

BSCCO/STO/BSCCO Structures by the MOD Method

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Abstract— $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (BSCCO) / SrTiO_3 (STO) / BSCCO trilayer structures were prepared by the metal-organic decomposition (MOD) method. In this study, annealing condition of BSCCO thin films prepared by the MOD method were investigated. High quality films having critical temperature (T_c) of 84 K were obtained on STO (001) substrate by a 2-step annealing process with 100% O_2 for 2 h at 870°C and 10% O_2 for 2 h at 885°C. The STO layer prepared by the MOD method was grown epitaxially on the BSCCO thin films, and the top BSCCO layer was also grown epitaxially on the STO layer. The BSCCO/STO/BSCCO structure showed a T_c of 77 K.

Index Terms—BSCCO/STO/BSCCO trilayer structure, critical temperature, crystal growth, MOD method.

I. INTRODUCTION

MULTILAYER structures consisting of superconductors and insulators are fundamental structures for integrating superconducting devices. However, it is not easy to prepare the multilayer structures for high- T_c superconductors. Conventionally, multilayers consisting of superconducting layers and insulating layers have been prepared using a pulsed laser deposition (PLD) method, a molecular beam epitaxy (MBE) method, or a sputtering method, etc [1]–[3]. These methods are of high cost due to requirement of vacuum processes. Recently, a metal-organic decomposition (MOD) method is attracting attention as one of the useful preparation techniques for high- T_c superconducting tapes and large-size films. For example, large area thin films of $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) with a huge critical current density of an order of 1 MA/cm² at 77 K have been obtained by the MOD method using trifluoroacetate [4]–[7]. However only a few reports have been published on the MOD method of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (BSCCO) [8].

BSCCO is considered to be a promising material for superconducting devices since it shows as an intrinsic Josephson effect [9], [10]. However, fabrication of superconducting integrated circuits has not been developed, because of the difficulty in preparation of the multilayers consisting of BSCCO layers and insulators. We consider that the MOD method is one of the most promising techniques to prepare high-quality multilayer structures not only for the tapes but for the superconducting electronics.

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In this study, optimal conditions to obtain high quality BSCCO thin films by MOD method were investigated, and BSCCO/STO/BSCCO trilayer structures were prepared by the MOD method.

II. EXPERIMENTS

A. BSCCO Thin Films

The BSCCO thin films were prepared by a using metal-organic (MO) solution (SKBSCCO-008, Kojundo chemical Lab.—Symetrix). The MO solution was spincoated on MgO (001) and STO (001) substrates by 2-step process using 1000 rpm for 5 s and 3000 rpm for 1 min. After the dry process on a hot plate at 120°C for 2 min, the films were annealed in air or O_2 or $\text{O}_2 + \text{N}_2$ (10:90) atmosphere at an annealing temperature between 500 and 885°C for 2 hour. The thickness of the thin films was approximately 40 nm.

B. BSCCO/STO/BSCCO Structures

The BSCCO/STO/BSCCO structures were prepared by using BSCCO solution (SKBSCCO-008) and a STO solution (STO-06, Kojundo Chemical Lab.). Bottom BSCCO layers were prepared as follow. The BSCCO solution was spincoated on STO (001) substrates by 2-step process using 1000 rpm for 5 s and 3000 rpm for 1 min. After the dry process on a hot plate at 120°C for 2 min, the layers were annealed by 2-step process in O_2 at 870°C for 2 h and in $\text{O}_2 + \text{N}_2$ (10:90) atmosphere at 885°C for 2 h. The STO layers were prepared by spincoating the STO solution on the bottom BSCCO layers, followed by the drying, and the annealing. Top BSCCO layers were prepared by the same procedure as that for the bottom layers. The spincoating of the BSCCO solution on the STO layers, followed by the drying, and annealing. Each process for the STO layers and the top BSCCO layers is under the same condition as used for the bottom BSCCO layers. Thickness of STO layers, top and bottom BSCCO layers was approximately 40 nm.

III. RESULTS AND DISCUSSION

A. BSCCO Thin Films

In order to analyze whether organic components remain in the films after the annealing process, the energy dispersive X-ray (EDX) analysis of the carbon content was carried out. Fig. 1 shows an intensity of characteristic X-ray emission from carbon atoms remaining in the films annealed at various temperatures. In the case of samples annealed in an O_2 atmosphere, the signal of carbon is as small as the background level. On the other hand, a large amount of carbon exists in the sample annealed

