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Process parameters optimization for laser deposition of high T_c superconducting thin films on Si and other substrate materials

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Abstract. Thin films of Y–Ba–Cu–O superconductor have been deposited on different substrates by pulsed excimer laser ablation from a superconducting pellet. The dependence of various process parameters such as substrate temperature, laser energy density, oxygen partial pressure, applied bias field and cooling rates on the quality of the films has been studied.

Keywords. Superconducting thin films; Y–Ba–Cu–O; Si; laser deposition.

1. Introduction

Soon after the discovery of high temperature superconductors (Bednorz and Muller 1986; Wu *et al* 1987), a wide range of techniques were investigated for deposition of thin films of these oxide-based systems including e-beam evaporation (Oh *et al* 1987), molecular beam epitaxy (Kaw *et al* 1987), pulsed laser evaporation (Ogale *et al* 1987), sputter deposition (Samekh *et al* 1987) etc. Among these, laser deposition (Wu *et al* 1989) is the simplest and rapid technique to produce thin films of excellent quality which are well-oriented, high density, having sharp transitions and high critical current densities in their as-deposited form.

In this paper we report process parameter optimization and successful synthesis of $Y_1Ba_2Cu_3O_{7-x}$ thin films on various substrates including silicon by pulsed excimer laser deposition technique. The object of the study has been to explore conditions for film deposition at low temperature ($<650°C$) since such temperatures reduce the film-substrate interdiffusion and can lead to crack-free and smooth films with high critical current density. We have investigated the dependence of thin film properties on various processing parameters such as substrate temperature, oxygen partial pressure, applied biased field, film thickness, effect of substrates etc. Optimized conditions have been used to deposit thin films of $Y_1Ba_2Cu_3O_{7-x}$ on c-$SrTiO_3$, c-ZrO_2, c-MgO and silicon (Wu *et al* 1989) with and without buffer layers. Yttrium-stabilized cubic zirconia has been used as the buffer layer because (i) it acts as a diffusion barrier between Si and YBaCuO, (ii) its dielectric constant is low (7·8) and therefore leads to faster electronic signal propagation and (iii) its high temperature reaction with YBaCuO thin films is minimal. The growth of YBaCuO thin film is dependent on the quality of ZrO_2 buffer layers deposited under various processing conditions and the thickness of the superconducting films on Si.

2. Experimental

The experimental arrangement is described elsewhere (Bendre *et al* 1989). Briefly, pulsed excimer laser (Lambda Physik EMG 200, $\lambda = 248$, 308 nm, pulse width 20 ns) was used to irradiate a bulk superconducting pellet with a nominal composition of $Y_1Ba_2Cu_3O_{7-x}$ and a transition temperature of 93 K. A stainless steel chamber supported with a Varian diffstack system was used for deposition. The laser energy density at the target was kept fixed at 2–2·5 J/cm^2. During deposition the target was rotated at 10 rpm to avoid texturing of the pellet surface. The substrates were mounted 2·5–3 cm away from the target and heated to different substrate temperatures up to 700°C in different experiments. The substrate temperature was measured by placing the Cr–Al thermocouple on the surface of the substrates. The oxygen partial pressure during deposition was kept from a few millitorr to about 200 millitorr and after deposition the substrates were cooled in 1 atm. O_2 pressure.

The electrical properties of the superconducting thin films were studied by conventional four-probe resistivity measurements. Contacts were made with silver paint and the transport current typically of 1 to 10 μA was used to measure low temperature resistivity. The critical current density was measured by laser patterning the films to obtain 20 μm wide microbridges. The structural and phase analysis was carried out by small angle X-ray diffraction technique (Rigaku rotaflex RU 200B) employing Seeman-Bohlin geometry using CuK_α radiation. For ZrO_2 buffer layers on Si, IR spectroscopy was also used as a supporting technique.

