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$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ sputtered films deposited using Bi-Sr-Cu-O and Ca-Cu-O targets

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$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Bi-based) films were simultaneously or alternatively deposited by a rf magnetron sputtering method controlling shutters of Bi:Sr:Cu = 4.3:1.8:0.6 and Ca:Cu = 1.9:1.0 targets, where the sputtering gas of $He:O_2$ = 4:1 and an *off-axis* geometry were used. From the results, we found that the films were $Bi_2Sr_2CuO_y$ (Bi-2201) phase although the composition of the films was approximately equal to that of an ideal $Bi_2Sr_2CaCu_2O_y$ (Bi-2212). This indicates that it is difficult to produce Bi-2212 single-phase films when the two targets were used at same substrate temperature. Therefore, the growth of the films may be dependent on the concentration of constituent elements supplied at the surface of the substrates.

Key words: BSCCO film, multi-targets, shuttering, sputtering, helium gas

1. INTRODUCTION

In order to fabricate high-T_c superconducting devices, it is necessary to get high quality $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Bi-based) superconducting thin films. So far they have been grown by metalorganic chemical vapor deposition (MOCVD) [1,2], molecular beam epitaxy (MBE) [3] and sputtering [4-6]. However, it is not easy to prepare high quality Bi-based films, since Bi-based superconductors have phases with different number of Cu-O layers. The Penning effect is known to produce active oxygen particles of oxygen atomic ion (O^+) and molecular ion (O_2^+) by using a mixture gas of He and O_2 [7-9]. Therefore, a high quality Bi-based film may be obtained by the sputtering gas.

In this study, we investigated the growth mechanism of Bi-based films simultaneously or alternatively deposited by a rf magnetron sputtering method using the targets of Bi-Sr-Cu-O and Ca-Cu-O, where the sputtering gas of $He:O_2$ = 4:1 and an *off-axis* geometry were used.

2. EXPERIMENTAL

The sputtering condition of the films is shown in Table I.

The Bi-Sr-Cu-O targets with compositions of Bi:Sr:Cu = 4.8~6.0:1.4~2.1:0.3~0.7 were prepared at 830℃ for 24h from the chemical powders of Bi_2O_3, $SrCO_3$, and CuO. The Ca-Cu-O targets with the compositions of Ca:Cu = 1.4~1.9:1.0 were prepared at 950℃ for 24h from the chemical powders of $CaCO_3$ and CuO. The diameter and the thickness of the targets were about 60mm and 4 mm, respectively. The sputtering gas of He+O_2 (He:O_2 = 4:1) was used.

We deposited Bi-based films by a rf magnetron sputtering method with two targets of Bi-Sr-Cu-O and Ca-Cu-O using an *off-axis* geometry, where the MgO (100) substrates were placed at the position perpendicular to the target. The total gas pressure and the substrate rotation speed were 75mTorr and 1 rpm, respectively. The rf powers of the Bi-Sr-Cu-O and the Ca-Cu-O targets were fixed at 100W. The Bi-Sr-Cu-O and the Ca-Cu-O contents in the films were controlled by shuttering. In order to prepare high quality the $Bi_2Sr_2CuO_y$ (Bi-2201) films clarify an optimum condition, when the shutter of the Ca-Cu-O target was closed.

The crystallinity, the composition and the surface morphology of the films were investigated with X-ray diffraction (XRD), electron probe micro analysis (EPMA) and scanning electron microscopy (SEM), respectively.

3. RESULTS AND DISCUSSION

We prepared Bi-2201 films using the targets of Bi:Sr:Cu = 4.8~6.0:1.4~2.1:0.3~0.7. Fig. 1 shows XRD patterns of the films prepared at various substrate temperatures (T_{sub}) using the target of Bi:Sr:Cu = 4.8:2.1:0.6. As shown in the figure, XRD peak was observed at about 29.6°, which was assigned to an impurity phase in the film prepared at 770℃. When the films were prepared at the T_{sub} of more than 790℃, the XRD peak were observed at about 21.8, 29.2 and 36.8°, which were assigned to (006), (008) and (00<u>10</u>) from a Bi-2201 superconductor, respectively. From the results, we found that the optimum T_{sub} for the Bi-2201 film with high crystallinity was 830℃, and that the composition of the film was Bi:Sr:Cu = 2.6:1.8:0.6. Therefore, this indicates that the compositions of the films are able to be controlled by the composition of targets.

