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DC-sputtered Bi(Pb)SrCaCuO films on single (MgO) and polycrystalline (MgO, CuO) substrates

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Abstract. Bi(Pb)SrCaCuO films have been deposited on single (MgO) and polycrystalline (poly MgO, CuO) substrates by DC sputtering. All the films became superconducting after post-annealing them in air. The films on single crystal MgO showed T_c onset at 120 K and T_c at 92 K. However, the extrapolated zero resistivity is obtained at 106 K. The ac susceptibility showed an onset at 106 K and a sharp transition at 85 K. The films on poly MgO and poly CuO had a $T_c = 72$ K. The preparation, X-ray diffraction and morphology of these samples are presented.

Keywords. DC sputtering; superconducting films; CuO substrate, MgO substrate; polycrystalline substrates.

1. Introduction

There have been considerable efforts recently to obtain thin films of high T_c superconductors required not only for various applications but also to understand their electronic behaviour. Several techniques such as electron beam evaporation (Naito *et al* 1987), laser deposition (Dijkamp *et al* 1987), cathodic sputtering (Hong *et al* 1987) etc. have been reported. Whatever be the technique involved, it is desirable to obtain such films both on single crystal and polycrystalline (poly) substrates. We wish to report here on BiPbSrCaCuO films deposited by DC sputtering on single-crystal MgO and unpolished polycrystalline MgO and CuO substrates.

2. Experimental techniques

The target material with a nominal composition of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3.5}O_y$ was prepared from respective oxides or carbonates by the well-established solid-state sintering techniques. The target consisted of several 12 mm diameter pellets pasted on to a copper block. At 2 to 3 cm from this copper block, several MgO (single and poly) and CuO (poly) substrates were placed on another metal disk. The target and the substrate holder were kept in a commercial vacuum set-up provided with a variable DC power supply (0 to 5 kV, 0 to 50 mA). MgO single crystal substrates (5 mm square) had (100) orientation. The poly MgO substrates were home-made. MgO powder was pressed into a pellet and sintered in air at 840°C for 5 h. CuO substrates were similarly, prepared. These polysubstrates showed no crystallographic orientation. Argon was used for sputtering. The pressure inside the vacuum chamber was 8×10^{-3} torr and the power used was around 20 watt. The sputtering time varied between 20 and 70 hours. The thicknesses of the samples varied between 5 and 30 μ. Indium was soldered on to

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the film surface at four points by ultrasonic welding for making electrical contacts. An alternating current (50 μA to 1 mA) was passed through the sample and the voltage monitored as a function of temperature. Four-probe method was used to evaluate the resistivity of the samples. The real part of the ac susceptibility (χ') was measured in a field of 5 Oe.

3. Results and discussion

The as-prepared films, whatever be the substrate, were generally very resistive. However, after heat-treating them in air they all became superconducting. For example, # 1(on single crystal MgO) was heated from room temperature to 850°C in 4 h and maintained at this temperature for 2 h and then cooled at 100°C/h. It shows a T_c onset at 120 K and T_c ($\rho = 0$) 92 K (figure 1). The width of the transition is 13 K. However, ρ extrapolates to zero at 106 K. The X-ray diffraction pattern of this film (CuK_α 40 kV, 20 mA) indicates the presence of both the low T_c and the high T_c phases (figure 2). Further, a majority of the peaks have a (00l) preferred orientation. The real part of the ac susceptibility further confirms the presence of both the high T_c and low T_c phases (figure 3). One can observe a first onset at 106 K followed by another one at 82 K. The second transition is quite sharp with a width of 3.5 K.

The sample (#2) deposited on to a sintered unpolished MgO substrate was heated to 500 C at 50 C/h, held there for 9 h. It was then taken to 855 C at 40 C/h, held there for 1 h and the temperature was reduced at a rate of 100 C/h. This film shows an onset at 120 K and T_c at 72 K with a width of 18 K (figure 1). However, ρ extrapolates to zero at 95 K. The X-ray pattern does not reveal the presence of high T_c phase. The details will be published elsewhere.

