

Structural and superconducting properties of orientation-ordered $Y_1Ba_2Cu_3O_{7-x}$ films prepared by molecular-beam epitaxy

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Superconducting $Y_1Ba_2Cu_3O_{7-x}$ films were produced by metal molecular-beam epitaxy with one electron beam and two thermal cells and a molecular oxygen-gas source. The films were epitaxially grown on $SrTiO_3(100)$ with an a -axis orientation perpendicular to the plane, and b and c axes ordered in the plane. A sharp resistive superconducting transition with $T_c(R=0)$ at 82 K was obtained. A lower limit of the average J_c in the plane is 10^3 A/cm² at 77 K, 5×10^4 A/cm² at 70 K, and 10^6 A/cm² at 4.2 K.

The advances in high-temperature superconductivity have progressed at an unprecedented pace in the past six months since the first discovery of T_c over 30 K in $La_{2-x}Ba_xCuO_{4-\delta}$ by Bednorz and Müller.¹ The attainment of superconductivity at 90 K in the Y-Ba-Cu-O system,² and later the identification of $Y_1Ba_2Cu_3O_{7-x}$ as the superconducting phase,³⁻⁵ are of immense importance in both science and technology. The superconducting oxide crystals prepared in thin-film form are vital for fundamental physical studies as well as for device applications. Recently several groups have succeeded in producing Y-Ba-Cu-O films with full superconductivity above 77 K using electron-beam coevaporation,^{6,7} or sputtering.⁸

In this work, we report properties of $Y_1Ba_2Cu_3O_{7-x}$ films prepared by molecular-beam epitaxy (MBE). The films are epitaxially grown on a $SrTiO_3(100)$ face. The orientation is the a axis perpendicular to the film plane, with the b and c axes ordered in the plane. Sharp superconducting resistive transitions with $T_c(R=0)$ above 77 K have been reproducibly achieved. A lower limit of the critical current density is 10^3 A/cm² at 77 K, 5×10^4 A/cm² at 70 K, and $\sim 10^6$ A/cm² at 4.2 K.

The superconducting films were prepared by the metal molecular-beam-epitaxy technique in a versatile ultra-high-vacuum deposition system previously used for producing rare-earth superlattices.^{9,10} The films reported here were made by thermal coevaporation from three separate sources simultaneously; Y from an electron-beam-heated evaporator, and Ba and Cu from the effusion cells. The deposition rate of each element was individually monitored and adjusted to yield the correct stoichiometry in the film. The oxygen was incorporated in the film during growth by introducing oxygen flow from a tube near the substrate. The O_2 flux is measured by an adjacent bare ion gauge, which can be rotated into the position aiming toward the outlet of the oxygen stream. Typical oxygen partial pressure near the substrate is 10^{-5} Torr, and is about one order of magnitude higher than the required O_2 flux at an oxide growth rate of 1.0 Å/sec. The background pressure is less than 2×10^{-10} Torr prior to O_2 doping, and is maintained at a low 10^{-7} Torr during growth. The growth temperature was varied from room temperature to 450°C. For most depositions it is kept at

$400 \pm 50^\circ C$. The film thickness is generally 9000 Å.

The substrates used in this study are primarily single-crystal $SrTiO_3(100)$. Earlier work showed that epitaxial single-crystal films of perovskite $Ba(Pb_{1-x}Bi_x)_3O_x$ were achieved by deposition on $SrTiO_3(100)$.¹¹ More recently, highly oriented $La_{1-x}Sr_xCuO_{4-\delta}$,¹² and $Y_1Ba_2Cu_3O_{7-x}$ (Ref. 13) with the c axis perpendicular to the film plane, were also made possible with this type of substrate. The in-plane (100) lattice constant of cubic $SrTiO_3$ is 3.9051 Å, and is within 0.4% mismatch with the lattice spacing of b or $\frac{1}{3}$ of the c axis of the orthorhombic $Y_1Ba_2Cu_3O_7$ phase.

The *in situ* reflection high-energy electron diffraction (RHEED) pattern of the $SrTiO_3(100)$ surface exhibits a 1×1 symmetry and clear Kikuchi arcs, indicative of a highly ordered surface. The as-grown film ~ 100 Å thick showed a RHEED pattern of diffuse background lacking any diffraction spots. A similar pattern persists when films become thousands of angstroms thick, indicating that the structure remains either amorphous or microcrystalline.

The as-grown film is insulating, and the appearance is dark and slightly transparent. The film remained stable for a short period (less than 15 min) of exposure to room air. Further stabilization was made by furnace annealing in O_2 at 500°C for about 2 h. The film turned opaque and black, and became slightly conducting. The superconducting phase is formed by further heat treatment in O_2 at 870–900°C for 1 h, then slowly furnace cooled.