3. Results and discussion

The low temperature electrical properties of $Y_1Ba_2Cu_3O_{7-x}$ thin films deposited on (001) oriented single crystal ZrO_2 substrates are shown in figure 1. Curve (a) corresponds to the film deposited at the substrate temperature of 520°C and the oxygen partial pressure of 5×10^{-3} torr. This shows semiconducting behaviour with onset around 92 K. Curve (b) corresponds to the substrate temperature of 520°C and an oxygen partial pressure of 4×10^{-2} torr. The improvement in the nature of the curve clearly indicates that oxygen can directly react with plasma plume and enhance the quality of oxygen stoichiometry in the film. However this condition is not optimum so as to get good-quality films. The nature of the curve is not metallic above onset. To further improve the oxygen stoichiometry and structural quality of the films the deposition was carried out at a higher substrate temperature of 650°C and an oxygen partial pressure of 1×10^{-1} torr followed by cooling at 1 atm oxygen pressure. The as-deposited films were found to be superconducting in this case with T_c of 92 K and J_c in excess of 5×10^5 A/cm^2 at 77 K. The corresponding low R–T behaviour is shown in figure 1c. Using the same parameters we could deposit the film with thickness of only 500 Å on c-ZrO_2 substrate and this film in its as-deposited form showed a zero resistance transition temperature of 85 K (see figure 1, curved).

We have also carried out an in-situ resistance measurement to monitor the quality and proper phase formation during deposition. It was found that the resistance of the film very much depends on its oxygen content. The change in resistance soon after the start of deposition is shown in figure 2. It is seen that after 20–25 and a pulse rate of 5 Hz, the resistance of the insulating substrates drops to 300 ohm followed by a gradual decrease to 100 ohm within 10 min. This indicates that the minimum thickness to achieve the proper stoichiometric film is of the order of 150–200 Å on ZrO_2 substrates, which is comparable to the reported value. After deposition, oxygen was leaked in the chamber at 1 atm pressure. The film deposited in oxygen shows quite an interesting

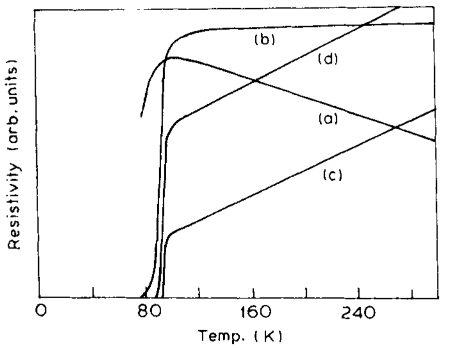

Figure 1. Low temperature resistivity measurements of the films deposited on c-ZrO_2.

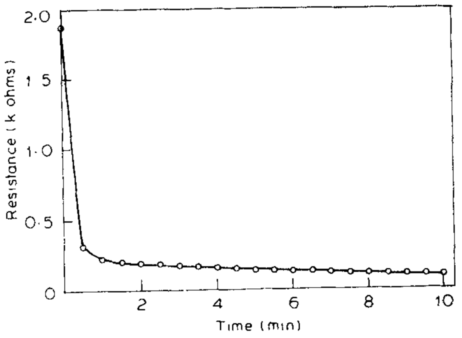

Figure 2. In-situ resistance measurement of YBaCuO during deposition.

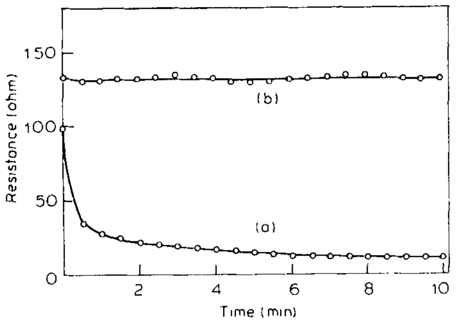

Figure 3. In-situ resistance measurement of the deposited film (a) immediately after deposition and oxygen atm pressure and (b) in-oxygen partial pressure of 100 mtorr.

