Formation and Intergrowth of the Superconducting Phase in the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$(n=2~4) System

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Superconducting $Bi_2Sr_2Ca_{n-1}Cu_nO_x$(n=2~4) thin films were prepared by single target DC-magnetron sputtering. And, that was compared with the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$(n=1~3) thin film fabricated by using the ion beam sputtering. Phase intergrowth among n=2-3, 3-4 and 4-5 phases was observed. The molar fraction of each phase in the mixed crystal of the deposited films was determined by x-ray diffraction analyses and investigated as a function of O_2 gas pressure during sputtering. We investigated the changes of the superconducting properties by molar fraction of each phase. Also, the thin film surface observation was carried out by atomic force microscope. The images show the average particle size decreases, and the distribution density of particles on the film surface was to increase with lower gas pressures. The fabrication conditions for selective growth of the single n=2, 3 and 4 phases in $BiSrCa_{n-1}Cu_nO_x$(n=2~4) thin film are discussed.

Keywords : Superconducting $Bi_2Sr_2Ca_{n-1}CunO_x$(n=2~4) thin films, Phase intergrowth,
DC-magnetron sputtering

1. INTRODUCTION

Human has been requested the development of new devices which has the function of high speed and high capacity since they have accumulated the huge amounts of information and knowledge. 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.

For such high-T_c superconducting thin film application, a high quality thin film fabrication is required and the growth mechanism at atomic scales must be investigated. Sticking coefficient gives various information that includes the overall processes of the thin film growth mechanism; atom adsorption, migration and coalescence into the structure or re-evaporation from the surface, etc. In situ growth by DC-magnetron sputtering has the technical advantage of preparing high quality superconducting thin films. As-grown superconducting films possess a smoother surface and better morphology compared with that undergoing post-annealing.

In this paper, we discuss the superconducting properties and the fabrication conditions for the single n=2, 3 and 4 phases and the mixed crystal of these phases in $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ thin films.

2. EXPERIMENTAL

The $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ system thin films on MgO (1 0 0) single-crystal substrates were fabricated by single target DC-magnetron sputtering using a single composite oxide target.

Sputtering targets were obtained by reacting the mixtures of Bi_2O_3 (99.9 %), $SrCO_3$ (99.9 %), $CaCO_3$ (99.9 %), and CuO (99.9 %) at 700 ℃ for 10 h followed by sintering at 750 ℃ for 5 h in air. Sputtering was carried out in pure oxygen and the substrate temperature was fixed at 680 ℃ during the growth process. First the substrate was mounted directly centered above the target with a target to substrate distance of 25 mm, and then a thermocouple was attached to the rear side of the substrate.

The applied discharge was 500 mA at 150 V, for a plasma ring. As a result of the film deposition rate was 0.8 Å/min, and the film thickness was 3000 Å for a deposition time of 1 h. Thin films were grown in the O_2 gas pressure from 0.2 to O.6 torr under substrate temperature of 680 ℃. Conditions for thin films fabrication was summarized inTable 1.

Table 1. Conditions for thin film fabrication.

Substrate temperature	680 ℃
O_2 gas pressure	0.2~0.6 Torr
Sputtering voltage and current	-150 V, 500 mA
Deposition rate	0.8 Å/s
Film thickness	3000 Å

The film structure was studied by using the x-ray diffraction and the resistivity was measured using the standard four-point probe geometry with silver paste contacts. A DC current density of 1 A/cm^2 was applied during measurement and the surface morphology was observed by atomic force microscopy(AFM).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the x-ray diffraction patterns of the deposited $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ system thin films fabricated by single target DC-magnetron sputtering using a single composite oxide target. The XRD patterns of the deposited films as a function of the O_2 gas pressure are shown in Fig. 1.

A continuous peak shift from 2212 phase, peak at 2θ = 5.8 °, to 2334 phase, peak at 2θ =4.2 °, is observed with decrease of the O_2 gas pressure. The individual 2212 and 2223 phases or 2223 and 2234 phases are mixed separately in the macroscopical domain, and the two individual (0 0 2) peaks, which are derived from both phases should be observed. Accordingly, (0 0 l) peaks at the midpoint between the individual 2212 and 2223 peaks or the 2223 and 2234 peaks mean that the two phases are not separated in microscopical domains. In case that the composition and the condition do not agree, the multi-system oxide, $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ is know as forming the various blending not only the oxides of each element but also the anomaly products such as Ca-Cu, Bi-Sr, Ca-Bi, Sr-Ca, Sr-Ca-Cu and so on[4]. It is reported that among these, CaCuO2 is formed as the oxide of Ca and Cu[5].

Figure 2 shows the variations of molar fraction of 2212, 2223, and 2234 phases by O_2 gas pressures.

