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Effect of annealing temperature on the structural–microstructural and electrical characteristics of thallium bearing HTSC films prepared by chemical spray pyrolysis technique

K K VERMA*, R S TIWARI[†] and O N SRIVASTAVA[†]

Department of Physics and Electronics, Dr R M L Avadh University, Faizabad 224 001, India

[†]Department of Physics, Banaras Hindu University, Varanasi 221 005, India

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Abstract. **In order to get good quality reproducible films of Tl : HTSC system, we have studied the different annealing conditions to finally achieve the optimized annealing condition. In the present investigation, Tl–Ca–Ba–Cu–O superconducting films have been prepared on YSZ (100) and MgO (100) single crystal substrates via precursor route followed by thallination. The post deposition heat treatments of the precursor films were carried out for various annealing temperatures (870°C, 890°C) and durations (1 and 2 min). The optimized thallination procedure occurred at 870°C for 2 min into good quality films with T_c ($R = 0$) ~ 103 K for YSZ and T_c ($R = 0$) ~ 98 K for MgO substrates, respectively. Further we have correlated the structural/microstructural characteristics of the films.**

Keywords. **Tl : HTSC films; optimized annealing condition; spray pyrolysis; precursor route.**

1. Introduction

Amongst the families of superconductors presently known, the Tl–Ca–Ba–Cu–O materials offer unique opportunities for the fabrication of superconducting devices. Because of their high T_c (~ 125 K) and high J_c, they are readily amenable to operation at liquid nitrogen temperature (~ 77 K). Uptil now, various methods for the preparation of HTSC thin films such as electron beam evaporation (Ramesh *et al* 1990; Ginley *et al* 1998a,b; Sugise *et al* 1998), sputtering (Lengfellner *et al* 1989; Lin and Wu 1989; Subramanyam *et al* 1990; Saito *et al* 1991; Ichikawa *et al* 1998; Zhou *et al* 1998), laser ablation (Betz *et al* 1989; Johs *et al* 1989), thermal flash evaporation (Barboux *et al* 1988; Ece and Vook 1989; Verma *et al* 1989), chemical spray pyrolysis (Kawai *et al* 1987; Gupta *et al* 1988; Saxena *et al* 1988; DeLuca *et al* 1991; Verma *et al* 1992) and spin coating (Rice *et al* 1987) etc have been employed. Out of these techniques, the simple chemical process like spray pyrolysis and spin coating are economically viable. Other advantages of these methods are that the oxide film is directly formed on the substrates and no powder handling is needed, the composition of the films is homogeneous and can be easily controlled. Substrate of any shape can be completely coated and the temperature required for processing is lower than those of the powder reactions. The present paper reports the fabrication of Tl : HTSC films on MgO (100) and YSZ (100) substrates by the spray pyrolysis technique. The recent report regarding high J_c ~ 10 Amp/cm^2 in the spray pyrolysed films has generated interest in this technique. A rather significant aspect of the present work is regarding the structural/microstructural correlation of the films with regard to T_c ($R = 0$). Recently Tl : HTSC films are in focus in regard to preparation of thin Tl : HTSC films (Lu *et al* 2003), microwave studies (Sundaresan *et al* 2003) and for substrate dependent surface morphology (Badica *et al* 2003).

2. Experimental

Since thallium is toxic, Tl–Ca–Ba–Cu–O HTSC films have been prepared by a two-step process. Firstly, Ca–Ba–Cu–O (precursor) films have been prepared by a downward spray of an aqueous methonolic solution containing nitrates (0·3 M) of Ca, Ba and Cu in the ratio, 2·2 : 2 : 3, on preheated (520 ± 10°C) MgO (100) and YSZ (100) single crystal substrates. The thallium incorporation was then carried out by diffusion of Tl_2O_3 vapour (derived from Tl_2O_3 powder) into the precursor film to eventually get the Tl–Ca–Ba–Cu–O superconducting films. The schematic set up of the spray pyrolysis technique has been previously described by us (Saxena *et al* 1988) for the synthesis of Y-based 123 : HTSC thin films. A systematic (pre-thallination) annealing of the precursor films (Ca–Ba–Cu–O) was carried out to take into account the following three factors—firstly, complete dissociation of the nitrates, secondly, improvement of the chemical homogeneity of the films and thirdly, improvement of the surface mor-