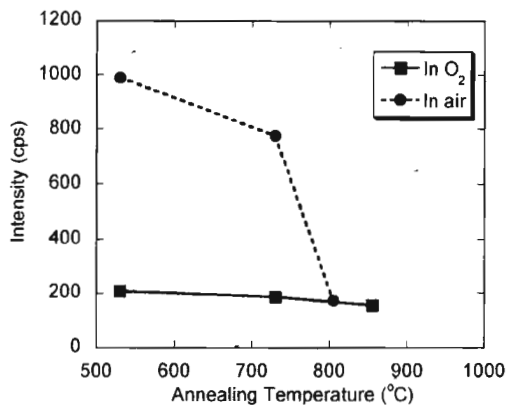


Fig. 1. Characteristic X-ray intensity of carbon atoms remaining in the films annealed at various temperatures in O_2 and in air.

below 800°C in air. This result indicates that the organic components are not decomposed and remain in the film even at temperature of 800°C . In contrast, the organic components are easily decomposed in O_2 atmosphere at temperature as low as 500°C . Usually, the MOD process is carried out by a three-step process as follows; 1) the drying process to evaporate organic solvent, 2) the pre-annealing process around 500°C to decompose metal-organic materials, and 3) the final annealing process to crystallize the materials. If a complete decomposition of organic components does not occur during process 2, crystallization process 3 may not proceed sufficiently. This may provide one reason why a preparation of BSCCO by the MOD method has failed in the previous studies.

Fig. 2 shows X-ray diffraction (XRD) patterns of the samples prepared at different temperatures (a) in air and (b) in O_2 on MgO(001) substrates. The (00 l) diffraction peaks of 2212 phase are observed for the annealing temperature between 780 and 805°C in air, and 805 and 880°C in O_2 . The diffraction peaks from 2201 phase are indicated by asterisks in Fig. 2. At the annealing temperature of 830°C , the 2212 phase was not obtained but the 2201 phase was obtained by the annealing in air as shown in Fig. 2(a). On the other hand, the 2212 phase was observed up to 880°C for samples annealed in O_2 . To compare these results, intensities of (008) peak of 2212 phase are plotted versus annealing temperatures in Fig. 3. A maximum of the (008) peak intensity is observed at 850°C for the O_2 -annealed sample, while the peak appears at 805°C for the air-annealed sample. In general, the 2212 phase can be obtained at higher annealing temperature for lower content of oxygen. We consider that the decomposition of 2212 phase at 830°C in air is due to some reaction between BSCCO crystal and residual organic components.

The R-T curves of samples that have the maximum intensity of (008) line are shown in Fig. 4. The sample (a) crystallized at 805°C in air shows T_c of 44 K, while the sample (b) crystallized in 100% O_2 at 850°C showed T_c of 60 K. Usually preparation of high quality BSCCO is considered to require conditions of higher process temperature and lower oxygen content. However, in the MOD method, such a condition is not favorable because of residual organic components in the films as mentioned above. Taking into account these results, a 2-step annealing process was employed to obtain high quality BSCCO thin film with an-

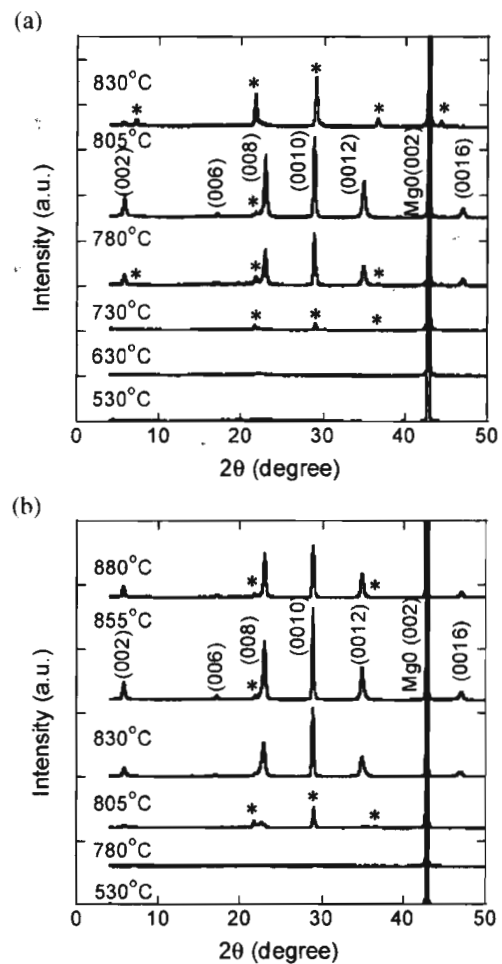


Fig. 2. XRD patterns of samples prepared with different annealing temperature (a) in air and (b) in O_2 . The diffraction peaks from 2201 phase are indicated by asterisks.

