

Improvements of Bi-Incorporation and Crystal Growth by Plasma Cleaning in Bi2201 Thin Film Preparations

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Ca-doped Bi2201 thin films were prepared at low temperatures by ion beam sputtering, and their growth mechanism was discussed in terms of a compositional transfer. In the deposited films at an oxygen partial pressure (P_O) of 1 mTorr and substrate temperatures (T_S) of 400-700°C, the Bi content and film thickness decrease drastically for $T_S > 600^\circ\text{C}$. However, they increase when P_O is increased to 3 mTorr. This is caused by a suppression effect on Bi_2O_3 re-evaporation from the films. Plasma cleaning of the substrate surface results in prominent improvements on the Bi-incorporation and crystallinity. The origin of these effects is proposed as an enhancement of early-stage nucleation.

Key words: Bi2201 thin film growth, Ion beam sputtering, Plasma cleaning, Composition, Bi-incorporation

1. Introduction

Recently, an important report was made by Migita et al.¹⁻³⁾ on Bi-related oxide thin film growth. They suggest that a self-limiting function of Bi content works in the preparation of Bi-Sr-Ca-Cu-O (BSCCO) thin films, and the Bi content decreases by re-evaporation of Bi_2O_3 at higher substrate temperatures (T_S)^{4,5)}. Thus the problems of the incorporation and re-evaporation of Bi element are quite important for elucidation of mechanism of BSCCO thin films. Laguës et al.⁶⁾ reported that the metallic Bi and Bi-oxide (Bi_2O_3) are very volatile then sticking rate of Bi decreases with increasing T_S , however it increases with increasing density of supplied oxygen. Ranno et al.⁷⁾ proposed that the Bi sticking rate is increased by supplying oxygen plasma. Dhare and Mason⁸⁾ reported that the Bi sticking rate gradually decreases with increasing T_S from room temperature to 600°C.

From our results obtained so far,⁹⁾ it is known that the Bi sticking rate rapidly decreases in higher T_S region but it is increased considerably by increasing oxygen partial pressure (P_O), and that it is not so much different for the oxygen molecular supply and plasma supply. Thus behaviors of Bi sticking are complicated, and probably depend on a method of deposition, co-deposition or sequential deposition, supply of activated oxygen, and T_S and P_O .

2. Experimental

Thin film depositions of Ca-doped Bi2201 ($\text{Bi}_2(\text{Sr}, \text{Ca})_2\text{CuO}_6$) were made by ion beam sputtering (IBS).¹⁰⁾ Targets were sputtered by 4 keV Ar^+ beam, and the target-a ($\text{Bi}_{1.17}\text{Sr}_{0.5}\text{Ca}_{0.44}\text{Cu}_1\text{O}_x$) was used for the main films. The target-b ($\text{Bi}_{1.62}\text{Sr}_{0.83}\text{Ca}_{0.41}\text{Cu}_1\text{O}_x$) was used to study plasma cleaning effects and the Bi sticking behaviors. In this target, the contents of Bi and Cu are slightly increased than the stoichiometry of 2201. The sputtered particles were deposited on a heated $\text{MgO}(100)$ substrate. The substrate temperature (T_S) was measured by a thermocouple pressed to the substrate surface. During the deposition, the oxygen molecules either plasma was supplied through a nozzle

located at 11 mm from the substrate. Thus the local oxygen partial pressure just above the substrate is higher than the average oxygen partial pressure (P_O) by factors of 5-10.

Two series of films were prepared. (1) Using the target-a, the films were deposited with supplying the molecules or plasma at $P_O=1.0$ mTorr at $T_S=400-700^\circ\text{C}$ for 12 h. Additional film was deposited with the molecular supply at $P_O=3.0$ mTorr at $T_S=650^\circ\text{C}$. Further, one film was deposited using the target-b with the same conditions after a plasma cleaning of the substrate surface by exposing it to the oxygen plasma at $P_O=4$ mTorr at $T_S=650^\circ\text{C}$ for 1 h. (2) Using the target-b, the films were deposited with supplying the molecules or plasma at $P_O=0.75$ mTorr at $T_S=500^\circ\text{C}$ for 1-3 h. Then additional film was deposited with the same conditions for 1 h after the plasma cleaning at $P_O=4.0$ mTorr at $T_S=500^\circ\text{C}$ for 5 h.

Crystallinity of the deposited films was estimated by XRD peak-width (FWHM) on $\theta-2\theta$ scan using $\text{Cu K}\alpha$ line. The film composition was measured by EDX analysis. Its film-correction was made by EPMA film-method suggested by JEOR.

