

## The Influence of Bi-Sticking Coefficient in Bi-2212 Thin Film

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### Abstract

Bi-thin films are fabricated by an ion beam sputtering, and sticking coefficients of the respective elements are evaluated. The sticking coefficient of Bi element exhibits a characteristic temperature dependence : almost a constant value of 0.49 below 730°C and decreases linearly with temperature over 730°C. This temperature dependence can be elucidated from the evaporation and sublimation rates of bismuth oxide, Bi<sub>2</sub>O<sub>3</sub>, from the film surface. It is considered that the liquid phase of the bismuth oxide plays an important role in the Bi(2212) phase formation in the co-deposition process.

**Keywords** : Bi-thin film, co-deposition, sticking coefficient, Bi(2201) phase, Bi(2212) phase

### 1. Introduction

High-T<sub>c</sub> superconducting thin film is expected to be a fascinating material for new electric devices. For its 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. This coefficient is defined in the present experiment as "the ratio of atom numbers concerned in the formation of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n</sub>Cu<sub>n+1</sub>O<sub>y</sub> (n≥0; BSCCO) structure against the incident onto the substrate." It gives fertile information that includes the overall processes of the film growth mechanism; atom adsorption, migration, and coalescence into the structure or re-evaporation from the surface, etc. 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<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>y</sub> (Bi(2212)) thin film using a co-deposition technique.

### 2. 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. A schematic diagram of the IBS system is illustrated in Fig. 1. 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°C under ozone gas pressures of 2×10<sup>-6</sup> to 4×10<sup>-5</sup> 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[1-2]. 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. This implies that the atom number of the incident Cu element was nearly equal to the component of the thin film. 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.

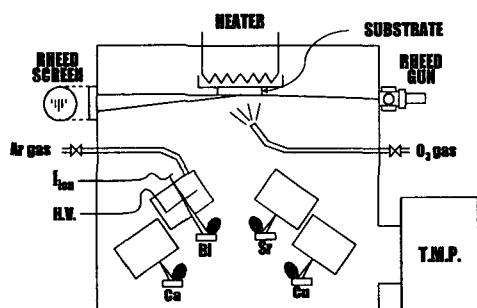


Fig. 1. Schematic diagram of the ion beam sputtering system set up for the present co-deposition process.

Generally, the sticking coefficient of the atom depends strongly on the crystal structure constructed in the thin film. Therefore, the crystal structure of the thin film was observed using the X-ray diffractometer (XRD) in order to investigate the sticking coefficient of the respective elements for BSCCO thin films.

### 3. Results and discussion

#### 3.1. Phase diagram

The phase diagram of BSCCO is shown in Fig.

2 as both functions of the ozone gas pressure and the inverse temperature.

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°C. Especially, a single Bi(2212) phase can be grown at sufficiently higher temperatures than 730°C. According to the XRD analysis, a little amount of CuO precipitate was observed, but no other impurity regarding Bi element was detected.

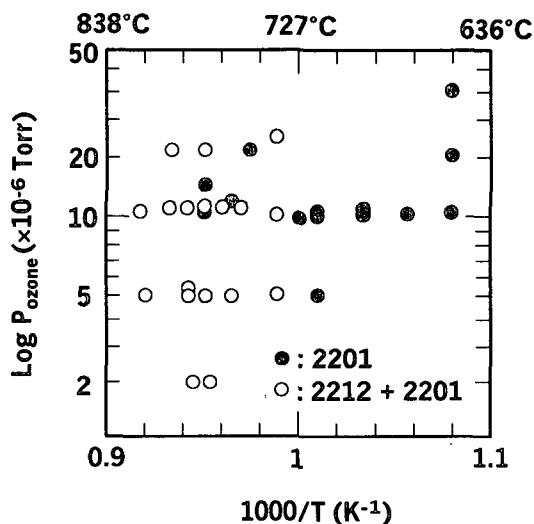


Fig. 2. Investigated phase diagram of Bi(2212) and Bi(2201) against inverse temperature and ozone gas pressure. Open circles indicate the appearance of Bi(2212) (+Bi(2201)) phase which means partial mixture of the Bi(2201) phase in the Bi(2212) host phase, and closed circles indicate the appearance of single Bi(2201) phase.

