Production of $YBa_2Cu_3O_{7-y}$ superconducting thin films *in situ* by high-pressure reactive evaporation and rapid thermal annealing

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A high-pressure reactive evaporation process has been used to produce smooth $YBa_2Cu_3O_{7-y}$ high T_c superconducting films without the necessity of a post-deposition oven anneal cycle. Augmented in some cases by rapid thermal annealing, the process has yielded films with zero resistance transition temperatures above 80 K, and critical current densities above 10^6 A/cm^2 at 4.2 K on both cubic zirconia and $SrTiO_3$ substrates.

Since the discovery of the new high T_c superconductor $YBa_2Cu_3O_{7-y}$ (hereafter referred to as YBCO)[1] there has been considerable progress in the production of thin films of this new material. Both reactive evaporation and reactive sputtering have been found to be capable of yielding films with relatively high transition temperatures and narrow transition widths.[2,3] With the use of $SrTiO_3$ substrates highly oriented growth of polycrystalline YBCO films has been obtained which has resulted in a marked increase in the critical current density that can be achieved in this material.[2] But to date all successful film growth techniques that have been reported have required a significant post-growth oxygen oven anneal cycle to form the metallic, superconducting phase of this ceramic system. The necessity of such annealing places a considerable burden on the processing of high T_c superconducting films for electronics applications, certainly on the possible formation of high T_c Josephson junctions. Moreover, extensive high-temperature anneal cycles exacerbates the problem of substrate-film interactions owing to the high reactivity of the high T_c ceramic. The development of a successful procedure for the relatively low-temperature growth of YBCO films that does not require a subsequent high-temperature oven anneal and that is capable of yielding high J_c values with substrates other than $SrTiO_3$ is a necessary next step in high T_c thin-film research and development.

Here we report on preliminary results from high-pressure reactive evaporation (HPRE) that demonstrate the feasibility of the deposition and *in situ* growth of the superconducting phase in high quality YBCO films on both $SrTiO_3$ and cubic zirconia substrates. We also describe the successful application of rapid thermal annealing (RTA) either for further improving films that are already superconducting or for replacing the oven anneal process for films that are not deposited in the superconducting phase. Together these results provide a new avenue for research leading to a successful high T_c thin-film technology.

Films were prepared on Al_2O_3, ZrO_2 (stabilized with 9.5% Y), or $SrTiO_3$ substrates at 400 or 700 °C by multiple source evaporation in an oxygen ambient. The three individual deposition rates (Y, Ba, and Cu) were monitored with three separate quartz crystal monitors, each with line of sight exposure to only one of the evaporation sources. Y and Ba were evaporated from two electron beam evaporators with feedback from the crystal monitors for rate control. Cu was deposited from a manually controlled thermal source. The total film growth rate was ~4.5 Å/s, with the individual rates controlled to yield the desired 1:2:3 composition.

The oxygen pressure was controlled to maintain a constant pressure of 0.65–1.0 mTorr. At this pressure the atomic mean free path is ~8 cm, so material is deposited on surfaces without line of sight exposure to the evaporation sources. Thus, the quartz crystal monitors were found to be not completely independent, the worst case being that 25% of the measured Cu rate was due to Y and Ba. This effect was predictable, however, and could be accommodated. In some cases, in an attempt to increase the oxygen content of the film, the chamber was backfilled with oxygen to 1 Torr while the film cooled. Typical elapsed time in cooling from 700 to below 200 °C was about 20 min.

After deposition, films which did not show good superconducting properties, as measured by room-temperature resistivity and transition temperature measurements, were annealed by a rapid thermal process in flowing oxygen. The substrate was placed on a silicon wafer in a quartz enclosure and illuminated with high-power lamps, bringing the film to an elevated temperature within 5 s. After 1–5 min at 700–900 °C the film was cooled to less than 200 °C in 3–5 min.

The films were characterized with four-probe resistivity measurements, Rutherford backscattering (RBS) analysis, and scanning and transmission electron microscopy. We defined the transition temperature T_c to be the temperature at which the superconducting resistive transition was complete, and ΔT_c to be the difference in temperature from 10% to 90% of the resistivity at the onset of superconductivity. Several of the better films were patterned with conventional photolithographic methods and etched with dilute nitric acid to produce a 100-μm line with a 20-μm width constriction for critical current and current-voltage (I-V) measurements.