3. Results and Discussion

3.1 Non plasma cleaning

The T_S -dependence of compositions is shown in Fig.1 for the Ca-doped Bi2201 films prepared at $P_O=1.0$ mTorr. The crystallinity of these films is excellent for $T_S>550^\circ\text{C}$ and slightly better for the molecular supply than for the plasma supply.^{9,11)} However, the crystallinity is not so fine for $T_S<550^\circ\text{C}$ but considerably better for the plasma supply compared with the molecular supply. The plasma energy must give excess energy for the crystal growth in the higher T_S region, while it must compensate shortage of thermal energy in the lower T_S region.

We can notice three characteristics in the film compositions in the lower $T_S(<600^\circ\text{C})$ region. The composition of Cu is decreased strikingly from the target composition. This is caused by a fact that Cu is

very difficult to be oxidized. The compositions of Sr and Ca are not so much different from the target. The composition of Bi is increased noticeably from the target then it compensates the decrease in Cu. Thus Bi is rather easily incorporated in the film at the low T_s . As a result, Cu is almost stoichiometric (20%), Bi is slightly larger (40-50%) and (Sr+Ca) is slightly smaller. There is some possibility that the slightly excess Bi gives good effects on crystal growth at low temperatures.^{12,13)} Though, the Bi-composition is drastically decreased above 600°C and finally the Bi cannot be incorporated in the films at 700°C. The crystallinity of the 2201 phase is fine at 600°C and it is the best at 650°C.^{9,11)} The crystallinity is poor and the film thickness is excessively reduced at 700°C. Therefore, the Bi is vigorously re-evaporated and it is hard to incorporate Bi in the film above 600°C. The Sr and Ca increase instead, however, the Cu does not increase so much as the Sr and Ca. The reason is that CuO formed at the surface is remarkably volatile.^{14,15)}

Although the composition of the film deposited at 650°C with the molecular supply is far from the stoichiometry, this film shows the finest crystallinity. Then we tried to obtain further excellent crystalline 2201 phase at 650°C. In order to suppress the Bi re-evaporation at 650°C, the film was deposited with the molecular supply at the increased P_o of 3 mTorr. It results in the increase in the Bi-composition to the stoichiometric value (40%) as shown in Fig.1 by the suppression effect. However, the film quality is much inferior than that of the film prepared at $P_o=1$ mTorr. The FWHM values of (006) peak are 0.12° for the 1 mTorr film while 0.48° for the 3 mTorr film. Reasons for this degradation might be a mixing of least amount of impurity phases induced by "excess oxidation power", and a "reduction of sputtered particles energy" caused by collisions with the supplied oxygen species in the gas phase.^{14,15)} The Bi-composition is slightly decreased as shown in Fig.1 when the film is deposited with the plasma supply at decreased $P_o=0.5$ mTorr at $T_s=540$ °C. This supports the "suppression effect" because the re-evaporation of Bi is promoted by reducing the pressure. Furthermore, the crystallinity is improved because the "sputtered particles energy" is not reduced so much. The sputtered particles energy becomes more important for the crystal growth as decreasing the temperature such as 540°C.

3.2 Plasma cleaning

We tried to improve the Bi-incorporation and nucleation at early stage of the crystal growth at $T_s=650$ °C by the plasma cleaning of the substrate surface before the deposition. This film was deposited at $P_o=3.0$ mTorr to suppress the Bi re-evaporation, and the target-b was used to enhance the Bi content in the film. The compositions are plotted in Fig.1. One characteristic of this result is that there is no trend of the large decrease in the Cu-composition from the target as observed in the films by the target-a. The Cu-composition is much larger in the target-a then the Cu re-evaporation is promoted except for the 20% Cu

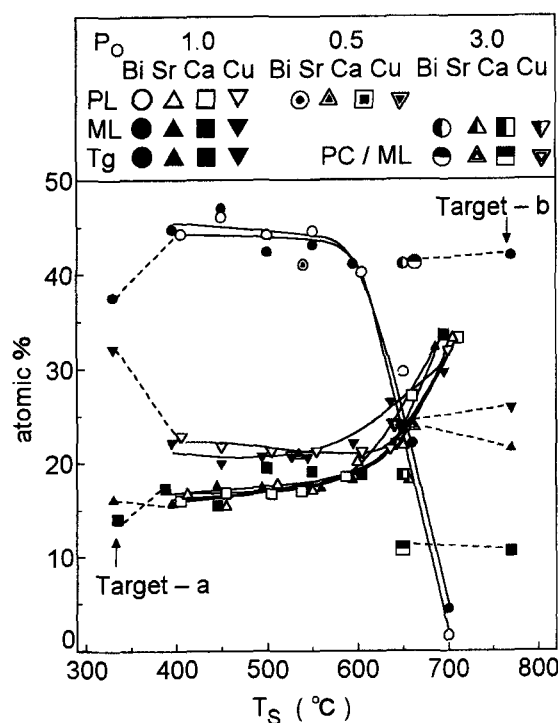


Fig.1. T_s -dependence of the compositions in the films. PL: plasma supply, ML: molecular supply, PC/ML: plasma cleaning and molecular supply, Tg: target. The plots connected to Target-b are from the target-b, and others from the target-a.

