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Preparation of Perovskite Bi-Sr-Ca-Cu-O Thin Films by Ion Beam Sputtering : Effects of Oxygen Molecules and Plasma

S. Uthayakumar[a], Shin-ichi Iwasaki[a], Kouji Yoshii[a], A. Gufran[a],
R. Dhanasekaran[b] and Tamio Endo[a*]
[a] Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan
Fax: +81-59-231-9471, e-mail: endo@elec.mie-u.ac.jp
[b] Crystal Growth Centre, Anna University, Chennai-600 025, India

Ca-doped and nondoped Bi2201 thin films were grown at low temperatures by ion beam sputtering with supplying oxygen molecule or plasma at various partial pressures (P_O). Crystallinity of the Ca-doped films is improved by the plasma only in the low P_O regions while that of the nondoped films is improved by the molecule in the whole region of P_O. It is proposed that sputtered particle energy and energy balance are important factors.

Keywords: Bi2201 thin films, Low temperature growth, Oxygen pressure, Oxygen plasma

1. INTRODUCTION

High temperature superconductors (HTS) are highly expected to be applied for high frequency devices [1] such as microwave filters [2]. Tunable microwave filters will be widely required as the next generation devices. The tunable filter may be realized by stacking ferromagnetic layers on HTS thin films [3,4]. In such a heterogeneous thin film stacking, surface flatness of the films and prevention of inter-diffusion are essentially important factors. In order to clear these demands, low temperature processing of thin films is most promising [5]. Of course, however, it is very difficult to grow good crystalline thin films at low substrate temperatures due to shortage of thermal energy. Then usually we need some other energies to grow the good crystalline thin films which can compensate the shortage of thermal energy.

Generally it is thought that active oxygen is inevitable for the low temperature growth of perovskite oxide thin films [6]. This must be true for low energy deposition techniques. However, it might not be always necessary for high energy deposition techniques such as PLD and sputterings. From this anticipation we tried to investigate a validity of oxygen plasma for the low temperature growth of Bi2201 thin films employing ion beam sputtering (IBS) since it is easy to control the oxygen supply. Bi2201 has the simplest perovskite structure among various HTS groups. Then it is easier to investigate impurity doping effects on the low temperature growth. It must be noticed that superiorly excellent crystalline Bi2201 thin films can be grown at a higher temperature of 650°C for the Ca-doped system [7,8], and at a 550°C for the nondoped system [9]. However, it is valuable to challenge the lower temperature process yet.

2. EXPERIMENTAL

The nondoped Bi2201 ($Bi_2Sr_2CuO_X$) and Ca-doped Bi2201 ($Bi_2(Sr,Ca)_2CuO_X$) thin films were deposited on MgO (100) substrate by IBS at low substrate temperatures (T_S). IBS system is shown in Fig.1 for the sputtering part. Ar gas is introduced into a discharge gap of 1.5 mm between anode (An) and cathode (Ca), and argon plasma (AP) is produced by electrical discharge applying a high voltage (V_a) of 4 kV on the anode of an ion gun. An and Ca are separated by a ceramic ring (C). Ar^+ ion beam is emitted through a cathode orifice of 1 mmΦ, and it is collimated by a copper collimator (Co) with 6mmΦ to focus the Ar^+ ion beam in a target (T) area. The ion beam diameter is 10-15 mmΦ, which is less than a diameter of 20 mmΦ of the target. The ion beam flux is monitored by a target current (I_t), which is ranging from 5 to 10 μA/cm^2.

The target (Bi-Sr-Ca-Cu-O) is sputtered by 4 keV Ar^+ ion beam and sputtered particles (SP) are deposited on the substrate (S). A distance between the ion gun and the target is 30 mm. The substrate is located under the target by 30 mm [10]. During the depositions, oxygen molecule (ML) or plasma (PL) was supplied from a plasma source at various oxygen partial pressures (P_O). The oxygen plasma was produced in the plasma source by discharging oxygen gas [7-12]. When the oxygen molecules were supplied, the oxygen gas was emitted from the same plasma source without the discharge. The P_O value was ranged from 0.1 to 6 mTorr for the depositions of nondoped Bi2201 at T_S=500°C