The chemical composition was determined by the Rutherford backscattering spectrometry (RBS). A typical spectrum with a 1.8-MeV He^+ -ion beam at normal incidence is shown in Fig. 1 for a sample with a nearly perfect stoichiometry of $Y_{0.91}Ba_{2.0}Cu_{3.0}O_{7-x}$. A separate measurement was made on a thin film 1000 Å thick deposited on Si(100) to analyze the oxygen content incorporated during deposition without heat treatment. The oxygen stoichiometry is approximately 7.0 with an accuracy of 5%. We note the fairly uniform depth profiles exhibited by Ba, Y, and Cu. However, the Sr front edge appeared in front of the Y back edge, indicative of diffusion occurring near the interface about 1000–2000 Å thick between the substrate and the deposits.

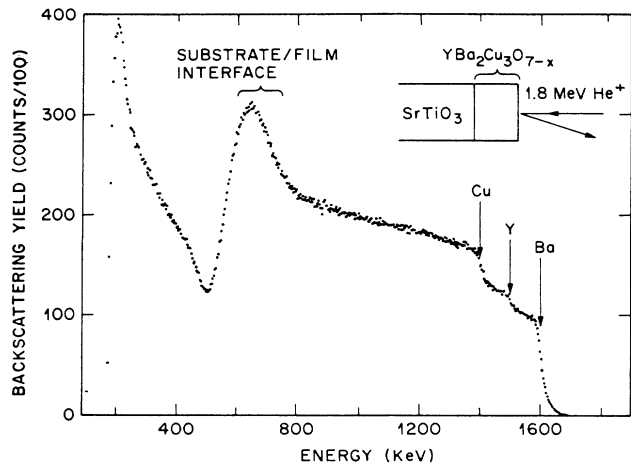


FIG. 1. Rutherford backscattering spectrum for a MBE-grown oriented $Y_{0.91}Ba_{2.0}Cu_{3.0}O_{7-x}$ film on $SrTiO_3(100)$.

Ion-channeling analysis was also performed on the same sample but was taken at a different spot 5 mm apart to evaluate its single-crystal quality. Spectra (I) and (II) in Fig. 2 are the results for 1.8-MeV He^+ incident along a random direction and the [100] direction of the film, respectively. The spot for the ion-channeling analysis is slightly Y deficient. An ion-channeling minimum yield, χ_{min} , of 46% was obtained, where χ_{min} is the ratio of the backscattered yield in the aligned condition to the yield in the nonaligned condition. Although χ_{min} is quite large compared to the value 5% expected for an ideally ordered single crystal, it is likely that the crystal underneath the surface layer of 1000 Å thick is of substantially better quality. The upper 1000 Å of the surface became disordered after long exposure to room moisture, and causes stray scattering of the ion beam. Hence the χ_{min} of 46%

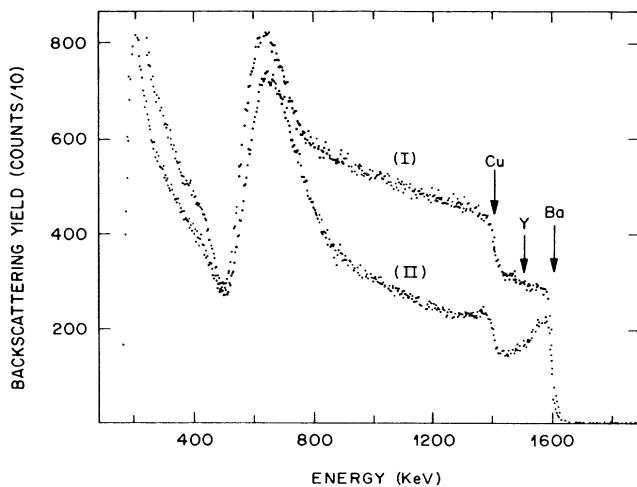


FIG. 2. Rutherford backscattering spectra for the 1.8 MeV He^+ incident along (I) a random direction, and (II) the [100] direction of the film.

could well be an overestimate.

The same $Y_{0.91}Ba_{2.0}Cu_{3.0}O_{7-x}$ film was structurally characterized on a four-circle diffractometer using $Cu K\alpha_1$ x rays from a rotating-anode source. An instrumental resolution of 0.010 \AA^{-1} full width at half maximum (FWHM) was achieved by using a singly bent pyrolytic-graphite monochromator, and a flat analyzer with slits of 0.5 mm before the monochromator and analyzer. The film was mounted in a He-gas-filled chamber to protect the film from possible chemical deterioration due to water vapor in the air. The rectangular-shaped $SrTiO_3(100)$ substrate had an in-plane long axis approximately parallel to [110].

