Use of Nd: YAG laser for *in situ* growth of thin films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

D S MISRA, A A C S LOURENCO and S B PALMER

Physics Department, University of Warwick, Coventry CV4 7AL, UK

Abstract. As-deposited superconducting films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with zero resistance at a temperature of ≈ 80 K have been successfully grown using a Nd:YAG laser. A substrate temperature in the range 450–550°C was found most appropriate. The use of a Nd:YAG laser instead of an excimer laser is likely to improve the cost effectiveness of the laser ablation technique.

Keywords. Superconducting thin films; laser ablation; thin films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

1. Introduction

High temperature superconducting materials are a new class of superconductors, previously unknown before the exciting discovery by Bednorz and Muller (1986). The most studied compound of this class of superconductors is $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (popularly known as 123) which shows zero resistance at 92 K. Although the transition temperature (T_c) of 92 K is quite high, the material is not completely free of technological problems. For example, the critical current density (J_c) of the bulk polycrystalline 123 is very poor (of the order of 100–200 A/cm² as compared to 10⁶ A/cm² in single crystals of 123 at 77 K). The low values of J_c are attributed to the presence of weak links in polycrystalline bulk 123, which are the results of high temperatures involved (≈ 930 – 940°C) during reaction and annealing. On the other hand, thin films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ grown epitaxially on SrTiO_3 substrates using laser ablation show J_c s comparable to the single crystals. This is achieved by depositing thin films on hot substrates ($T_s \approx 700^\circ\text{C}$) in the flow of molecular oxygen (Koren *et al* 1989). These films show superconducting behaviour without any post-annealing.

Considerable effort is being made to reduce the deposition temperature further. Thin films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ grown at 550–600°C in the presence of an oxygen plasma using laser ablation technique show superconducting properties comparable to single crystal (Singh *et al* 1989; Witanachchi *et al* 1989). However, all the films deposited so far by laser ablation are grown using excimer lasers which are relatively costly and not always user friendly. Cost effectiveness of the laser ablation technique is reduced further by the fact that one has to spend money periodically on the maintenance of such a laser. It is therefore desirable that the deposition of the films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with comparable superconducting properties to single crystals be achieved using a Nd:YAG laser which is much cheaper and also relatively safe.

2. Experimental

We have designed and fabricated a laser ablation deposition system using a cross-shaped cell made of pyrex glass (see figure 1). A Nd:YAG laser ($\lambda \approx 1.06 \mu\text{m}$, pulse

Figure 1. Apparatus for laser ablation deposition of thin superconducting films. (1, substrate holder; 2, substrate; 3, heater; 4, target; 5, anode (high tension electrode); 6, quartz window; 7, biconvex quartz lens; 8, needle valve for O_2 flow; 9, valve to pump; 10, stainless steel target holder rod; 11, pyrex glass cross).

width ≈ 35 ns and energy range ≈ 200 – 400 mJ) was used for the deposition of the samples. The laser beam was focused using a quartz lens. Target was a sintered pellet of $Y_1Ba_2Cu_3O_{7-\delta}$ held on a stainless steel holder which can be rotated from outside. $SrTiO_3$ substrates (100 orientation) polished to an optical finish, were held on a stainless steel block which can be heated to $\approx 650^\circ\text{C}$. Oxygen was taken near the substrates using a fine capillary tube. A high tension electrode was present in the system to generate a plasma of oxygen to facilitate the growth of the superconducting films at ≈ 450 – 550°C . The distance between the target and substrate was 2 cm.

The surface of the superconducting films was characterized using a scanning electron microscope and the composition determined using energy dispersive X-ray analysis (EDAX) and secondary ion mass spectroscopy (SIMS). Gold contacts were deposited onto the surface of the films for resistance measurements. Resistance was measured as a function of temperature using a conventional dc four-probe technique in an Oxford Instruments continuous flow cryostat. Films were tested for superconductivity in as-deposited form and no post-annealing was done.

3. Results and discussion

We find that the important parameters which lead to the growth of as-deposited superconducting films are substrate temperature (T_s), partial pressure of oxygen (p_{O_2}), repetition rate of laser (f), laser fluence (E) and the cooling procedure. All the films are deposited at $T_s > 450^\circ\text{C}$ and $E \approx 25$ – 30 J/cm². The composition of the film which is a sensitive function of E is similar to the target to within 1–2 at% from EDAX and SIMS measurements. As-deposited films are black, shiny and have a mirror like surface.

