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SUPERCONDUCTING THICK-FILMS FROM A Y-Ba-Cu-O PRECURSOR

MAURIZIO SACCHI[a], FAUSTO SIROTTI, BRUNO MORTEN AND MARIA PRUDENZIATI

Dipartimento di Fisica, via Campi 213/a 41100 Modena, Italy

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We have prepared screen-printed films of the Y-Ba-Cu-O compound starting from a spray-pyrolysis precursor powder. BeO ceramic substrates are confirmed to be inert with respect to the film up to about 1000°C. Electrical properties of oxygen annealed films are investigated, evidencing excellent superconducting behaviour, both in terms of T_c (≃91 K) and J_c (>10^2 A·cm^{-2} at 77 K).

Key words: thick film, super conduction, high temperature superconductors

INTRODUCTION

Potential applications of high-T_c superconducting thick-film devices have attracted a great scientific and technological interest during the last two years[1–5]. The problem of film/substrate interaction has been widely investigated[1–3] and a few suitable materials identified. In a previous paper[3], we pointed out the good characteristics of ceramic beryllia (BeO) with respect to the Y-Ba-Cu-O superconductor, the structural and morphological properties of BeO supported films being comparable to those of the sintered bulk material. Nonetheless, extremely low values of the superconducting current density J_c were observed (J_c(20 K) ≃1 A·cm^{-2}), due to poor intergrain connections. To overcome this limitation, a precursor powder has been employed as a starting material, instead of powdered ceramic $YBa_2Cu_3O_7$.

EXPERIMENTAL

The Y-Ba-Cu-O precursor was prepared by using the spray-pyrolysis method, starting from an aqueous solution of Y-nitrate and Ba- and Cu-acetates. The resulting powder contains small $BaCO_3$ crystals (<20 μm) and CuO-like and Y_2O_3-like clusters (~10 Å diameter), as shown by our detailed structural investigation[6,7]. An organic vehicle (α-terpineol, ethyl-cellulose and buthil-carbitol acetate) was added (≃30% by weight) to obtain a paste suitable for screen printing. Films 35–40 μm thick were prepared on commercial 99.5% beryllia (Brush & Welldmann, Ther-

[a] present address: L.U.R.E. Centre Universitaire Paris-Sud 91405 Orsay, France

malox 995) substrates and kept for 1 h at 980°C in air. Part of these samples was subsequently annealed for 2 h at 440°C in flowing oxygen. Heating and cooling rates were always 1.5 deg/min.

NON ELECTRICAL MEASUREMENTS

X-ray diffraction (XRD) patterns relating to BeO supported and oxygen annealed films showed the presence of the $YBa_2Cu_3O_{7-x}$ orthorombic phase[7], and further evidence for a fully oxygen content ($x \simeq 0$) was given by the X-ray absorption spectra around the copper K-edge which are very sensitive to the oxygen depletion in the superconducting phase[8,9].

Local morphology and composition of the films have been investigated by Scanning Electron Microscopy (SEM) and X-ray energy dispersive spectroscopy (XEDS). SEM image of Fig. 1 shows an extremely dense and close structure, where no voids are observed. When compared to previous films prepared from sintered bulk materials[3], this picture gives a strong evidence for the influence of the initial grain size and local homogeneity on the final morphology of the films. XEDS analysis of the local composition (sampled volume ~10 μm^3) gave no indication for the presence of second phases as confirmed from XRD measurements carried out on the same sample.