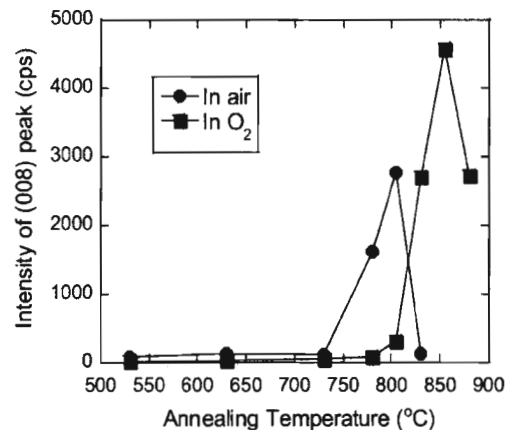


Fig. 3. Intensities of (008) peak of samples are plotted of annealing temperature.

nealing in O_2 at 870°C and in $N_2 + O_2$ (90:10) at 885°C on STO (001) substrate. Consequently, the sample prepared by the 2-step process shows T_c of 84 K as shown in Fig. 4(c).

B. BSCCO/STO/BSCCO Structures

Fig. 5 shows XRD patterns of (a) a BSCCO single layer, (b) a STO/BSCCO structure deposited STO layer on BSCCO layer

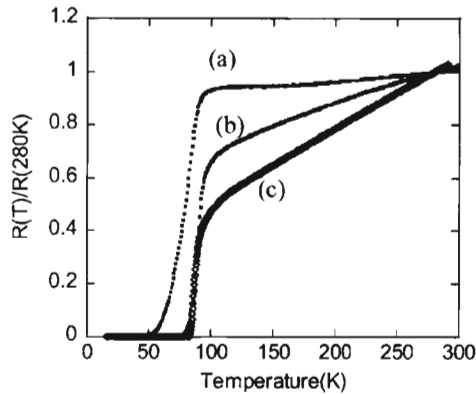


Fig. 4. R-T curves of BSCCO samples annealed at (a) 805°C in air for 1 hour, (b) 855°C in O₂ for 1 hour, (c) 870°C in O₂ for 2 hour and 885°C in 10% O₂ for 1 hour on STO substrate.

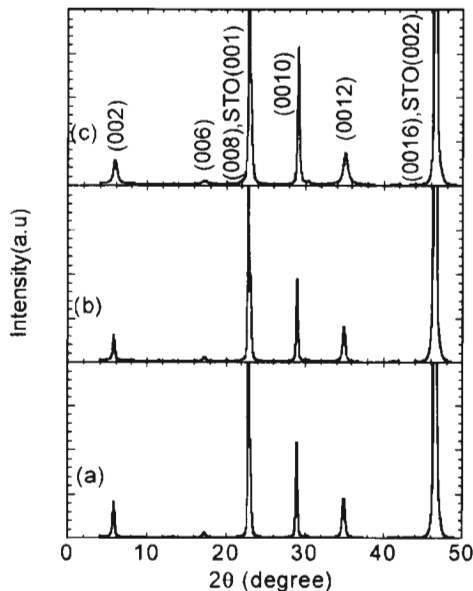


Fig. 5. XRD patterns of (a) BSCCO single layer, (b) STO/BSCCO structure and (c) BSCCO/STO/BSCCO structure.

and (c) a BSCCO/STO/BSCCO structure. The $(00l)$ diffraction peaks of the BSCCO and the STO are observed for all the samples, and any other secondary phases are not observed. The full width at the half maximum (FWHM) of (0012) peaks of BSCCO single layer, STO/BSCCO structure and BSCCO/STO/BSCCO structure were 0.37° , 0.38° and 0.69° , respectively. This indicates that crystallinity of the top BSCCO layer is poor compared with that of the bottom BSCCO layer.

In order to investigate the epitaxial relationship of the top BSCCO, the bottom BSCCO and the STO layers, the reflective high-energy electron beam diffraction (RHEED) patterns were investigated. Fig. 6 shows the RHEED patterns of (a) the BSCCO single layer, (b) the STO/BSCCO structure and (c) the BSCCO/STO/BSCCO structure. The electron beam incidence is parallel to STO $[100]$. Weak streak patterns are observed in the BSCCO single layer and the BSCCO/STO/BSCCO structure. We consider that the low intensity in the RHEED patterns is due to ex-situ RHEED analysis, because the sample surface may have been damaged by an exposure in air. On the other hand, a

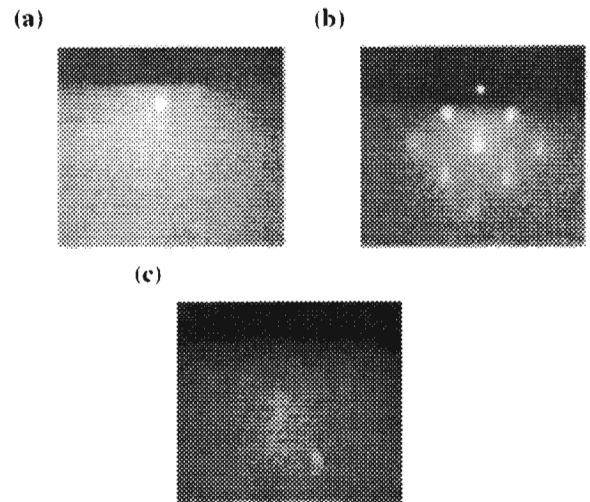


Fig. 6. RHEED patterns of (a) BSCCO single layer, (b) STO/BSCCO structure and (c) BSCCO/STO/BSCCO structure.