#### 3.2. Sticking coefficient of Bi element

The sticking coefficient of Bi element is plotted against the inverse temperature in Fig. 3. In

comparison of the data both in Fig. 2 and Fig. 3. We can recognize certain correlation between the Bi(2212) phase formation and the Bi sticking coefficient. In contrast, 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. In Fig. 3, 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°C and that with a linearly decreasing value for temperatures over 730°C. This critical temperature point can be elucidated as follows.

The melting temperature of Bi metal is 271°C, much lower than the film growth temperature. Therefore, pure Bi element can hardly exist on the substrate. Most of the Bi elements are subjected to oxidation in the presence of the ozone gas and only remain as bismuth oxides on the surface.

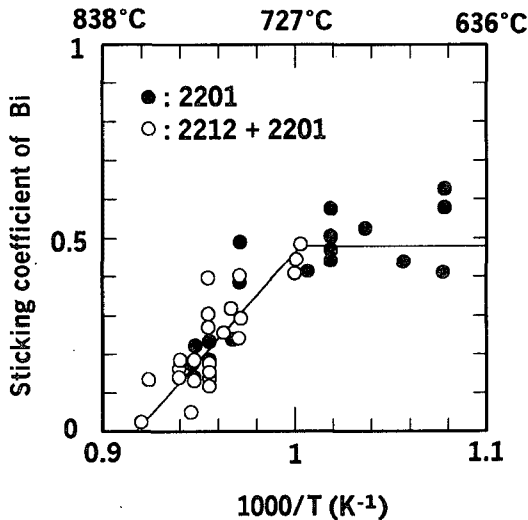


Fig. 3. Observed sticking coefficient of Bi element against inverse temperature of the substrate. Open circles indicate the appearance of Bi(2212)(+Bi(2201)) phase, and closed circles indicate that of single Bi(2201) phase.

The most stable bismuth oxide is  $\text{Bi}_2\text{O}_3$  with a melting temperature of 824°C[4]. The enthalpy with respect to the evaporation  $H_v$  and sublimation  $H_s$  of the volatile bismuth oxides had been reported[5] as  $\Delta H_v(\text{Bi}_4\text{O}_6) = 37.2$  and  $\Delta H_v(\text{Bi}_2\text{O}_3) = 56.7$  kcal/mol ranging from 1098 to 1193K, and  $\Delta H_s(\text{Bi}_4\text{O}_6) = 55.9$  and  $\Delta H_s(\text{Bi}_2\text{O}_3) = 66.1$  kcal/mol ranging from 1003 to 1098K, respectively.  $\text{Bi}_4\text{O}_6$ , the dimer of  $\text{Bi}_2\text{O}_3$ , is considered as the most probable evaporation species, referring to the difference of enthalpy between  $\text{Bi}_4\text{O}_6$  and  $\text{Bi}_2\text{O}_3$ . This fact has been supported by the vapor pressure measurement of bulk Bi(2212) polycrystal using a transpiration method[6].

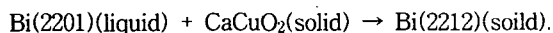
Next, let us consider temperature dependence of the total vapor pressure of  $\text{Bi}_2\text{O}_3$  which stays on the substrate. Vapor pressures of solid and liquid  $\text{Bi}_2\text{O}_3$  were given by Il'in[4]. The latent heat  $\Delta H_L$  of  $\text{Bi}_2\text{O}_3$  due to the phase transition from solid to liquid was calculated as 73.32 kcal/mol from the data. The lowering of melting point( $T_{mp}$ ) under the evacuated condition can be elucidated using this latent heat in terms of the Clapeyron-Clausius law. Namely,  $T_{mp}$  results in 773°C at  $10^{-3}$  Torr and 709°C at  $10^{-4}$  Torr.  $T_{mp}$  of 730°C is realized at  $2.22 \times 10^{-4}$  Torr, which is higher than the present experimental condition of ozone pressure between  $2 \times 10^{-6}$  and  $4 \times 10^{-5}$  Torr. This result can be understood well when we consider both the effect of gas injection toward the substrate and the strong oxidizing potential of ozone gas. In consequence, the liquid phase of  $\text{Bi}_2\text{O}_3$  is formed on the substrate over 730°C, and this liquid phase plays an important role for the Bi(2212) phase formation.