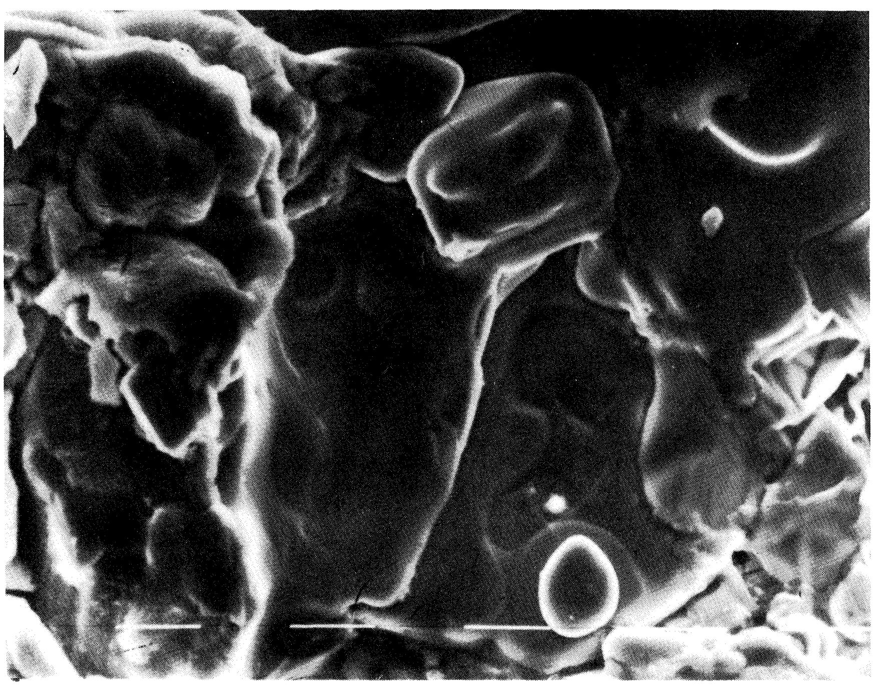

FIGURE 1 SEM image of a BeO supported Y-Ba-Cu-O superconducting film. Thermal treatment is 1 hour at 980 C in air + 2 hours at 440 C in flowing oxygen. Each white bar is 10 μm.

ELECTRICAL MEASUREMENTS

Four-points electrical measurements were performed in the range 10–300 K (±0.1 K) using a liquid-He cryostat and an electric heater. The programmable current generator (I = 10^{-9} – 10^{-1} A with plus and minus polarities) and a multimeter (sensitivity = 50 μV) were driven by a personal computer through a specifically developed code which simultaneously controlled the thermostatic conditions during the measurement. Electrical contacts on the samples were obtained by fixing with Ag-paint four Pt-wires at the corners of a 5mm × 5mm square. Contributions to the potentials from metallic heterojunctions were made negligible by inverting the current sign and relating the resistivity to the mean value

$$V(T) = \frac{V^+(T) - V^-(T)}{2}$$

Due to the initial fluidity of the Ag-paint, the geometry of the 4-contacts is not fully reproducible and exact resistivity values can hardly be deduced by voltage measurements. Measurements of the room temperature resistivity for each sample using a conventional 4-points rig of known geometry allowed the calibration of the ρ(T) curves. Fig. 2 shows the typical resistivity behaviour obtained for the oxygen annealed films: the sharp transition at ~91K and the steep rise towards higher temperatures are typical of the Y-Ba-Cu-O superconducting phase with full oxygen content. Current dependence of the resistivity is shown in the right panel of Fig. 2, on an expanded temperature scale. Temperature parameters of the superconductive transition are summarized in Tab. I. The onset and midpoint temperatures

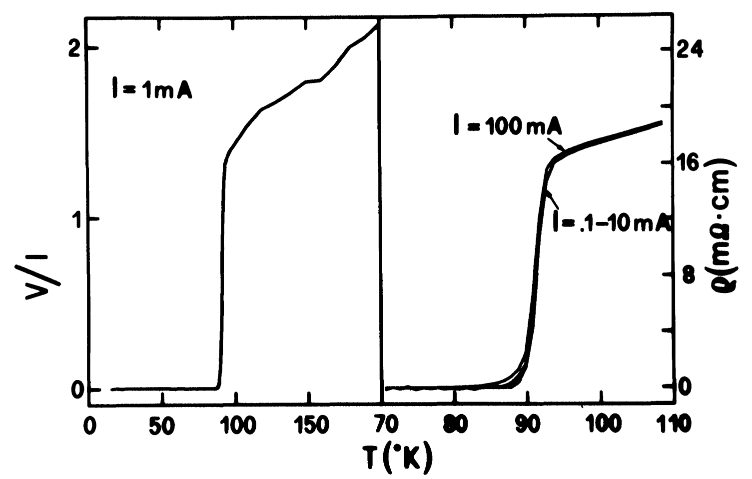

FIGURE 2 *left panel*: Resistivity ρ(T) as a function of temperature for an oxygen-annealed sample. ρ(T) is obtained by normalizing the V(T) curve at the resistivity value obtained at T = 300 K using a conventional 4-points rig of known geometry. *right panel*: ρ(T) curves obtained for different measuring currents (I = 10^{-4} – 10^{-1} A). Note the expanded temperature scale.

