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EPITAXIAL ORDER AND RESISTIVITY OF HIGH TEMPERATURE SUPERCONDUCTORS GROWN ON $SrTiO_3$

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Thin films of $YBa_2Cu_3O_{7-\delta}$ grown on ⟨001⟩-oriented $SrTiO_3$ substrates attain zero resistance at a temperature of $T = 92$ K and have a superconducting critical current, j_c, of more than 3×10^6 Acm^{-2} at $T = 77$ K. A low resistivity superconducting Cu-rich phase shows great promise for epitaxial growth on $SrTiO_3$ substrates because of an improved lattice match in the growth direction and strong epitaxial ordering due to the presence of the new phase.

There is interest in fabricating films of high temperature superconductors both for basic physics research and possible device application [1–3]. We report progress in making very high quality thin films of $YBa_2Cu_3O_{7-\delta}$ on ⟨001⟩-oriented $SrTiO_3$ substrates using vapor deposition of Y, BaF_2 and Cu in a high vacuum chamber. In addition, a new low resistivity phase [4] which displays improved epitaxial growth and a small lattice mismatch of approximately −0.05% to the $SrTiO_3$ substrate has been grown. It should be possible to create single crystal, epitaxial films of this phase on $SrTiO_3$ substrates.

We use a turbo-pumped vacuum deposition chamber with a base pressure of 5×10^{-8} Torr. The system is equipped with two electron-gun and two thermal evaporation sources. The deposition rate of BaF_2 is controlled by a quartz crystal monitor and the Y and Cu rates are controlled using a Sentinel III detector [5]. During deposition the chamber is backfilled with pure, dry O_2 gas to a pressure in the $(5–10) \times 10^{-6}$ Torr range. The incorporation of O_2 into the film prevents phase segregation of Y, Cu and BaF_2. All the films described here were fabricated by depositing Y, Cu, BaF_2 at a combined rate of around 10 Å/s onto unheated ⟨001⟩-oriented $SrTiO_3$ substrates.

After removal from the deposition chamber, the samples are transferred into a two-inch diameter tube furnace with a slow flow ($\sim 5 \times 10$ liter/min) of O_2 gas bubbled through H_2O. A typical anneal cycle starts by increasing the sample temperature to 500 °C and then maintaining this temperature for 15 min. The sample is then annealed at 800 °C for 30 min or 700 °C for 60 min. Finally, the sample is maintained at 500 °C for 5 min, cooled to room temperature in 2–3 min, and removed from the furnace for electrical and structural characterization. After annealing, our thin films are typically 1000 to 1500 Å thick and appear shiny and black in color. Thicker films (up to 10,000 Å) have also been made using the method described above.

The water vapor present during annealing is required to convert BaF_2 in the as-deposited films to BaO, by the reaction: $BaF_2 + H_2O \rightarrow BaO + 2HF$. As written this reaction is endothermic with a change in Gibbs free energy $\Delta G°$ of approximately +53 kcal/mol at 800 °C (+56 kcal/mol at 700 °c) [6]. Using these values to calculate an equilibrium constant and assuming a water vapor pressure appropriate for a saturated gas stream at room temperature, one obtains an equilibrium pressure of HF in the range of a milliTorr. How-

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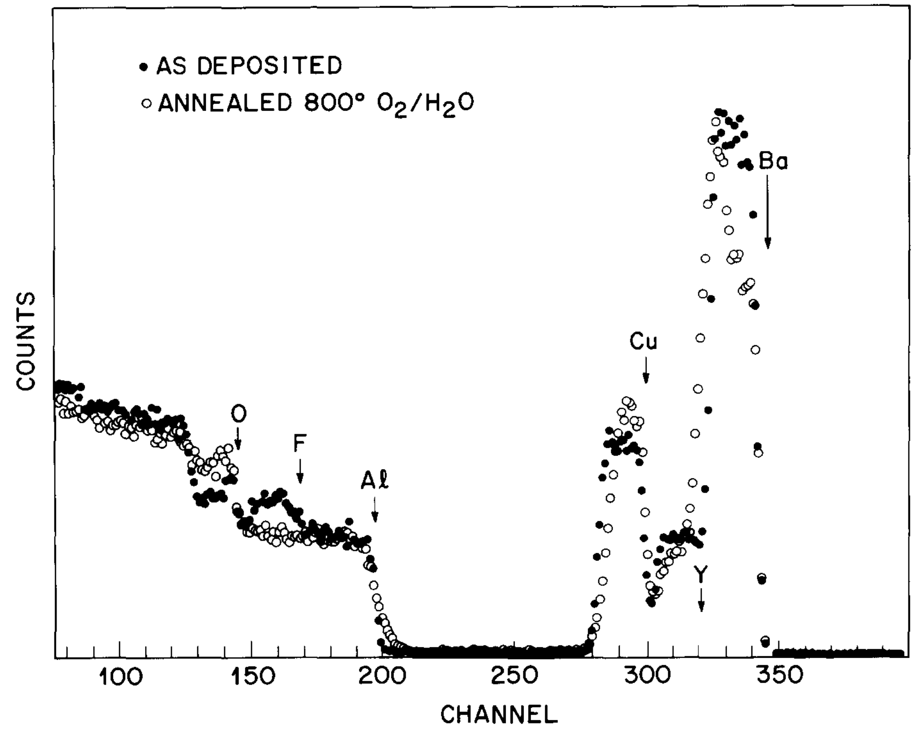

