Preparation of Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O superconducting films by conventional techniques

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Abstract. High temperature superconducting films of Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O have been deposited on different substrates using conventional techniques, like flash evaporation and spray pyrolysis. The microstructural investigation of the films by SEM technique reveals the partially oriented nature of the crystallites. In the case of spray-deposited Bi–Sr–Ca–Cu–O HTSC films it has been found that film/substrate mismatch is not the decisive factor for the superconducting transition temperature T_c .

Keywords. HTSC films; flash evaporation; spray pyrolysis; microstructure; film substrate mismatch.

1. Introduction

With the recognition of the fact that high critical current densities ($\sim 10^4$ to 10^6 A/cm²) can readily be reached in thin film forms of high temperature superconductors, increasingly greater emphasis is being paid on the development of various methods for the deposition of thin films of HTSC materials. A large variety of techniques such as electron beam deposition, magnetron sputtering, laser ablation, metal-organic deposition etc have been successfully used. However, conventional techniques like spray-pyrolysis and flash evaporation are of much interest because of their easy accessibility and cost viability.

This paper reports our results on the deposition of Y–Ba–Cu–O film on MgO substrate by flash evaporation, a technique for deposition of films whose constituents have different vapour pressures (Hatou *et al* 1988; Ece and Vook 1989; Yasuda *et al* 1989). This technique can give thin films with composition and structure as that of the parent material.

The other technique employed by us for deposition of Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O thin films is the technique of spray pyrolysis. Here again the deposition method is easy to employ and is viable for routine deposition (Hsu *et al* 1989).

We have monitored the microstructural characteristics and details of substrate-film interaction. Attempts have been made to present a correlation between these properties and superconducting characteristics of the films deposited by the aforesaid techniques.

2. Experimental

YBa₂Cu₃O_{7-x} pellets were prepared by the conventional solid-state reaction of Y₂O₃, BaCO₃ and CuO. A mixture of these materials in the stoichiometric ratio (Y:Ba:Cu = 1:2:3) was thoroughly mixed and fired at 900°C for 12 h in air and 500°C for 4 h in flowing oxygen. The pellets were then tested and found to correspond to the standard 123 orthorhombic phase. The pellets were ground into fine particles.

The experimental set-up of this technique was reported earlier (Verma *et al* 1989). Flash evaporation was done by dropping fine particles of Y–Ba–Cu–O on a Mo boat maintained at a high temperature, under a vacuum of $\sim 10^{-5}$ torr. The films were deposited on three different substrates viz. MgO, ZrO₂ and YSZ. The substrate temperature during deposition was kept at $400 \pm 10^\circ\text{C}$. The as-deposited film on MgO was highly resistive, but annealing at 900°C for 2 h and finally at 600°C for 1 h in flowing oxygen reduced the electrical resistance to a few ohms at room temperature.

The superconducting films of Bi–Sr–Ca–Cu–O were prepared by spray pyrolysis technique which involves deposition of chemical precursors (metal nitrates) onto suitable substrates, through a nozzle using oxygen as the carrier gas. The experimental set-up was discussed earlier by Saxena *et al* (1988). To prepare Bi–Sr–Ca–Cu–O films, 0.3 M solution of nitrates of Bi, Sr, Ca and Cu are mixed in the ratio 2:2:2:3 and sprayed over heated ($400 \pm 10^\circ\text{C}$) single crystal MgO, SrTiO₃ and YSZ substrates. The films were first annealed in air for 15 min at 800°C . Then the temperature was raised at a rate of $\sim 20^\circ\text{C}/\text{min}$ and the films were quenched when the temperature reached 880°C . The films were further annealed in air at 840°C for 15 min and quenched. The details of film-substrate interaction will be described later.

The films so formed were characterized through X-ray diffraction by employing a Philips powder diffractometer (PW 1710) equipped with graphite monochromator. The film composition and morphology were investigated in SEM mode of Philips microscope CM-12 having EDAX PV9900 attachment. The electrical resistivity was measured as a function of temperature by applying Van der Pauw technique. For this current was supplied from a Keithley programmable current source (model-220) and voltage was measured by a nanovoltmeter (model-181).

3. Results and discussion

A typical variation of resistance with temperature of the Y–Ba–Cu–O flash-deposited film on MgO substrate is shown in figure 1. In the films deposited by us so far T_c onset

Figure 1. Variation of resistance with temperature for a flash-deposited thin film of YBa₂Cu₃O_{7-x} formed on a single crystal of MgO.

and T_c zero was at ~ 93 K and ~ 80 K respectively. The critical current density J_c obtained was ~ 600 A/cm².