TABLE 1
Parameters of the superconductive transition for different measuring currents

	$I = 10^{-4}$	$I = 10^{-3}$	$I = 10^{-2}$	$I = 10^{-1}$
$T_{ons.}$	94.0	94.0	94.0	94.0
T_o	87.4	86.3	84.0	77.8
T_C	90.8	90.8	90.8	90.8
ΔT	2.5	2.7	2.9	3.3
	$J_c(77\ K) \simeq 200\ A\cdot cm^{-2}$			
	$\rho(300\ K) \simeq 25\ m\Omega\cdot cm$			

T_{ons} and T_c are scarcely affected by the value of the measuring current in the range 10^{-4}–10^{-1} A. On the contrary, the temperature of zero resistivity T_o continuously shifts downwards as current increases, and consequently larger transition widths ΔT are found. This lowering of T_o at constant T_c values clearly indicates the crossing of the critical current density J_c as the measuring current is increased. J_c is an extremely important parameter for many practical applications. Its value in sintered materials is not just related to the crystalline structure (e.g. oxygen content or impurity concentration, in our case), but also to microstructural aspects like grain orientation or interconnection. It has been shown that mono-oriented single-phase $YBa_2Cu_3O_7$ thin films can have critical current density at 77 K as high as 10^6 $A\cdot cm^{-2}$ [10]. On the contrary, sintered ceramic bulk samples have typically $J_c \simeq 10^2$ $A\cdot cm^{-2}$ at the same temperature[11].

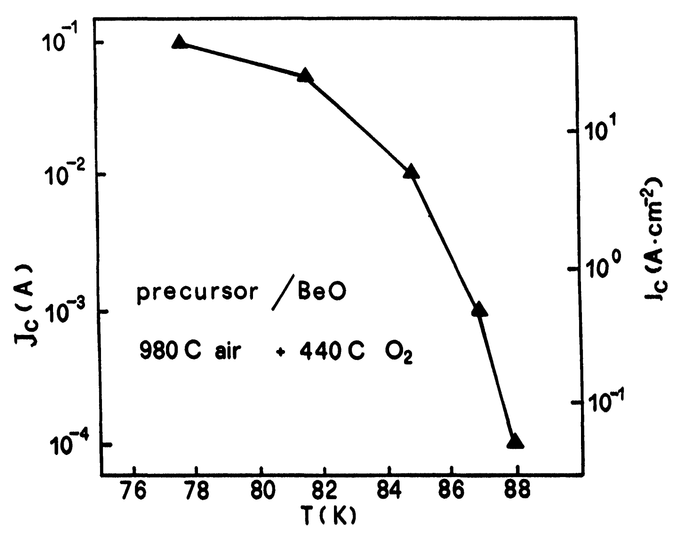

FIGURE 3 Critical current density J_c as a function of temperature. An effective section of $2\cdot 10^{-3} cm^2$ is assumed.

In screen printed films the situation is usually even worst with respect, for example, to pressed pellets due to the poorer compaction before sintering. Our previous best results starting from ceramic powder were of about 10^2 A·cm^{-2} at 20 K, and no measurable J_c at 77 K was found[3].

Critical current density values as a function of temperature are reported in Fig. 3 for the films discussed in this paper. J_c at 77 K is of the order of 10^2 A·cm^{-2}, assuming an effective section of $5 \cdot 10^{-1} \times 4 \cdot 10^{-3}$ cm^2 for the superconducting electrical transport. The exact value has not been determined due to the upper limit of 10^{-1} A in the current generator. Appreciable superconducting current density of several A·cm^{-2} can be applied up to temperatures of about 85 K. To our knowledge, this is the first time that similar results are found in Y-Ba-Cu-O screen-printed films.

In conclusion, we have shown the extreme importance of starting from a finely grain sized and intimately mixed precursor in the preparation of thick superconducting films. The heat treatment at 980°C on BeO substrates followed by oxygen annealing leads to dense $YBa_2Cu_3O_7$ films. Their excellent electrical properties, particularly in terms of critical current density, confirm the good quality of intergrain connections.

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