresponds to that particular temperature where the sticking coefficient of Bi element begins to decrease. The gradual decrease of sticking coefficient of Bi element corresponds to the increase of Bi_2O_3 vapor pressure in a temperature region higher than the melting point of solid Bi_2O_3, presented by Il'in[6].

Bi atoms arrive onto the surface and are oxidized partly to bismuth oxides. Bi itself or Bi_2 molecule would re-evaporate from the substrate immediately. Even for bismuth oxide, Bi_2O_3, sublimation or evaporation takes place by the formation of the dimer Bi_4O_6, since it has also a finite resident time. When the substrate temperature comes to exceed the melting temperature of Bi_2O_3 in the vacuum, the evaporation increases and the sticking coefficient decreases. This behavior of the sticking coefficient of Bi element is reflected on the formation of BSCCO phases. The Bi(2201) phase can be easily formed in wide temperature regions so long as the compositional ratio is satisfied. Whereas, it is difficult to transfer into the Bi(2212) phase in the temperature region lower than the melting point of Bi_2O_3 in spite of adjusting the compositional ratio.

Consequently, the Bi(2212) phase is formed in the thin film from the Bi(2201) phase melted partially with the aid of the liquid phase of Bi_2O_3 via the following reaction,

$$Bi(2201)(liquid) + CaCuO_2(solid) \rightarrow Bi(2212)(soild).$$

This reaction must be initiated by releasing the Sr-O-Cu bond along the c-axis, and insertion of $CaCuO_2$ takes place by cutting the bond between (Sr and O-Cu) or (Sr-O and Cu) as shown in Fig. 4. In consequence, Bi(2212) phase will be constructed substantially with the aid of Bi_2O_3 liquid phase.

This model is also in accordance with the fact that in the bulk synthesis Bi(2212) phase is formed via Bi(2201) phase from the raw materials.

Ⅳ. Concluding remarks

The sticking coefficient of Bi element in BSCCO film formation was observed to show a unique temperature dependence : it was almost a constant value of 0.49 below about 730 ℃. This behavior of the sticking coefficient was explained consistently on the basis of the evaporation and sublimation processes of Bi_2O_3.

It was concluded that Bi(2212) thin film constructs from the partial melted Bi(2201) phase with the aid of the liquid phase of Bi_2O_3 as illustrated in Fig. 3.

The idea of this liquid-phase-mediated crystal growth may be also applied to the fabrication of Tl-type or Hg-type superconducting thin films.

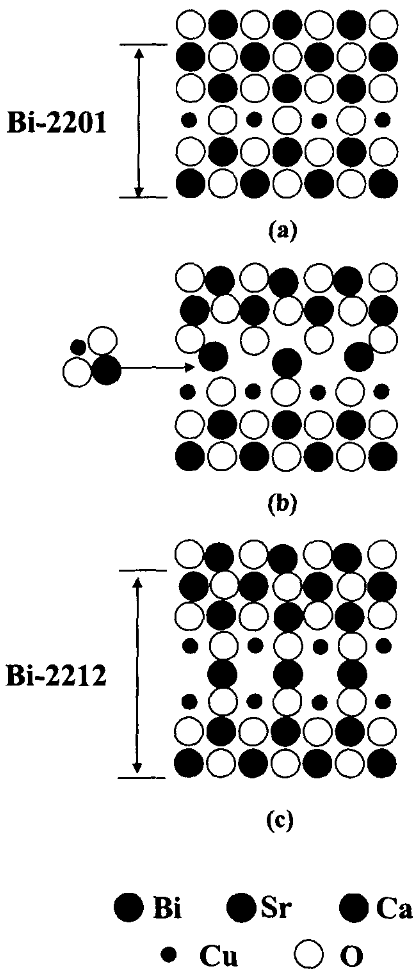

Fig. 4. A model for Bi(2212) thin film growth.
(a) Formation of the Bi(2201)
(b) Partial melting of Bi_2O_3 and insertion of $CaCuO_2$
(c) Formation of the Bi(2212) phase.

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