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In situ growth of $Y_1Ba_2Cu_3O_{7-x}$ superconducting thin films using a pulsed neodymium:yttrium aluminum garnet laser with CO_2 laser heated substrates

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By replacing the resistive heater with a CO_2 laser to heat the substrates together with concentered oxygen stream blowing onto the substrate during deposition, high quality $Y_1Ba_2Cu_3O_{7-x}$ thin films with nearly perfect *c*-axis orientation and $T_{c0} = 87$ K were grown *in situ* without subsequent slow cooling in oxygen atmosphere or any further heat treatment. The rapid quenching, from typically 600 °C to room temperature in less than 50 s of the as-deposited films, excludes the possibility of further oxygen incorporation during the cooling process and indicates that the *in situ* growth may have completed during deposition under proper deposition conditions.

The capability of producing smooth, stoichiometric, and more importantly, *in situ* growth at temperatures compatible with semiconductor technologies, has made the laser ablation method one of the most viable techniques in fabricating high T_c superconducting thin films for electronic applications.[1-11] Parameters such as the input laser energy density, the substrate temperatures, as well as the oxygen partial pressure (P_{O_2}) during deposition and subsequent cooling are the most crucial ones for growing high quality films *in situ*. It is generally agreed that the laser energy density with optimum values of 2–5 J/cm^2 was the key to obtaining the right stoichiometry, since it determines what was contained in the laser plume reaching the substrate.[3-5] The substrate temperature, which determines the mobility of the particles on the surface after reaching the substrate, was usually between 400 and 750 °C, depending on the particular system used. The effects of P_{O_2}, however, are still controversial. In most early reports where, due to the limitations of heater oxidation, lower P_{O_2} was used during deposition, either subsequent heat treatment at lower temperatures ($\approx$400 °C) or slow cooling in oxygen atmosphere was required to obtain superconductivity.[1-11] Recently, with modifications on the substrate heating, the role of P_{O_2} both during deposition and subsequent slow cooling on the morphology and oxygen incorporation processes in the films was investigated extensively.[12-14] However, since all the films were subjected to a relatively slow cooling rate in high P_{O_2}, the effects of P_{O_2} on growth mechanisms during deposition were hidden to some extent.

In this letter, we report a simplified process for the laser ablation technique in which the resistive heater is replaced with a CO_2 laser to heat the substrates. With this modification, the problems of outgassing from the vacuum seal and oxidation of the heating element commonly encountered by using the resistive heater were avoided. Thus, a wide range of P_{O_2} can be accessed during deposition. In addition, instead of near the target, the oxygen was introduced as concentered streams directed onto the substrate *via* a ring-shaped Pyrex tube with equally spaced holes. It was found that after the CO_2 laser was turned off at the completion of deposition, it took less than 50 s for the films to cool down to room temperature. This corresponds to at least a tenfold increase in the cooling rate as compared to the rate for the resistively heated substrate holders. Since the as-quenched films all display better results than films subjected to slow cooling or any further treatment, it seems that the *in situ* growth of these highly oriented films must have been completed during deposition. This result is in contrast to the commonly accepted mechanism[14,15] in that the nonsuperconducting tetragonal phase should form first during deposition at higher temperatures, followed by a tetragonal-to-orthorhombic phase transition due to oxygen intake at an early stage of the cooling process. If this is indeed the case, the rapid quenching, realized by our laser heating and a concentered oxygen stream may provide a unique benefit in producing the correct stoichiometry.

Figure 1 shows the schematic diagram of the system used in the present study. The vacuum chamber is made of a Pyrex/glass tube, 8 and 30 cm in diameter and length, respectively. Prior to deposition, the chamber was first evacuated to a background pressure of about 0.02 Torr by a rotary pump and then back filled to the desired P_{O_2}. The oxygen was introduced *via* several small holes with $\approx$1 mm diameter around a ring-shaped Pyrex tube, which was placed in the middle between the target and the substrate. The holes were arranged such that the oxygen streams were centered at the substrate. In many previous studies the oxygen was introduced near the target in order to get the greatest excitation. However in the present design, since the target-to-substrate distance is only about 3 cm, the excitation effect due to the energetic particles produced by the laser beam should be about the same during their whole travel course. The recombination effect due to the higher P_{O_2} used may become important, and we felt that it was more beneficial to have the excitation take place near the substrate surface in order to enhance the oxygen incorporation during deposition.

