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Study of Josephson effects in microbridges of Bi–Sr–Ca–Cu–O films made by spray pyrolysis

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Abstract. Superconducting Bi-Sr-Ca-Cu-O (2212) films were prepared by spraying stoichiometric aqueous solutions of nitrates of bismuth, strontium, calcium and copper on heated MgO (100) substrates and subsequent annealing in air. The R–T curves of the films show metallic behaviour above the superconducting transition temperature. T_c ($R = 0$) is observed between 80 and 85 K. Annealing temperature has a profound effect on T_c ($R = 0$) and on the orientation of the film. Annealing in air in near-melting region yields highly oriented films with c-axis perpendicular to the substrate. These films show a sharp superconducting transition with zero resistance at 85 K. Microbridges of the dimensions of 50 μm × 50 μm have been patterned photolithographically followed with chemical etching. The I–V characteristics of the microbridges show Josephson effects due to the presence of grain boundary weaklinks. The temperature dependence of the critical current for these microbridges suggest formation of superconductor-normal-superconductor type weaklinks.

Keywords. High temperature superconductors; Josephson effect; microbridge; Bi–Sr–Ca–Cu–O films; spray pyrolysis

1. Introduction

Spray pyrolysis (Mooney and Radding 1982) is a simple method of thick film preparation and is a useful and general technique for obtaining fine powder (Setaka *et al* 1988) and thick films (Sears and Gee 1988). The atomized aqueous solution of metallic salts is conveyed by a carrier gas on the surface of a heated substrate to attain salt decomposition by the pyrolytic process right on the heated substrate surface. The film formation accompanies the decomposition process. The method is used for preparing Y–Ba–Ca–Cu–O (Reddy *et al* 1989) and Bi–Sr–Ca–Cu–O (Walia *et al* 1989) films.

In the present study Bi–Sr–Ca–Cu–O films were prepared by spraying stoichiometric (2212) aqueous solution of nitrates of the constituent elements on (100) MgO-heated substrates. T_c and orientation of the film has been found to depend very much on annealing temperature. Microbridges were patterned using photolithography. The effect of microwave radiation on the I–V characteristic of the microbridge is also studied.

2. Experimental

The films were prepared using the experimental set-up for spraying as described elsewhere (Walia *et al* 1989). The aqueous solution containing nitrates of bismuth,

Table 1. Details of the heat treatment and the corresponding transition temperatures for four films

Sample No.	Heat treatment	Melted	Transition onset	Temperature (K) offset
1	870°C (5 min) + cooling (6°C/min) 850°C (15 min) + slow cooling (2°C/min)	no	85	68
2	875°C (5 min) + cooling (6 min) + 850°C (30 min) + slow cooling (2°C/min)	no	87	75
3	880°C (5 min) + cooling (6°C/min) 850°C (45 min) + slow cooling (2°C/min)	Partially melted	91	83.5
4	885°C (5 min) + cooling (6°C/min) 850°C (1 h) + slow cooling (2°C/min)	yes	91	85

strontium, calcium and copper in the atomic ratio of 2212 was prepared by dissolving a suitable amount of bismuth oxide, strontium carbonate, calcium carbonate, and copper oxide in a dilute solution of nitric acid with 25% methanol to enhance the speed of evaporation during deposition. The films were deposited on heated (100) MgO substrates and subsequently annealed in air for 10 min. at 800°C (pre-heating). The cycle of spraying and preheating was repeated up to four times to control the film thickness. This yielded good films with thickness $\sim 5\,\mu$m. These films were given annealing treatments for achieving superconducting properties. The annealing treatments given, are summarized in table 1. A $50 \times 50\,\mu$m bridge was patterned on the film using photolithography technique. Dilute phosphoric acid was used as an etchant. The effect of microwave radiation on the microbridge was studied by mounting the patterned film at $3\lambda/4$ distance away from the shorted end of the wave guide. R–T and I–V measurements were carried out using the standard four-probe technique.

3. Results and discussion

Figure 1 shows R–T curves for films 1 to 4. Annealing conditions and T_c of these films are summarized in table 1. T_c of the films is found to depend very much on the annealing conditions. Partial melting at the first step has been found essential for giving high T_c. Figures 2(a) and 2(b) show X-ray diffraction patterns of films 4 and 3 respectively. It is evident that for the melted film most of the peaks corresponds to (00l) planes indicating that it is highly oriented with C axis perpendicular to the surface of the substrate. For film 3 annealed at a slightly lower temperature, other reflection planes were also present.

Figure 3 shows the R–T curves of the Bi–Sr–Ca–Cu–O film before and after patterning of the microbridge. This shows that photolithographic patterning slightly reduces the T_c of the film. Figure 4 shows the variation of the critical current density J_c, with the reduced temperature t ($= T/T_c$) for the microbridge. The curve clearly does not conform to the characteristics expected from the relation derived for superconductor-insulator-superconductor tunnel junctions (Ambegaokar and Baratoff 1963). According to this relation I_c varies linearly with $(1 - t)$ near T_c and shows a

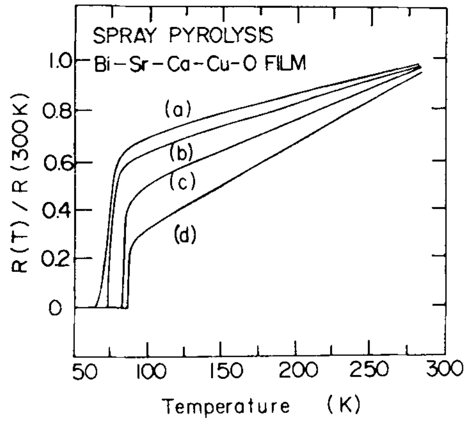
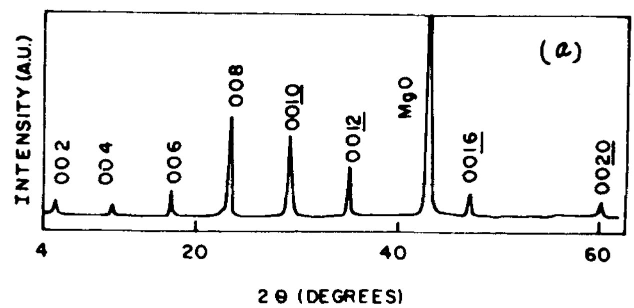