Table I sputtering condition

Target	Bi-Sr-Cu-O	Ca-Cu-O
Target composition	Bi:Sr:Cu= 4.8~6.0:1.4~2.1:0.3~0.7	Ca:Cu= 1.4~1.9:1.0
rf power	100 W	
Sputtering gas	He+O_2 (He:O_2=4:1)	
Sputtering time	4 h	
Total gas pressure	75 mTorr	
Substrate Temperature (T_{sub})	770~850℃	
Substrate	Polished MgO (100)	

We prepared the Bi-2201 films using the targets with various compositions. Although the figures were not shown, we found that the compositions of the Bi-2201 films were dependent on those of the targets. The composition of the film prepared using the target of Bi:Sr:Cu = 6.0:1.8:0.6, was Bi:Sr:Cu = 1.9:2.0:1.2 and approximately equal to that of an ideal Bi-2201 superconductor.

Fig. 2 shows XRD pattern of the film prepared at 830℃ using the target of Bi:Sr:Cu = 6.0:1.8:0.6. The prepared film was a Bi-2201 single-phase and did not include any impurity phases. The FWHM (full-width-half-maximum)

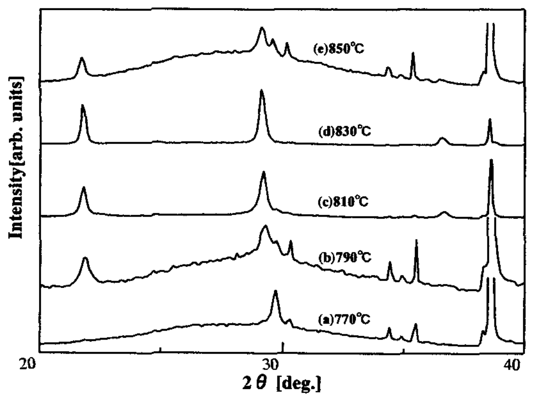

Fig.1 XRD patterns of the films prepared at various substrate temperatures (T_{sub}) using the target of Bi:Sr:Cu = 4.8:2.1:0.6

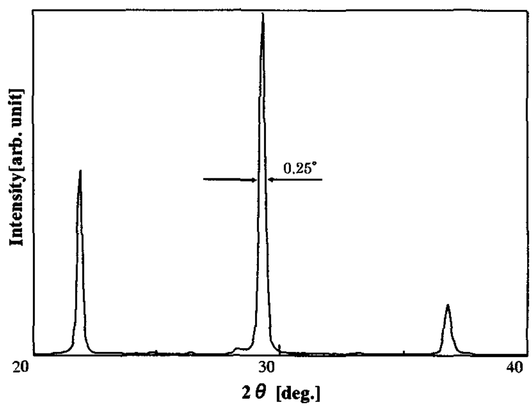

Fig. 2 XRD pattern of the film prepared at 830℃ using the target of Bi:Sr:Cu = 6.0:1.8:0.6

value of the Bi-2201 (008) peak was 0.25°. Therefore, this indicated that the Bi-2201 film was a high crystallinity.

Fig.3 shows shuttering patterns in this work. T_1 and T_2 represent opening and closing time of the shutter for the Bi-Sr-Cu-O target, respectively. T_3 and T_4 represent opening and closing time of the shutter for the Ca-Cu-O target, respectively.

Fig. 4 shows XRD patterns of the films prepared at 830℃ using two targets of Bi-Sr-Cu-O and Ca-Cu-O, where the shuttering condition were (a) T_1 = 0s, T_2 = 120s, T_3=0s, T_4 = 25s and (b) T_1 = 0s, T_2 = 120s, T_3=0s, T_4 = 60s. From the results, we found that the Bi-2201 phase of the films were dominant in both (a) and (b).

