In situ resistance of $Y_1Ba_2Cu_3O_x$ films during anneal

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Measurements of electrical resistance of thin films of the high-temperature superconductor $Y_1Ba_2Cu_3O_x$ have been carried out between 100 and 800 °C, and in the range between roughly 0.1 and 1 atm of ambient oxygen. Results are reported for both quick and slow heating, and also for sudden changes in oxygen partial pressure. At constant temperature we observe that the response to the oxygen partial pressure is both quick and reversible. We show evidence that quick heating is preferable, and we also observe features in the resistance similar to those reported in bulk samples and interpreted as an order–disorder transition of oxygen in the one-dimensional Cu-O chains.

There has been great progress in the short time since the discovery of high-temperature superconductivity in certain Cu oxides[1–4] in producing thin films[5] with properties approaching those of the bulk ceramics. Films of $Y_1Ba_2Cu_3O_x$ (YBC oxide) have shown transition temperature onsets near 100 K and zero resistance[6] by 90 K. Films have been produced[5] with oriented grains that carry supercurrents approaching theoretical limits near 10^6 A/cm^2. Still, all of these samples require post-deposition processing, involving heating in the presence of oxygen. Developing procedures to optimize this post-processing has been a trial and error process.

In bulk ceramic samples Freitas and Plaskett[7] have shown the sensitivity of high-temperature resistivity measurements to subtle changes due to oxygen uptake and ordering in the temperature range between 300 and 800 °C. They were able to study the behavior of known superconducting samples during a heating process after the formation of the proper superconducting phase. Gurvitch and Fiory[8] have obtained similar results. Our work extends such measurements to thin films, and in addition studies the growth of the superconducting phase at high temperature.

We have studied films made both by electron beam (*e*-beam) evaporation[5] and by dc magnetron sputtering.[9] In either case the films were about 1000 nm thick, deposited on clean unoriented single-crystal sapphire or magnesium oxide substrates, and had 10 MΩ resistance or so, as-deposited. The films came out of the deposition systems with a smooth shiny black appearance and good adhesion.

Our resistance measurements were made in a four-probe configuration, using platinum-40% rhodium wire 1 mm in diameter. Four such wires were passed through an insulating ceramic sleeve, and each bent into the shape of a short coil spring at the end. The sample could then be inserted into these four short springs assuring good mechanical contact. The wire used withstood repeated cycles to over 900 °C in oxygen, without losing its springiness, and without excessive corrosion. Insertion of the samples into the platinum rhodium springs was not suitable for delicate substrates such as silicon. Therefore, all samples discussed were deposited on robust single-crystal wafers, particularly sapphire and MgO.

The ceramic sleeve with platinum-rhodium wires supporting the sample at one end could slide into a tube furnace with flowing oxygen and/or helium. Unless otherwise stated the exhaust end of the furnace tube (through which the sample was inserted) was left open, thus diluting the flowing gas with oxygen and nitrogen from the room atmosphere. Switching the gas flow from oxygen to helium changed the oxygen partial pressure inside the furnace tube from 0.75 to 0.075 atm, according to our rough estimate.

The resistance measurements reported here were dc, except as noted, using current levels of 1 mA or less. The current polarity was occasionally reversed to make sure that thermal emf's could be ignored.

Figure 1 shows data for a sample that was *e*-beam evaporated onto a MgO substrate,[5] and then warmed slowly to 820 °C and cooled slowly (< 5 °C per minute) both ways in flowing oxygen. The as-deposited film at room temperature had a resistance of several MΩ. The resistance dropped rapidly as the sample was warmed. A peak in resistance was observed at about 700 °C, followed by a precipitous drop from roughly 4000 to about 200 Ω at 800 °C. The peak at 700 °C was observed in about half of our samples. We found that going much over 800 °C in these slowly warmed samples would always result in a nonreversible resistance rise. The precipitous drop at 750 °C was a universal feature of these films, and apparently corresponds to the creation of

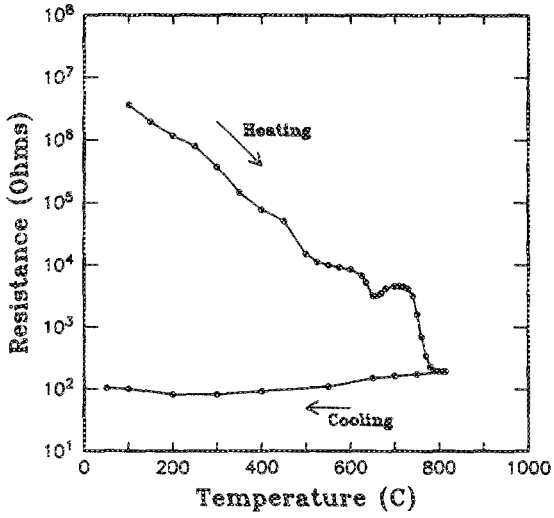

FIG. 1. Resistance vs temperature for an as-deposited YBC oxide film on a magnesium oxide single-crystal substrate. Both warming and cooling proceeded at less than 5 °C per minute.