A representative sample of X-ray diffraction pattern is shown in figure 2. The pronounced intensity of (001) reflections e.g. (005) line indicates the formation of partially oriented film with the c -axis normal to the substrate surface.

Figure 3 shows the EDAX of Y–Ba–Cu–O flash-evaporated film. The composition ratio of Y:Ba:Cu as determined was 1:2:3:4:3. Our result indicates that Cu-rich films exhibit pronounced grain growth. This is in keeping with other results (see e.g. Hamdi

Figure 2. X-ray diffraction pattern of the flash-deposited $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film. The characteristic diffraction lines reveal the orthorhombic phase ($a = 3.824$ Å, $b = 3.891$ Å, $c = 11.685$ Å).

Figure 3. EDAX of Y–Ba–Cu–O thin film.

Figure 4. SEM of flash-deposited Y-Ba-Cu-O film on MgO substrate showing basal-oriented crystallites.

Figure 5. Variation of resistance with temperature for spray-deposited films of Bi-Sr-Ca-Cu-O on single crystal substrates (MgO, SrTiO₃ and YSZ).

et al 1988). Figure 4 shows the SEM of Y-Ba-Cu-O film. One observes platelet-shaped crystals which have preferential growth parallel to *a-b* plane. The morphology of the film is in conformity with the XRD result shows enhancement in the intensity of (001)-type reflections.

In the case of spray-deposited film, R-T monitoring reveals a striking result that the film lattice/substrate mismatch does not affect the transition temperature. As shown in figure 5, the R-T curves for the three film configurations, viz. Bi-Sr-Ca-Cu-O/MgO, Bi-Sr-Ca-Cu-O/SrTiO₃ and Bi-Sr-Ca-Cu-O/YSZ lead to the same transition

Table 1.

Substrate and substrate structure	Lattice mismatch for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($a = 5.399 \text{ \AA}$; $b = 5.414 \text{ \AA}$; $c = 30.904 \text{ \AA}$)		
	along a	along b	along c
MgO (F.C.C. NaCl type) $a = 4.20 \text{ \AA}$	$M_a = 8.87\%$	$M_b = M_a = 8.87\%$	$M_c = 5.05\%$
SrTiO ₃ (Perovskite cubic) $a = 3.90 \text{ \AA}$	$M_a = 1.92\%$	$M_b = M_a = 1.92\%$	$M_c = 1.08\%$
Y-stabilized ZrO ₂ (fluorite cubic) $a = 5.16 \text{ \AA}$	$M_a = 4.63\%$	$M_b = 4.92\%$	$M_c = 0.18\%$

Figure 6. A model of possible planes of matching for Bi-Sr-Ca-Cu-O films over MgO, SrTiO₃ and YSZ.

temperature. The calculated value of lattice mismatch is given in table 1. It may be noted that the largest mismatch is for Bi-Sr-Ca-Cu-O/MgO and the smallest value corresponds to Bi-Sr-Ca-Cu-O/SrTiO₃. A model of the film/substrate matching is shown in figure 6. The J_c of these films measured on some films was in the range of $\sim 100\text{--}500 \text{ A/cm}^2$.

The microstructural characteristics as monitored by SEM for spray-deposited film is shown in figure 7. It appears that the platelet characteristic of the film where the film is parallel to a - b plane is more obvious in the case of film deposited on SrTiO₃. Curled petal-shaped growth morphology and some cylindrical-shaped growth of crystallites are seen in films on MgO and YSZ.

Figure 7. SEM of spray-deposited Bi-Sr-Ca-Cu-O film on (a) MgO, (b) YSZ (c) SrTiO₃ substrates showing curled petal-shaped growth morphology and some cylindrical shaped crystallites (marked by arrow).

4. Conclusion

Both flash evaporation and spray pyrolysis techniques can be employed for deposition of high temperature superconducting thin films. The present study reveals that flash evaporation under appropriate conditions can easily lead to partially-oriented 123 film.

With regard to spray pyrolysis technique our investigation brings out that HTSC film/substrate lattice mismatch is not the decisive factor for higher T_c . For Bi–Sr–Ca–Cu–O HTSC films it has been found that all three substrates lead to formation of films with approximately the same transition temperature T_c . Microstructural characteristics investigated in the present case suggest that the basal-oriented platelet crystallites are formed for the film on SrTiO₃ substrate.

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