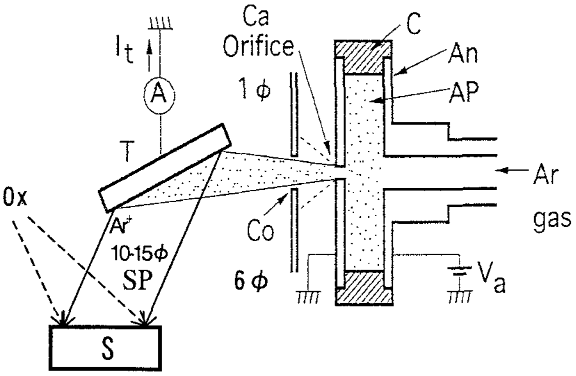

Fig.1 A schematic diagram of the ion beam sputtering system. See text for notations. A: current meter.

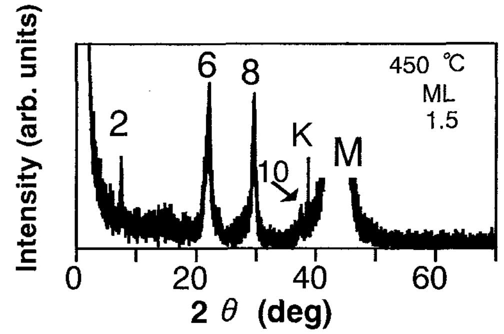

Fig.2 XRD pattern of the 30% Ca-doped Bi2201 thin film deposited at 450°C at 1.5 mTorr with ML. M, K : MgO peaks.

and Ca-doped Bi2201 at T_S=450°C and 500°C.

The deposited films were characterized by XRD and their crystallinity was estimated by averaged FWHM of (006) and (008) peaks on θ-2θ scan (Av.Δ_θ). The surface morphology of the films was observed by AFM and their roughness was estimated by the average values of R_Z.

3. RESULTS AND DISCUTTION

XRD patterns are shown in Fig.2 for the 30% Ca-doped Bi2201 thin film deposited at T_S = 450°C with ML at P_O = 1.5 mTorr, and in Figs.3 and 4 for the 30% Ca-doped Bi2201 thin films deposited at T_S = 500°C with ML and PL, respectively, at various P_O indicated. Attached numbers indicate (00*l*) indices. The XRD of all the films showed c-oriented Bi2201 phase. The XRD pattern of 450°C film (Fig.2) is not good but the main peaks of Bi2201 phase are clearly observed even though T_S is ultralow. The XRD patterns are excellent for 500°C films (Figs.3 and 4) except for the films with very low and high P_O values. Peaks (B') from impurity Bi214 (Bi_2SrO_4) phase are observed for the ML films at higher P_O but they are not observed for the PL films. Then the impurity growth is suppressed by the plasma. Figures 5 and 6 show Av.Δ_θ vs P_O for the 30% Ca-doped Bi2201 films deposited with the supply of ML or PL at T_S=450°C and 500°C, respectively. Figure 7 shows Av.Δ_θ vs P_O for the nondoped Bi2201 films deposited at T_S=500°C. Grossly speaking, they all show that the values of Av.Δ_θ increase both in the lower and higher P_O regions for ML and PL. The larger Av.Δ_θ indicates deterioration of crystallinity which is generally caused by shortage and excess of oxidation power at the low and high P_O regions, respectively. Av.Δ_θ always increases faster with increasing P_O in the higher P_O regions for PL than for ML. This is caused by the stronger (excess) oxidation power for PL than for ML in such higher P_O regions.

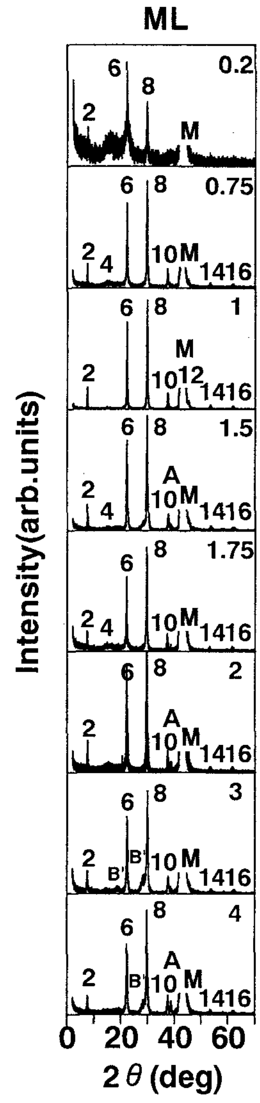

Fig.3 XRD patterns of the 30% Ca-doped Bi2201 thin films deposited at 500°C at various P_o with ML. B': impurity Bi214 phase, A: CuO.