The film showed evidence of three-dimensional order with the a -axis film normal to the surface. A θ - 2θ scan along ($h00$), showing (100) and (200) peaks from both the substrate and the film, is plotted in Fig. 3. The absence of c -axis ordering normal to the film is indicated by both the values of the lattice parameter associated with the (100) and (200) peaks, and the lack of peaks with d spacings near (001), (002), (004), and (005). Powder patterns show a (005) peak with an intensity only slightly less than the (006) peak. The small peak at the (005) 2θ position (not visible in Fig. 3) indicated that c -axis order-

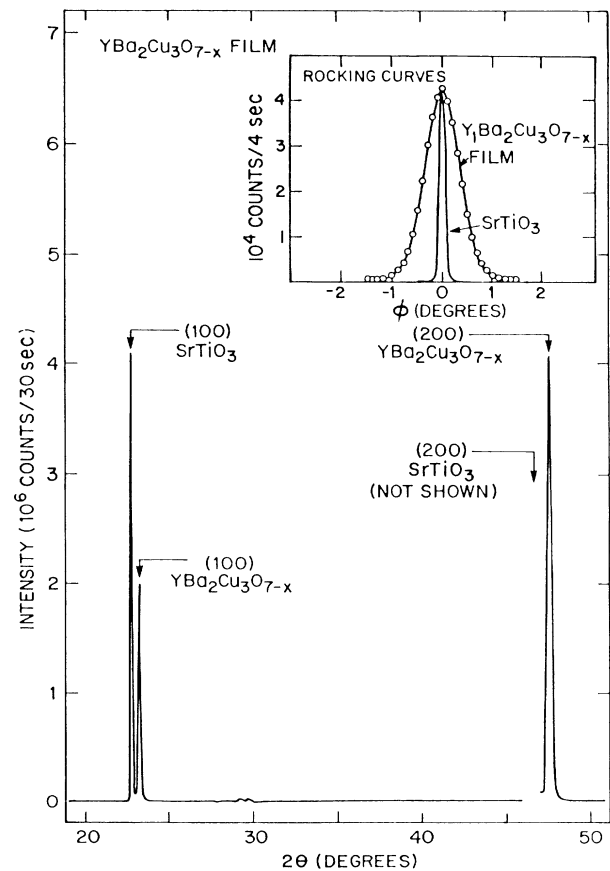


FIG. 3. X-ray θ - 2θ scan normal to the film. The inset compares the rocking curves of the (200) planes of the substrate and the film.

ing normal to the substrate was less than one part in 1000. Both the (100) and (200) $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ peaks were broader than resolution with widths of 0.011 \AA^{-1} and 0.018 \AA^{-1} , respectively. This suggests a real-space correlation length on the order of 100–300 \AA . The amount of misalignment of the ordered grains was measured by a rocking curve through the (200) $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ peak. The rocking curve shown in the inset of Fig. 3, was about 0.82° wide and centered on the same position as the substrate peak. A small amount (less than 1%) of BaCuO_2 is detected.

Three-dimensional ordering of the film was demonstrated by observing diffraction peaks with in-plane components. Figure 4 shows θ - 2θ scans through (211) reflections where $l=0-5$. Scans along both the SrTiO_3 [2 k 0] and [20 l] directions showed peaks with $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ c axis parallel to SrTiO_3 [010], while other regions grew with the c axis parallel to [001]. (The in-plane twinning means that a unique [010] or [001] direction cannot be defined for critical-current measurements.) Off-axis diffraction peaks had longitudinal widths and rocking curves similar to the on-axis ($h00$) peaks.

A measurement of the lattice parameters was obtained by making radial scans through sixteen diffraction peaks of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ film and fitting the observed 2θ positions with a powder diffraction least-squares refinement program. This procedure gave lattice parameters for the film of $a=3.821(6) \text{ \AA}$, $b=3.900(6) \text{ \AA}$, and $c=11.68(2) \text{ \AA}$ in good agreement with neutron-diffraction data from $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ ceramic samples.¹⁴

The superconducting transitions were measured by the standard 4-point measurement using the ac method with a modulation current of 0.2–1.0 μA . Figure 5 is resistivity versus temperature of the same sample of nearly perfect stoichiometry. The room-temperature resistivity is 1800 $\mu\Omega \text{ cm}$, and the resistivity ratio $R(300 \text{ K})/R(90 \text{ K})$ is 2.5. The resistive T_c onset is 90 K, and the 10% and 90% transitions are at 84 and 83 K, respectively. The fully-zero-resistance state is reached at 82 K. No resistance tail was seen. Our studies showed samples of varying compositions share similar onsets of 90 K. However, the resistive transition temperature ($R=0$) is highest when the composition is closest to the ideal stoichiometry. Furthermore,

films grown on SrTiO_3 show reproducible transition widths much sharper than those deposited on other types of substrates like Al_2O_3 or MgO . The resistivities of the off-stoichiometry samples are generally higher by about a factor of 2.

