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Superconducting Bi-Ca-Sr-Cu-0 Films by RF Magnetron Sputtering

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Thin films of high-T_c superconductor were prepared by RF magnetron sputtering from sintered Bi-Ca-Sr-Cu-0 targets. The effects of annealing conditions on the superconducting properties of the films were studied. Films with a sharp transition were obtained by sintering films at about 860 °C. The resistivity shows an anomaly in the high temperature ranges 420 K $\leqslant$ T $\leqslant$ 630 K. This anomaly is similar to that observed in bulk Bi-Ca-Sr-Cu-0 samples. Pb doped Bi-Ca-Sr-Cu-0 films show a sharp superconducting transition with $T_c(50\%) = 82$ K and a zero resistance at 77 K. The critical current density is about 5 X 1 0^3 A/ cm^2 at the reduced temperature t = 0.9 for Pb doped films, where t = T/T, and $T_c(50\%) = 82$K.

Recently a new class of superconducting compound, the Bi-Ca-Sr-Cu-O system[1,2] was found with transition temperature ranging from 80 K to 105 K. The nominal transition at 85 K has been attributed to the phase $Bi_2CaSr_2Cu_2O_y$[2]. For many applications as well as fundamental studies, it is essential to prepare this new high T_c oxide in the form of thin films. Recently Ichikawa et al[3] have reported thin films of Bi-Ca-Sr-Cu-0. Many activities[4-8] are focusing on exploring ways of preparing high quality films. This paper presents preliminary results for Bi-Ca-Sr-Cu-0 thin films that were prepared by rf sputtering with particular targets and different annealing conditions.

Ceramic targets were used in the magnetron sputtering system. They were prepared according to the following procedures. Powders of Bi_2O_3, $CaCO_3$, $SrCO_3$ and CuO were first ground thoroughly and sintered in air at 880 °C for about 20 mins. The annealed powder was reground and then sintered in air at 870 °C for another 10 hrs. It was then pressed into a flat target and the target annealed in air for 1 hr. Targets prepared this way are flat and have T_c at about 85 K (50% resistive transitiqn). Targets were mounted in a planer magnetron (US gun II) sputtering system. Typical sputtering conditions are listed in

Table I. Single crystals of MgO(100) were selected as substrate. Six samples were deposited simultaneously in a single run so that one can study the effects of annealing on the super-

TABLE I. Sputtering conditions in preparing Bi-Ca-Sr-Cu-0 films.

Substrate	MgO(100)
Sputtering gas $Ar:O_2$ ratio	7:3
Gas pressure	50 mtorrs
rf power	125W
Substrate temperature	~100°C
Growth rate	2Å/sec
Target to substrate distance	4cm

conducting properties. A vertical rotatable sample holder was designed in this sputtering system. The as-sputtered films were amorphous. Post annealing was required to obtain superconducting films. The nominal composition was determined from ICP-AES. The electrical resistivity was measured by LR400 (Linear Research Inc.) using a four-probe method. Silver paste was used for electrical contacts. Different annealing conditions were studied in this work. All samples reported here were quickly brought to the annealing temperature in minutes.

Figure l(a) shows typically the temperature dependence of the normalized resitivity, R(T)/R(300K), for the Bi-Ca-Sr-Cu-0 samples sputtered from a (2-l-2-2) target. The films show a nominal composition of about (2-0.59-1.39-1.50). Samples were furnace cooled, taking 8 hrs to room temperature. Film b was annealed in air at 880 °C for 30 minutes, it has a superconducting transition temperature, T_c (50% resistive transition) at 84 K and a transition width, ΔT_c (10% – 90%) = 90K – 80K. Figure 1 (b) shows the temperature dependence of the normalized resistivity, R(T)/R(300K), for Bi-Ca-Sr-Cu-0 samples sputtered from a (2.2-l-2-2.2) target. The films show a nominal composition of about (2-0.92-l .29-1.97). The films have a thickness of about 1.5μm determined from a surface profile instrument (Dektak 3030). Sample f was annealed in air at 870 °C for 30 minutes. The sample was then furnace cooled from 870 °C to 700 °C in about 30 minutes and kept at 700 °C for 1 hour. After this process, the sample was furnace cooled to room temperature. The room temperature resistivity is 9.2mΩcm. Sample f has T_c(50%) = 82K and ΔT_c (10% – 90%) = 88K – 76K. Figure l(c) shows the temperature dependence of the normalized resistivity, R(T)/R(300K), for sample g. It has a nominal composition of about (2-0.61-1.08-2.22). Sample g was annealed in air at 860 °C for 30 minutes and furnace cooled to room temperature. The room temperature resistivity is about 12.6mΩcm. It has T_c(50%) = 86K and AT, (10% – 90%) = 91K – 80K. The results reported here show that superconducting films can be successfully prepared by sputtering a single ceramic target, being annealed at 860 °C then cooled in a furnace.

