Reactive deposition of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ 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 $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ 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 $3 \times 10^5 \text{ A/cm}^2$ 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. $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ 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 $Y_1Ba_2Cu_3O_{7-x}$ superconductor thin films from an unreacted but stoichiometric and homogeneous mixture of Y_2O_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_2O_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/cm². 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 1×10^{-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/cm² 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–ZrO₂ (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 $20 \times 200 \mu\text{m}$ microbridge obtained by excimer laser dry etching (Inam *et al* 1987; Ogale 1991). The films were also characterized by XRD technique using CuK_α 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.

3. Results and discussion

The XRD spectra of the powder mixture, a pellet prepared from such a mixture at 400°C and a superconducting 123 pellet prepared at high temperature are shown in figures 1a–c respectively. Comparison of these figures shows that the pellets prepared at 400°C are simply composed of unreacted Y_2O_3 , $BaCO_3$ and CuO individual grains and there is no observable solid state reaction except perhaps at the intergrain boundaries. The resistivity data for a 0.7 μm thick superconductor film from the unreacted 123 target (sintered at 400°C) deposited on $Y-ZrO_2$ (100) substrate under optimized process parameters ($T_s = 680^\circ C$ and oxygen partial pressure of 200 mTorr) are shown in figure 2a. The resistivity behaviour reflects a good quality film having T_c of

Figure 1. X-ray diffraction patterns of (a) stoichiometric mixture of Y_2O_3 , $BaCO_3$ and CuO , (b) pellet of unreacted mixture, prepared at 400°C and (c) single phase $Y_1Ba_2Cu_3O_{7-x}$ pellet.

Figure 2. (a) Resistance vs temperature characteristics of $Y_1Ba_2Cu_3O_{7-x}$ film deposited from unreacted pellet. (b) X-ray diffraction pattern of $Y_1Ba_2Cu_3O_{7-x}$ film deposited from unreacted pellet.

89 K and a transition width (ΔT_c) of about 1 K (see inset of figure 2a). This transition width is sharper than the transition width of the films prepared by high temperature post-annealing process reported by DeSantolo *et al* (1988). The critical current density of the film was 3×10^5 A/cm² at 77 K. This is indeed a lower limit because no extra precautions were taken to avoid reduction in J_c due to film edge effects (Tinkham 1975). Similar superconducting properties were also obtained for the films deposited from unreacted pellets prepared at 100°C and 700°C (results not shown). Thus, the temperature factor used to prepare a mechanically stable target does not seem to be very important. Figure 2b shows the XRD pattern of the film deposited from an unreacted pellet prepared at 400°C. Very strong (001) reflections of $Y_1Ba_2Cu_3O_{7-x}$ were observed. This indicated that the film was highly oriented with its *c*-axis normal to the substrate.

SEM micrograph of the superconductor films deposited from an unreacted pellet is shown in figure 3a. In figure 3b we show for comparison the morphology of a film

Figure 3. SEM micrographs of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ film deposited from (a) unreacted pellet and (b) single phase $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ pellet.

prepared from a single-phase superconducting target. The film deposited from a single-phase superconducting pellet (figure 3b) has small particles ($< 0.5 \mu\text{m}$) on a fairly smooth surface with a network of grain boundaries. This is typical for Y-ZrO_2 substrate. The morphology of the film observed in figure 3a is similar to that in figure 3b except for a few large particles of $\sim 1 \mu\text{m}$. These particles are probably due to removal of weakly coupled grains from the unreacted pellet. We feel optimistic that the density of these can be reduced by fine powder synthesis of targets or by use of a lateral laser beam for in-flight vaporization (Korean *et al* 1990). EDAX measurements of the superconductor thin films revealed that the films deposited from 123 single-phase superconducting pellet and the unreacted pellet have the proper composition of Y, Ba and Cu within 2–3% of each other in contrast to the composition variation observed by DeSantolo *et al* (1988). This implies that the low temperature processing conditions significantly affect the superconducting and microstructural properties of the films.

The morphology of the unreacted pellet before and after laser treatment was also examined. The SEM micrograph of the unreacted pellet is shown in figures 4a and 4b. It has powder particles of 1–3 μm diameter. On the other hand, the morphology of laser-irradiated surface (at energy density of 2 J/cm^2 , after few hundred shots), shown in

Figure 4. SEM micrographs of (a) unreacted pellet and (b) laser-processed pellet.

figure 4b shows large smooth structures which reveal a morphology similar to what is observed upon melting and resolidification (Rashmi *et al* 1989b). During this process, there is a possibility of chemical reaction between small grains of Y_2O_3 , $BaCO_3$ and CuO thereby leading to the formation of large grains of the reacted material. We are carefully examining the morphology variation as a function of number of pulses and

laser energy density. Our preliminary data showing an interesting variation will be reported separately. The fact however remains that in the laser deposition technique it is the stoichiometric quantity of ions and neutrals evaporated by the laser deposition that is giving the required stoichiometry in the film irrespective of whether the target material is single-phasic or multiphasic as long as the desired ion composition is maintained in the target.

4. Conclusions

We have shown that high quality high- T_c superconductor thin film can be deposited by an *in situ* laser ablation process involving a target composed of an unreacted mixture of Y_2O_3 , $BaCO_3$ and CuO . The films have properties which compare favourably with those of good quality superconducting films obtained from single-phase superconducting target. In our view, this feature can be used in novel ways in laser deposition experiments for superconductors as well as other material systems.

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