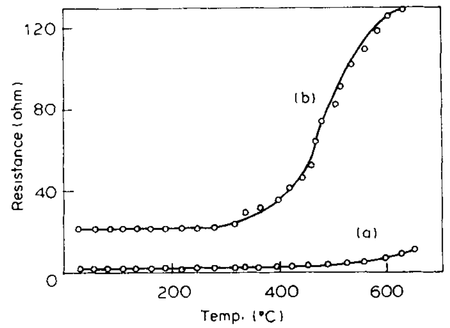

Figure 4. In-situ resistance measurement during slow cooling process (a) oxygen of 1 atm pressure and (b) 100 mtorr.

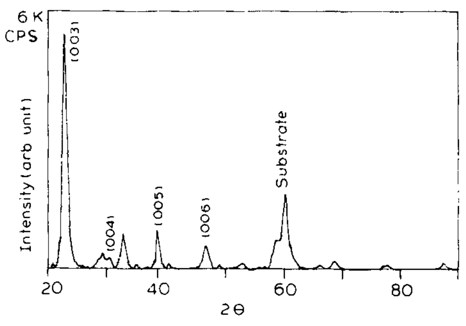

Figure 5. Low angle XRD patterns of as-deposited superconducting thin film.

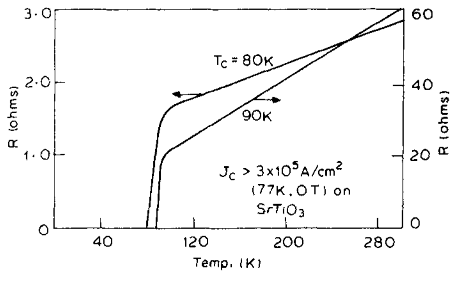

Figure 6. Resistance vs temperature of superconducting thin film deposited on (a) $SrTiO_3$ and (b) MgO.

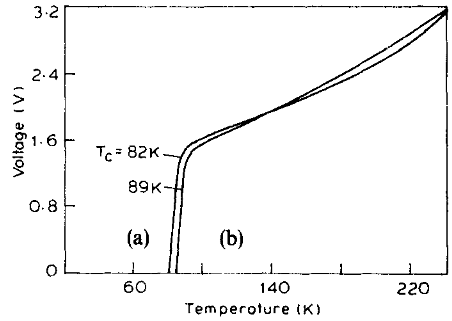

Figure 7. Resistance vs temperature for 2 films deposited at 550°C (**a**) without field bias and (**b**) with field bias of 130 V/cm.