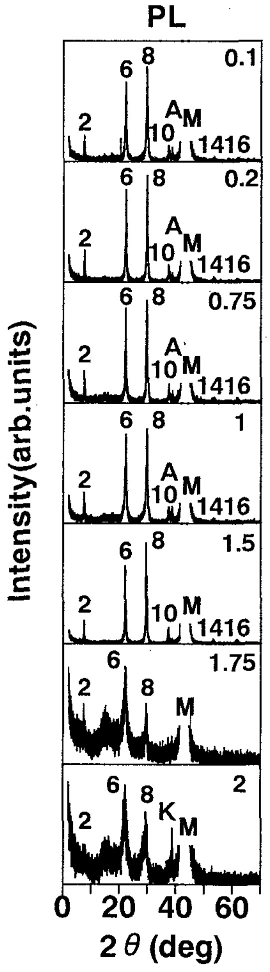

Fig.4 XRD patterns of the 30% Ca-doped Bi2201 thin films deposited at 500°C at various P_o with PL.

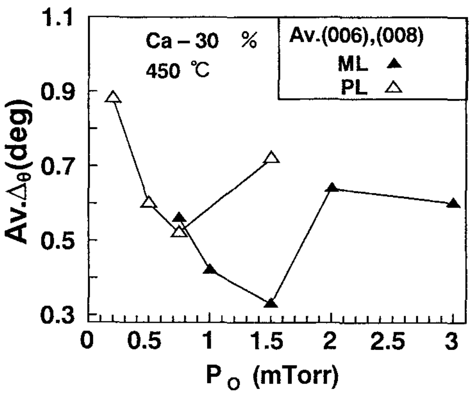

Fig.5. Av.Δ_θ vs P_O for the 30% Ca-doped films deposited at T_S=450°C.

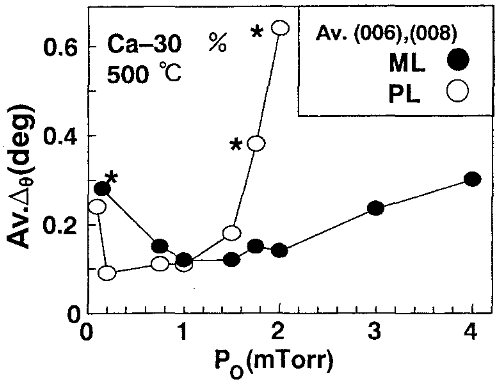

Fig.6. Av.Δ_θ vs P_O for the 30% Ca-doped films deposited at T_S=500°C.

There is the other reason for the deterioration in the higher P_O regions, that is, collisions between sputtered particles (SP) and the supplied oxygen species [11]. We believe this is more feasible. Kinetic energy of SP is quite important for the low temperature growth, it can enhance surface migration of the deposited particles and formation of the crystal structure compensating shortage of thermal energy. The sputtered particles lose much more energy by this collision in the higher P_O region, then they cannot assist the surface migration. It results in the deterioration. Collision cross section is larger for PL than for ML due to Coulombic interaction for PL, then SP lose much more energy leading to the higher deterioration for PL at the same P_O.

3.1 Ca-doped film at 450°C

Though the crystallinity of Ca-doped films deposited at 450°C (Fig. 5) is poor in average due to the shortage of thermal energy, the plasma clearly improves the crystallinity in the lower P_O region [12]. The best P_O value is 0.75 mTorr for PL. While, it is improved by ML in the higher P_O region, and the best P_O is 1.5 mTorr. The highest quality film with Av.Δ_θ=0.33° is obtained by ML at this T_S. These results cannot be explained exactly but we believe that energy balance among the ① thermal energy, ② sputtered particle energy after the collision, ③ activated oxygen energy by the collision, and ④ plasma energy, is a critical factor in this system [12].

