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Thin superconducting oxide films

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Studies of superconductivity in thin films of La-Sr-Cu-O and Y-Ba-Cu-O have resulted in samples completely superconducting at 87 K and with onsets as high as 97 K. The high-T_c materials show a strong Meissner effect which agrees with the temperature dependence of the resistance. Critical current densities in excess of 300 A/cm^2 have been measured close to T_c in the Y-based materials.

Within the past year superconducting materials with superconducting transition temperatures in excess of 90 K have been fabricated and studied.[1-5] These bulk materials are generally referred to as oxide superconductors and for the most part consist of compounds of La, Sr, Cu, and O (Refs. 1 and 6) or Y, Ba, Cu, and O (Refs. 2–5). They can be most easily formed by sintering the constituent oxides at high temperatures. A typical good superconducting compound is $La_{1.8}Sr_{0.2}CuO_4$, which has a T_c at about 40 K, or $Y_1Ba_2Cu_3O_y$, which has a superconducting transition in the 90-K range. The latter compound appears to be the superconducting phase[3,4] in the $Y_{1.2}Ba_{0.8}CuO_4$ compound reported earlier.[2] These materials represent an exciting new development in both science and technology and interest in their properties is widespread. Of equal interest, particularly for applications, is the possibility of making high-T_c films. In this Rapid Communication we describe our work in fabricating such films by vapor deposition from three metal sources in a partial pressure of oxygen. Superconducting films have been successfully fabricated in both the La and the Y system, and we will describe the results in this Rapid Communication. Previous work on the bulk superconductors surprisingly showed that the measured critical currents were generally quite low—a few hundred A/cm^2.[2,7] These low values assumed a uniform distribution of the current. However, the current may flow in narrow channels and previous work has shown that the current may actually flow in percolating or grain-boundary-like regions.[6,8] This would lead to higher local current densities. It is quite important to understand these effects in films, as many applications require relatively high critical currents.

The vapor deposition system consisted of an ultrahigh vacuum system with three 10-kV electron beam heated sources. The deposition rates could be controlled over the range of 0.01–1 nm/sec and the substrate temperature could be varied from -100 to 700 °C. The substrates used generally consisted of sapphire wafers commercially available with both c- and a-axis orientation. Plates of MgO were also used as substrates both with a ⟨110⟩ and a ⟨001⟩ orientation. In general, only small differences were found in the final films among the above substrates. The three electron guns were filled with the desired three metals, e.g., La, Sr, and Cu or Y, Ba, and Cu, and the rates adjusted to give the nominal desired composition at the substrate plane. It was initially found that films made at room temperature in a high vacuum were often unstable upon removal to room ambient and were not superconducting. It was also observed that the films were not totally uniform in appearance or composition, suggesting corrosion reactions. X-ray data on the La-Sr-Cu-O compositions confirmed that many of the diffraction peaks of the tetragonal K_2NiF_4 were present after an oxidizing anneal. In order to avoid the deterioration of the films and obtain stable films at room ambient, samples were made in a partial pressure of oxygen with presure up to 10^{-3} Torr at elevated substrate temperatures, typically around 450 °C. Film thicknesses were between 0.1 and 1 μm and were relatively smooth in the as-deposited state. The ac resistance versus temperature data for these films were generally taken using four terminal pressure contacts, while susceptibility measurements were made using a superconducting quantum interference device (SQUID) magnetometer. The applied current was kept small during the R-vs-T measurements, typically around 1 μA; smaller currents were also used. The Y-based films showed a strong Meissner effect, while the La films showed a correspondingly weaker effect. While powder x-ray patterns were taken to monitor the structure, this work will be reported in a subsequent paper. The visual appearance of the films is also of interest as the as-grown La material appeared almost dark and metallic with a positive resistance ratio of 1.1 to 1.5 down to 4 K, while the Y films were dark and high resistance as-deposited. These as-deposited films did not generally go superconducting. With a low-temperature anneal in oxygen (<500 °C) the La films became insulating; however, with a subsequent 650 °C and higher heat treatment in O, the films became metallic again and generally were superconducting at low temperatures. The Y-based films required higher temperatures, generally between 900 and 950 °C. The films became thicker and rougher after the oxygen annealing.

