Growth of high T_c superconducting thin films using molecular beam epitaxy techniques

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(Received 3 August 1987; accepted for publication 24 August 1987)

Thin films of the high-temperature superconductor $DyBa_2Cu_3O_{7-x}$ have been grown on $SrTiO_3$ substrates using molecular beam epitaxy techniques. Reflection high-energy electron diffraction patterns observed during deposition indicate incomplete oxidation of copper and growth of oriented metallic copper microcrystals in a matrix of amorphous barium and dysprosium oxides. After post-growth anneal the films exhibited sharp superconducting transitions with zero resistance observed as high as 89 K and critical current densities of 4.8×10^5 A/cm^2 at 4.2 K and 3.9×10^4 A/cm^2 at 77 K.

Since the discovery of high T_c superconducting perovskites,[1,2] enormous progress has been made toward a better understanding of the fundamental properties of these materials as sample quality has improved. Most of the work on the 90 K superconductors has focused on bulk samples of $YBa_2Cu_3O_{7-x}$, although various groups[3,4] have shown that substitution of certain rare earth atoms in place of Y in the 1:2:3 structure does not alter the superconducting properties. We have grown thin films of $DyBa_2Cu_3O_{7-x}$ (DBCO), using molecular beam epitaxy (MBE) techniques, that are highly oriented and exhibit sharp transitions and critical current densities comparable to the best reported to date.[5-7] Although these films must be annealed at high temperatures in oxygen to form the superconducting phase, our low growth rate in conjunction with *in situ* reflection high-energy electron diffraction (RHEED) provides a unique opportunity to study the nucleation of the film on the substrate which may prove extremely important in determining the final film properties.

The films reported here were grown in a modified Varian 360 MBE system. Standard MBE furnaces were used to provide beams of copper, barium, and dysprosium; their fluxes were measured by rotating an ionization gauge into the growth position and monitoring each cell's beam equivalent pressure individually. Flux stability was adequate to provide compositional control to within one percent. After growth, measurements of average film composition were made using electron microprobe; this provided a calibration of beam equivalent pressure ratios measured with the ionization gauge. Oxygen was introduced near the growing film by means of a precision leak valve which metered the flow of oxygen from an atmospheric pressure manifold into a tube that terminated several inches from the substrate station. The oxygen beam was stable to about ten percent over several hours. The system vacuum was maintained by a turbomolecular pump. The machine also included a RHEED system for *in situ* growth diagnostics.

We have grown, in increasing order of success, films on {100} Si, $\{1\bar{1}02\}$ sapphire, {100} yttria stabilized cubic ZrO_2, and {100} $SrTiO_3$. These were chosen to give approximate lattice matching. No superconductivity was observed on Si and a highest zero resistance temperature of 89 K was achieved on $SrTiO_3$. The three runs described here (VSC062,63,64) were all done on $SrTiO_3$ and utilized similar growth conditions: the O_2 pressure was about 7×10^{-6} Torr at the substrate position and the substrate temperature ranged from 600 to 750 °C, as indicated by a thermocouple in contact with a molybdenum block to which the substrate was bonded. A growth rate of approximately 0.64 Å/s was utilized, the final film thicknesses being about 1 μm.

Figure 1 includes a sequence of RHEED photographs for VSC064. In Fig. 1(a) we show the RHEED pattern of the substrate prior to growth, exhibiting streaks characteristic of a smooth surface. The electron beam is incident along a ⟨100⟩ azimuth. The presence of Kikuchi lines is indicative of good surface quality and the 1/2 order streaks indicate a 2-fold surface reconstruction. Figure 1(c) shows the pattern 2 min after the beginning of the growth; the streaks essentially have disappeared, having been replaced by a spot pattern characteristic of a rougher surface but also showing preferred orientations for the growing film. Figure 1(b) shows a much later point in the growth of VSC064—about 2/3 of the total time. The sharp spots are replaced by broken rings indicating some registry of the film to the substrate as well as the presence of large amounts of randomly oriented polycrystalline material.

The RHEED patterns provide information about the nature of the growth occurring. Identification of the spots as due to diffraction from crystalline DBCO is not consistent with its known structure; the spacing inferred from spots labeled "A" in Fig. 1(c) is about 5% smaller than that of DBCO. It is, however, consistent with the lattice constant of metallic copper. Furthermore, spots "B" are spaced by a factor of $\sqrt{2}$ more than spots A, suggesting that the RHEED pattern contains a superposition of ⟨100⟩* and ⟨110⟩* reciprocal lattice vectors.