The laser beam used was a frequency-doubled neodymium: yttrium aluminum garnet (Nd:YAG) laser, 532 nm in wavelength, 20 ns in pulse width, 70 mJ per pulse, and

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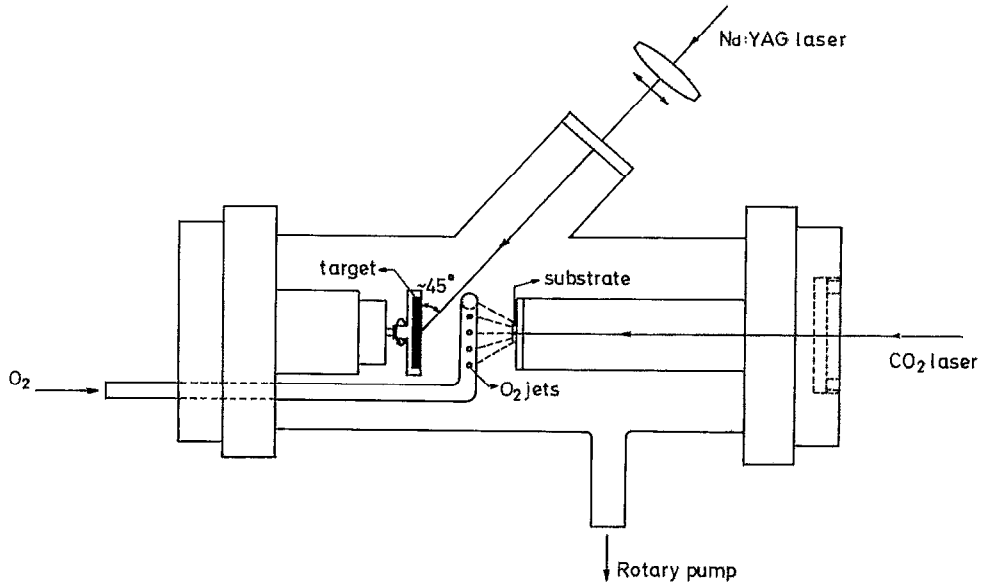

FIG. 1. Schematic diagram for the deposition system used in the present work. Notice that the substrate is heated by a CO_2 laser and the oxygen streams are concentered on the substrate *via* a ring-shaped pyrex tube.

10 Hz repetition rate. The beam was focused through an anti-reflection (AR) coated window on the target at an incidence angle of 45°. The area of the elliptical spot was about 3 mm^2 and the energy density estimated was about 2.5 J/cm^2. The holder of the focus lens can also be translated off the optical axis to focus the spot on a different part of the target. The target was a 2-mm-thick, 2.2-cm-diam disk, of bulk $Y_1Ba_2Cu_3O_{7-x}$ prepared by solid-state reaction and had a T_{c0} of 88 K. It was rotated by a dc motor with a speed of 2 500 rpm ($\cong$ 40 Hz) to maintain uniform ablation as well as to reduce the splashing of microscopic particulates on the substrate.[16]

Both resistive heater and CO_2 laser were used to heat the substrates in the present study. The Ni-Cr-Fe wire was wrapped around a ceramic rod to form the resistive heater. A metallic block was used as substrate holder in this case. However, due to outgassing and oxidation problems as commonly encountered by using a resistive heater, the resulting films all had relatively lower T_c's, and degraded superconducting properties. As an alternative, a homemade CO_2 laser (cw) with a maximum output power of 80 W was used to heat the substrate. The laser beam was directed through an AR-coated ZnSe window (see Fig. 1) and focused onto a 2-mm-thick quartz plate with a beam diameter of about 12 mm, which virtually covered the whole quartz plate to obtain a uniform heating. The substrates [both $SrTiO_3(100)$ and $MgO(100)$ single crystals] were then attached to the quartz plate using a high heat conducting ceramic cement. Temperatures were measured either on the metallic block or on the quartz plate by a thermocouple placed near the substrates. In addition to the lower power requirement, there were several significant features with the use of the CO_2 laser. Besides the simpler structure, the vacuum chamber was found to be cleaner, mainly due to the elimination of outgassing and heater oxidation. The cooling rate after deposition was also higher. Typically, it took only about 50 s by the laser heating method, whereas it took 8–10 min for the resistive heating sources to cool down to near room temperature.

With the modifications in the deposition systems described above, several deposition parameters, namely the substrate temperature, the substrate materials, the energy fluences, the oxygen partial pressure during deposition, and the cooling rate after deposition were investigated. The optimum conditions for P_{O_2} and the laser energy density to produce the best results were 0.2 Torr[17] and 2.5 J/cm^2, respectively. For the MgO substrate, only the measured substrate temperatures between 500 and 600 °C gave superconducting as-deposited films, and films deposited at 550 °C showed the best T_{c0}, around 82 K. At temperatures above 600 °C, all the films on MgO substrates showed semiconducting behavior, presumably because the interactions between the substrate and the depositing materials became more pronounced at these higher temperatures. For $SrTiO_3$ substrates, the substrate temperature that gives the best results was 650 °C with $T_{c0} \simeq$ 87 K, which is comparable to the best results obtained by any other processes. Figure 2 shows two of the temperature dependent resistance [$R(T)$] curves for typical films deposited on different substrates

