Preparation of superconducting thin films of calcium strontium bismuth copper oxides by coevaporation

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Superconducting films of Ca-Sr-Bi-Cu oxides have been prepared by coevaporation of CaF_2, SrF_2, Bi, and Cu, followed by post-oxidation in wet O_2. The films were characterized by four-probe resistivity measurements, Rutherford backscattering, transmission electron microscopy, x-ray diffraction, and Hall measurements. Zero resistance was achieved at ~80 K, although evidence of traces of superconductivity at higher temperatures was seen in resistivity and Hall data. The critical current at 4.2 K was 1.0×10^6 A cm^{-2}. The films were epitaxial on ⟨100⟩ and ⟨110⟩ $SrTiO_3$ substrates. The electrical and structural properties of the films were insensitive to film composition over a wide range of stoichiometries.

Recently, several groups have observed bulk superconductivity in ceramic samples of oxides in the Ca-Sr-Bi-Cu system.[1-4] Many of these samples appear to contain more than one superconducting phase, with the possibility of as many as three distinct onset temperatures, approximately 80, 105, and 120 K. So far only the lowest T_c component has been isolated and identified: single crystals of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$ have been grown from a flux: single-crystal resistivities were measured, and its crystal structure was determined.[3] A crystal structure determination was also made on a crystal of similar composition extracted from a ceramic specimen.[4] Isolation of the higher T_c components remains elusive.

We report the preparation of thin superconducting films of calcium strontium bismuth copper oxides by coevaporation of CaF_2, SrF_2, Bi, and Cu, followed by post-oxidation in wet oxygen. This is an adaptation of a technique successfully used for preparing high-quality films of $Ba_2YCu_3O_7$.[5] The films showed zero resistance at 80 K, although evidence of a minor component with a higher T_c was seen in resistivity and Hall measurements. Over a rather wide range of composition, the electrical and structural properties were insensitive to film stoichiometry. The films have been characterized by four-probe resistivity measurements, Rutherford backscattering (RBS), transmission electron microscopy (TEM), x-ray diffraction, and Hall measurements.

To deposit our films, we used multiple-source evaporation from a combination of thermal and electron beam (*e*-beam) sources. The pressure before deposition was typically less than 10^{-7} Torr. CaF_2 and SrF_2 (optical grade) were evaporated as a mixture from a single resistivity heated boat. Bi was evaporated from a resistively heated boat, while an electron beam was used to evaporate Cu. A few films were also prepared with the addition of Y (*e*-beam evaporated from a fourth source) or Pb (mixed with the Bi charge). The evaporation rates for the sources were maintained by feedback control using the output from quartz crystal monitors (for the fluorides and Bi) and Sentinel III monitors[6] (for Cu and Y). In the Ca-Sr-Bi-Cu films, 12 different metal ratios were deposited, with Ca:Sr molar ratios from 1:2.99 to 1:0.80, Bi from 16 to 26 mol %, and Cu from 33 to 49 mol %. Film composition was determined by RBS on unannealed films deposited on sapphire.

For the post treatment, films were heated in flowing O_2 bubbled through water. Typical conditions were 15 min at 725 °C, followed by 5 min at 850 °C. The samples were then cooled to room temperature over the course of a few minutes. The electrical properties of the films were quite sensitive to the temperature and duration of the high-temperature step, with too low a temperature giving incomplete reaction, and too high a temperature or too long a time leading to degradation due to interaction with the substrate. The cooling rate appeared to make little difference in the properties, nor was it necessary to perform an extended anneal at lower temperatures as is required with $Ba_2YCu_3O_7$ films. The annealed films were black and shiny. Typical film thicknesses, measured on photolithographically patterned bridges, were 3000 to 5000 Å.

The substrates used were single-crystal $SrTiO_3$, both ⟨100⟩ and ⟨110⟩ orientations, and sapphire. No fully superconducting films could be prepared on sapphire due to extensive substrate reaction.

Four-probe resistance measurements were performed for the films, using fluxless In soldering for the contacts. For quantitative measurements of resistivity, Hall voltage, and critical current, bridges were fabricated in the films using photolithography and wet etching in dilute acid. Figure 1 shows the variation of resistivity with temperature for a film with composition $Ca_{1.00}Sr_{1.58}Bi_{2.35}Cu_{3.94}O_x$. The resistance shows an approximately linear dependence on temperature from $T = 300$ K down to about $T = 120$ K, with a projected intercept close to zero at $T = 0$. In the vicinity of 110–120 K, there is a small but noticeable change in slope. Around 90 K, the resistance begins to drop off more rapidly, with zero resistance achieved near 80 K. This resistivity data is representative of our results for all the compositions tried. In all cases, the films showed metallic behavior and zero resistance in the range 78–83 K. Most films showed the small break in resistance at 110–120 K as well. Indeed the behavior of $\rho(T)$ appeared to be very insensitive to film composition.