The resistivity of some of the films deposited on to poly CuO substrates after heat-

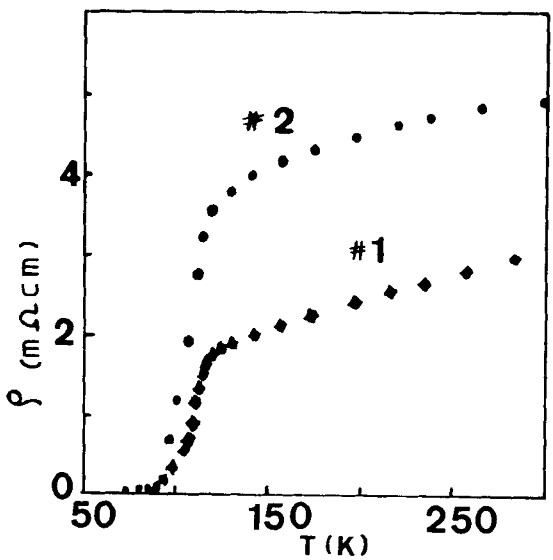

Figure 1. Resistivity (ρ) as a function of temperature. (◆) #1 film deposited on single crystal MgO. (●) #2 film deposited on polycrystalline MgO. To get the actual value of ρ of this sample divide the ordinate by 2.

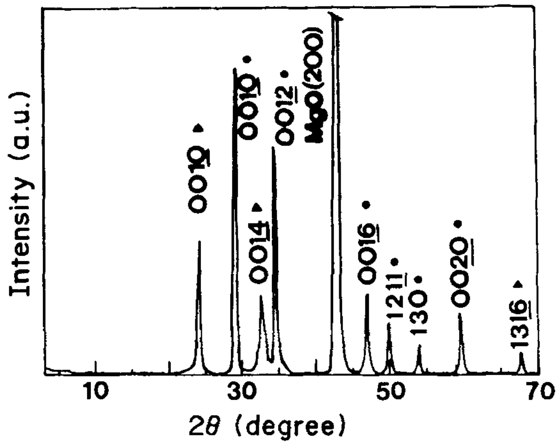

Figure 2. X-ray diffraction pattern of #1. (▲) denotes high T_c and (●) low T_c reflections.

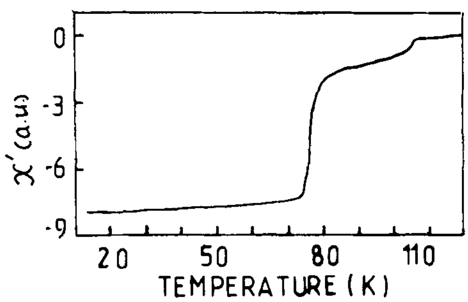

Figure 3. Real part of the ac susceptibility (χ') of #1, in arbitrary units, as a function of temperature.

treatment is shown in figure 4. #3 was kept at 500 C (heating rate 50 C/h) for 4 h and taken to 850 C with a heating rate of 40 C/h. It was held there for 1 h and cooled to 20 C at a rate of 80 C/h. ρ of this sample increases from an initial value of 2.5 mΩ cm as T decreases but shows a T_c onset at 72 K. Zero ρ is observed only at 40 K with a width of 20 K. #4 was heat-treated at 855 C but without the intermediate step at 500 C. ρ of this sample decreases as T decreases. T_c onset is observed at 112 K with T_c at 50 K. The width of the transition is around 50 K. However, if one extrapolates the resistivity curve from 100 K, zero ρ is obtained at 75 K. The heat-treatment cycle of #5 was similar to that of #4 but with an intermediate step at 500 C. The T_c onset is observed at 105 K and T_c at 72 K with a width of 10 K. However, the extrapolated zero ρ can be seen to occur at 90 K. None of these films on CuO on X-ray analyses show Bragg peaks corresponding to the high T_c phase. The details will be published elsewhere.