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$Y_1Ba_2Cu_3O_x$. Cooling before this drop would always give a negative temperature coefficient, while cooling from a temperature higher than the temperature of the drop always gave a metal-like positive temperature coefficient of resistance.

The lower branch of the curve shows the behavior as the sample cooled. This particular sample was measured in a two-probe configuration, and the resistance rise at low temperature on the cooling branch is certainly due to added contact resistance as the sample cooled and the platinum-rhodium contacts contracted. (Comparison of two- and four- probe measurements always showed agreement above 400 °C.)

The superconducting behavior of this sample is shown in Fig. 2 as curve a. The resistance (four-probe lock-in measurement, 1 μA excitation) begins to drop anomalously at about 100 K, drops steeply at about 80 K, but does not go to zero until about 30 K. Curves of this same qualitative shape and quantitative width were always observed in our films after a slow-warming anneal in oxygen. This was true of both electron beam coevaporated samples, and dc magnetron sputtered samples.

Curves b and c in Fig. 2 were for films deposited on the same wafer as film a, but annealed differently. These films were heated to about 900 °C in half a minute in flowing helium and then cooled slowly in flowing oxygen, as described in Refs. 5 and 10. The width, onset, and normal state resistance of these two films were all improved by this quick heating procedure. Curve c had a width of only 5° and is completely superconducting above 83 K.

It is interesting that there is a visual difference between films that have been heated quickly, and those that were heated slowly. The slow films all showed a fine grain structure and appeared blue-gray to the naked eye, with moderately specular reflection. Fast heated films had large grains, readily observed in optical microscopes, were dark gray, and very diffuse optical scatterers. Evidently the quick heating allows faster crystallite growth, whereas slow heating is presumably dominated by nucleation rates and yields smaller

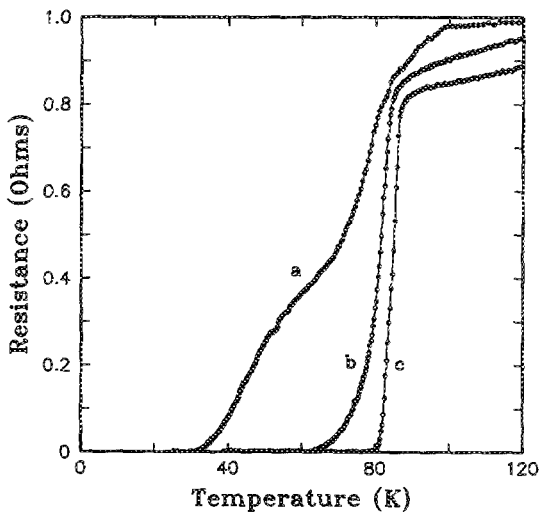

FIG. 2. Superconducting transitions for three films deposited on the same wafer, showing the deleterious effects of slow warming of the as-deposited film.

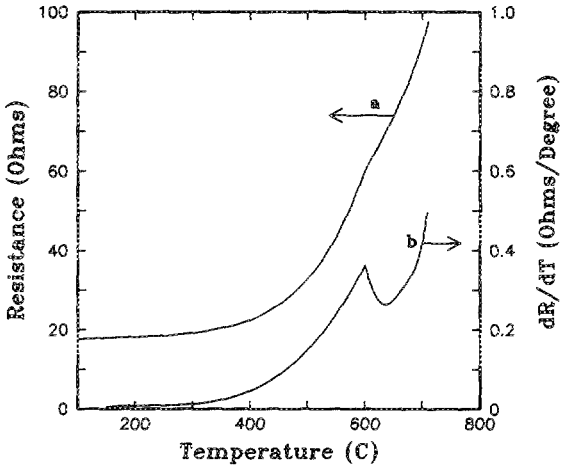

FIG. 3. High-temperature resistance and dR/dT for the film corresponding to curve b in Fig. 2. The bump due to ordering of oxygen is evident in both curves.

grains. It is possible that the differences in superconducting properties between the fast and slow heating procedures could all be explained by grain boundary effects.