While x-ray data were useful in understanding properties of the films we found it more beneficial to use chemical analysis to obtain the film composition. Using these data we attempt to make films in the composition range near the reported bulk values. For the La compounds the aimed for stoichiometry was $La_{1.8}Sr_{0.2}CuO_4$ and the measured composition was within 20% of this value. For the Y-based samples the $Y_1Ba_1CuO_4$ and $Y_1Ba_2Cu_3O_y$ atomic ratios were sought. Again it was possible to get within 20% of the desired composition as verified using chemical

analysis. The value of y that gave the best T_c to date was about 8. The data as shown in the figures are from different runs and composition and are within about 15% of the aimed for value. It appears that the exact composition is not necessary to see the high-T_c superconductivity in agreement with work on bulk materials. Some variation over the plane of the substrates is also observed. However, knowledge of the chemical composition is of great value in adjusting the vapor deposition rates, temperature, and background pressure. The atomic percents in the atomic formulas have been normalized to a copper value of 3. On this basis the oxygen value was generally around 9 ± 2, although the error in this value was larger because it is determined by difference after analyzing for all the metal constituents.

Resistance versus temperature data for $La_{1.9}Sr_{0.31}CuO_4$ thin film generally showed broad transitions which had onsets at about 38 K and were completely superconducting at around 8 K. Just below room temperature the resistance drops in metallic fashion and as the temperature is lowered further a small rise (presumably due to localization effects) occurs. This behavior is seen for most of our La-based films, particularly those with broad transitions. Such behavior is presumably due to both the off stoichiometry and the fact that while the x-ray data show many of the correct peaks, some extra phase peaks are present. The films do not appear to be a single phase and full epitaxial growth of the films is not observed. While the onset T_c is generally high, some films are not completely superconducting at 4 K.

The Y-based films are more spectacular in their high-T_c behavior. Figure 1(a) shows the R versus temperature for a film of composition $Y_{0.75}Ba_{1.35}Cu_3O_{7.7}$. The onset of superconductivity is clearly observed to be about 97 K, and the films are generally completely superconducting at about 50 K. There is still some microscopic evidence for the existence of a second phase in the films which is also indicated by the two different slopes in Fig. 1(a). Closer study of the x-ray diffraction of these samples should make it possible to identify the phases present. However, in a subsequent run at a somewhat different composition, a much higher final transition temperature is observed with a narrower transition width. These results are shown in Fig. 1(b), where the onset of superconductivity is at 97 K and the samples are completely superconducting at 87 K. Many of the films continue to show small tails on the R-vs-T curves, resulting in a lower T_c and indicating the existence of a second phase. The atomic composition for these films is about $Y_{0.87}Ba_{1.53}Cu_3O_{11}$ with some variation over the substrate plane. The oxygen value has an uncertainty of about 20%, while the metal values are good to a few percent. However, superconductivity above liquid nitrogen temperature has been clearly observed in the films as well as the bulk, opening many new possibilities for both scientific and applied studies. These films also have a strong Meissner effect, showing the diamagnetic onset corresponding to the resistive onset. These results are indicated in Fig. 2 for the higher-T_c sample. The susceptibility was measured using a SHE SQUID magnetometer with the applied field parallel to the film plane. The diamagnetic signal from this sample is easily detected in

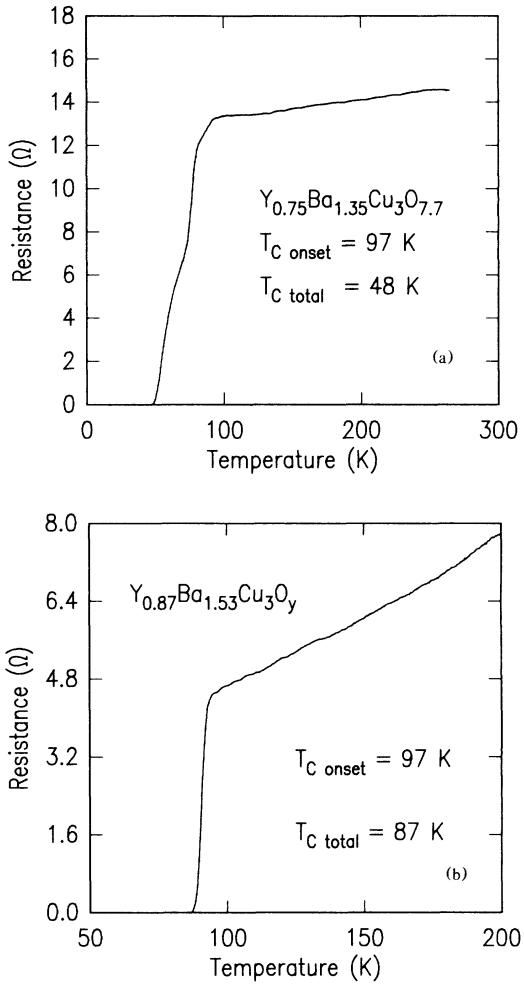

FIG. 1. Resistance vs temperature for two yttrium-based films of about 400-nm (as-deposited) thickness. The value for y for these films is 9 ± 2.