The superconducting critical current at 4.2 K was 1×10^6 A cm^{-2}. A dc current was used, and the material was

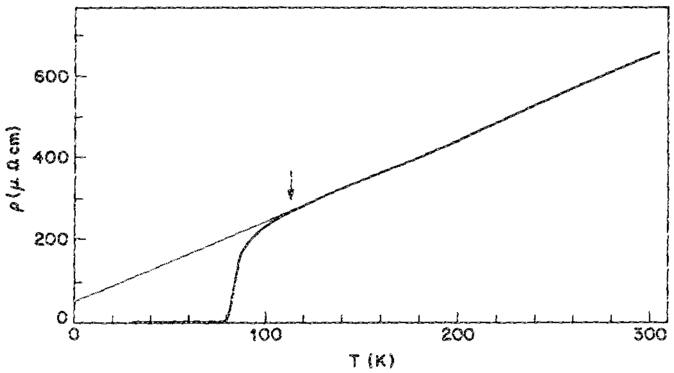

FIG. 1. Temperature dependence of the resistivity (heavy line) for a film of composition $Ca_{1.00}Sr_{1.58}Bi_{2.35}Cu_{3.94}O_x$, grown on ⟨100⟩ $SrTiO_3$. A weak, although characteristic break in slope at $T \sim 115$ K is indicated with an arrow. The fine line shows the projected intercept of the linear portion of $\rho(T)$ at $T = 0$.

considered to have reached the normal state when its resistivity was $> 1 \times 10^{-3}\ \mu\Omega$ cm.

Addition of Pb to Ca-Sr-Bi-Cu oxides has been reported to give a higher T_c in multiphase ceramic samples.[3] However, in our films, at two different levels of Pb substitution for Bi, we saw no noticeable effect on $\rho(T)$. The level of Pb substitution for Bi was approximately 10 and 25%, based on the amount of Pb added to the evaporation charge. Due to overlap with the Bi peak, it was not possible to determine the actual amount of Pb by RBS. It was clear that Pb had actually been incorporated into the superconducting phase, because the x-ray diffraction lines for these films were shifted in a manner consistent with a slightly longer c axis. Addition of Y appeared to give a slightly higher $T_{c(\mathrm{onset})}$, but the temperature for $R = 0$ was unchanged.

The Hall voltage was measured as a function of applied magnetic field, B, for the film of Fig. 1, over the same temperature range as for the resistivity measurements. Data from this experiment in the vicinity of the superconducting transition are shown in Fig. 2. In the normal state one obtains a straight line with a positive slope, showing that the dominant carriers are holes. These data are preliminary, but a hole concentration of 4.6×10^{21} cm^{-3} at RT, decreasing linearly to around 3.5×10^{21} cm^{-3} at $T = 150$ K, can tentatively be assigned to the data, assuming a naive one-band model for the conductivity. As the material enters the superconducting state, the Hall voltage vs B plot develops some curvature at small values of B field. This phenomenon has been observed previously for $Ba_2YCu_3O_7$ films,[7] and appears to be a very sensitive measure of the presence of traces of superconductivity. In this sample one can see a deviation from straight-line behavior at approximately 108 K, indicating that some portion of the material is in the superconducting state at this temperature.

X-ray diffraction measurements were performed on the films on a four-circle diffractometer with a rotating anode Cu x-ray source. Figure 3 shows a θ-2θ scan for the film whose resistivity data are shown in Fig. 1. One can see a series of diffraction lines from the film which fall into two sets. One set corresponds to the $(00l)$ lines of the 84 K superconducting phase reported in the single-crystal x-ray studies,[3,4] which has a c axis of 30.89 Å. The other set, about an order of magnitude less intense than the first, corresponds to the $(00l)$ lines of a phase with a c-axis spacing of 24.5 Å. This spacing has been identified with a semiconducting phase of composition $M_2Bi_2CuO_6$, where M is a mixture of Ca, Sr, and/or Bi.[3] Both sets of lines are aligned with the substrate; rocking curves show a width of about one degree. No lines with indices other than $(00l)$ are seen for either phase in this scan, indicating that these phases have an essentially 100% c-axis normal orientation. Some out-of-plane reflections were also located, showing that the phases are indeed epitaxial. For the films on ⟨110⟩ $SrTiO_3$ substrates, we anticipated finding an orientation having the c axis in the plane of the film. However, these samples also showed a c-axis normal orientation, giving θ-2θ scans almost identical to those seen for the ⟨100⟩ substrates. One feature that was only observed in the x-ray scans of the ⟨110⟩ samples was a set of diffraction peaks from a different phase, also aligned with the sub-

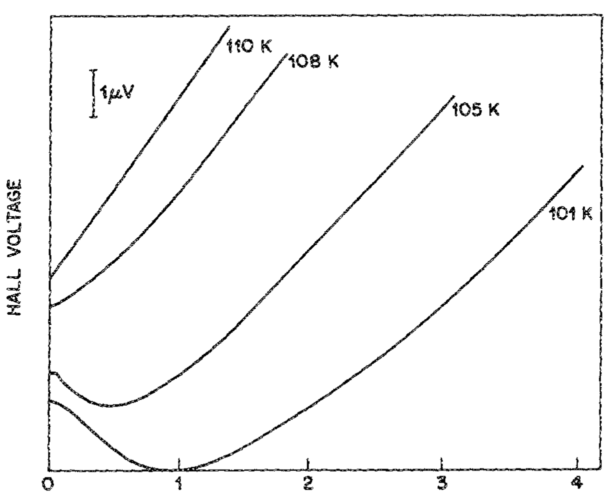

FIG. 2. Hall voltage vs magnetic field B for the film of Fig. 1, at temperatures near T_c. The curves have been offset for clarity.