The critical current was measured by the transport method in the van der Pauw configuration without lithographic patterning. Hence, the values reported here are the lower limits of the actual critical current density J_c due to heating. The directions of the applied current were approximately along the [013] or [0 $\bar{1}$ 3] axis for the ease of placing electrical contacts. No difference in J_c between the two directions was found. This is expected since two axes are equivalent directions for electric transport. Further measurements of J_c along the in-plane [010] (b axis) and [003] (c axis) are underway. Because of the twinning of b and c axes previously found by x-ray analysis, the in-plane transport anisotropy may well be substantially weaker.

At $T=77 \text{ K}$, a J_c averaged in plane by the transport method is 10^3 A/cm^2 , and at $T=70 \text{ K}$, J_c rapidly increases to $5.0 \times 10^4 \text{ A/cm}^2$. Also magnetization hysteresis was measured with a superconducting quantum-interference device (SQUID) magnetometer with a field applied parallel to the film plane.¹⁵ The preliminary results indicate that J_c at 4.2 K is about 2 orders of magnitude higher than that at 70 K. The results suggest that the critical current at 77 K is limited by the fact the temperature is too close to the $R=0$ transition temperature. It is expected that the J_c can be drastically improved when only a slight increase of $T_c(R=0)$ by about 5 K is made.

Possible causes for the slightly lowered $T_c(\text{onset})$ and $T_c(R=0)$ in present films are speculated; one is due to the deviation from the ideal stoichiometry. Although the lattice parameters agree within present experimental accuracy with the values determined for the 90 K $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ ceramic sample, the film could be slightly oxygen deficient and the lattice parameters change very little. The second possibility is due to the coherency strain from the epitaxial growth in matching with the underlying SrTiO_3 lattice. This is evident by the slightly expanded b axis lattice spacing in approaching SrTiO_3 . The third cause is the chemical substitution of Sr or Ti into the Ba

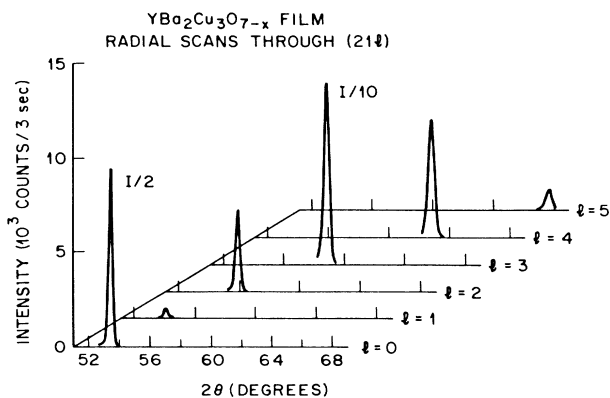


FIG. 4. X-ray θ - 2θ scan through (21 l) reflections, $l=0-5$.

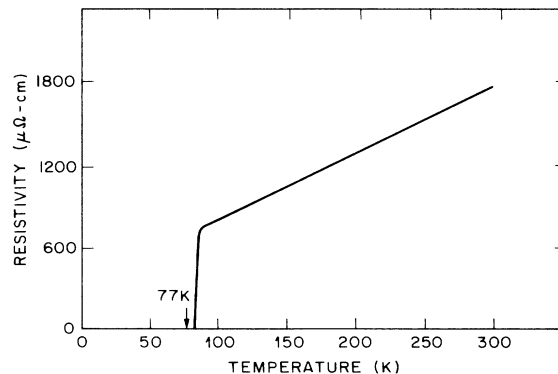


FIG. 5. Resistivity vs temperature for the same film of $\text{Y}_{0.91}\text{Ba}_{2.0}\text{Cu}_{3.0}\text{O}_{7-x}$.

or Cu site due to interdiffusion with the substrates. A 10% substitution of Cu by Ti is known to decrease the total transition temperature by about 10 K.¹⁶

In conclusion, we have demonstrated that using the molecular-beam-epitaxy technique compatible with thin-film semiconductor technology, highly orientation ordered epitaxial $Y_1Ba_2Cu_3O_{7-x}$ films can be prepared with good superconducting properties and high current carrying capacities. Further optimizations of the preparation method may lead to important applications in hybrid devices or structures combining both superconductors and semiconductors.

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