Typical resistivity versus temperature data are shown in Fig. 1. None of the films grown on Al_2O_3 showed a superconducting transition as deposited, the best films exhibiting a room-temperature resistivity ρ_{RT} of 40–400 mΩ cm. After a conventional furnace anneal at 750–850 °C with a long (3–6 h) cooling time the films showed a wide transition (~30 K) reaching zero resistance at 55–60 K. Similar results were obtained with 2–5 min RTA's at 750–850 °C, with longer anneals having no further effect on the room-temperature resistivity. Higher temperature RTA's (> 875 °C) degraded

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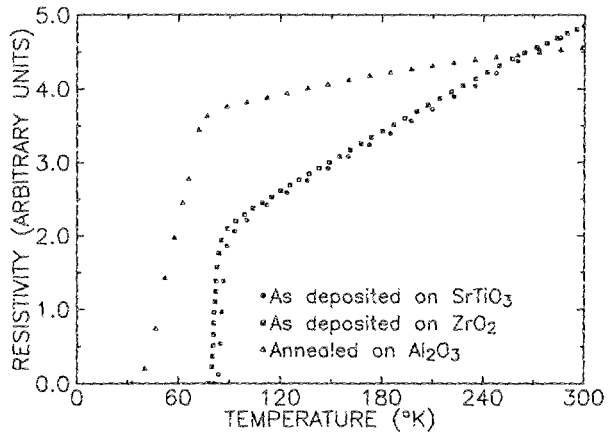

FIG. 1. Typical resistivity vs temperature measurements for films grown on Al_2O_3, Y-stabilized ZrO_2, and $SrTiO_3$. The film on Al_2O_3 was rapidly thermal annealed.

the superconducting transition. We believe the poor quality of the films on Al_2O_3 is due to reaction of the substrate with the film, as indicated by the RBS analyses in Fig. 2(a). The as-deposited films show very little or no interdiffusion of the

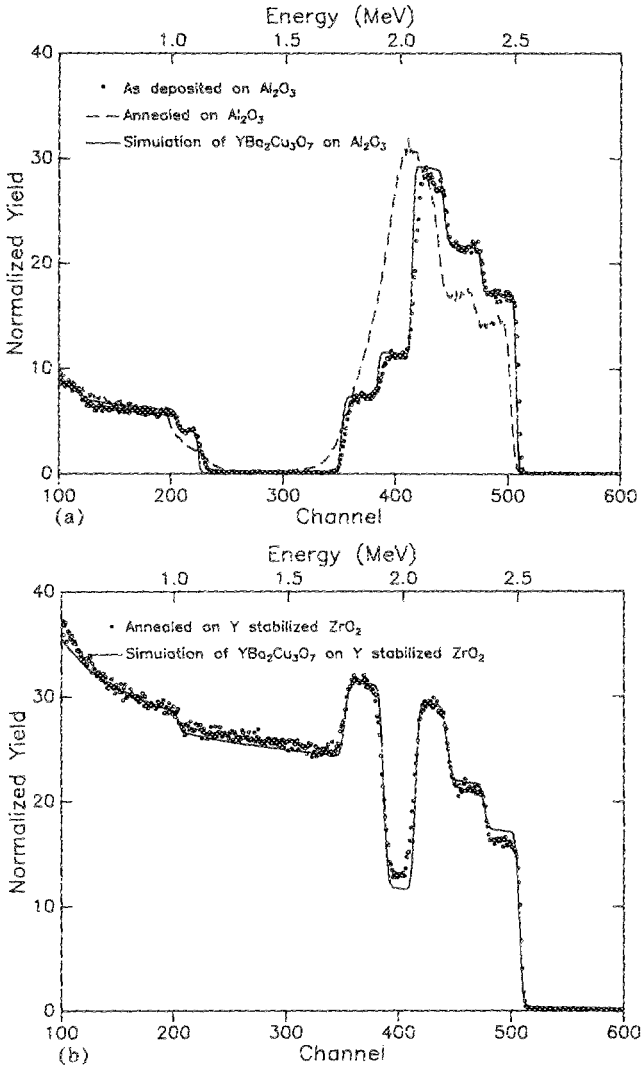

FIG. 2. Typical RBS data (a) film grown on Al_2O_3 before and after RTA, (b) film grown on ZrO_2 after a RTA at 800 °C for 2 min.

Al into the film, while the annealed films have substantial interdiffusion.

On ZrO_2 (stabilized with 9.5% Y) or $SrTiO_3$ substrates films showing good superconducting transitions could be grown without a post-deposition anneal as shown in Fig. 1. When the deposition chamber was backfilled with 1 Torr of oxygen while the film cooled, the films produced on Y-stabilized ZrO_2 had typical T_c's of 77–79 K, ΔT_c of 2–4 K, and ρ_{RT} of 0.5–3 mΩ cm. On $SrTiO_3$ a film with $T_c = 81$ K, $\Delta T_c = 4$ K, and $\rho_{RT} = 2.5$ mΩ cm was obtained. When the backfill was not performed but the oxygen pressure was held at the deposition pressure of 0.65 mTorr while the film cooled, the resulting film still exhibited a superconducting transition, although it was a poor one. The transition width and room-temperature resistivity were both relatively large, 30 K and 4.5 mΩ cm, respectively. This indicates that while the proper phase was being grown, the oxygen content of the resultant film was low. This film was annealed at 800 °C for 2 min with the rapid thermal process, which improved the transition temperature to 81 K and the width to 3 K. These values are typical of the films produced with a backfill, indicating that both the backfill to 1 Torr while the film cooled and RTA are equally effective at introducing a suitable amount of oxygen into the film. Figure 2(b) shows the RBS results for a 1-μm YBCO film on zirconia. The quality of the film and lack of substrate reaction is evident.

