Superconducting Bi-Sr-Ca-Cu-O films formed diffusion of metallic bismuth on $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrates

KIEJIN LEE and GWANGSEO PARK

Department of Physics, Sogang University, C.P.O. Box 1142, Seoul, Korea

Abstract. Superconducting Bi-Sr-Ca-Cu-O films have been prepared on $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrates by thermal evaporation of metallic Bi layer and heat-treatment at 830°C for a few minutes in air. The zero resistance temperature of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ film of $1\text{--}2\ \mu\text{m}$ in thickness is about 70 K. The surface diffusion process of Bi on the granular structure of $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ was observed by scanning electron microscope and thermogravimetry analysis. The stripe pattern of superconducting film, typically $2\ \mu\text{m}$ thick and $0.3\ \text{mm}$ wide, is formed by using a mask.

Keywords. Bi-Sr-Ca-Cu-O; metallic bismuth; surface diffusion.

Following the discovery of the Bi-Sr-Ca-Cu-O superconductor (Maeda *et al* 1988) with $T_c(\text{offset})$ of 110 K, many researchers have focused their effort on the fabrication of superconducting films for both scientific and technological purposes. A wide variety of techniques have been employed for the fabrication of films of Bi-Sr-Ca-Cu-O superconductor (Nagata *et al* 1980; Deshmukh *et al* 1988; Nakamori *et al* 1988; Rice *et al* 1988) and most of them were applied to MgO and SrTiO_3 single-crystal substrates. However, these crystal substrates are usually produced as small pieces which implies a limitation in actual device applications. The formation of superconducting films on such substrates as alumina, silicon and quartz has not been so successful mainly due to active reaction and inter-diffusion between the substrates and the superconducting films at high temperatures. This problem might be solved by using as substrate the part of the compositions of high T_c superconducting oxide compound. This method has several advantages; substrates are inexpensive and are relatively easy to make them into arbitrary shapes. Also, the degradation effect by interface reaction is not crucial but improves the adhesion of film. As reported earlier (Lee *et al* 1989), Bi-Sr-Ca-Cu-O films of $100\ \mu\text{m}$ thick with zero resistivity above 100 K were prepared by diffusing Bi-Pb-O oxide mixture into Sr-Ca-Cu-O compound substrate and heat-treatment at 830°C and 850°C for 12 h and 6 h in air atmosphere, respectively. In the present work, we have prepared the Bi-Sr-Ca-Cu-O film by diffusion of a metallic Bi into the $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrates. This method provides an easy pattern formation by using a mask and comparing it with the patterning of high T_c superconducting films usually including resist lithography followed by wet or dry etching for pattern transfer (Matsui *et al* 1988; Shih and Qiu 1988; Tsuge *et al* 1988; Harriott *et al* 1989).

Sr-Ca-Cu-O substrates were prepared by the standard ceramic process. Starting powders of SrCO_3 , CaCO_3 and CuO of reagent grade were weighed to be Sr:Ca:Cu = 2:2:4 in atomic ratio. After having sufficiently ball-milled, the mixture was calcined at 900°C for 12 h twice and then reground. The fine powder was then pressed into pellets at $5\ \text{ton}/\text{cm}^2$, and the substrates produced by sintering at 950°C for 24 h. Metallic Bi was thermally deposited on the $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrates in a vacuum and heat-treated at $760\text{--}880^\circ\text{C}$ for 1 min to 2 h under air atmosphere. Through

heat-treatment, Bi diffused into the substrate twice as thick as the originally evaporated thickness. The transition behaviour and the microstructure of the film were studied by resistivity measurement and X-ray diffraction(XRD) analysis respectively. The morphology of the films during heat-treatment was observed by scanning electron micrographs(SEM) and energy-dispersive X-ray analysis(EDX).

Figure 1 shows the photograph of the film pattern produced by using a metal mask. The film was prepared by deposition of Bi (about $1\text{ }\mu\text{m}$ thick) on the $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrate and heat-treatment at 830°C for several minutes in air. The resistivity measurement of the lines of 0.3 mm width shows onset temperature (T_{c0}) at 85 K and zero resistance (T_{cz}) at 70 K . The line width of an as-deposited Bi film did not change through heat-treatment at 830°C .

Figure 1. A photograph showing the pattern produced by using metal mask and heat-treated at 830°C for 1 min in air atmosphere.

Figure 2. The transition behaviour of the films prepared with the heat-treatment temperature (solid square: high T_{c0} (onset) phase; solid circle: low T_{c0} (onset) phase; solid triangle: T_{c0} (offset)).

The variation of T_c with heat-treatment temperature was studied by measuring the resistivity of the films fired at 760–880 °C for a few minutes under air atmosphere. The average heating rate was about 400 °C/h and then furnace-cooled. Figure 2 shows the definite dependence of T_c on firing temperature for the sample of as-deposited Bi film with 1 μm in thickness. As the heat-treatment temperature increases above 800 °C, the T_{cz} increases rapidly up to 70 K at 830 °C and then decreases slowly, while no superconducting phases were obtained in the temperature range up to 800 °C and above 880 °C. For heat-treatment at temperatures above 830 °C and periods longer than 10 min, the film showed gradually widening transition behaviour and eventually a typical semiconducting behaviour. For the film heat-treated at 880 °C, the resistivity showed a semiconducting behaviour which was identified as a $\text{Bi}_2\text{Sr}_2\text{Cu}_1\text{O}_y$ phase by the analysis of XRD. The fact that superconducting phase cannot be obtained at temperatures below 800 °C even for long firing time might imply that Bi atom does not seem to diffuse into the substrate until Bi is oxidized to form Bi_2O_3 . To see this point clearly, we tried heat-treatment of the as-deposited film in N_2 atmosphere and found that the film showed an insulating behaviour which is the same as that of substrate itself. EDX analysis was carried out on the film heat-treated at 830 °C in N_2 . The ratio of Bi:Sr:Ca:Cu for the main phase was observed to be 0.374:12.504:4.719:32.311 with many clusters separated from the main phase. One thus concludes that metallic Bi simply evaporates and diffusion does not take place as a Bi atom itself but as a Bi^{+3} ion in Bi_2O_3 only after reaction with oxygen atoms, and thus O_2 must be supplied for diffusion. Also, the optimum firing temperature of 830 °C seems to be related to the melting point of Bi_2O_3 (820 °C).

