Reactive deposition of $Y_1Ba_2Cu_3O_{7-x}$ superconductor films by pulsed laser ablation from an unreacted mixture of $Y_2O_3$, $BaCO_3$ and $CuO$

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Abstract. Superconducting thin films of $Y_1Ba_2Cu_3O_{7-x}$ have been deposited on (100) Y–ZrO$_2$ substrates by pulsed excimer laser ablation from an unreacted mixture of $Y_2O_3$, $BaCO_3$ and $CuO$. The films deposited at substrate temperature of 680°C and oxygen partial pressure of 200 mtorr were found to be superconducting with zero resistive transition temperature of 89 K and critical current density of over $3 \times 10^5$ A/cm$^2$ at 77 K. These results are compared with those obtained by laser ablation from a sintered superconducting pellet.

Keywords. Superconductor thin films; laser ablation.

1. Introduction

Pulsed laser ablation has proved to be a successful technique for depositing good quality thin films of high-$T_c$ superconductors (Moorjani et al 1988; Wu et al 1988; Koren et al 1989; Venkatesan et al 1989; Singh and Narayan 1990) and other materials (Koinkar et al 1989; Rashmi et al 1989a, b; Richter 1990). It has been established that this technique can lead to a true transfer of stoichiometry of the target material to the deposited film. However, the precise nature of the process is yet to be well understood. Various studies have been devoted to examine the effects of laser wavelength (Koren et al 1989), laser energy density (Venkatesan et al 1988), deposition angle (Venkatesan et al 1988), substrate temperature (Vispute et al 1991), ambient gas pressure (Inam et al 1988; Ohkubo et al 1989; Singh et al 1989; Ying et al 1989), external field biasing (Witanachchi et al 1988; Singh et al 1989) etc on the ablation process and film quality. Optimum process parameters have thus been identified to obtain high quality superconducting thin films at low temperatures by a totally in situ process.

In all the laser deposition experiments performed to date a single-phase reacted material (e.g. $Y_1Ba_2Cu_3O_{7-x}$ superconducting pellet) was invariably used as a target. There is one report by DeSantolo et al (1988) wherein the unreacted composite target of $Y_2O_3$, $BaF_2$ and $CuO$ materials has been used for superconductor film synthesis. The method involves post-deposition annealing treatment at high temperature which has many disadvantages, such as (i) formation of impurity phases due to chemical reaction between the substrate and film (Wu et al 1987) resulting in loss of stoichiometry of the film material, (ii) formation of unwanted surfaces due to surface evaporation (Dijkkamp et al 1987; Naito et al 1987) and (iii) high temperature thermal cycling leading to crack formation in the YBaCuO film (Hideomi et al 1987) because of mismatch in thermal expansion coefficients of YBaCuO and substrate material. Therefore, high temperature processing for thin film preparation should be avoided.

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In this study we have attempted to deposit Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ superconductor thin films from an unreacted but stoichiometric and homogeneous mixture of Y$_2$O$_3$, BaCO$_3$ and CuO by pulsed excimer laser ablation technique. The focus of this work was to prepare high quality superconducting thin films at low processing temperature by in situ process using unreacted target. It was observed that good quality films can be deposited from such pellets without any post-annealing treatment. This was important for the following reasons: (i) control of microstructural properties of deposited films by varying the target composition becomes easy and it should be possible to deposit metastable forms of oxides which cannot be synthesized by conventional thermodynamic routes (in the case of superconductors this can be useful for deliberate introduction of pinning centres to enhance critical currents ($J_c$)), (ii) ablation from a mixed target is an interesting vaporization problem wherein different optical and thermal properties of individual grains are encountered, and (iii) elimination of single-phase target preparation, which is a critical and time-consuming process, is technologically significant.

2. Experimental

In our experiments, the pellets of unreacted material were prepared by (i) mixing commercially available Y$_2$O$_3$, BaCO$_3$ and CuO powders in stoichiometric proportion (1:2:3) in acetone; (ii) drying the mixture under IR lamp and (iii) pressing the mixture into a pellet form at a pressure of 5 tons/cm$^2$. Such pellets were then heated in air at different temperatures up to a maximum of 700°C for 3 h. These pellets were then characterized by X-ray diffraction (XRD) technique to ensure that no observable reaction of powders occurred. The pellets were then used as targets for laser deposition. A typical pellet was mounted in the deposition chamber which could be evacuated to a base pressure of 1 x 10$^{-7}$ torr. A KrF excimer laser ($\lambda = 248$ nm, pulse width = 20 ns, Lambda Physik) was used for ablation and was made incident on the target surface at an angle of 45°. The energy density at the target was kept at 2 J/cm$^2$ and a pulse repetition rate of 5 Hz was used during deposition. The target was slowly rotated during irradiation to avoid texturing of its surface. The substrates were mounted in front of the target at a distance of 5 cm and were heated to a temperature of 650–700°C. Here the substrate temperature refers to the surface temperature measured by placing a Cr–Al thermocouple on the substrate surface itself. The process parameters used were essentially the same as those optimized for deposition from a single phase superconducting 123 target to obtain good quality superconducting films on Y–ZrO$_2$ (100) substrate (Vispute et al 1991). The deposition rate was about 0.7 Å per pulse and the film thickness deposited was 7000 Å in all cases. The films were characterized by four-probe electrical resistivity measurement. The pattern used for measurement of the critical current density was in the form of 20 x 200 μm microbridge obtained by excimer laser dry etching (Inam et al 1987; Ogale 1991). The films were also characterized by XRD technique using CuK$_\alpha$ radiation. Scanning electron microscopy (SEM) was used for studying the surface morphology of the pellet as well as the superconductor films, whereas energy-dispersive analysis of X-ray (EDAX) measurements was made for determination of elemental composition.