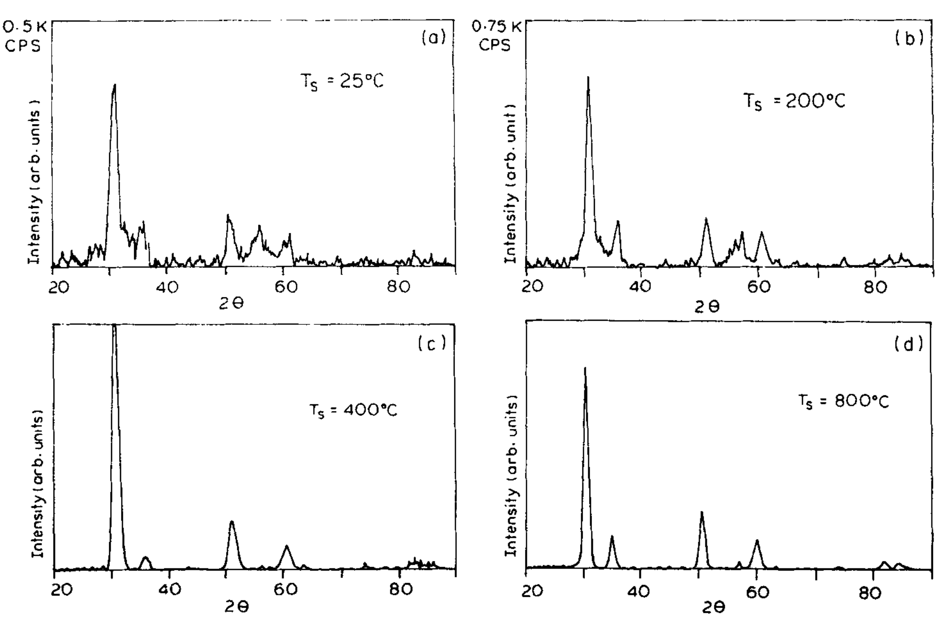

Figure 8. Low angle XRD patterns of ZrO_2 thin films on Si deposited at T_s(**a**) 25°C, (**b**) 200°C, (**c**) 400°C and (**d**) 800°C.

resistance behaviour (figure 3a). Immediately after introducing oxygen, the resistance dropped from 100 ohm to 20 ohm in 2 min showing that the deposited film may be oxygen-deficient. When no oxygen was leaked into the system after deposition the resistance remained almost constant (figure 3b). During slow-cooling process, the temperature dependence of resistance for the films cooled in oxygen with a partial pressure of 1×10^{-1} torr was found as shown in figure 4. The corresponding low temperature electrical properties showed that the film cooled in oxygen is metallic with T_c of 92 K while the film cooled in 1×10^{-1} torr is semiconducting. We therefore believe that the optimized process parameters for the as-deposited superconducting thin films are higher oxygen partial pressure ($1–2 \times 10^{-1}$ torr) and substrate temperature in the range of 600–650°C followed by slow-cooling in oxygen ambient at higher pressure.

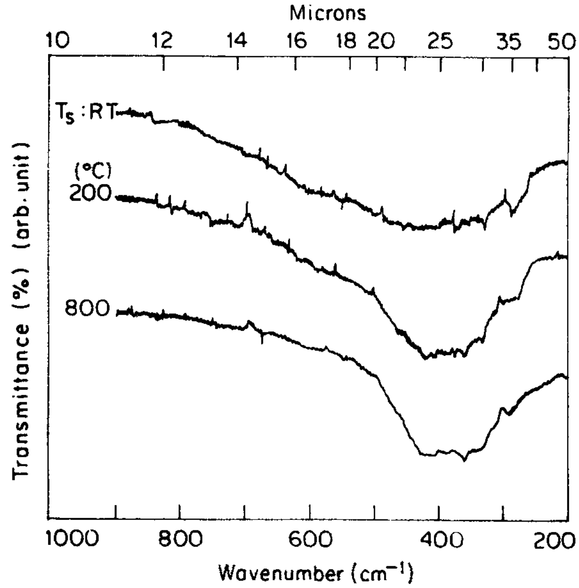

Figure 9. IR spectra of ZrO_2 thin films on Si deposited at T_s.