Fig. 1. RBS data for films on sapphire substrates as deposited (closed circles) and after annealing at 800 ° C for 15 min in flowing wet oxygen (open circles). Note the loss of the fluorine signal after the anneal.

ever, this represents a pessimistic estimate of the energetics of fluorine removal, since the formation of the superconducting oxide phase, being more stable than BaO, would provide an additional driving force.

The fact that this fluorine removal does take place, and that it is necessary for the formation of the superconducting oxide phase, was explored experimentally. Films were deposited as described above on single crystal sapphire substrates. These samples were annealed in flowing wet oxygen at progressively higher temperatures, then examined by Rutherford back scattering (RBS) to determine the fluorine content of the films. For heating times of 15 min, samples heated at 700 ° C or below show a fluorine RBS signal substantially the same as for an unannealed sample. These films are a transparent brown color and are insulating. A sample heated at 800 ° C in wet oxygen for 15 min, by contrast, shows no evidence of fluoride in the RBS spectrum, is black in color, and electrically conducting. Fig. 1 shows the RBS spectrum of a sample before and after this 800 ° C anneal. The loss of fluorine signal in the RBS spectrum coupled with the conversion from an insulating to a conducting film demonstrates the role of water vapor in the annealing process (a sample heated to 800 ° C in *dry* oxygen is brown in color and insulating). In fig. 1 it can also be seen that this brief 800 ° C anneal causes the leading edge of the aluminum peak and the back edge of the barium peak to broaden, indicating interdiffusion of the film with the substrate. RBS measurements on samples annealed in wet oxygen at 700 ° C for longer times (30 min or more) also show the loss of the fluorine signal, consistent with the fact that superconducting films can be obtained at 700 ° C with longer annealing times.

Depending on the composition of the film, as measured by RBS prior to annealing, two types of superconducting material can be formed: $YBa_2Cu_3O_{7-\delta}$ and a Cu-rich phase whose composition has been estimated as $Y_2Ba_4Cu_8O_{20-\delta}$ [4]. Electrical measurements are performed using a

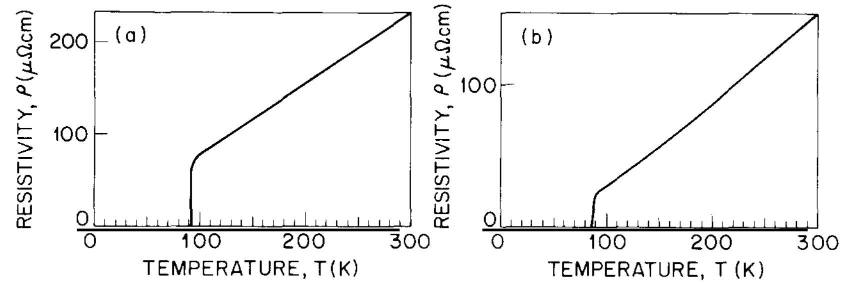

Fig. 2. (a) Resistivity, ρ, as a function of temperature T for a 1400 Å thick film of single phase $YBa_2Cu_3O_{7-\delta}$. (b) Resistivity as a function of temperature for a 1400 Å thick film of the low resistivity Cu-rich film.

standard four-terminal Hall bridge geometry which was photolithographically defined and chemically etched in dilute HCl. The bridge pattern is 50 μm wide and 500 μm long.