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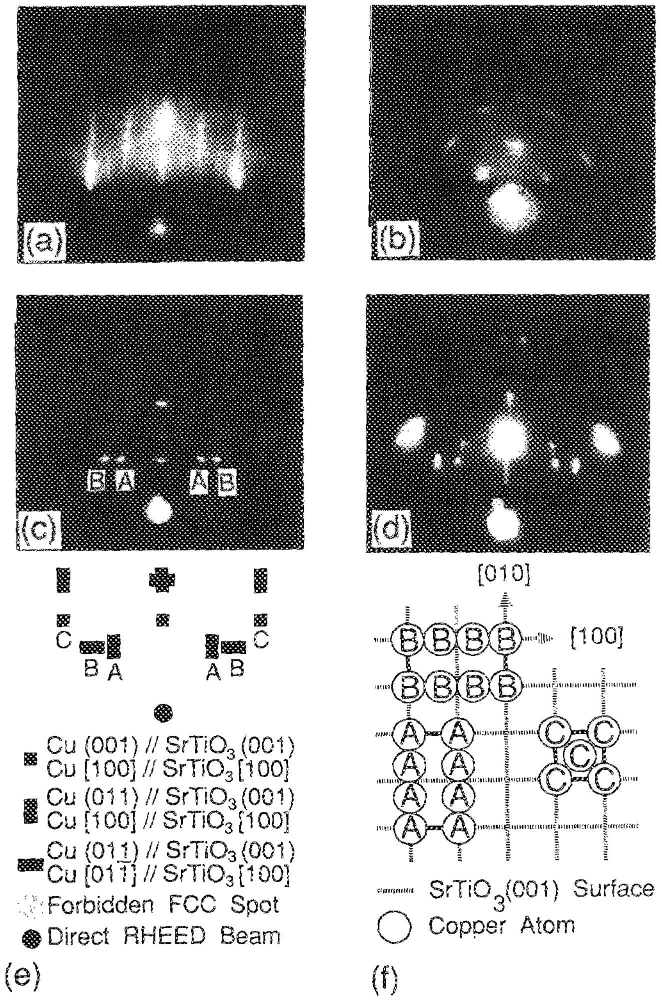

FIG. 1 RHEED pattern observed on [100] azimuth (a) from clean $SrTiO_3$ (001) prior to growth, (b) after ~6000 Å growth of DBCO, (c) after 80 Å of growth of DBCO, (d) after ~100 Å of growth of Cu film on $SrTiO_3$. (e) Calculated RHEED pattern, same azimuth, for epitaxial growth of Cu on $SrTiO_3$ (001) for the three configurations shown in (f).

To check this hypothesis, we deposited copper alone onto a $SrTiO_3$ {100} substrate at 600 °C. Analysis of the RHEED pattern, Fig. 1(d), indicated that the copper was depositing primarily with {100} and {110} planes parallel to the interface. Copper deposited in the presence of an oxygen flux yielded similar results. The brightest spots in the initial RHEED pattern of DBCO films, Fig. 1(c), are identical to the spots corresponding to Cu{110} on $SrTiO_3${100}, seen in Fig. 1(d) and illustrated in Figs. 1(e) and 1(f). The Cu⟨100⟩ mismatch is 7.4% while the 3:2 matching shown for the Cu⟨100⟩ direction gives a mismatch of 1.8%. This results in the lowest observed areal lattice mismatch of low index Cu planes to the $SrTiO_3$ substrates. Figures 1(c) and 1(d) also show spots indicating the growth of Cu{100} on $SrTiO_3${100}. The differing relative intensities of the spots reflect the detailed distribution of grain orientations obtained under the two growth conditions.

Both the general correspondence of the observed RHEED patterns as well as a detailed explanation of the observed spots indicate the growth of metallic copper. We conclude that deposition under the conditions described here does not lead to oxidized copper but presumably to small island growth of metallic copper in a matrix of amorphous Ba and Dy oxides. It would appear that a significant reason for the requirement for an extended oxygen anneal cycle to convert the films to the proper phase is the relative inertness and segregation of copper in the film.

Further confirmation of island growth of copper came from *in situ* Auger spectroscopy of the copper film deposited on $SrTiO_3$. A total of 150 Å was deposited which, assuming an escape depth for ~450 eV electrons from the substrate material through copper of ~15 Å, should in the case of a uniform film lead to attenuation of the Auger peaks by a factor $\sim 2\times 10^4$. The observed attenuation of ~4 indicates the coverage was not uniform. Of course the nucleation conditions may be altered in the case of co-deposited films, but the Auger data do provide support for the inference drawn from the RHEED observations.

The DBCO films as grown are not superconducting and are unstable in air. After an initial 6-h anneal at 650 °C in flowing oxygen, x-ray diffraction studies show that there is no 1-2-3 phase or metallic copper present. The films are subsequently annealed at 750 °C for 1 h, then 850 °C for 1 h.[5] Both x-ray diffraction and resistive measurements indicate that the 1-2-3 superconducting phase does not form until the final high-temperature heat treatment.