Figure 1. Normalized resistance vs temperature curves for 5 μm thick Bi–Sr–Ca–Cu–O film 1–4 (marked as (a)–(d) in the figure) (for annealing conditions see table 1).



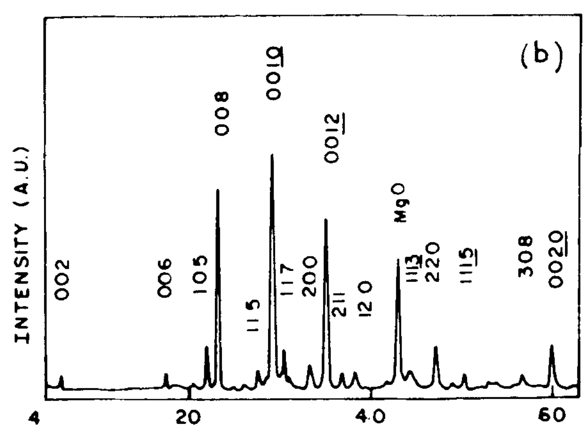


Figure 2. X-ray diffraction patterns of Bi–Sr–Ca–Cu–O film on MgO (100) (**a**) highly-oriented, (**b**) partially-oriented.

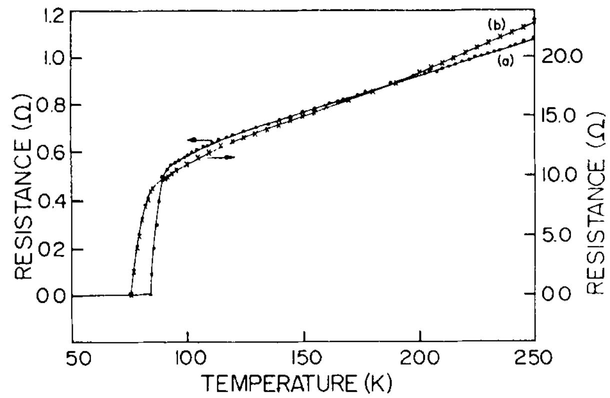


Figure 3. *R–T* curve of Bi–Sr–Ca–Cu–O film (**a**) before and (**b**) after patterning by photolithography.

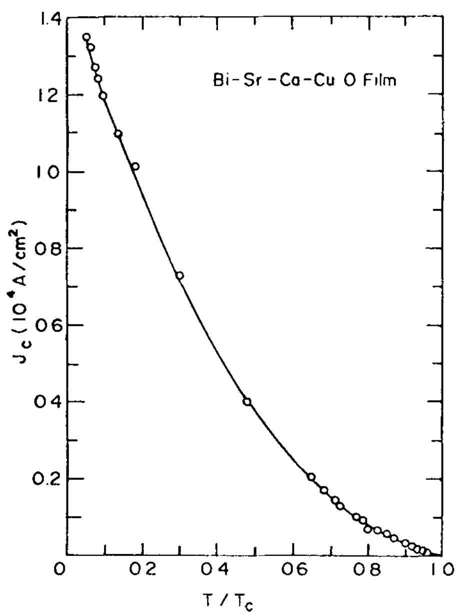


Figure 4. Variation of J_c of the bridge with reduced temperature t ($= T/T_c$).

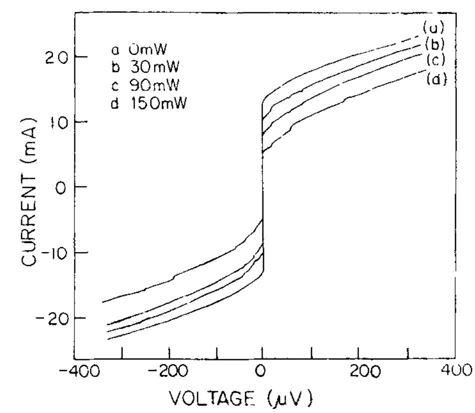


Figure 5. I–V curve for the microbridge for different incident microwave power.

convex profile with respect to the temperature axis at lower temperature. The I_c almost assumes a constant value for $t < 0{\cdot}5$. This shows that the Josephson weak links in the present case no more have insulating boundaries (barriers). In the case of the barrier being a normal metal the curves should show superconductor-normal metal-superconductor (SNS) behaviour involving proximity-induced coupling effects. In this case, according to de Gennes (1964) $I_c \propto (1-t)^2$ for temperature closer to the transition temperature. For temperatures which are much lower than transition temperature, the model predicts a sharp increase in the value of I_c. The present results can be explained qualitatively with the help of de Gennes model. We find I_c to vary as $(1-t)^{1\cdot 8}$ at temperatures near the transition temperature and a concave profile with temperature axis being observed for lower temperatures.

Figure 5 shows the I–V characteristics of the microbridge at 4.2 K for several values of applied microwave power. As the microwave power was increased from 0 to 150 mW, the amplitude of the critical current falls gradually and Shapiro steps corresponding to Josephson voltage-frequency relation are clearly observed. The frequency of the microwave being 9·86 GHz.

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