Superconducting properties of high-T_c Bi-Sr-Ca-Cu-O thin films

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Polycrystalline thin films of the high-T_c Bi-Sr-Ca-Cu-O system have been grown on MgO substrates using an rf magnetron sputtering technique. The Bi-Sr-Ca-Cu-O thin films with a sharp superconducting transition were obtained after the post-annealing. The best sample exhibits the transition temperature of around 110 K with zero-resistance temperature of about 100 K. The critical current density of the Bi-Sr-Ca-Cu-O system is estimated to be 10^5 to 2×10^5 A/cm^2 at 77 K.

Much attention has been paid to the new high-T_c oxide superconductor of Bi-Sr-Ca-Cu-O system. In the Bi-Sr-Ca-Cu-O system, two phases of superconductors with different T_c are present; one is $T_c \sim 80$ K and the other is $T_c \sim 120$ K.[1] The higher-T_c phase appears near the composition ratio of 1:1:1:2 for Bi-Sr-Ca-Cu. The Bi-Sr-Ca-Cu-O system frequently comprises the two different phases. Their crystal structure and the superconducting properties have not yet been well understood. Recently, we made thin films of the Bi-Sr-Ca-Cu-O system by sputtering and evaluated their superconducting properties. In this paper, we will describe the effects of the depositions on the superconducting properties and a critical current density for the Bi-Sr-Ca-Cu-O system.

Thin films of the Bi-Sr-Ca-Cu-O system were prepared by an rf-planar magnetron sputtering similar to that in previous works.[2] The target was complex oxides of Bi-Sr-Ca-Cu-O which were made by sintering a mixture of Bi_2O_3 (99.999% pure), $SrCO_3$ (99.9% pure), $CaCO_3$ (99% pure), and CuO (99.9% pure) at 880 °C for 8 h in air. Typical sputtering conditions are listed in Table I. Single crystals of (100) MgO were selected for the substrates. The target composition was changed from the $Bi_1Sr_1Ca_1Cu_2O_x$ composition so as to get an optimum value in the sputtered films.

It is well known that the crystalline superconducting films are prepared by (i) sputtering at a low substrate temperature (below cyrstallizing temperature) with post-annealing, or (ii) sputtering at high substrate temperature (above crystallizing temperature).[3,4] Previous experiments suggest that the high-temperature phase will increase in the thin films prepared at the high substrate temperature.[5] So in this experiment, the substrate was kept at a higher temperature than 700 °C.

TABLE I. Sputtering conditions.

Target	Bi-Sr-Ca-Cu-O (100ϕ)[a]
Substrate	MgO(100)
Sputtering gas Ar:O_2 ratio	0.67–1.5
Gas pressure	0.5 Pa
rf power	150 W
Substrate temperature	700–800 °C
Growth rate	80 Å/min

[a]Diameter measured in mm.

The composition of the films was determined by inductively coupled plasma-emission spectrometry and electron-probe x-ray microanalyses. Resistivity measurements were done using a standard four-probe method with gold electrodes deposited on the film surface in vacuum. The diamagnetization was measured by an rf superconducting quantum interference device (SQUID) susceptometer in a dc magnetic field of 10 Oe.

The as-sputtered films showed polycrystalline phase and were superconductive with a black color. Most of the as-sputtered films showed the transition temperature of around 80 K with a broad transition width of 40–50 K. The sharp transition was observed after post-annealing in O_2.

The superconducting properties of the sputtered films were affected by the sputtering conditions and the post-annealing process. Post-annealing in an O_2 atmosphere was done as follows; the sputtered films were annealed at 890–900 °C (top temperature) for 20 min and subsequently kept at 850–865 °C (holding temperature) for 5 h. Table II shows typical experimental results. In Table II, the top and the holding temperatures for the post-annealing are listed. $T_{c_{on}}$ signifies the temperature where the superconducting transition starts and $T_{c_{off}}$ signifies the temperature where the zero resistivity of films is achieved. It is seen that the transition temperature of the sputtered films is dependent on the target composition. The thin films sputtered from the Bi-rich target generally showed the low-temperature phase with a $T_{c_{on}}$ of 80 K (sample 1). When both Bi and Ca in the target were enriched and the higher temperature annealing was done, the resultant films showed the high-temperature phase with a $T_{c_{on}}$ of 110 K superimposed on the low-temperature phase with a $T_{c_{off}}$ of 69 K (sample 2). And when the substrate temperature was raised to 800 °C and the sputtered film was annealed in the same manner as that for sample 2, this sample exhibited a sharp transition at about 110 K and zero resistance at about 100 K without the shoulder (sample 3).