XRD analysis was carried out to identify the phase of Bi-Sr-Ca-Cu-O films. Figure 3 shows a diffraction pattern of the film heat-treated at 830 °C. Most of the X-ray peaks correspond to the low T_c $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ phase, together with a minor $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrate phase and a small amount of $\text{Bi}_2\text{Sr}_2\text{Cu}_1\text{O}_y$ phase.

The morphology of the films was studied by SEM to observe the temperature dependence of diffusion process. Some SEM photographs of the cross-sections and surface of the films at each heat-treatment temperature under air atmosphere are shown in figure 4. The as-deposited metallic film, typically 1 μm in thickness, has a clear boundary and the surface with small pores as shown in figure 4a. Figures 4b and 4c show the films heat-treated at 400 °C and 800 °C, respectively. As the temperature increases up to 400 °C, the surface becomes rough and bulky due to

Figure 3. XRD patterns of Bi-Sr-Ca-Cu-O film heat-treated at 830 °C for 1 min in air atmosphere.

Figure 4. SEM photographs of the surface and cross-section of sample heat-treated for various temperatures. (a) ambient temperature, (b) 400°C, (c) 800°C and (d) 830°C for 1 min in air atmosphere respectively.

Figure 5. SEM image of the cross-section of the Bi-Sr-Ca-Cu-O film, which was prepared by deposition of Bi of about $0.5\ \mu\text{m}$ thick on $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrate and heat-treated at 830°C for 1 min in air atmosphere.

oxidation. At 800°C , plate-like superconducting phase starts to show up but the connectivity does not seem to be good enough to give a finite T_{c2} . By the *in situ* thermogravimetric analysis of the film, we find that the weight decreases until 350°C by evaporation and then increases exponentially with temperature until 700°C by the oxidation of Bi. At 830°C as shown in figure 4d, the superconducting grains grow to produce a better connectivity.

In order to see how the superconducting phase grows as Bi atom diffuses into the substrate, a SEM photograph of the film cross-section was taken by focusing the interface. Figure 5 shows the interface of the film heat-treated at 830°C for a few minutes in air. The resulting film was about $1\ \mu\text{m}$ thick with plate-like Bi-Sr-Ca-Cu-O grains grown on the substrate grains. The dendrite structure produced by diffusion of Bi into the substrate is clearly seen in figure 5. This type of structure is generally recognized in the reaction of liquid phase (Bi_2O_3) with solid phase(substrate). We note that the *c*-axis of the microcrystal of the superconducting grain is favourably aligned parallel to the substrate surface. Such crystallization may be energetically very stable for a film produced at the interface by reaction between a liquid Bi_2O_3 and a solid substrate phase. The structure of this film was identified as a 2212 low T_c phase by XRD, and the T_{c2} and J_c at 70 K were 70 K and about $10^3\ \text{A}/\text{cm}^2$, respectively. The dendrite structure was produced by diffusion of Bi into the substrate.

In summary, we have prepared Bi-Sr-Ca-Cu-O films typically $0.5\text{--}1\ \mu\text{m}$ thick on $\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ substrates by Bi diffusion method. The best film heat-treated at 830°C for a few minutes in air has shown T_{c2} at 70 K with a low T_c phase. In this method the interdiffusion between film and substrate provides an excellent adhesion without any degradation of the superconducting properties and the possibility of a well-aligned microstructure to increase J_c if the orientation of the substrate grains can be controlled.

References

- Deshmukh D, Rothe E W, Reck G P, Kushida T and Xu Z G 1988 *Appl. Phys. Lett.* **53** 2698
- Harriott L R, Polakos P A and Rice C E 1989 *Appl. Phys. Lett.* **55** 495
- Lee K, Lee J and Park G 1989 *Proc. BHTSC, Beijing* (in press)
- Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn J. Appl. Phys.* **27** L209
- Matsui S, Takado N, Tsuge H and Asakawa K 1988 *Appl. Phys. Lett.* **52** 69
- Nagata H, Takano A, Kawaski M, Yoshmoto M and Koinuma H 1980 *J. Am. Ceram. Soc.* **72** 680
- Nakamori T, Abe H, Kanamori T and Shibata S 1988 *Jpn J. Appl. Phys.* **27** L1265
- Rice C E *et al* 1988 *Appl. Phys. Lett.* **52** 1828
- Shih I and Qiu C X 1988 *Appl. Phys. Lett.* **52** 1523
- Tsuge H, Matsui S, Matsukura N, Kojima Y and Wada Y 1988 *Extended abstracts Int. Conf. on Solid State Devices and Materials, Tokyo*