Resistivity, ρ, as a function of temperature, T, is shown in fig. 2a for a 1400 Å thick film of the pure $YBa_2Cu_3O_{7-\delta}$ phase. The resistivity at $T=$ 300 K (ρ_{300K}) is 233 $\mu\Omega$ cm and $\rho(T)$ decreases linearly extrapolating to $\rho(T=0K)=0$ $\mu\Omega$ cm. For this sample $\rho(T)$ can be fit with the function $\rho(T)=a_1T$ using $a_1=0.78$ $\mu\Omega$ cm K^{-1} giving a resistivity ratio $\rho_{300K}/\rho_{100K}=3$. The superconducting transition is very abrupt with a width $\Delta T \leq 1$ K and zero resistance occurs at $T=92$ K. The superconducting critical current, j_c, is measured at a fixed temperature by detecting the constant current level at which the first 1 μV of voltage is developed across the bridge. In this and other films we have obtained $j_c > 3 \times 10^6$ A cm^{-2} with the sample immersed in boiling liquid nitrogen ($T \sim 77$ K). With decreasing temperature, j_c increases to greater than 10^7 A cm^{-2} at 4.2 K. In fig. 2b we show $\rho(T)$ for a film containing a large fraction of Cu-rich material (see X-ray data below). This film has a resistivity ratio of 5.6 and $\rho(T)$ displays some positive curvature. In addition, extrapolation of $\rho(T)$ to $T=0$ gives a negative intercept. For this film, $\rho(T)$ can be fit with the function $\rho(T)=a_0+a_1T+a_2T^2$ using $a_0=-24$ $\mu\Omega$ cm, $a_1=0.47$ $\mu\Omega$ cm K^{-1}, and $a_2=3.8\times10^{-4}$ $\mu\Omega$ cm K^{-2}. The width of the superconducting transition is $\Delta T=3$ K and zero resistance occurs at $T=87$ K. Typical values for j_c in these films are around 1×10^6 A cm^{-2} at $T=77$ K.

In order to determine whether the Cu-rich phase is a superconductor we measured the DC magnetization of our films. Results for a predominantly Cu-rich phase sample are shown in fig. 3. The data were obtained using a quantum design SQUID magnetometer in an applied magnetic field of 25 Oe oriented in the plane of the film. The transition temperature (as determined by the onset of diamagnetism) of 82 ± 1 K, is about 5 K less than that of similar films of pure $YBa_2Cu_3O_{7-\delta}$ and the large Meissner fraction, 48%, is consistent with

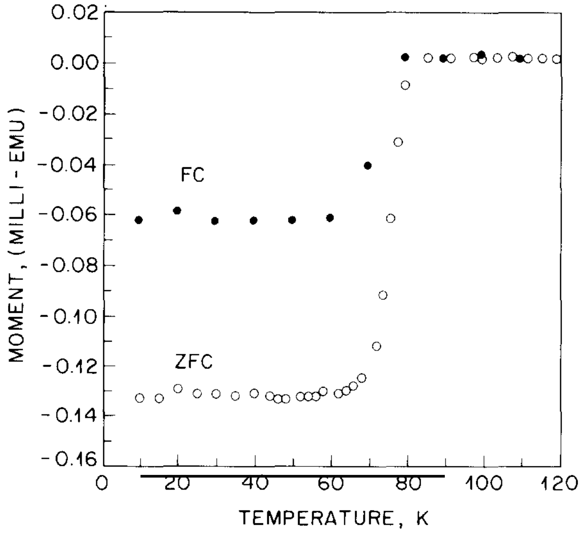

Fig. 3. Magnetization of a Cu-rich film as a function of temperature in a magnetic field of 25 Oe applied in the plane of the film. Open circles show total flux exclusion at low temperature and are data taken warming after cooling in zero magnetic field. Full circles are data taken cooling in a field and give a 48% Meissner effect. The difference between the two sets of data corresponds to flux pinned in the film.

bulk superconductivity. In addition, Hall effect data for such a film [7] show that the carrier density at $T = 100$ K is approximately seven times larger than that found in films of the pure $YBa_2Cu_3O_{7-\delta}$ compound. Since the resistivity increases and the carrier density decreases with oxygen removal in the $YBa_2Cu_3O_{7-\delta}$ compound [8,9], the above results cannot be interpreted as simply the effect of oxygen deficiency. Thus we tentatively conclude that superconductivity in the Cu-rich phase is intrinsic and not attributable to the minor fraction of $YBa_2Cu_3O_{7-\delta}$ present or to proximity effects.

