Crystal growth of (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O thin films fabricated via post annealing

Zon Mori and Shinichiro Koba

Department of Mechanical and Intelligent Systems Engineering, National Institute of Technology, Kumamoto College, Yatsushiro, Kumamoto 866-8501, Japan

E-mail: mori@kumamoto-nct.ac.jp

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Abstract

Post-annealing of superconducting Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ (BSCCO) thin films deposited by sputtering is essential for obtaining a single 2223 phase. However, optimum annealing temperature is limited to a very narrow range, needing to pass liquid phase for 2223 crystallization while not exceeding re-evaporation point. In this study, we optimized annealing conditions and observed the crystal growth process. As a result, single phase 2223 thin films with critical temperature of 108 K were obtained at 850 °C, while mixed phase thin films of 2223 and 2212 were grown above 855 °C. This is due to the re-evaporation of the thin film compounds, and these results reflect the recrystallization process after melting.

Introduction

A superconducting Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ (BSCCO) system has three main stable phases, namely, Bi$_2$Sr$_2$CaCu$_2$O$_x$ (2201), Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ (2212), and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (2223). The electrical properties of these phases are strongly influenced by the number of CuO$_2$ planes. It is known that the superconducting transition temperature ($T_c$) of a BSCCO system is 20 K for $n = 1$ (2201), 80 K for $n = 2$ (2212) and 110 K for $n = 3$ (2223). The high $T_c$ of the 2223 system compared to 2212 and sufficient temperature margins provided by liquid nitrogen motivates its ongoing research and development. The three phases have only slightly different activation energy for formation, attracting mixed crystals or intergrowth during fabrication. Hence, establishing a fabrication process of single 2223 phase is indispensable to develop applications of BSCCO systems.

One of the most important applications of BSCCO systems is the fabrication of long multifilamentary superconducting wires through powder-in-tube (PIT) method [1]. However, the critical current density ($J_c$) of BSCCO multifilamentary superconducting wires by PIT is lower than Y$_1$Ba$_2$Cu$_3$O$_x$ (YBCO) coated conductors. This is because the in-plane crystal grains in the BSCCO system act as weak links for current transport [2–5]. To improve the $J_c$ of a BSCCO system, it is necessary to reduce the number of grain boundaries. Essential to this is an understanding of the crystal growth of 2223 superconductors. In the future, development of the 2223 superconducting wire with sufficient critical current density that can be used in liquid nitrogen is expected. In this study, crystal growth processes during annealing and the micro-crystal structure of 2223 thin films were studied.

Experimental

The BSCCO thin films were prepared by radio frequency (RF) magnetron sputtering using a four-source multi-target system. The targets were: (1) Bi (metal), (2) Pb (metal), (3) Sr$_2$Ca$_2$Cu$_2$O and (4) Ca$_2$Cu$_2$O. It is known that the superconducting properties of BSCCO system can be increased by doping with Pb. Doping of Pb onto Bi sites reduces the anisotropy of crystal structure and relaxes the inner strain of crystal structure [6]. The substrate was polished MgO (100) single-crystal. The thin film composition was controlled by adjusting the sputtering
power of each target, and for this study the thin film composition was set to Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$. The substrate temperature during deposition was set to 650 °C. The Ar and O pressures were kept at 2.0 Pa and 3.0 Pa, respectively, during deposition. The typical thin film thickness was 200 nm. These deposited thin films were post-annealed at 845 °C–865 °C for 1–20 h in a tube furnace in air. During annealing all thin films were enclosed between two sintered compacts with a depression. The sintered compact was prepared with the same composition (Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$) as the thin films. This allowed the vapor pressure of each element surrounding the thin films to be kept at the same conditions. The sintered compacts were replaced for each experiment. Details of the sputtering process and properties of the thin films including the effects of Pb doping have been reported elsewhere [7].

The film structure was studied by x-ray diffraction (XRD) using Cu Kα radiation. Electric transport was conducted by four-point probe geometry. The surface morphology was observed by a scanning electron microscope (SEM) and scanning ion microscope (SIM). To observe the cross-section, the specimen was milled by a low-voltage Gentle Mill ion beam workstation together with a high-voltage focused ion beam (FIB). The incident direction of the FIB was set to [110] of MgO and the thin films were coated with W/C/Pt-Pd prior to processing.

Results and discussion

The XRD patterns of the thin films annealed at 845 °C–865 °C for 10 h are shown in figure 1. For all samples, typical peaks of the 2212 or 2223 phases and the preferred orientation with the c-axis perpendicular to the substrate plane are shown. C-axis-oriented 2212 (00 l) and 2223 (00 l) phases are labeled with open and closed circles, respectively. Thin films with a single 2212 phase and 2223 phase grew at 845 °C and 850 °C, respectively. On the other hand, films with a mixed phase of 2223 and 2212 grew at 855 °C or higher. As shown in SEM micrographs in figure 2, the crystal structure of the thin films appeared to be strongly influenced by the annealing temperature. Although some small holes were seen, the surface of the thin film annealed at 845 °C and 850 °C was observed to be smooth and uniform. On the other hand, flaky, discontinuously arrayed island microcrystals were observed on the thin film annealed at 855 °C or more. These structures reflected the recrystallization after melting. It is known that some liquid phases lead to the formation of a 2223 phase [8, 9]. The presence of the liquid phase narrows the temperature windows of annealing, because re-evaporation of the elements easily take place when thin film was melted. The 2223 phase commences at a temperature slightly higher than melting point so delicate temperature control during annealing is essential for obtaining continuous thin films.