Films showing good transitions as deposited were also annealed in an attempt to further improve the superconducting properties. Typically, a 2-min anneal at 750–850 °C improved T_c by about 2 K and decreased the room-temperature resistivity by 20–60%. If the film started with a slightly wide transition (4 K) the anneal would improve it to about 2.5 K, although no further improvement was observed in films which began with transition widths of 2–3 K. More significantly, the contact resistance was usually improved by at least a factor of 4 by any rapid thermal anneal. This suggests that the surface of the film and the grain boundaries are either oxygen deficient or off stoichiometry as deposited, but are improved by the annealing process.

An as deposited, unannealed film on $SrTiO_3$ was thinned and examined with transmission electron microscopy.[4] Electron diffraction showed that the c axis was predominantly parallel to the plane of the film with the (110) axis also in the plane of the film. Figure 3 is a transmission electron image showing rectangular grains, ~100 by 500 nm in size, with the a-b planes evident. Adjacent grains often have their c axes perpendicular, so the properties of these films will not exhibit the anisotropies expected of a film with a preferred c axis orientation. In contrast, selected area diffraction of an annealed film on ZrO_2 revealed two distinct types of regions. One has irregular 1 μm sized grains with the c axis perpendicular to the film, the other has rectangular grains with either the a or b axis perpendicular. Differing results reported by other groups[2,3] indicate that the film orientation is very process dependent, so further investigation could produce *in situ* films with a preferred c axis orientation normal to the film.

The temperature dependence of the directly measured critical current density J_c of a patterned YBCO film on both

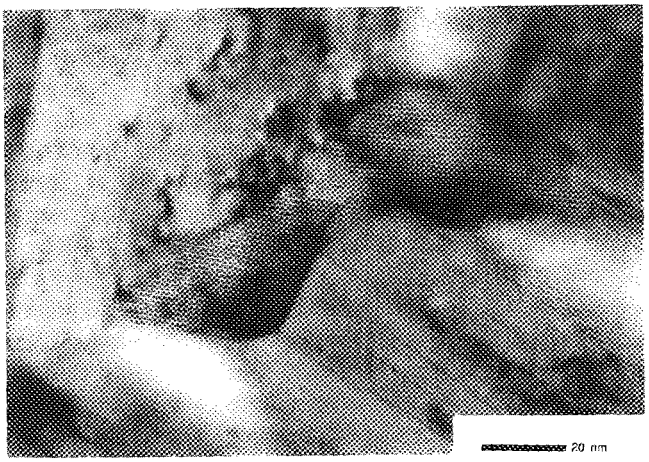

FIG. 3. TEM image of YBCO film grown on $SrTiO_3$, courtesy of B. C. De Cooman and C. B. Carter.

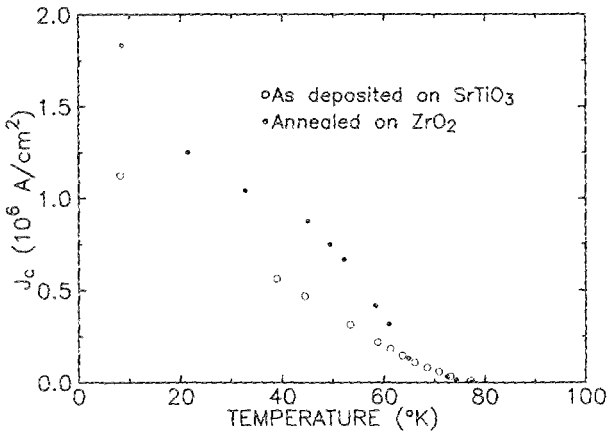

FIG. 4. Critical current measurements from YBCO films on cubic zirconia and $SrTiO_3$.

a $SrTiO_3$ and a ZrO_2 substrate is shown in Fig. 4. Because of the somewhat depressed value of T_c in these films the measured J_c at 77 K is low, but it rises quasi-linearly to $J_c \sim 10^6$ A/cm^2 at 4.2 K for both films. Note that the two different substrates yield similar results, with the measured J_c for the film on ZrO_2 being slightly higher. The temperature dependence of J_c is not as predicted from conventional superconductivity theory, and this serves to further establish that here J_c is still limited by weak coupling between superconducting regions. The measured temperature dependence is similar to the indirectly measured J_c results reported earlier on YBCO films on $SrTiO_3$ which had a predominate c-axis orientation normal to the substrate.[2]

The depressed T_c values and the temperature dependence of J_c of the films grown by HPRE indicate that the films are as yet still somewhat inhomogeneous or lack the optimum oxygen stoichiometry. RBS analysis has indicated that, in some instances, Y:Ba:Cu ratios have been obtained that are within a few percent of the desired 1:2:3 value. Of course fluctuations in the deposition rates could lead to local variations in this composition and even minute amounts of secondary phases at grain boundaries could be significant here. Less than ideal oxygen stoichiometry or variation in the oxygen content through the film are also possible sources of the reduced T_c.

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