The resistive transitions were measured using the four-point technique with silver paint contacts and low current densities. In all cases where the composition was close to being stoichiometric and the growth was on $SrTiO_3$, the samples had sharp transitions with onsets of 92–88 K and normal state resistivities decreasing linearly with temperature as shown in Fig. 2.

A more sensitive test of film quality is the critical current density. Magnetization hysteresis loops have been measured in a vibrating sample magnetometer in fields up to 15 kOe. We use the Bean formula to obtain the average critical current density: $J_c = 30M(H)/R$, where R is the average radius of the sample (in cm) and $M(H) = \Delta M(H)/2$ is half the change in magnetization across the hysteresis loop (in emu/cm) for fields perpendicular to the plane of the sample. Our best film, sample VSC064, has a J_c at 3 kOe of 4.8×10^5 A/cm^2 at 4.2 K and 3.9×10^4 A/cm^2 at 77 K. Sample VSC062 has a slightly lower J_c, while that of VSC063 is

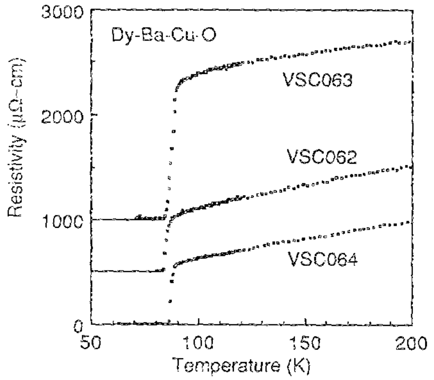

FIG. 2. Resistivity vs temperature for VSC062, 063, 064. Data from VSC062, 063 have been displaced upward for clarity.

TABLE I. Summary of superconducting thin-film properties.

Sample No.	$T_{\text{substrate}}$ (°C)	Composition[a]	Orientation ⊥ to film	T_c (10%–90%) (K)	J_c at[b] $H_\perp = 3$ kOe
062	650–600	$Dy_{17}Ba_{37}Cu_{46}$	$a,b > c$	88–84	3.1×10^5 at 4.2 K 2.2×10^4 at 77 K
063	740	$Dy_{16}Ba_{34}Cu_{50}$	$a,b > c$	91–88	7.7×10^4 at 4.2 K
064	600–640	$Dy_{18}Ba_{34}Cu_{48}$	$a,b \gg c$	92–89	4.8×10^5 at 4.2 K 3.9×10^4 at 77 K

[a] Electron microprobe.

[b] 20% uncertainty.

lower by an order of magnitude (see Table I). It is also interesting to note that the magnetization density is a factor of 30 lower for all three samples when the field is in the plane of the sample.

The difference between these three samples is seen more clearly when we examine the x-ray diffraction data. All three samples are highly oriented, but have differing preferred grain orientations relative to the substrate. The thin film in sample VSC064 shows strongly preferred *a*- or *b*-axis grains perpendicular to the plane to the film (the long axis, *c* in the plane of the substrate), with some *c*-axis oriented grains, as well as a small amount of random orientation. Samples VSC062 and VSC063 show more *a* or *b* orientation than *c* orientation, but not nearly as much as sample VSC064. A small amount of random orientation also exists in VSC063, while VSC062 shows none. Furthermore, in the plane of the film all three samples have the oriented grains aligned both along the (100) axes of $SrTiO_3$ as well as along the (110) axes. Each film has $BaCuO_2$ as an impurity phase, although in VSC062 and VSC064 it appears in trace amounts, while VSC063 shows much more. This could explain the low J_c found in VSC063, presumably due to $BaCuO_2$ at grain boundaries. These results indicate that the average critical current density is not only dependent on the degree of crystallographic orientation of the 1-2-3 phase,[6] but also the presence of small amounts of impurity phase in the films as well.

In conclusion, then, we have successfully grown high T_c superconducting thin films in a MBE system with properties comparable to the best reported to date. In addition, we have investigated by RHEED the initial stages of the deposition in the temperature range 600–750 °C and have shown that copper does not oxidize during growth under the conditions we have employed but rather forms islands of metallic copper in an amorphous matrix of oxides of Dy and Ba. The copper, however, is oxidized after an extended 650 °C anneal in flowing O_2, and after even higher temperature anneal steps the proper superconducting phase forms.

We gratefully acknowledge numerous illuminating discussions with the entire Stanford high T_c group, as well as those with R. Barton on the x-ray studies, and the able technical assistance of Y. Desai and H. A. Luong. This work was supported in part through National Science Foundation–Material Research Laboratory at the Center for Materials Research at Stanford and the Joint Services Electronics program through contract number DAAG29-84-K0047. ESH acknowledges the support of an IBM fellowship and DGS acknowledges the support of a Semiconductor Research Corporation fellowship.

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