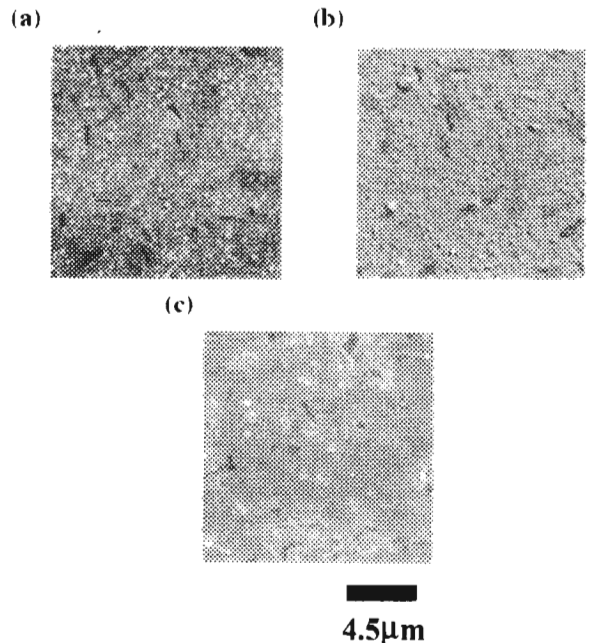


Fig. 7. SEM images of (a) the BSCCO single layer, (b) the STO/BSCCO structure and (c) the BSCCO/STO/BSCCO structure.

spot pattern was observed in the STO/BSCCO structure. These indicate that the bottom BSCCO layer, the STO layer and the top BSCCO layer are grown epitaxially, where $[100]$ or $[010]$ azimuth of BSCCO is parallel to $[110]$ azimuth of STO.

Fig. 7 shows scanning electron microscope (SEM) images of (a) the BSCCO single layer, (b) the STO/BSCCO structure and (c) the BSCCO/STO/BSCCO structure. Many precipitates of 100–200 nm are observed in Fig. 7(a). The surface of the STO layer is more rough than that of the STO substrates due to many precipitates in the bottom BSCCO layer, but it is smoother than that of the bottom BSCCO layer and the surface of the top BSCCO layer is smoother than that of the bottom BSCCO. Large terraces of $> 1 \mu\text{m}$ are observed in the top BSCCO layer and there are few precipitates, although the crystallinity is worse

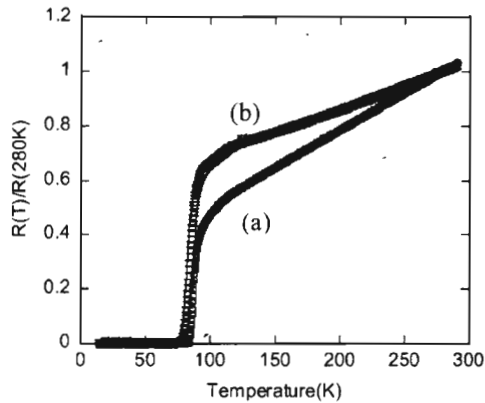


Fig. 8. R-T curves of (a) the BSCCO single layer and (b) the BSCCO/STO/BSCCO structure.

as discussed above. We consider the reason is that many steps on the STO layer promote the nucleation of the BSCCO crystal, and large grains grow on top BSCCO layer.

Fig. 8 shows R-T curves of (a) the BSCCO single layer and (b) the BSCCO/STO/BSCCO structure. The BSCCO single layer and the BSCCO/STO/BSCCO structure shows T_c of 84 K and 77 K, respectively. It is considered that the deterioration of the T_c of the BSCCO/STO/BSCCO structure is due to the low crystallinity of the top BSCCO layer. In order to improve the electrical properties of the BSCCO/STO/BSCCO structure, an improvement of the flatness of the bottom layer is strongly required.

IV. CONCLUSION

The BSCCO thin films and the BSCCO/STO/BSCCO trilayer structures were successfully prepared by MOD method. The annealing in O_2 seems to play a significant role for decomposition of the organic components. This assumption is justified by the fact that high-quality BSCCO thin films are obtained using the 2-step annealing process.

XRD and RHEED measurement showed that the bottom BSCCO layer, the STO layer and the top BSCCO layer in the BSCCO/STO/BSCCO structures were grown epitaxially. The BSCCO/STO/BSCCO trilayer showed the T_c of 77 K, while the single BSCCO layer showed the T_c of 84 K.

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