### 3.3. A model of Bi(2212) film growth process

In the thin film fabrication via the co-deposition process, the Bi(2212) phase appears above about 730°C, while the single Bi(2201) phase exists below about 730°C as shown in Fig. 2. This corresponds to that particular temperature where the sticking coefficient of Bi element

begins to decrease in Fig. 3. The gradual decrease of sticking coefficient of Bi element corresponds to the increase of  $\text{Bi}_2\text{O}_3$  vapor pressure in a temperature region higher than the melting point of solid  $\text{Bi}_2\text{O}_3$ , presented by  $\Pi'$  in [4].

A possible model of the Bi(2212) thin film growth is proposed by taking account of the behavior of Bi element on the substrate surface as follows. Bi atoms arrive onto the surface and are oxidized partly to bismuth oxides. Bi itself or  $\text{Bi}_2$  molecule would re-evaporate from the substrate immediately. Even for bismuth oxide,  $\text{Bi}_2\text{O}_3$ , sublimation or evaporation takes place by the formation of the dimer  $\text{Bi}_4\text{O}_6$ , since it has also a finite resident time. When the substrate temperature comes to exceed the melting temperature of  $\text{Bi}_2\text{O}_3$  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  $\text{Bi}_2\text{O}_3$  as shown in Fig. 3, in spite of adjusting the compositional ratio. This implies that it requires intervention of the  $\text{Bi}_2\text{O}_3$  liquid phase for the formation of Bi(2212) phase. 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  $\text{Bi}_2\text{O}_3$  via the following reaction,



This reaction must be initiated by releasing the Sr-O-Cu bond along the c-axis, and insertion of  $\text{CaCuO}_2$  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  $\text{Bi}_2\text{O}_3$  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.

#### 4. Conclusion

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  $730^\circ\text{C}$  and decreased linearly over about  $730^\circ\text{C}$ . This behavior of the sticking coefficient was explained consistently on the basis of the evaporation and sublimation processes of  $\text{Bi}_2\text{O}_3$ . It was concluded that Bi(2212) thin film constructs from the partial melted Bi(2201) phase with the aid of the liquid phase of  $\text{Bi}_2\text{O}_3$  as illustrated in Fig. 4.

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, since the melting temperatures of thallium oxides ( $596^\circ\text{C}$  for  $\text{Tl}_2\text{O}$  and  $717^\circ\text{C}$  for  $\text{Tl}_2\text{O}_3$ ) and the decomposition temperature of mercury oxide ( $500^\circ\text{C}$  for  $\text{HgO}$ ) are found well below their bulk synthesis temperatures.

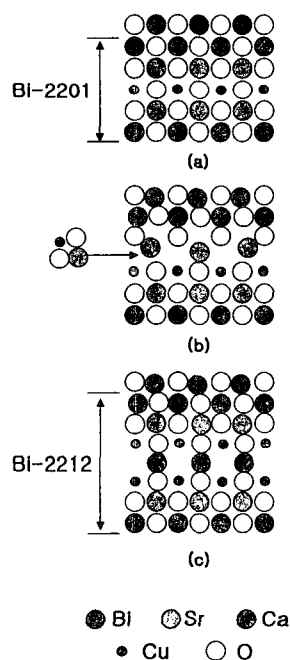


Fig. 4. A model for Bi(2212) thin film growth.

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