EPITAXIAL ORDER AND RESISTIVITY OF HIGH TEMPERATURE SUPERCONDUCTORS GROWN ON SrTiO$_3$


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Thin films of YBa$_2$Cu$_3$O$_{7-\delta}$ 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 $3 \times 10^6$ A cm$^{-2}$ 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$_2$Cu$_3$O$_{7-\delta}$ 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 $5 \times 10^{-8}$ 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$_2$O. 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$_2$O $\rightarrow$ BaO + 2HF. As written this reaction is endothermic with a change in Gibbs free energy $\Delta G^\circ$ 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-
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: YBa2Cu3O7−δ and a Cu-rich phase whose composition has been estimated as Y2Ba4Cu6O20−δ [4]. Electrical measurements are performed using a
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, \( \rho \), as a function of temperature, \( T \), is shown in fig. 2a for a 1400 Å thick film of the pure \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) phase. The resistivity at \( T = 300 \text{ K} \) (\( \rho_{300K} \)) is 233 \( \mu \Omega \text{ cm} \) and \( \rho(T) \) decreases linearly extrapolating to \( \rho(T = 0\text{K}) = 0 \) \( \mu \Omega \text{ cm} \). For this sample \( \rho(T) \) can be fit with the function 
\[
\rho(T) = a_0 + a_1 T + a_2 T^2
\]

The superconducting transition is very abrupt with a width \( \Delta T \leq 1 \text{ K} \) and zero resistance occurs at \( T = 92 \text{ K} \).

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 \( 82 \pm 1 \text{ K} \), is about 5 K less than that of similar films of pure \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) and the large Meissner fraction, 48%, is consistent with
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$_2$Cu$_3$O$_{7-\delta}$ compound. Since the resistivity increases and the carrier density decreases with oxygen removal in the YBa$_2$Cu$_3$O$_{7-\delta}$ 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$_2$Cu$_3$O$_{7-\delta}$ present or to proximity effects.

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$_2$Cu$_3$O$_{7-\delta}$ and the absence of any significant reflections with indices other than (001) 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$_2$Cu$_3$O$_{7-\delta}$ 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.

![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.](image)

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.
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Both lateral directions with $a \equiv b \equiv 3.868$ 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$_2$Cu$_3$O$_{7-\delta}$ 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$_2$Cu$_3$O$_{7-\delta}$ film, the ratio of the aligned backscattered yield to the random yield (taken in the Ba region of the spectrum) is $X_{\text{min}} = 30\%$. This indicates that the film is polycrystalline with $\sim 70\%$ of the crystallites oriented with the (001) SrTiO$_3$ substrate. For the low resistivity films, $X_{\text{min}}$ is measured to be $13\%$, demonstrating a degree of crystalline order approaching that of bulk single crystals of YBa$_2$Cu$_3$O$_{7-\delta}$ which typically show $X_{\text{min}} \sim 5\%$. 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$_2$Cu$_3$O$_{7-\delta}$ with superconducting critical currents of more than $3 \times 10^6$ 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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