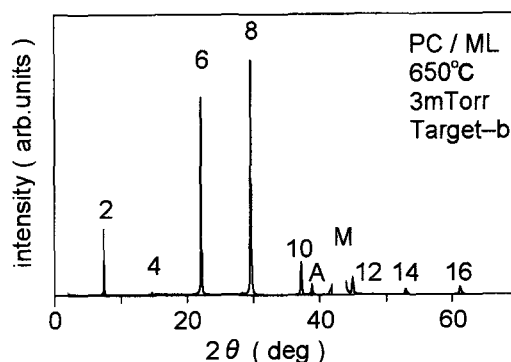


Fig.2. XRD pattern for the plasma-cleaned film. Numbers in the figure indicate (002), (006)··· peaks. M: MgO peak, A: CuO.

needed to form the 2201 phase. However, the Cu-composition is originally small in the target-b then the Cu re-evaporation is least to keep the 20% Cu in the film. The other characteristic is that the Bi-composition in the film is slightly decreased from the target. In the case of target-a, the Bi-composition is increased from the target to keep the 40% (or more than 40%) Bi in the film because the Bi-composition is smaller than 40% in the target. Though, the Bi-composition is larger than 40% in the target-b then it is automatically decreased in the film. Whereas, the (Sr+Ca) is smaller than 40% in the target-b then they

are increased. Thus self adjustment function effectively works in this deposition after the plasma cleaning. Accordingly the exceptionally high quality crystalline 2201 phase can be grown. Its XRD pattern is shown in Fig.2, the FWHM of (006) peak is only 0.07° .

As discussed above, the compositional transfer from the target to the film is the important factor. We define the transfer rate $T_r(i)$ for each element (i) as

$$T_r(i) = \frac{C_f(i)}{C_t(i)}, \quad (i = \text{Bi, Sr, Ca, Cu}), \quad (1)$$

where C_t and C_f are compositions in the target and film, respectively. The $T_r(\text{Bi})$ is plotted in Fig.3. In the case of target-a, $T_r(\text{Bi})$ is larger than 1 because the system works to increase the Bi for $T_s < 600^\circ\text{C}$. However, the re-evaporation dominates over this function for $T_s > 600^\circ\text{C}$, then $T_r(\text{Bi})$ becomes less than 1 violently. Though, when P_O is increased from 1.0 to 3.0 mTorr, $T_r(\text{Bi})$ can recover to more than 1 even at 650°C . On the other hand, in the case of plasma-cleaned film using the target-b under the same conditions of T_s and P_O , $T_r(\text{Bi})$ becomes just less than 1 to keep the stoichiometry.

3.3 Re-evaporation

In Fig.3 the Bi sticking rates in ① Bi_2O_3 and ② BSCCO thin film preparations obtained by Migita et al.¹⁾ are also shown for the comparison. According to this result, the Bi_2O_3 film cannot be deposited by its re-evaporation for $T_s > 600^\circ\text{C}$. Our result of $T_r(\text{Bi})$ also shows the rapid decrease for $T_s > 600^\circ\text{C}$, then the re-evaporation of Bi must be performed in the form of Bi_2O_3 in our experiment. The reason why $T_r(\text{Bi})$ does not drop to zero above 600°C , is that the Bi atoms should be incorporated simultaneously with the other elements. The situation is the same with the BSCCO

system ② obtained by Migita et al., rather the re-evaporation of Bi_2O_3 from their films occurs at higher T_s than from our films. The origin for this difference is in the difference in Bi supplying method. They supply the metallic Bi in atomic layer-by-layer deposition. The difference of oxidant may also be one of the origins, they use ozone. We employ the co-deposition method and the deposition rate is ultralow such as an order of 10^{-2} Å/s. Therefore, the deposited Bi can be re-evaporated before the following particles cover this Bi atom. This is one of the basic reasons why the Bi cannot be deposited above 700°C in our system.