*Author for correspondence (kkverma23@yahoo.com)

phology of the precursor films via the coalescence of the grains in the films. The precursor films were annealed in the box furnace at 500 ± 2°C for 15 min and then the films were taken up to a temperature of 600 ± 5°C in a span of 30 min. The annealed precursor films were then placed in a closed pt-boat with Tl_2O_3 powder, which in turn was enclosed in a heated silica tube maintained under O_2 gas flow for carrying out thallination. Various anealing temperatures (870°C, 890°C) and durations (1 and 2 min) were tried in order to get good quality Tl : HTSC films. To achieve the annealing temperature, the microprocessor controlled Heraus furnace was kept initially at 980 ± 2°C. The tube containing precursor film and Tl_2O_3 powder was inserted into the furnace. In about 5 min, the desired annealing temperature was obtained. The films were kept at the temperature for 30 s, and then quenched in ambient atmosphere by quickly pulling the tube out of the furnace. Resistance of the films as a function of temperature was monitored by the well known four-probe Van-der-pauw technique. For this, current was supplied from a Keithley nanometer (model-220) and voltage was measured by the Keithley nanometer (model-181). The surface morphology was examined by scanning electron microscope utilizing Philips EM (CM-12) electron microscope. XRD analysis was carried out by employing Philips X-ray powder diffractometer (PW1710).

3. Results and discussion

The central motivation of the present work has been to optimize the annealing condition in order to get good quality Tl : HTSC films and also to establish possible structural/microstructural correlation of the films with T_c (R = 0) Figures 1(a)–(d) show the variation of resistance as a function of temperature for the Tl : HTSC films deposited on MgO (100) and YSZ (100) single crystal substrates