Results of superconducting onset temperatures and zero-resistance temperatures of the films deposited at different parameters are summarized in table 1. Films deposited at $T_s \approx 450^\circ\text{C}$, $p_{O_2} \approx 80$ mtorr, $f = 1$ Hz and $E \approx 30$ J/cm² shows semi-

conducting behaviour in the temperature range $300\text{ K} \geq T \geq 60\text{ K}$. Superconducting onset in the above films begins at 50–60 K, yet the zero resistance is not achieved down to 15 K, the lowest temperature of measurement. Increase in T_s and p_{O_2} results in films with onset temperature $\approx 85\text{--}90\text{ K}$ but the zero resistance is achieved only at $\approx 20\text{ K}$ due to the presence of a long low temperature tail. Significant changes take place in the superconducting properties of the films when they are deposited at higher repetition rate (f) of the laser and are fast-cooled. Normalized resistance of

Table 1. Summary of the growth parameters for the deposition of YBCO films using Nd:YAG laser.

Deposition parameters	Nature above onset	T_i (onset) (K)	T_c (zero) (K)
$T_s \approx 450^\circ\text{C}$, $p_{O_2} \approx 50\text{ mtorr}$ $f = 1\text{ Hz}$ and $E \approx 30\text{ J/cm}^2$	Semicond.	50–60	< 15
$T_s \approx 500^\circ\text{C}$, $p_{O_2} \approx 180\text{ mtorr}$ $f = 1\text{ Hz}$ and $E \approx 30\text{ J/cm}^2$	Semicond.	75	20
$T_s \approx 540^\circ\text{C}$, $p_{O_2} \approx 180\text{ mtorr}$ $f = 2\text{ Hz}$ and $E \approx 30\text{ J/cm}^2$	Semicond.	90	12
$T_s \approx 540^\circ\text{C}$, $p_{O_2} \approx 180\text{ mtorr}$ $f = 5\text{ Hz}$ and $E \approx 30\text{ J/cm}^2$	Semicond.	90	65
$T_s \approx 540^\circ\text{C}$, $p_{O_2} \approx 180\text{ mtorr}$ $f = 10\text{ Hz}$ and $E \approx 30\text{ J/cm}^2$ (fast-cooled)	Metallic	90	81

Figure 2. Normalized resistance vs temperature plots of the three films of $Y_1Ba_2Cu_3O_{7-\delta}$ deposited at various repetition rate of laser. Films deposited at 2 Hz and 5 Hz are cooled at $\approx 0.5\text{ K/min}$. Cooling rate for the film deposited at 10 Hz is $\approx 30\text{ K/min}$.

the films deposited at $f = 2$ Hz, 5 Hz and 10 Hz keeping other parameters the same is plotted as a function of temperature in figure 2. Films deposited at 2 Hz and 5 Hz show semiconducting behaviour with their resistance increasing by a factor $\simeq 1.2$ in the temperature range $300\text{ K} \geq T \geq 90\text{ K}$. Onset of superconductivity for both films begins at 90 K, but the film deposited at $f = 5$ Hz has a much sharper transition than that deposited at $f = 2$ Hz. Zero resistance for the film deposited at $f = 5$ Hz is achieved at 65 K as compared to $\simeq 12\text{ K}$ in the one deposited at $f = 2$ Hz. On the other hand the film deposited at 10 Hz shows metallic behaviour above the superconducting onset which begins at 90 K. The superconducting transition is much sharper when compared to those deposited at $f = 2$ Hz and 5 Hz and the zero resistance is achieved at 81 K.

It is interesting to note that as-deposited superconducting films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ can be grown using a Nd:YAG laser. The wavelength of the Nd:YAG laser used in the present work is $1.06\text{ }\mu\text{m}$ corresponding to an energy of $\sim 1\text{ eV}$ as compared to the energy $\sim 5\text{--}10\text{ eV}$ of an excimer laser. The energy of Nd:YAG laser is also much smaller than ionization potential of copper, barium and yttrium. The Nd:YAG laser also may not be strong enough to break the molecular oxygen. This may imply that the mechanism of growth of 'as-deposited' superconducting films using laser ablation is much more complicated than appears at first sight. The influence of repetition rate of the laser on the superconducting properties of the films is also very significant. However, the film deposited at $f = 10$ Hz was also fast-cooled (cooling rate $\simeq 30\text{ K/min}$). Fast cooling may prevent the evaporation of oxygen from the film. Efforts are continuing to optimize the parameters to get films with much sharper transition and higher zero resistance temperature.

4. Conclusion

We have shown that as-deposited superconducting films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ can be grown using a Nd:YAG laser. The superconducting onset temperature and zero resistance temperature are similar to those obtained in the films deposited using excimer lasers. Use of a Nd:YAG laser instead of an excimer laser should improve the cost effectiveness of the laser ablation technique.

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