However, Migita et al.²⁾ reported that the Bi sticking rate begins to decrease at the higher temperature of 730°C and reaches zero at 830°C in the BSCCO film preparation using the same deposition technique of IBS even though their system has the same order of growth rate with us. It should be noted that they employ the ozone and deposit the films at much lower P_O of orders of 10^{-6} – 10^{-5} Torr. We deposit the films at much higher P_O of 10^{-3} Torr, and furthermore the local oxygen pressure is still higher than P_O values by the factors of 5–10. In this situation, the sputtered Bi particles have high possibility to make collisions with the supplied oxygen species from the nozzle in the gas phase.^{14,15)} Thus the Bi particles must form the Bi_2O_3 molecules in the gas phase before landing on the film surface, resulting in the prompt re-evaporation.

Ranno et al.⁷⁾ suggest that the Bi-incorporation can be enhanced by the oxygen plasma. To the contrary, the Bi-incorporation rates are almost the same for the molecular and plasma supplies in our experiment as shown in Figs.1 and 3. Though, it must be noted that the Cu-incorporation is enhanced by the plasma for $T_s < 550^\circ\text{C}$ as shown in Fig.1. This indicates that the oxidation of Cu is promoted by the plasma.

3.4 Early stage

The fact that the plasma cleaning of the substrate surface results in the excellent crystal growth, predicts critical effects at early stage of the growth. To elucidate such the effects, we prepared the films at

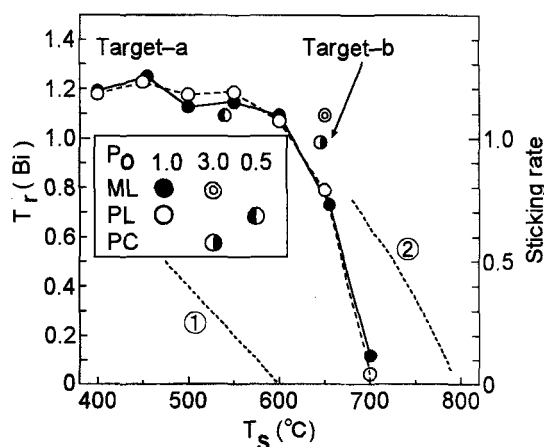


Fig.3. T_s -dependence of $T_r(\text{Bi})$. Bi sticking rates for ① Bi_2O_3 films and ② BSCCO films by Migita et al.¹⁾

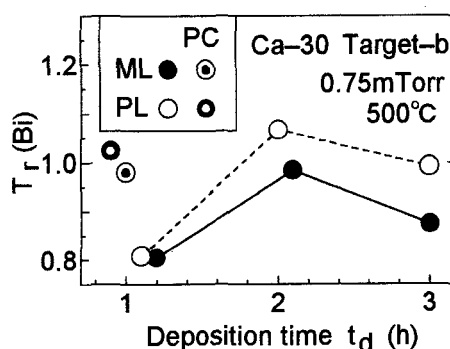


Fig.4. t_d -dependence of $T_r(\text{Bi})$ for the non plasma-cleaned and plasma-cleaned (PC) films.

$T_s=500^\circ\text{C}$ at $P_O=0.75$ mTorr for shorter deposition times (t_d) of 1, 2 and 3 h.¹⁶⁾ The Bi transfer rates $T_r(\text{Bi})$ are plotted in Fig. 4. The values of $T_r(\text{Bi})$ at $t_d=1$ h are much smaller than those at 2 and 3 h, indicating that it is hard for the Bi to be incorporated at the early stage of the growth on the MgO surface. The both films at 1 h have the poorest crystallinity because of the Bi deficiency. However, the plasma cleaning results in the increase in $T_r(\text{Bi})$ at 1 h as shown in Fig. 4, and in the prominent improvement of the crystallinity.¹⁶⁾ This indicates that the plasma cleaning can adjust the Bi-incorporation by activating the substrate surface then enhance the crystalline nucleation at the early stage. The epitaxial growth conserves this excellent crystallinity up to the longer deposition times.

4. Summary

Ca-doped Bi2201 thin films were prepared by IBS and T_s -dependence of the Bi transfer rate was investigated. The Bi transfer rate is high at the lower T_s region while it decreases rapidly above 600°C by the re-evaporation of Bi_2O_3 . However, it is increased with increasing P_O by the suppression effect even at the high T_s such as 650°C . The deposition system has the self adjustment facility in the transfer rate and this results in the excellent crystal growth. The plasma cleaning has the prominent effects on the Bi-incorporation and the early nucleation, then can enhance the self adjustment facility.

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