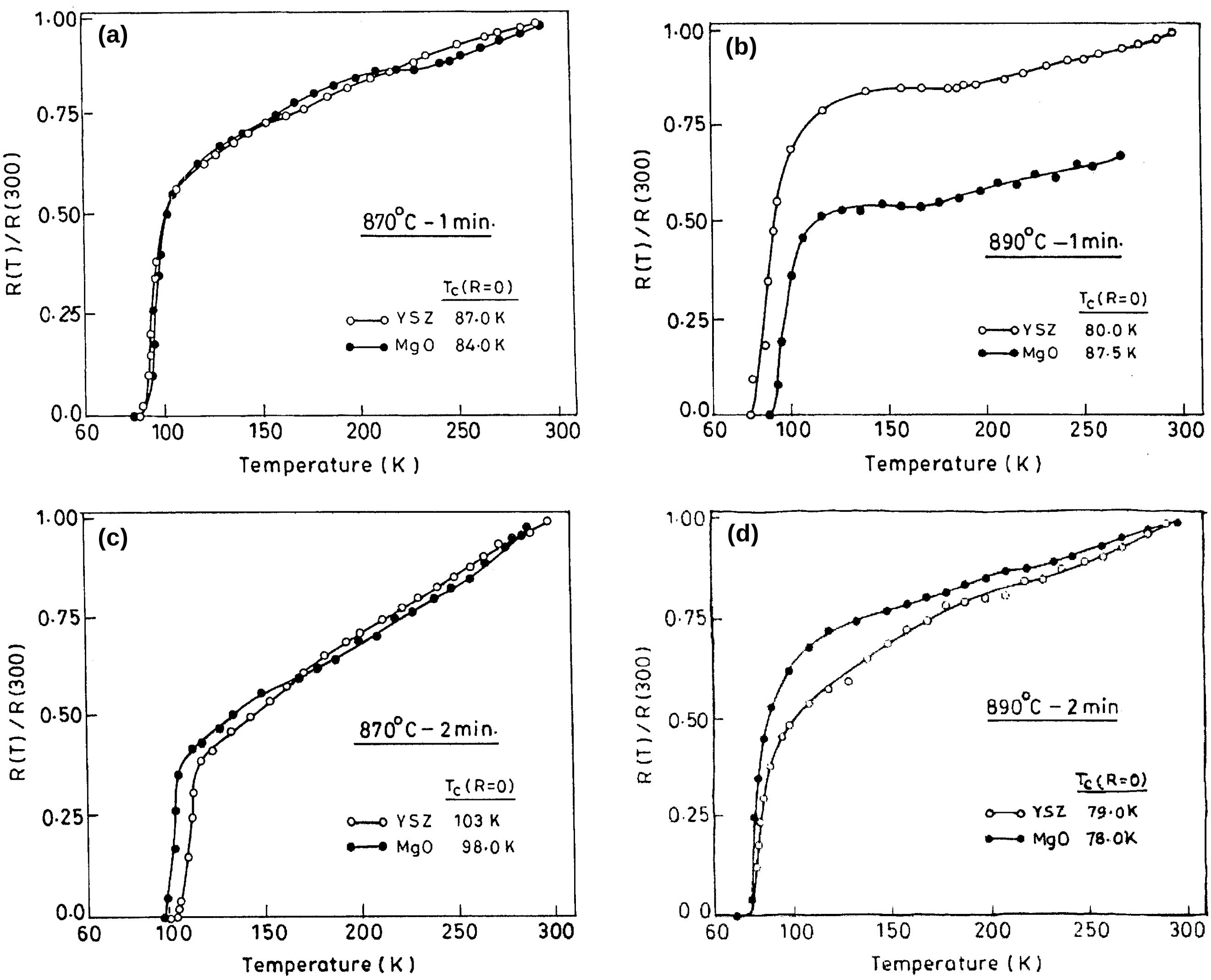

Figure 1. Resistance vs temperature curve of the Tl–Ca–Ba–Cu–O HTSC film on MgO (100) substrate and YSZ substrate after thallination at (**a**) 870°C for 1 min, (**b**) 890°C for 1 min, (**c**) 870°C for 2 min and (**d**) 890°C for 2 min.

under the annealing temperatures (duration) of 870°C (1 min), 890°C (1 min), 870°C (2 min) and 890°C (2 min), respectively. Figure 1(a) exhibits the *R–T* behaviour of Tl : HTSC film prepared after annealing at 870°C for 1 min. The metallicity of the film before the T_c (onset) on YSZ (100) is better than that of MgO (100). The T_c ($R = 0$) for the films are ~ 84 K (MgO) and ~ 87 K (YSZ), respectively. The slightly higher T_c ($R = 0$) on YSZ (100) may be due to this better metallicity of the film. Figure 1(b) shows the *R–T* behaviour of Tl : HTSC film prepared after annealing at 890°C for 1 min. The T_c ($R = 0$) for the films are ~ 87·5 K on MgO and ~ 80 K (YSZ), respectively. Figure 1(c) shows the *R–T* behaviour processed at 870°C for 2 min. The T_c ($R = 0$) are ~ 98 K on MgO and ~ 103 K on YSZ, respectively. Figure 1(d) shows the *R–T* behaviour of the Tl : HTSC films prepared after annealing at 890°C for 2 min; the T_c ($R = 0$) are 78 K (MgO) and ~ 79 K (YSZ), respectively. Figure 2(a) shows the XRD pattern of the Tl–Ca–Ba–Cu–O films on MgO substrates annealed for 870°C (1 and 2 min) and 890°C (1 and 2 min); in this pattern we observed that the intensity of the 0012 (2212) peak increased as we went from 870°C (1 min) to 890°C (2 min), however, it is absent for 890°C (1 min). In comparison to films processed at 870°C (1 min)–890°C (1 min), 2223 phase becomes the dominant one for 890°C (2 min). The presence of several 001 lines of 2223 phase exhibits the partially oriented nature of the films. Figure 2(b) shows the XRD patterns of the Tl–Ca–Ba–Cu–O films on YSZ (100) substrate.

These patterns show that the intensity of the 0014 (2223) line has increased as we went from 870°C (1 min) to 890°C (2 min) and the 2223 phase becomes dominant. Figure 3 is a representative scanning electron micrograph of the films. This shows the presence of platelet shaped crystallites.