spite of the small film volume (6.9×10^{-6} cm^3). The MgO substrate has not been subtracted, but its contribution is small, as can be seen by the behavior above 100 K. The diamagnetic susceptibility was measured while cooling in an applied magnetic field of 100 G to determine the Meissner effect. Under these conditions the sample exhibits about one third of the calculated Meissner susceptibility ($\frac{1}{4}\pi$). The sample was also cooled in zero field and 100 G applied at 5 K. The latter procedure measures the superconducting current's diamagnetic shielding and is a more sensitive way of detecting transition and onset temperatures. The data show that large diamagnetic-susceptibility effects are present at the temperature where the resistive transition is complete. The resistive onset temperature is also detectable in the diamagnetic signal. It should also be observed that the resistance continuously decreases from room temperature with a resistance ratio of about 3 prior to the beginning of superconductivity.

Critical currents were studied in these films by measuring the current-voltage characteristics using an ac conduc-

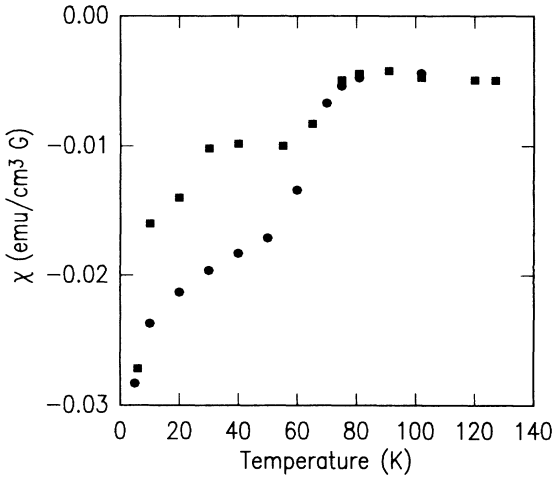

FIG. 2. Temperature dependence of the diamagnetic susceptibility for the Y film of Fig. 1(b) measured in a 0.01-T field. The sample was studied both by cooling in zero field (●) and in the 0.01-T field (■). The zero-field cool-down measurements were taken while warming in the applied field.

tance modulation technique, i.e., the dc I-V characteristic was measured by using a small ac voltage to determine the slope, leading to data of the resistance as a function of voltage. These data could then be integrated digitally to give the I-V results. The current at which 1 μV appeared was taken to be the critical current. The sample configuration was that of a flat film and heating at the contacts did not permit an accurate determination of the temperature dependence of the current. For the La-based material with a T_c at 8 K, the critical current at 4.2 K was about 3 μA, leading to a current density of about 1 A/cm^2. The high-T_c Y film could only be measured near the transition ($\simeq$77 K) and showed a critical current density of about 300 A/cm^2. These values are in the range of those found in bulk materials. Much higher currents are needed to drive the samples normal, and the resistance that first appears at the critical current is not the normal resistance. At this resistance the films appear to be in a mixed state, possibly exhibiting flux flow resistance. The La films also show current steps at nonzero voltages indicating a somewhat granular, polycrystalline structure in general agreement with the x-ray observations. In this regard, it should be observed that the above current densities assume a uniform current distribution which is apparently not the case. Thus local current densities should be considerably higher, particularly if the current path is through grain boundaries or a percolating network. As greater control of the sample geometry becomes available more detailed studies of the critical current can be achieved.

Thus, we have clearly shown that the high-T_c superconductors can be grown as thin films with onset T_c up to 97 K and with a strong Meissner effect. Some critical currents have been obtained for these films and indicate the granular, multiphase composition. As the film fabrication develops and uniform films of the correct composition and single phase are developed, the critical current should increase and applications for the high-T_c superconductors should grow.

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