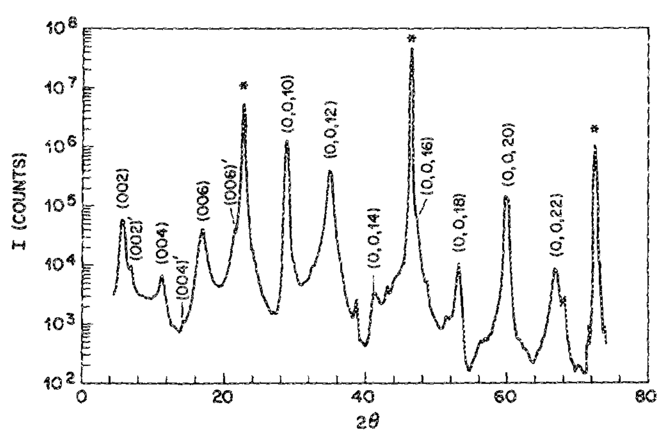

FIG. 3. θ-2θ x-ray diffraction scan for a film of Ca-Sr-Bi-Cu oxide on ⟨100⟩ $SrTiO_3$, measured with Cu K_α radiation. The diffraction lines from the 80 K superconducting phase and a related semiconducting phase are designated $(00l)$ and $(00l)'$, respectively. The $(h00)$ lines from the $SrTiO_3$ substrate are indicated with an asterisk.

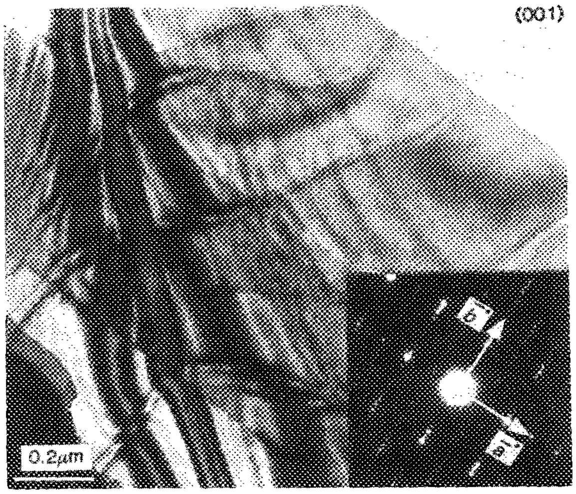

FIG. 4. Transmission electron micrograph of a film of composition $Ca_{1.00}Sr_{1.46}Bi_{1.29}Cu_{3.55}O_x$ grown on ⟨100⟩ $SrTiO_3$. The electron diffraction pattern shown in the inset was obtained with the electron beam along [001].

strate, with a lattice spacing of 6.5 Å or some multiple. As far as we are aware, no such phase has been identified in bulk studies. This phase appears to be present on the level of a few percent of the film, varying from sample to sample. The amount of this phase could not be correlated with any features in the resistivity data. On both ⟨100⟩ and ⟨110⟩ substrates, the x-ray diffraction patterns were found to be remarkably similar for widely different film compositions.

A transmission electron micrograph of a film of composition $Ca_{1.00}Sr_{1.46}Bi_{1.29}Cu_{3.55}O_x$ grown on ⟨100⟩ $SrTiO_3$ is shown in Fig. 4, obtained using a Phillips 420T electron microscope operated at 120 kV. The micrograph was performed on a thin section of the film overhanging a cleaved edge of the sample. The electron diffraction pattern shown in the inset was taken with the electron beam directed along [001], and shows the same lattice spacings along the *a* and *b* directions as were reported for the 84 K superconducting phase in the single-crystal studies.[3,4] These data confirm the presence of the 84 K superconducting phase, and demonstrate the highly crystalline nature of these films.

In conclusion, we have prepared superconducting films of Ca-Sr-Bi-Cu oxides with zero resistance at 80 K. These films are epitaxial with ⟨100⟩ and ⟨110⟩ $SrTiO_3$ substrates, with the *c* axis of the superconductor oriented normal to the plane of the film in both cases. The electrical and structural properties of these films were not a sensitive function of film composition. It appears that tight control of film composition is not as crucial as for films of $Ba_2YCu_3O_7$. Evidence of a higher T_c component, with a transition temperature near 108 K, was clearly seen in resistivity and Hall measurements.

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