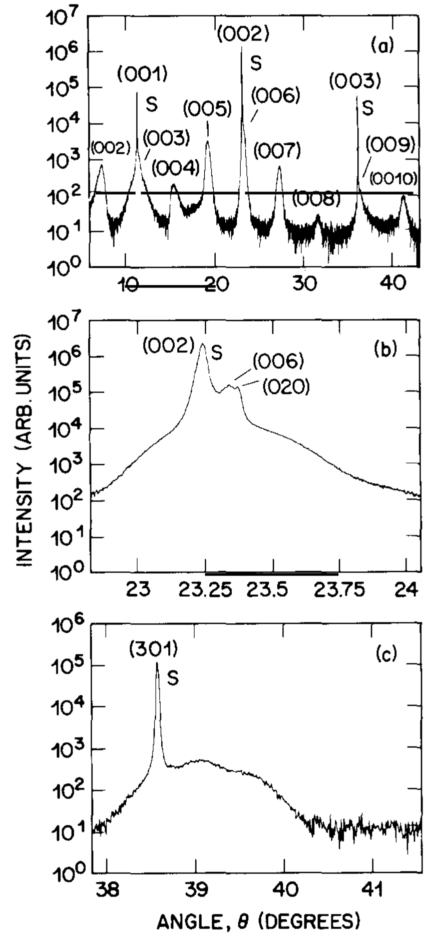

Fig. 4. (a) X-ray diffraction scan of the film used to obtain the data shown in fig. 1a. Peaks from the $SrTiO_3$ substrate are indicated with an S. (b) HRXRD scan in the vicinity of the $SrTiO_3$ (002) reflection. (c) HRXRD scan in the vicinity of the $SrTiO_3$ (301) reflection.

The X-ray characterization was carried out with a high-resolution X-ray diffractometer (HRXRD) which utilized a four-crystal monochromator [10]. In fig. 4a we present the angular diffraction pattern scanned along the [001] growth direction, of the sample whose resistivity data are shown in fig. 2a. The X-ray data show the crystalline material to be pure $YBa_2Cu_3O_{7-\delta}$ and the absence of any significant reflections with indices other than (00*l*) indicates a large degree of preferred orientation along [001]. In fig. 4b, a HRXRD scan taken in the vicinity of the (002) reflection of $SrTiO_3$ ($a_0 = 3.905$ Å) shows two closely spaced peaks; one can be identified as the (006) reflection of $YBa_2Cu_3O_{7-\delta}$ with a lattice parameter $c = 11.671$ Å and a perpendicular lattice mismatch of -0.4%; the second peak is ascribed to the (020) reflection with $b = 3.884$ Å. From the intensity ratio of these two peaks we calculate that approximately 70% of this material grows with the *c*-axis (and 30% with the *b*-axis) perpendicular to the (001) substrate plane. The angular scan of the low resistivity sample (fig. 5a) reveals the presence of $YBa_2Cu_3O_{7-\delta}$ and the recently discovered Cu-rich phase [4] which has extra Cu–O planes along the [001] stacking direction with $c = 27.19$ Å ($\cong 7 \times a_0((SrTiO_3))$). For both phases primarily the (00*l*) reflections are observed, indicating strong epitaxial growth along [001]. From the intensity ratios we estimate that at least two thirds of the thin film material consists of this new phase. The HRXRD scan in the vicinity of the $SrTiO_3$ (002) reflection (fig. 5b) shows this two-phase material to be very closely matched along [001] with a very small perpendicular mismatch $\lesssim -0.05\%$ as compared to -0.4% for the pure $YBa_2Cu_3O_{7-\delta}$ film. Furthermore, there is no indication of orientations along any of the other axes. This result shows that the low-resistivity Cu-rich phase material grows with considerably better epitaxial ordering than the pure $YBa_2Cu_3O_{7-\delta}$ film.