The quick heating of the samples that produced curves b and c in Fig. 2 did not allow the recording of meaningful resistance versus temperature curves, but the subsequent slow cooling did. Such a curve for the film corresponding to curve b in Fig. 2 is shown in Fig. 3. Curve a in this figure is the resistance of this film, and curve b is the slope, dR/dT. The first thing to notice is the metal-like positive temperature coefficient of resistance over the whole range. This behavior was repeated quantitatively during three cycles to 750 °C and back in flowing oxygen. The steep rise in resistance above 400 °C corresponds to the known loss of oxygen as the sample is heated above this temperature. The dramatic effect on resistance has to do with the contribution of each new oxygen atom to the carrier density. (The very high resistivity of these films implies mean free paths no larger than the cell size, and makes it likely that oxygen content would have a negligible effect on mobility.)

A bump is visible in Fig. 3 in the resistance data at about 600 °C. The derivative, curve b, shows this feature much more clearly. Similar features have been observed by Freitas and Plaskett[7] in resistance measurements of bulk ceramic samples, although at somewhat higher temperatures. They have shown convincing evidence that this bump corresponds to an order–disorder transition in the oxygen chains, which is associated with the tetragonal–orthorhombic phase transition observed by x-ray and neutron diffraction experiments. Our data demonstrate that this phase transition can also be observed by resistance measurements in thin films. We note that this bump is most evident in films with the sharpest superconducting transitions, and is probably a good high-temperature indicator of superconducting performance.

Figure 4 shows the influence of a helium atmosphere on the resistance during anneal. This plot is for a sputtered film on sapphire, and depicts vividly the rapid change in resistance as the flowing gas is switched between helium and oxygen. The curve begins at high temperature in oxygen, cooling

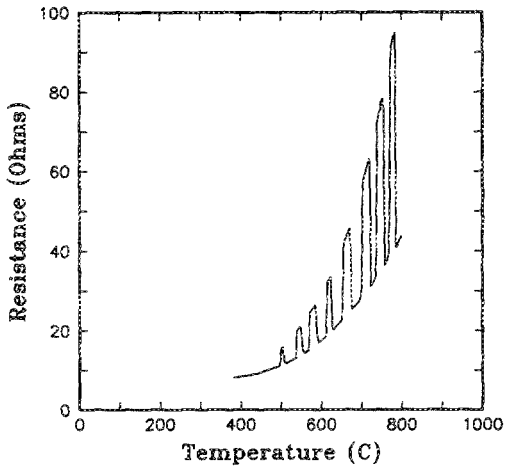

FIG. 4. High-temperature resistance of a film on sapphire, with the flowing gas switched back and forth between helium and oxygen. On the time scale of switching the gases, the response in resistance was a virtual step function, and was completely reversible to below 500 °C.

at about 4 °C per minute. Just below 800 °C the oxygen gas is turned off and a similar flow of helium is substituted. The resistance responds about as fast as the gas can be changed, and shoots up from around 40 Ω to over 90. As the sample continued to cool the flowing gas was repeatedly switched back and forth, showing the reversibility of the process down to around 500 °C. Below 500 °C changes in resistance became much less reversible. At 450 °C, for example, equilibrium was not achieved after 15 min, more than an order of magnitude increase in time.

It should be pointed out that the data in Fig. 4 were obtained with the exit end of the furnace open, so that with helium gas flowing there was still a substantial amount of oxygen present. The furnace for this sample had a 7.5-cm bore, and the sample was about 50 cm from the open end. Gas flow was measured by a flow meter calibrated for air, and was kept at 3 l per minute for both gases. With the end open, room air could account for half the atmosphere in the tube, so that with helium flowing, the partial pressure of oxygen could have been as much as 0.1 atm.

When the open end of the tube was capped off to minimize infiltration of room air, the resistance with helium flow was at least an order of magnitude higher. These observations are consistent with those of Freitas and Plaskett, although with their bulk samples, they had no way to observe the extreme speed of response to changes in ambient oxygen.

In summary, we have shown evidence that the superconducting YBC oxide forms from the deposited mixture in films at a temperature of 750 °C. However, the best superconducting performance was achieved by rapid heating to about 900 °C in flowing helium, followed by slow cooling to room temperature in an oxygen flow.[5,10] The resistance during this process can be monitored to observe the absorption and ordering of oxygen, and to control the annealing process.

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