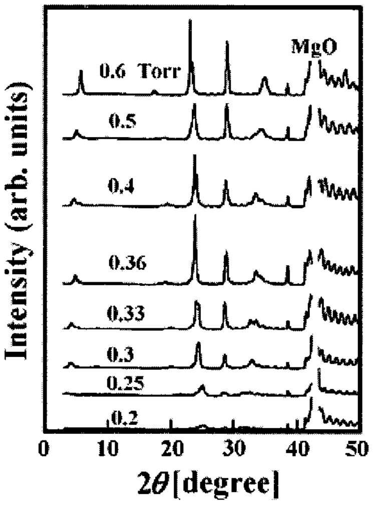

Fig. 1. X-ray diffraction patterns of $Bi_2Sr_2Ca_2Cu_3O_x$ system thin films at various O_2 gas pressure.

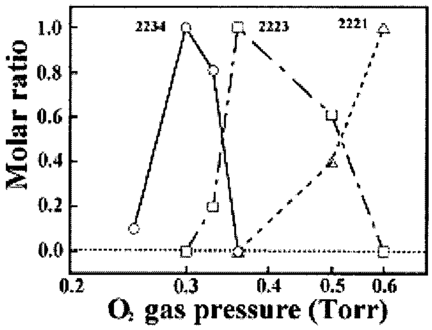

Fig. 2. Variation in molar fraction of 2212, 2223, and 2234 phases in deposited $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ thin films.

It is well known that the 2212 phase can grow at a wide temperature and pressure range compared with 2223 or larger n phase, and in our case, small shoulders are observed for 0.5, 0.4, and 0.36 Torr films. However, the main peaks showed gradual shifts toward low angle with pressure, and thus, the peak position was estimated from the maximum in this study. The crystal structure of thin films is very sensitive to the O_2 gas pressure. The $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ phase of larger n is proportional to the lower O_2 gas pressure.

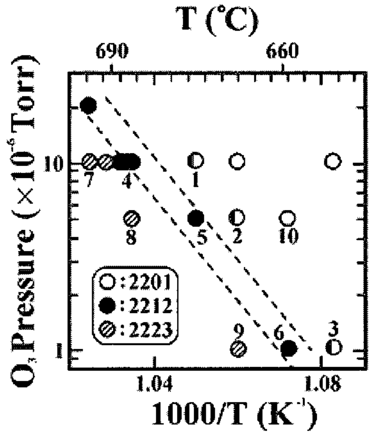

Fig. 3. Phase diagram of thin films fabricated by using the ion beam sputtering.

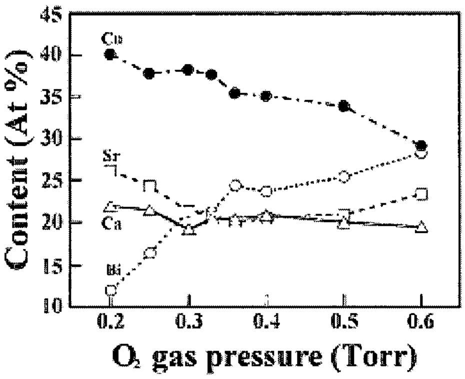

Fig. 4. Variation in compositions of each element by O_2 gas pressure.

Similar results were obtained for the ion beam sputtering deposition using the O_3 gas. Figure 3 represents the phase diagram of thin films fabricated by using the ion beam sputtering. The superconducting thin films fabricated by using the evaporation method and an effusion cell employed. Metal targets of Sr, Ca, and Cu were simultaneously sputtered by Ar ion or atom beans generated by saddle field type cold cathode guns. 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 660 and 720 ℃. Highly condensed ozone gas was obtained by a silica gel adsorption method[6].

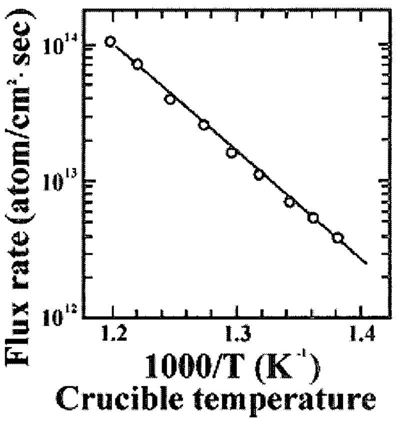

Fig. 5. Characteristics of faraday cup.

The horizontal line indicates the reciprocal number of the substrate temperature(K) and the vertical line indicates the log of the O_3 gas pressure of the oxidation gas. In Fig. 3. ○ indicates the formed thin film of 2201 phase, and ● indicates that of 2212 phase, and ⊘ indicates that of 2223 phase. The mixed marks of Fig. 3 indicates that the peak of XRD does not include the 2201 single crystal [(002) peak location = 7.24 °], the Bi2212 single crystal [(002) peak location = 5.75 °] and the 2223 single crystal [(002) peak location = 4.77 °]. Comparing formation regiens of each phase on the regular substrate temperature lineal, as the O_3 gas pressure transfer form high pressure to low pressure, the crystal structure of the thin film transfer as 2201 → 2212 → 2223. This tendency agrees with the pressure dependence observed for the solid-state reaction.

The variations of the chemical composition of the films by O_2 gas pressure were studied and the results are shown in Fig. 4.