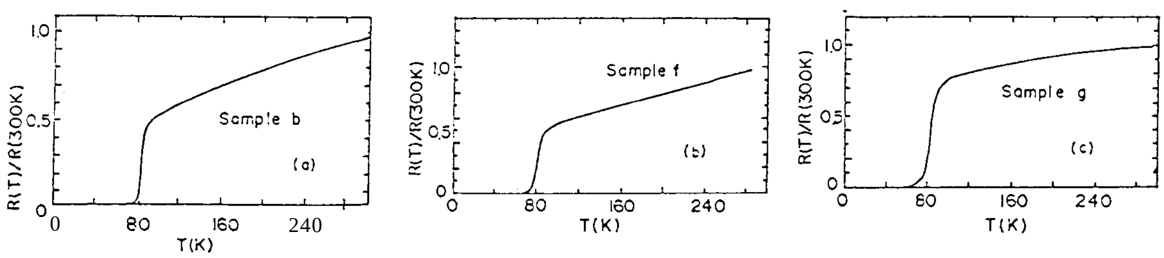

FIG. 1 Temperature dependence of R(T)/R(300K) for (a). sample b (b). sample f and (c). sample g.

The powder X-ray diffraction pattern has been taken for most samples. The X-ray was from a copper target. Figure 2 shows the diffraction peaks for sample k. The data shows predominately 2-l-2-2 phases with c axis perpendicular to the surface. Other phases are also present.

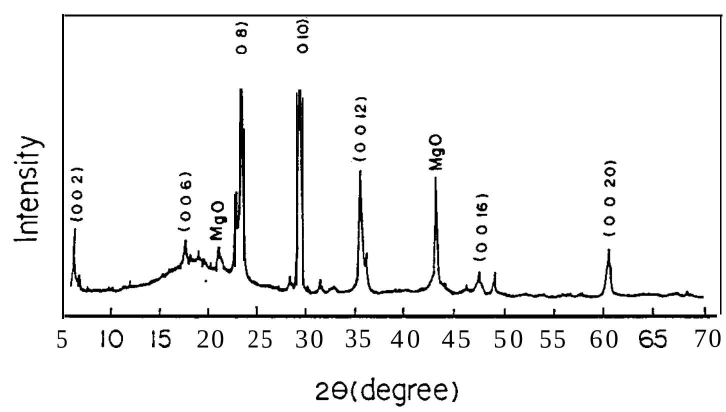

FIG. 2 Powder X-ray diffraction data of sample k.

We have also studied the critical current, I,, for Pb doped Bi-Ca-Sr-Cu-0 films. The films were prepared with sintered Bi, Pb, $Ca_3Sr_{2.5}Cu_{3.2}0_x$ The films were subjected to a rapid heating at 850K for 3.5 h in air and quenched to room temperature in minutes. The film (sample k) prepared this way has a superconducting temperature T_c(50% resistive) at 82K and zero resistance at 77K as shown in Figure 3. The geometry of the sample was in a stripe shape with a width of about 0.2cm and the film has a thickness of about 0.8μm. The voltage probes were 0.3cm apart. The temperature of the sample was controlled by a temperature controller (Model 130, Linear Research Inc.) which is stable to within 0.1 K. We make contact to the film with silver paint extending across the superconducting region. The I-V characteristic was collected automatically by IBM PC/XT via IEEE488 interface. Heating effect was not found in the I, measurement as the current is biased below the critical value, I_c. The value of the critical current was chosen to be the one at which the generated voltage rose to 1μV. The critical current density is about 5 $\times 10^3$ A/cm^2 at the reduced temperature t $= T/T_c =$ 0.9 and T_c(50%) = 82K. This value of critical current density is about one order of magnitude larger than that of undoped film at the same reduced temperature.

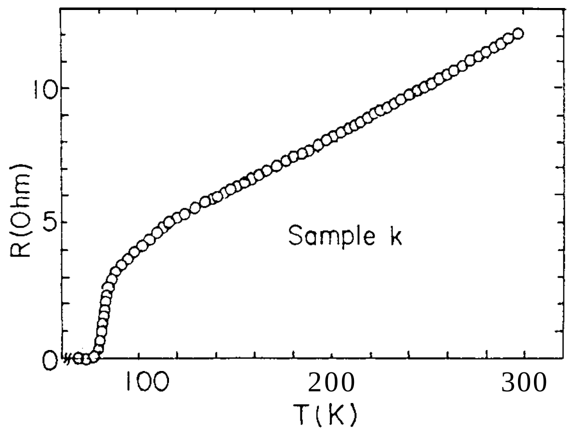

FIG. 3 Temperature dependence of resistance for sample k. The superconducting transition temperature (50% resistive) is at 82K and a zero resistance is 77K.