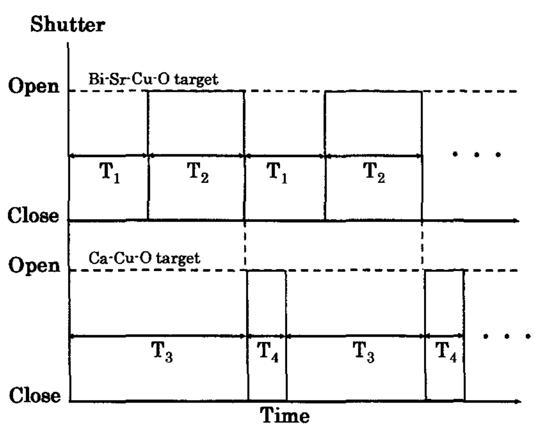

Fig. 3 shuttering patterns used in this work

Although the figures were not shown, the films were prepared using the delay time after the formation of one Bi-Sr-Cu-O/Ca-Cu-O unit. The result indicates that the films were XRD peaks from a Bi-2201 phase, although the composition of (b) was Bi:Sr:Ca:Cu = 2.7:2.1:0.8:1.4, which was approximately an ideal composition of Bi-2212.

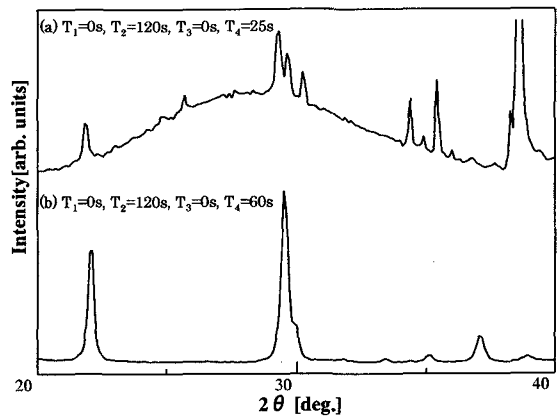

Fig. 4 XRD patterns of the films prepared at 830℃ using two targets of Bi-Sr-Cu-O and Ca-Cu-O with different shuttering conditions of (a) and (b)

Fig. 5 shows XRD patterns of the films prepared at 830℃ using two targets of Bi-Sr-Cu-O and Ca-Cu-O, where the shuttering condition were (a) T_1 = 2s, T_2 = 10s, T_3 = 0s, T_4 = ∞s, (b) T_1 = 2s, T_2 = 5s, T_3 = 0s, T_4 = ∞s and (c) T_1 = 8s, T_2 = 10s, T_3 = 0s, T_4 = ∞s. As shown in the figure, $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) film of (a), which

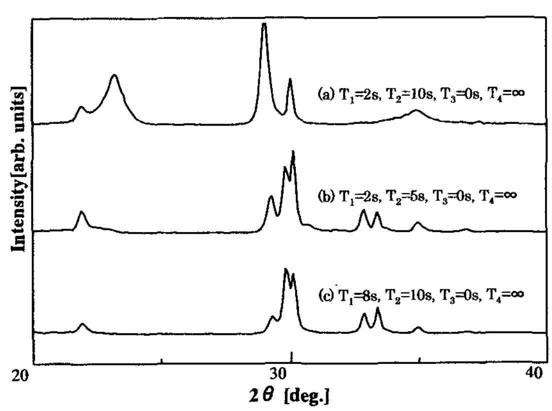

Fig. 5 XRD patterns of the films prepared at 830℃ using two targets of Bi-Sr-Cu-O and Ca-Cu-O with various the shuttering conditions of (a), (b) and (c)

was approximately equal to the composition of a Bi-2212 superconductor, were prepared by controlling the shutter of the Bi-Sr-Cu-O target, while the shutter of Ca-Cu-O target was always opened. The compositions of (b) and (c) films, which were different from composition of a Bi-2212 superconductor was the Bi-2201 phase and the impurities phase. Although the figures were not shown, we prepared the Bi-2212 films by a rf magnetron sputtering method with two targets of Bi-Sr-Cu-O and Ca-Cu-O. The c-axis-oriented Bi-2212 films were prepared by changing the Ca-Cu-O rf powers [10].

4. CONCLUSIONS

Bi-based films were deposited by a rf magnetron sputtering method controlling shutters of the Bi-Sr-Cu-O and Ca-Cu-O targets. From the results, we found that the films were a Bi-2201 phase although the composition of the films was approximately equal to that of an ideal Bi-2212. This indicates that it is difficult to produce Bi-2212 single-phase films when the two targets were used at same substrate temperature. Therefore, the growth of the films deposited using shuttering may be dominated by the concentration of constituent elements supplied at the surface of the substrates.

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