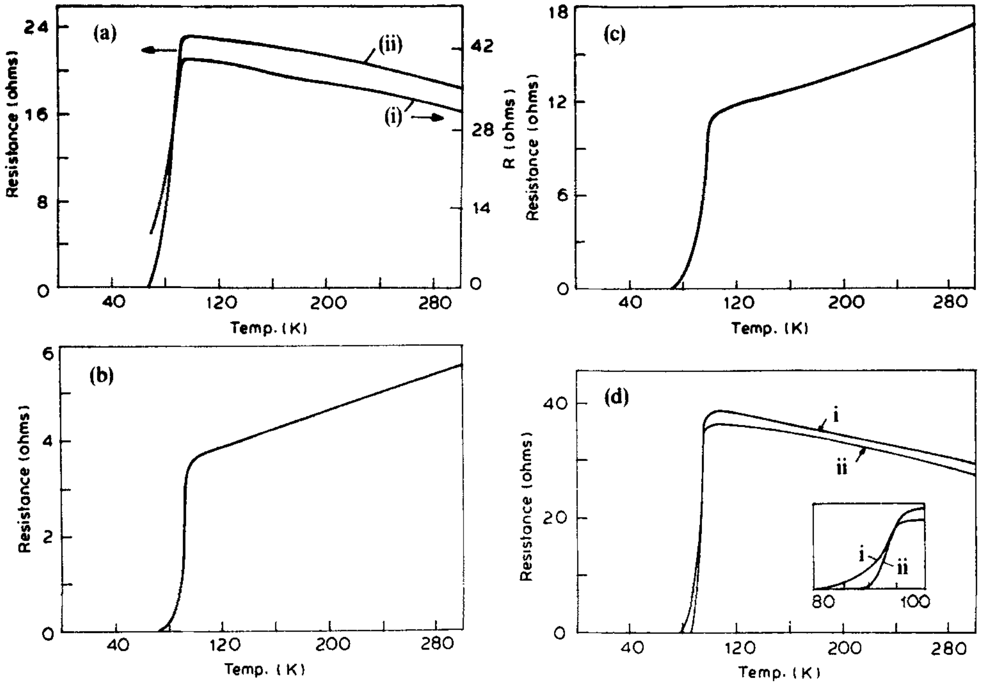

Figure 10. Resistivity as a function of temperature for superconductor thin films on Si with ZrO_2 buffer layers (**a**) only Si(i), ZrO_2 deposited at 25°C(ii). (**b**) ZrO_2 deposited at 200°C. (**c**) ZrO_2 deposited at 800°C. (**d**) 1·5 μm thick film (i), 2·5 μm thick film (ii).

The small angle XRD pattern of the as-deposited thin film (figure 5) shows that it is mainly oriented towards the c-axis perpendicular to the substrate surface.

Using the same parameters as for ZrO_2, films were deposited on c-$SrTiO_3$ (001) and MgO (001) substrates. The low temperature resistivity measurement for these cases is shown in figure 6. Clearly the optimized parameters for c-ZrO_2 work equally well for $SrTiO_3$ and MgO substrates. We have also studied the effect of field biasing on the quality of the superconducting thin films. Figure 7a corresponds to the T vs R plot for the film deposited at $T_s = 550°C$ without field biasing. Figure 7b corresponds to $T_s = 550°C$ and a field biasing of 130 V/cm. It is evident that plasma-assisted deposition shows improvement in the quality of the thin film.

For deposition of superconducting thin films on silicon, ZrO_2 barrier layers (thickness 0·3– 0·4 μm) were deposited by pulsed excimer laser at different conditions. Thin films of YBaCuO were deposited on these substrates under the same conditions optimized for films on ZrO_2 substrates. The X-ray diffraction pattern of the ZrO_2 thin films deposited at various conditions is shown in figure 8. The film deposited at the substrate temperature of 25°C (room temperature) is amorphous in nature with small crystalline grains. The improvement in structural quality of ZrO_2 with increase in substrate temperature clearly indicates that high substrate temperature is essential for grain growth and proper stoichiometry. These results were confirmed by IR spectroscopy (see figure 9). The superconducting thin films (thickness $\sim 0{\cdot}7\,\mu$m) were deposited at substrate temperature of 650°C and an oxygen partial pressure of $1-2 \times 10^{-1}$ torr. The low temperature electrical measurements are shown in figure 10. The film deposited on Si without buffer layer showed semiconducting nature with onset at 93 K and a broad transition. The film deposited on buffer layer at room temperature was also semiconducting but T_c was higher than the previous case. However the superconducting films deposited on Si with ZrO_2 at 200°C and 800°C were metallic with T_c of 71 K without post-annealing step. In the case of thicker films of superconductors (1·5–3 μm) T_c was improved to 87 K. The corresponding electrical properties of the films are shown in figure 10(e).

4. Conclusion

Thin films of YBaCuO superconductor were deposited on different substrates which includes c-ZrO_2, c-$SrTiO_3$ and c-MgO and Si (with ZrO_2 buffer layers) by pulsed excimer laser technique. The various process parameters have been optimized to get good quality thin films in single-step process on these substrates. The films have been characterized by small angle XRD and resistivity measurements.

Acknowledgements

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