Figure 1 shows the resistivity versus temperature characteristics and x-ray-diffraction (XRD) patterns obtained from the samples (samples 1 and 3 in Table II).

In sample 1, with a $T_{c_{off}}$ of 69 K, there appear periodic

TABLE II. Properties of the sputtered films of Bi-Sr-Ca-Cu-O system.

Sample No.	Bi:Sr:Ca:Cu in target	Substrate temperature (°C)	Annealing temperature (°C) Top	Holding	Tc_{on} (K)	Tc_{off} (K)
1	1.6:1:1:3	700	890	850	80	69
2	1.6:1:1.5:2	700	900	865	110	69
3	1.6:1:1.5:2	800	900	865	110	100

peaks caused by diffraction of the preferentially oriented axis of the film. The lowest multiple of lattice spacing of this axis is estimated to be 15.32 Å. This x-ray spectrum will teach the crystal structure of the low-temperature phase. Its crystal structure may be a layered structure of Bi-O, Cu-O, and (Ca,Sr)-O with $c=30.646$ Å, similar to the value observed in the ceramics.[1]

For sample 3 with Tc_{off} of 100 K, the broad oriented peaks are superimposed on periodic sharp peaks, which correspond to the low-temperature phase observed in sample 1. It is estimated that the broad oriented peaks result from the high-temperature phase itself. At present, the crystal structure of the high-temperature phase is not understood.

It was considered that sample 3 with zero resistivity at about 100 K comprises the low-temperature phase and the high-temperature phase, although the resistivity shows a sharp transition at around 100 K. These considerations were confirmed by measurements of the diamagnetization as shown in Fig. 2. The diamagnetization was observed below 100 K corresponding to the high-temperature phase and a shoulder appeared at 80 K corresponding to the low-temperature phase.

Critical currents in sample 3 were studied by measuring the current-voltage characteristics under a zero magnetic field. The film was deposited on MgO substrate and its dimensions were 1 mm wide, 5 mm long, and 0.25 μm thick. Typical results are shown in Fig. 3. The films showed a critical current density of about 10^4 A/cm^2 at about 90 K and the current density will exceed 10^5 A/cm^2 at 77 K. It is considered that the currents measured at the temperature range of 77–100 K may chiefly consist of the current flow in the high-temperature phase, since the currents in the low-temperature phase will scarcely flow at the temperature above 77 K.

As described above, sample 3, showing zero resistivity at 100 K, comprises the high-temperature and the low-temperature phase. The diamagnetization measurements