Figure 4 shows typically the high temperature resistance as a function of temperature. The arrows indicate the direction along which the resistivity was taken. Both heating and cooling were carried out in flowing oxygen. The heating rate was about 5°C/min. Four Pt-wires was connected to the sample by silver paints. Upon heating the resistance increases continuously. A precipitous increase at 425K was followed by a sharp decrease at 525K. The resistivity dropped from 26mΩcm to 18.5mΩcm between 500K and 600K. The resistivity increases monotonicly for T > 630K. As the sample was cooled from 800K, the resistivity continuously decreases to a room temperature value of 16.3mΩcm. Upon reheating the sample the change in resistivity simple follows the cooling curve and never

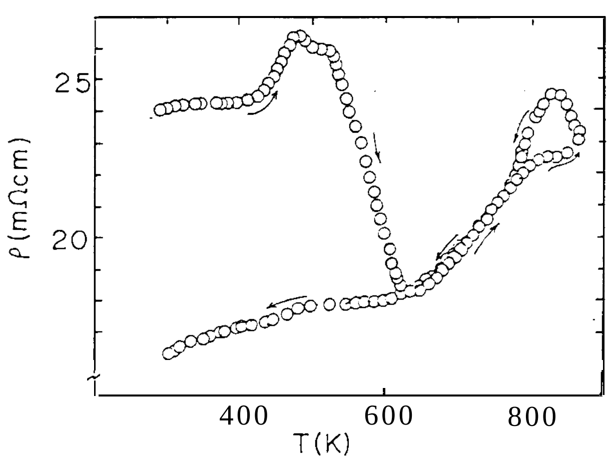

FIG. 4 High temperature electrical resistivity for sample f.

shows any features observed in the first heating cycle. The high temperature resistivity anomaly may arise from any of the following (1). A relaxation process, (2). an oxygen loss, or (3). an oxygen related thermodynamic process. Reason (1) is less likely, because in an relaxation process cne can only decrease the resistance instead of introducing a peak in the resistance curve. Reason (2) may happen in the heating, however, it is not responsible for the resistivity anomaly because a loss of oxygen can cause an increase in resistivity as in the case of $YBa_2Cu_3O_{7-y}$. Therefore, we think it is not the main cause for the resistivity anomaly. Reason (3) may be responsible for the resistivity anomaly because the DTA data in 0, show an exotherm at the resistivity peak. This indicates that there is an oxygen related thermodynamic reaction in the heating. The resistivity anomaly between T = 420K and 630K in the first heating cycle is similar to that observed in the bulk Bi-Ca-Sr-Cu-0 samples.[9]

Semiconductive films has been prepared to study localization. The films were deposited by rf-magnetron sputtering from a ceramic target ($Bi_{2.2}CaSr_2Cu_{2.2}O_y$) at a low rf power of 30W. The deposition rate was 1 Å/sec. The film has a thickness of about 36008. After deposition the film was subject to a rapid heating and rapid quenching process. The film temperature was brought quickly to 860 °C in air in minutes and held at 860 °C for 30 mins. It was then quenched to room temperature. Samples prepared this way are semiconducting. Its surface is shining and uniform. Figure 5 shows lnR versus $T^{-1}, T^{-1/2}, T^{-1/3}$, and $T^{-1/4}$ (dashed curves) for sample h. According to the theory of Mott[10], if the density of states at Fermi level is finite, but the electron states are localized, we expect the resistance of the semiconductive films to obey the following relation:

$$R(T) = R_0 \exp[+B/(k_B T^a)] \quad , \tag{1}$$

where R_0 is a constant, B an energy parameter, and k_B the Boltzmann constant, a = 1/4 if the carriers are localized in three dimensions, and a = 1/3 if the carriers are localized in two dimensions. In the present Bi-Ca-Sr-Cu-0 sample the temperature follows Eq. (1) with a =

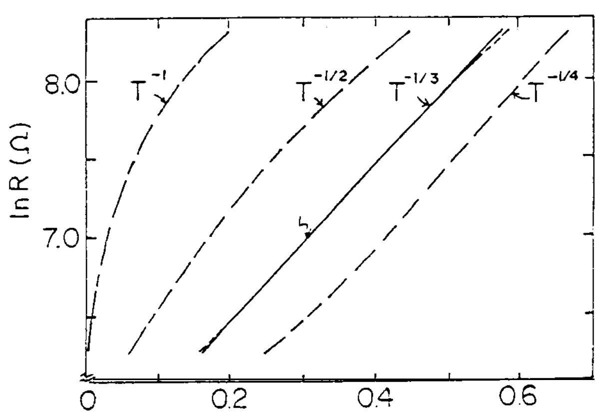

FIG. 5 Temperature dependence of lnR as a function of $T^{-1}, T^{-1/2}, T^{-1/3}$ and $T^{-1/4}$ (dashed curves) for sample h. The solid curve is the theoretical data based on Eq. (1)

1/3. The solid curve is the theoretical data based on Eq. (1) with $R_0 =$ 241.0751 and B = 4.929k_B ($J/K^{2/3}$) derived from least square fitting. The data indicate that the electron states are localized in two dimensions in the thin films reported here.

In this work, thin films of Bi-Ca-Sr-Cu-0 have been successfully prepared using targets -with different compositions. The critical current density of Pb-doped Bi-Ca-Sr-Cu-0 films shows an enhancement in I_c compared with that of undoped samples. Localization was found in films with semiconductive properties. The localization is perhaps due to the randomized oxygen vacancies in the Bi-Ca-Sr-Cu-0 films.

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