The Bi composition was observed to decrease and the Cu concentration to increase with lowering O_2 gas pressures. The compositions of Sr and Ca were constant in this gas pressure range. The vapor pressure of Bi is much higher than that of other construction elements of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$[7]. Thus, at a fixed substrate temperature, increase of Bi vapor pressure by lowering the O_2 gas pressure leads to Bi deficiency in the deposited thin film. All these films were deposited using the same set of targets with cationic composition of 2:2:2:3. Thus, a continuous phase shift via mixed crystal by varying O_2 gas pressure indicates that the crystal growth was dominated by the effects of low sticking coefficient of Bi atoms. In ion beam sputtering case, even in the high substrate temperature re-evaporating Bi element a lot, to get a stable element molecular, Bi element was supplied by the evaporation method using the faraday cup.

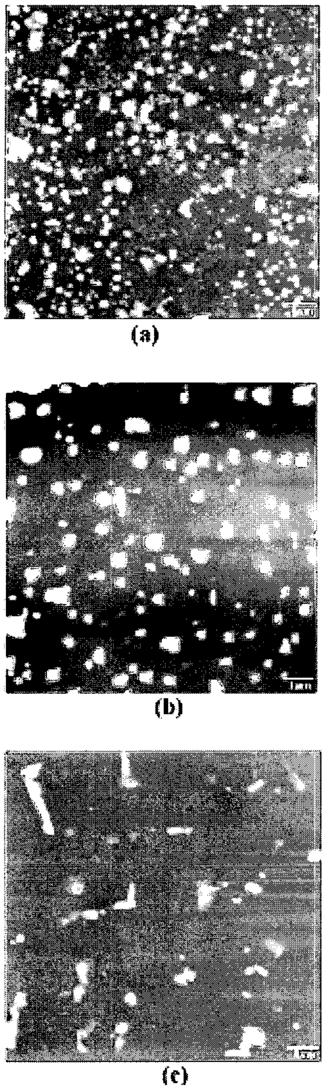

Fig. 6. AFM images of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ thin films.

Figure 5 represents the characteristics of the faraday cup. The vapor atoms spouted in the chamber can be regarded as molecular flow, the distribution is determined by the distribution of the plain evaporation source. In this case, the intensity of the molecular beam from the faraday cup becomes only the function of the temperature and does not rely on the quantity of the material in the faraday cup[8]. Therefore, by the fine temperature control, the stable supply of Bi element is always possible, and the excellent control equal to Ar ion bean gun can be realized. The quantity of evaporation By using the faraday cup could be 10~100 times as much as that by using the sputtering method.

On the other hand, it is well known that thermodynamical phase stability increases in the order of 2234<2223<2212. A phase transition from the more stable phase to the less stable one needs a thermodynamical driving force, e.g., entropy rise due to partial melt or re-evaporation and so on. In the case of the single target sputtering under study, oxygen introduced into the deposition chamber supplied ions for target bombardment as well as oxidizing species. Accordingly, these two factors, low sticking coefficient of Bi element and thermodynamical driving force, promote crystal structure of $n \gg 3$ at low O_2 gas pressures. One of the most essential factors for the selective growth of each single 22 (n-1)n phase is oxidizing atmosphere during the deposition.

The thin film surface observation was carried out by AFM, and their images are shown in Fig. 6.

The small rectangular particles with a dimension of about 0.3~0.1 μm in diameter were dispersed on the film surface. The average particle size decreases, and the distribution density of particles on the film surface is observed to increase with lower gas pressures. These particles may come from excess Cu atoms in the deposited thin film as shown in Fig. 4.

4. CONCLUSION

$Bi_2Sr_2Ca_{n-1}Cu_nO_x$ superconducting thin films were fabricated by single target DC-magnetron sputtering using a single composite oxide target. And, it was compared with the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ thin film fabricated by using the ion beam sputtering.

The crystal structure of deposited thin films was systematically shifted to a larger n phase by lowering the O_2 gas pressure. Among the optimum O_2 gas pressure for the single phase fabrication of 2212, 2223, and 2234 phases, intergrowth of these phases was observed. The molar fraction of each phase was estimated by XRD analysis, and the relationship with sputtering gas pressure was discussed. Bi deficiency was also observed at low O_2 gas pressures. This suggests that $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ thin film growth by single target sputtering is mainly dominated by the low sticking coefficient of Bi atoms as well as by the thermodynamical driving force promoting $n \geq 3$ phase at low oxygen atmosphere. AFM images show the average particle size decreases, and the distribution density of particles on the film surface was to increase with lower gas pressures.

The multi-system compound such as oxide superconductor exists a lot as the stabile phase and the metastable phase. So, to get the planned phase, it is important to determine the reaction path that the anomaly is not generated, but the process of the formation of the thin film is basically the reaction of nonequilibrium, so it is difficult to determine the reaction path. However, O_2 gas pressure and temperature dependence which are the important parameters related to the fabrication of the superconducting thin film of the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ system are thought to supply the various information about explanation of the crystal growth mechanism of the oxide high temperature superconductor of the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ system.

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