Figure 3 shows the variation of XRD patterns with annealing time. The annealing temperature was fixed at 855 °C. Since 855 °C is slightly higher than the optimum annealing temperature from the results of figures 1 and 2, the change with the annealing time can be clearly observed as compared with 850 °C. In addition, position of the grain boundary can be easily confirmed because the island like structure was clearly seen. The main phase of
the thin films coincides with the 2212 phase initially, gradually decreasing as the 2223 phase grew with annealing time. SEM micrographs are shown in figure 4. The surface of the thin films was smooth and uniform during short annealing, with voids becoming noticeable at 10 hours or later. These results suggest that the 2212 phase formed at the initial stage of annealing decomposed over a relatively long time before reforming into the 2223 phase through aggregation after the liquid phase.

Figure 5 shows the SIM image of thin film annealed at 855 °C for 10 hours observed from an oblique direction. The crystallographic relationship between the substrate and the island can be seen. Flaked crystals are stacked in layers to form particles with square shape 3 to 10 μm in size. Planer crystals closer to the substrate are square while crystals that grew on the upper layer are of indeterminate shape. Lattice parameter of the MgO is 0.42 nm (a-axis), and the Bi-system is 0.38 nm (a-axis). These structures are related to the relaxation process of lattice mismatch between MgO and Bi-system.

Thin films with high crystallinity are favored by annealing at high temperatures where atom diffusion is active. If the annealing temperature is too high, however, re-evaporation occurs, so the annealing temperature is limited to a very narrow range. As shown in figure 6, the superconducting transition temperatures of thin films
Figure 4. SEM micrographs of the surface of BSCCO thin films shown in figure 3.

Figure 5. SIM micrograph of BSCCO thin film surface annealed at 855 °C. The crystallographic direction of MgO is shown.

Figure 6. Temperature dependence of resistivity of thin films annealed at 850 and 855 °C.
annealed at 850 and 855 °C were 108 K and 77 K, with no transition observed in 865 °C annealing for 10 h (shown in figure 2) due to the discontinuity between crystal islands.

Figure 7 shows a cross-section of the stacked crystal in figure 5. Planer crystals were observed to grow in three steps. The height of each step was 55–70 nm with the end face of each step perpendicular to the substrate, reflecting the anisotropy of the Bi-superconductor crystal structure. The tints of the three layers appear to differ from one another, the cause for which is unclear at present. Figure 8 shows a high-resolution TEM micrograph of the planer crystal from figure 5. The c-axis length of the half unit cell of the section indicated by two black triangle tips is 1.88 nm (2223). The arrangement of the constituent atoms in the crystal can be clearly observed. The section between the white triangle tips is composed of the 2212 phase (half unit = 1.53 nm). The growth conditions of the 2212 and 2223 phases partially overlap, with the 2212 phase relatively stable over a wide range allowing growth in Bi-deficient conditions. Excess atoms such as Ca or Cu were thought to be swept away from the thin film, forming oxides at the edge of the islands. Figure 9 shows a cross section of the boundary between islands. While a nearly uniform 2223 single phase can be seen, a tilted grain boundary is observed in one part of the thin film. Figure 10 shows a pole figure (115) of the same sample. The BSCCO thin film on MgO substrate has a uniform bi-axial oriented texture with four symmetric poles, hence the orientation mismatch between the grain boundaries can be considered to be 90 degrees. These structures demonstrate part of the forming process of the thin film, with the formation of grain boundaries resulting in a lower $J_c$. Although TEM observations of thin film grain boundaries annealed at 850 °C were not performed due to the difficulty in identifying their location, they are thought to exist to some extent as the several voids are observed in figure 2. Therefore, an annealing process which prevents island-like growth is essential for the fabrication of thin film.
with high $J_c$. One method to resolve this problem is to provide sufficient Bi atoms during annealing, the study of which is currently underway.

**Summary**

In this study, variations of the crystal structure of BSCCO superconducting thin films under different annealing conditions were observed. Thin films were deposited by sputtering, followed by post-annealing at 840 °C–860 °C for 1–20 h. The crystal structure of these thin films was greatly influenced by the annealing temperature and time. Re-evaporation and condensation from the liquid phase of the thin films were observed over 855 °C. Crystal growth started from the 2212 phase gradually progressing to 2223 structure during the liquid phase. In the process of liquid phase aggregation, grooves between crystal islands were formed, obstructing the flow of electrical current. Therefore, as the formation of grain boundaries during post-annealing is inevitable, use of sufficient Bi vapor or a deposition process without post-annealing should be studied to obtain BSCCO thin films with high $J_c$.

**ORCID iDs**

Zon Mori @ https://orcid.org/0000-0002-1873-7188
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