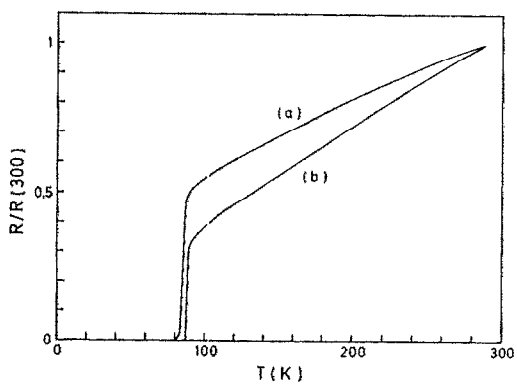

FIG. 2. Typical $R(T)$ curves for films deposited on (a) $MgO(100)$ at 550 °C and (b) on $SrTiO_3(100)$ at 650 °C. The resistances were normalized to that of room temperature ones. The linearity of curve (b) in $R(T)$ for $T > T_c$ and the extrapolation for $R(T)$ to $R \simeq 0$ at $T = 0$, indicates the high quality of film (b).

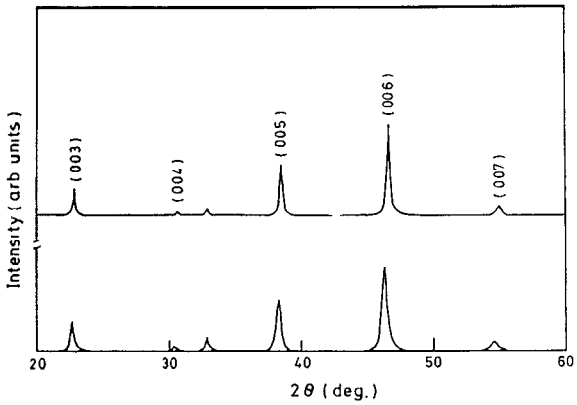

FIG. 3. Typical θ-2θ x-ray diffraction patterns for films deposited on MgO (bottom) and on $SrTiO_3$ (top) substrates, showing the highly c-axis oriented nature of these laser-ablated YBCO films. Notice that the diffraction peaks for the substrates were substracted from the pattern by an installed software and are not shown in the figure.

under the optimum conditions described above. The films on $SrTiO_3$, in particular, shows a linear $R(T)$ for $T > T_c$ that extrapolated to nearly $R = 0$ at $T = 0$, indicating the good quality of these films. It is interesting to note that any further annealing treatments and/or slow cooling processes that we used to try to incorporate more oxygen turned out to be unnecessary or even harmful. Figure 3 shows two examples of x-ray diffraction patterns taken by the usual θ-2θ scan. As can be seen from the pattern, films produced by the present method all show strong preferred growth orientation with the c axis oriented normal to the substrate surface, as usually observed. All these results demonstrate the feasibility of using the simpler design presented in this letter to fabricate high quality films.

We now give a brief discussion on the possible mechanism for the *in situ* growth of the films. Perhaps the main differences for our system as compared to others[1–15] were the rapid cooling rate realized by using laser heating and direct blowing of the concentered oxygen on the substrate immediately after deposition, as well as introducing the oxygen right on the substrate surface instead of near the target. It has been pointed out that only the tetragonal phase can be formed *in situ* for films deposited at relatively low P_{O_2} due to the outdiffusion of oxygen at the substrate temperatures used.[12,14,15] Recently, several groups have raised the P_{O_2} to the range used in the present study, and found that P_{O_2} does have strong influences on both the film morphology[13] and the oxygen content[12,14] in the resulting films. The generally accepted film formation process to date is that the tetragonal phase forms during deposition even at the early stage of cooling due to the rapid oxygen in-diffusion at temperatures above 400 °C. A rough estimate using the diffusion constant of about 5×10^{-14} cm^2/s taken from the literature, however, yields a time much longer than the cooling rate measured.[14] Although possibilities such as the misoriented grain boundaries and various types of defects may improve the agreement between this model and the measured oxygen contents, it seems inadequate to provide a reasonable explanation for our case, in that the cooling rate was more than an order of magnitude higher. As has been suggested by Ying *et al.*,[15] it is possible to have the superconducting orthorhombic phase form directly provided that the oxygen out-diffusion could be suppressed, or at sufficiently high P_{O_2}. Considering our high P_{O_2}[17] and the arrangement of oxygen streams used, it seems that, at least in our case, the superconducting phase was formed *in situ* during deposition with virtually correct stoichiometry.

In summary, we have made a series of studies to obtain optimum deposition parameters in a modified laser ablation process which gives high quality superconducting films *in situ*. The high P_{O_2} possible by using a CO_2 laser to heat the substrates allows the superconducting phase to form *in situ* during deposition. The simplicity and effectiveness of the present technique in fabricating high quality films may also have important implications in technological applications.

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[16] J. T. Cheung and H. Sankur, CRC Crit. Rev. Solid State Mater. Science **15**, 63(1988). In this article it has been demonstrated that about 50% of the particulates can be removed from the substrate with a target rotation speed of 100 Hz in a similar laser ablation process.
[17] The pressure was measured as the average value in the chamber. Due to the special arrangement in the present system, the P_{O_2} is considered to be higher right around the substrate.