Some of the reasons for not observing $T_c = 100$ K in our samples could be as follows: (i) deviations from the ideal composition necessary to stabilize the high T_c phase, (ii) improper annealing treatment and (iii) chemical interaction of the substrate with the film. Of these, the first two reasons seem to be quite probable. In fact, Dew *et al* (1989) have shown that an optimum target composition of $Pb_{1.1}Bi_{2.2}Sr_2Ca_2Cu_3O_y$ resulted in films with $T_c = 106$ K obtained by RF sputtering. It should be noted that the

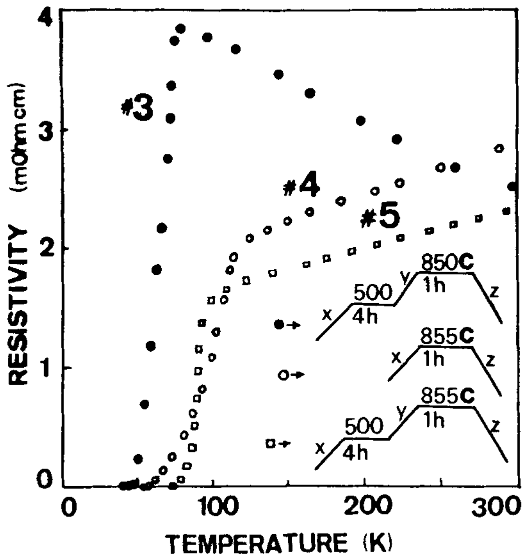

Figure 4. Resistivity as a function of temperature of the films deposited on poly CuO substrates. The annealing conditions for each film are indicated. $X = 50\,C/h$; $Y = 40\,C/h$; $Z = 80\,C/h$.

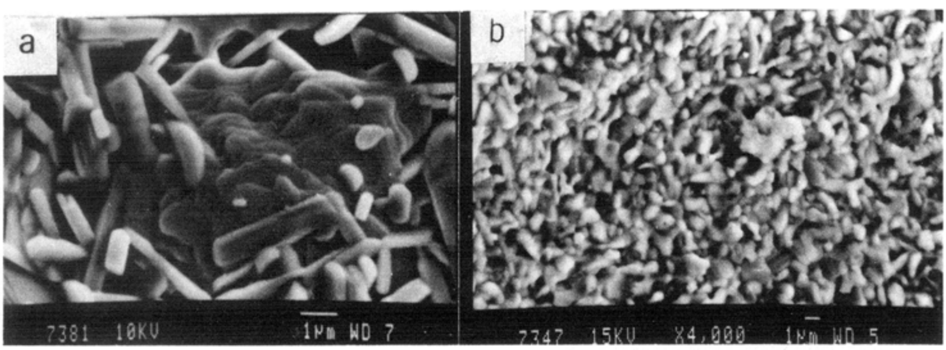

Figure 5. Scanning electron microphotographs of the surface of (**a**) #1 and (**b**) #2.

optimum value of Pb is above the value determined in the case of bulk samples (see for example Kijima *et al* 1988). Further, the importance of annealing the films in oxygen at 865 C was also pointed out (Dew *et al* 1989). However, it should be noted that even without the addition of Pb, films on single crystal MgO with $T_c = 102\,K$ have been obtained (Yoshitake *et al* 1988; Mukaida *et al* 1989; Wasa *et al* 1988). These authors did observe Bragg reflections corresponding to both the high and low T_c phases in their samples. The third cause, namely the chemical reaction of the substrate with the film is unlikely to be a major one at least in the case of MgO substrates. In the case of CuO, however, the out diffusion of Ca, Sr, Bi and Pb into the CuO substrate could affect the properties. This has to be checked by detailed secondary ion mass spectrometer studies. On the other hand, a small diffusion of Cu into the film is not expected to be harmful to the film properties.

The scanning electron microphotographs (SEM) of the surface of #1 and #2 are shown respectively in figures 5a, b. The crystallites of #1 (single crystal MgO substrate) have well-defined shapes—needle shape and flakes—and show some orientation whereas those of #2 (poly MgO substrate) have no well-defined shapes and above random orientation.

4. Conclusions

Superconducting films of BiPbSrCaCuO obtained by DC sputtering from a single target on to single crystal MgO substrates have $T_c = 92$ K and show onsets at 106 K and 82 K in ac susceptibility measurements. The films on unpolished polycrystalline MgO and CuO substrates have a $T_c = 72$ K. The data obtained on CuO indicate the possibilities of obtaining sputtered superconducting films on CuO buffer layer film on alumina (for example) or on oxidized Cu wires.

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