3.2 Ca-doped film at 500℃

The Ca-doped films deposited at 500°C also show the crystalline improvement by PL at the low P_O region (Fig.6). This result clearly shows the absolute improvement by PL because the minimum Av.Δ_θ value is smaller for PL (0.09°) at P_O=0.2 mTorr than for ML (0.12°) at P_O= 1 and 1.5 mTorr. The energy balance and the plasma energy must play some role for this improvement. As a whole, the crystallinity is improved at 500°C compared with 450°C owing to the higher thermal energy.

3.3 Nondoped film at 500°C

The nondoped films deposited by ML at 500°C (Fig.7) show the better crystallinity (Av.Δ_θ = 0.1° at P_O=2 and 4 mTorr) than the Ca-doped films (Fig.6) in the same P_O region. This obviously means that the pure Bi2201 crystal can be grown with the higher crystallinity than the impurity doped Bi2201 crystal. A striking feature for the plasma supply is that there is no improvement effect by PL compared with ML in the whole P_O region for the nondoped system.

3.4 Surface morphology

An example of surface morphology is shown in Fig.8 using SEM photograph for the 30% Ca-doped film deposited at 450°C at 1.5 mTorr by ML. The surface is very smooth when the film is deposited at very low temperature. We evaluated the surface roughness by R_Z for the Ca-doped films deposited at 500°C. Grossly R_Z values decrease with increasing P_O both for ML and PL, indicating that the growth mode

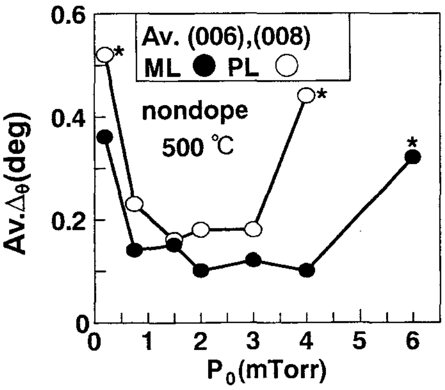

Fig.7. Av.Δ_θ vs P_O for the nondoped films deposited at T_S=500°C.

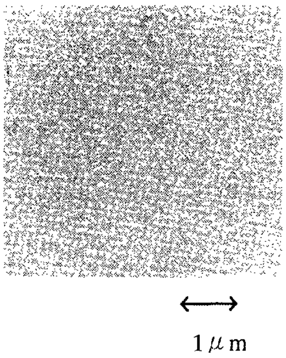

Fig.8 SEM photograph of the 30% Ca-doped film deposited at 450°C with ML at 1.5 mTorr.

gradually changes from 3D to 2D. This may be due to the optimization of SP energy by the collision. The plasma apparently reduced the surface roughness, then it can enhance multiple nucleation [7].

3.5 Mechanism [7-12]

We believe that Bi2201 grows with Sr-plane on the most surface area during the deposition. A surface energy is higher for the Ca-doped phase than for the nondoped phase since the former has Sr-Ca mixed plane on the surface while the latter has single Sr atom. Then the Ca-doped phase has strain energy and higher entropy energy. The supply of thermal energy and SP energy is sufficient for the nondoped phase with the lower surface energy, then it can be grown well by ML. While, the Ca-doped phase with the higher surface energy needs additional energy, namely, the plasma energy. The plasma energy induces the higher order of Sr-Ca arrangement and the reduction of surface energy, resulting in the higher crystallinity and the smoother surface.

4. SUMMARY

The Ca-doped and nondoped Bi2201 thin films were grown at the very low temperatures of 450°C and 500°C with supplying oxygen molecules or plasma, and the oxygen partial pressure dependence and the oxygen plasma effects were investigated on their crystallinity. For the Ca-doped films the plasma can improve the crystallinity in the low P_O region, while the nondoped films are improved by the molecules. We suggest that the collisions between SP and oxygen, and the total energy or energy balance, are the important factors on the low temperature growth. The surface morphology is also improved by the plasma. We proposed the improvement mechanism by the plasma.

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