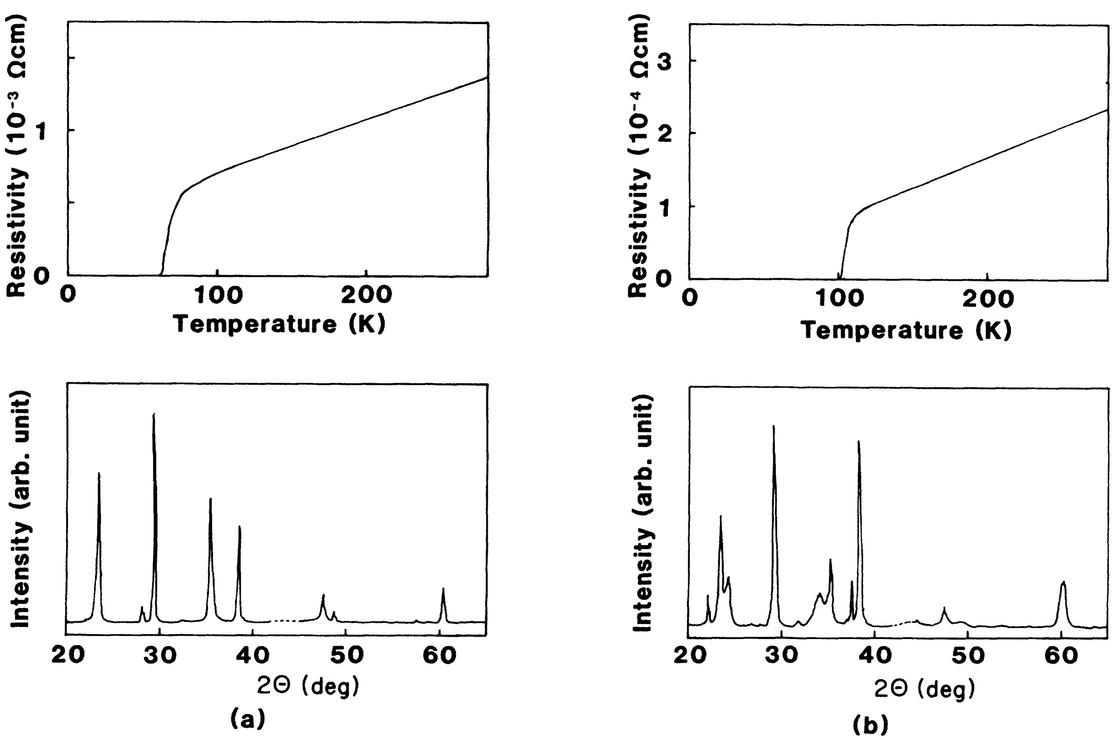

FIG. 1. The temperature dependence of the resistivity (upper) and x-ray diffraction patterns (lower) for Bi-Sr-Ca-Cu-O films; (a) sample 1 and (b) sample 3 in Table II. The peaks at 38.2° are corresponding to the Au electrodes.

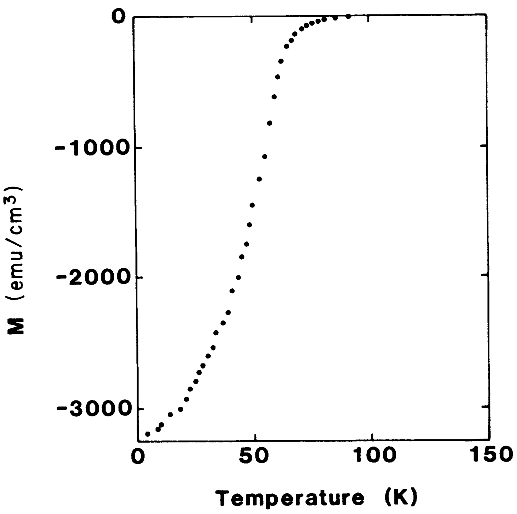

FIG. 2. Diamagnetization of the sputtered Bi-Sr-Ca-Cu-O film (sample 3 in Table II).

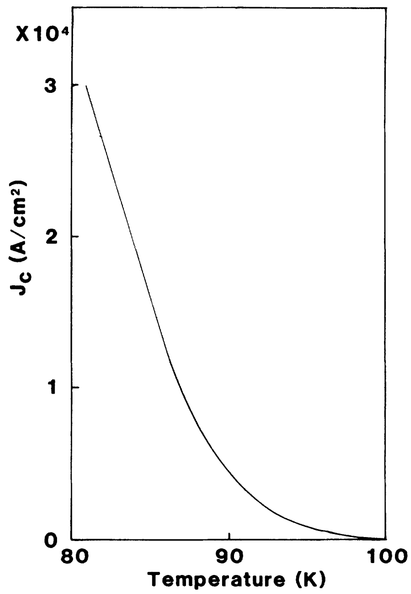

FIG. 3. Critical current density for the sputtered Bi-Sr-Ca-Cu-O film (sample 3 in Table II).

suggest that the volume ratio of the high-temperature phase in sample 3 is only 5–10%. So, it is reasonably concluded that the Bi-Sr-Ca-Cu-O system with a single high-temperature phase will exhibit the critical current density of 10^6 to 2×10^6 A/cm^2 at 77 K. These values are in the range of those found in the Y-Ba-Cu-O system. It is very interesting that the sharp superconducting transition is observed at about 100 K under the presence of a high-temperature phase of only 5–10%. The composition of the high-temperature phase will surely precipitate on the surface of the crystallites of the low-temperature phase and form a current channel.

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