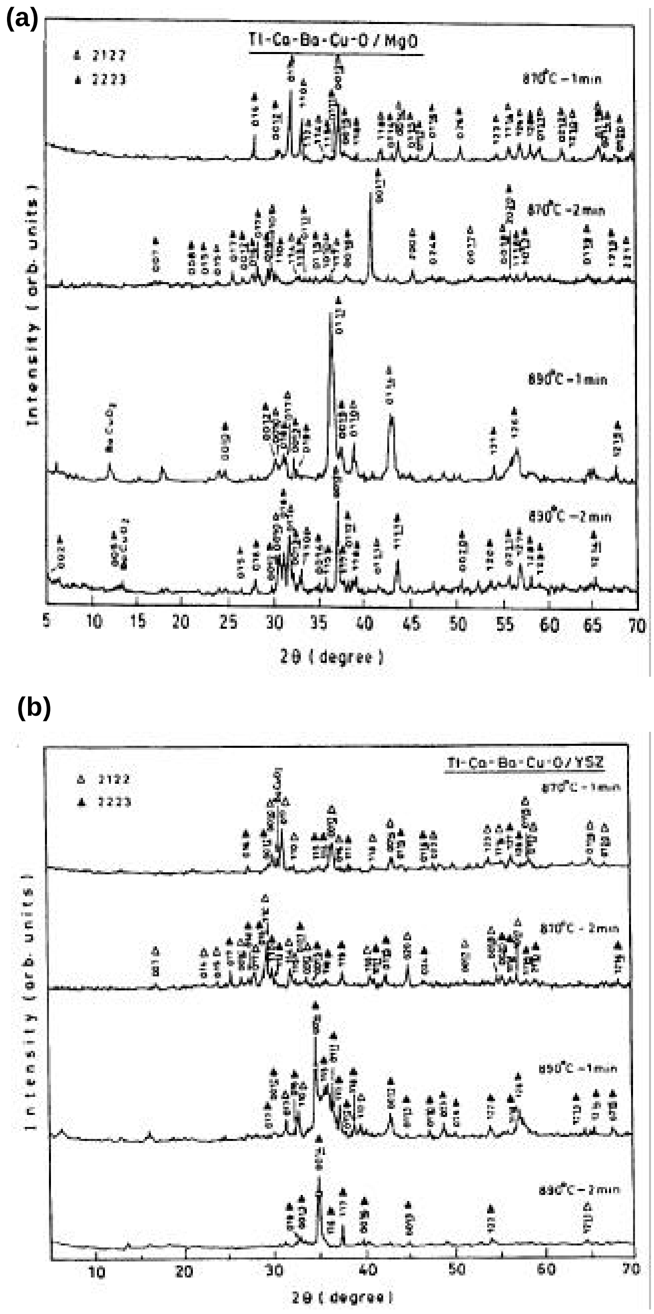

Figure 2. X-ray diffraction patterns of the Tl–Ca–Ba–Cu–O HTSC film on (**a**) MgO (100) substrate after thallination at 870°C (1 and 2 min) and 890°C (1 and 2 min) and (**b**) YSZ (100) substrate after thallination at 870°C (1 and 2 min) and 890°C (1 and 2 min).

4. Conclusions

Tl–Ca–Ba–Cu–O HTSC films on MgO (100) and YSZ (100) single crystal substrates have been synthesized by precursor route i.e. by a two-step process. The gross structural and microstructural characterization of the films was carried out by X-ray diffraction and scanning electron microscopic techniques. It has been found that the films are mostly of bi-phasic nature (2212/2223) with 2223 as dominant phases. A definite influence of anneal-

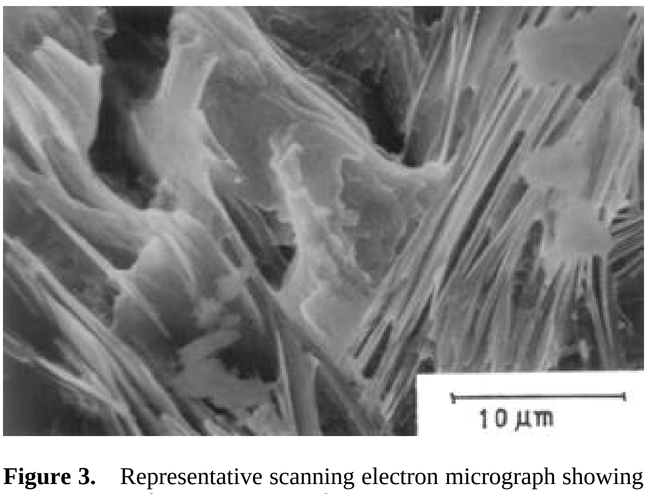

Figure 3. Representative scanning electron micrograph showing the presence of platelet nature of crystallites.

ing of the precursor film on the T_c ($R = 0$) of the thallium HTSC films has been found. The T_c ($R = 0$) depends sensitively on the post annealing temperature and duration. In regard to the critical transition temperature, the most suitable temperature and time duration was found to be 870°C and 2 min. This corresponds to the best observed T_c ($R = 0$) viz ~ 98 K and ~ 103 K for Tl : HTSC film on MgO (100) and YSZ (100) substrates. It can be concluded from these observations that the YSZ (100) is best suited for the deposition of Tl : HTSC films.

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