To obtain information about the lateral mismatch, HRXRD scans of both samples were taken approximately 71.5° out of the [001] growth direction, in the vicinity of the (301) and (031) reflection of $SrTiO_3$. The scans of the pure $YBa_2Cu_3O_{7-\delta}$ film show a very broad peak next

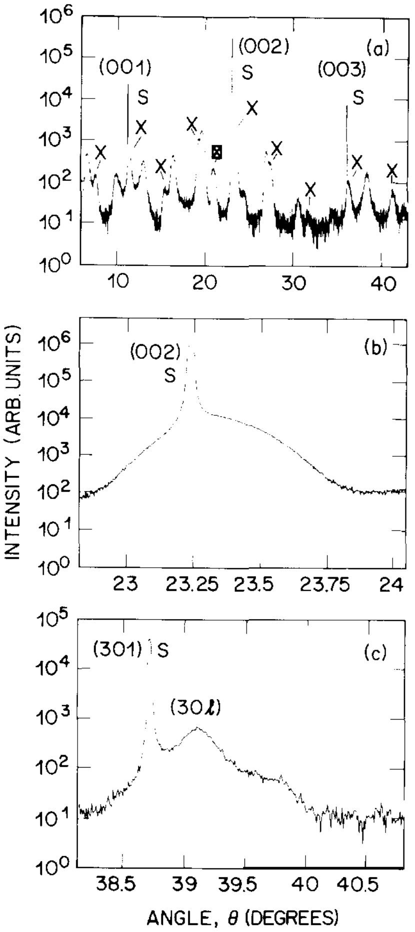

Fig. 5. (a) X-ray diffraction scan of the film used to obtain the data shown in fig. 1(b). Peaks from the $YBa_2Y_3O_{7-\delta}$ phase are indicated with X and substrate peaks are indicated with an S, and the remaining peaks can be identified with the low resistivity Cu-rich phase. Some Cu_2O crystals which are on the surface of the film show up as a peak indicated with ⊠. (b) HRXRD scan in the vicinity of the $SrTiO_3$(002) reflection. (c) HRXRD scan in the vicinity of the $SrTiO_3$(301) reflection.

to the substrate peak (see fig. 4c) which, in part, may be ascribed to the (303) reflection. This peak, broadening indicates a large degree of random orientation throughout the film resulting in a poorly defined lateral mismatch. On the other hand, the same HRXRD scans of the Cu-rich sample show a well-defined peak next to the substrate peak in fig. 5c which can be identified as the (303) and (307) reflection of $YBa_2Cu_3O_{7-\delta}$ and the new Cu-rich phase, respectively. A lateral mismatch of approximately −1.0% is calculated in both lateral directions with $a \cong b \cong 3.868$ Å. Our X-ray data show that the presence of the new Cu-rich phase in the low resistivity film results in a much higher degree of epitaxial order, both in the growth and lateral directions, as compared to the pure $YBa_2Cu_3O_{7-\delta}$ film.

It is also interesting to note that the low resistivity film does not seem to grow commensurate with the substrate, but rather maintains a fairly large lateral mismatch of −1.0%, resulting in a nearly zero mismatch along the [001] growth direction. The excellent *c*-axis lattice match implies that epitaxial growth of the low resistivity phase starts at steps in the surface of the ⟨001⟩ $SrTiO_3$ substrate. The substrate and film c-axes align and oriented single-crystal growth proceeds from these nucleation sites. Recent transmission electron microscope studies appear to support this model [11].

The X-ray data are reinforced by 2 MeV He^+ RBS and channeling results. For the pure $YBa_2Cu_3O_{7-\delta}$ film, the ratio of the aligned backscattered yield to the random yield (taken in the Ba region of the spectrum) is $\chi_{min} = 30\%$. This indicates that the film is polycrystalline with ~ 70% of the crystallites oriented with the ⟨001⟩ $SrTiO_3$ substrate. For the low resistivity films, χ_{min} is measured to be 13%, demonstrating a degree of crystalline order approaching that of bulk single crystals of $YBa_2Cu_3O_{7-\delta}$ which typically show $\chi_{min} \sim 5\%$. The channeling data for both types of superconducting films indicate that the disorder is lowest near the surface and increases toward the substrate.

In conclusion, films of single phase $YBa_2Cu_3O_{7-\delta}$ with superconducting critical currents of more than 3×10^6 A cm^{-2} at liquid nitrogen temperature can be grown on $SrTiO_3$. However, due to a higher degree of epitaxial ordering and an improved lattice match, the low resistivity Cu-rich phase is better suited for growth of single crystal thin film superconductors on ⟨001⟩-oriented $SrTiO_3$ even though this material has a lower superconducting transition temperature.

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