Properties of high-temperature superconducting films of the Y-Ba-Cu-O system grown from the melt

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Results of electrical and magnetic measurements carried out for polycrystalline superconducting films in the Y-Ba-Cu-O system grown from the melt by a new technique are reported. The superconducting transition temperature is $T_c \sim 90$ K, and the transition width is 5–10 K. The resistance is found to be a power function of the current in the low-temperature wing of the extended phase transition of the films.

Bednorz and Müller's discovery[1] of high-temperature superconductivity and the subsequent synthesis of Y-Ba-Cu-O ceramics with a superconducting transition temperature T_c above the temperature of liquid nitrogen[2] have stimulated a search for a technology for synthesizing thin films and coatings based on high-temperature superconductors of the Y_2O_3-BaO-CuO system. Researchers are presently devoting their efforts primarily to the deposition of high-temperature superconducting films through sputtering or of ceramics in the Y_2O_3-BaO-CuO system, for either the separate components of the system or in a mixed technology.

The magnetron sputtering method has now been adopted most widely because of the relatively high deposition rate (5–10 nm/s) and the availability of suitable technological apparatus.[3–8] It should be noted, however, that the results of the use of this method are presently limited in comparison with those achieved by the method of electron-beam sputtering from several sources. An apparatus of this type has produced[9] high-quality single-crystal films with $T_c \approx 90$ K and a transition width $\Delta T_c \approx 1$ K.

Notable among the other sputtering methods which are being used are the methods of low-frequency plasma sputtering[10] and the pulsed laser sputtering of ceramics.[11,12] There is also the method of molecular-beam epitaxy.[13] The synthesis of oriented films with $T_c \approx 82$ K has recently been reported.[13] The use of emulsions and suspensions of ground powders of Y-Ba-Cu-O ceramics to synthesize superconducting coatings is being reported.[11,14,15]

In this letter we report the results of a study of films of the Y-Ba-Cu-O system grown from the melt. The method is based on the ability of the binary system BaO-CuO to form a melt over a certain interval of the mole fractions of the components. As the third component in the system we used single-crystal yttrium oxide (an active substrate). The results which we are reporting here are of a preliminary nature. In this stage of the research we were testing the possibility in principle of reproducibly synthesizing high-quality superconducting films of a definite thickness which did not require special technological approaches for their deposition.

The films were deposited on an unoriented polished substrates of single-crystal yttrium oxide, synthesized by induction melting of a powder of the type ItO-Mgr oxide in a cold crucible. The substrate, 2 mm thick, was in contact with the melt to the point of complete wetting for several minutes. The subsequent operations of thermoreactor diffusion and annealing resulted in the formation of a polycrystalline superconducting film. The thicknesses of the films were 5–10 μm. The annealing was carried out in either an oxygen atmosphere of air at 850 °C, followed by a cooling at a rate of 200 deg/h.

The quality of the resulting superconducting films was determined by measuring the temperature dependence of the resistance R by a standard two-probe method.[16] The current contacts and the probe contacts were fabricated by the deposition of indium. The resistance of the current contacts was no more than a few ohms. For the electrical measurements we used films with typical dimensions of 0.8×0.5 cm.

Figure 1 shows the temperature dependence of R, normalized to the room-temperature value, measured during the passage of a direct current $I = 500\ \mu$A. Curves 1 and 2 correspond to films which have been annealed in oxygen, while curve 3 corresponds to a film which spent part of the time in air. We see that for the best of these samples the superconducting transition occurs at $T_c \approx 90$ K in a fairly narrow temperature interval $\Delta T_c \approx 5$ K (we are ignoring here the tail on the phase transition which stretches down to low temperatures; we will discuss this tail below).

It also follows from the data in Fig. 1 that as the temperature is lowered from room temperature to the beginning of the transition, the decrease in R is monotonic and "metallic." The relative change in the resistance is 10–15%. At room temperature the values of R for the various samples lay in the range 2–10 Ω. A metallic conductivity is usually observed in the normal phase of single-phase superconducting ceramics and high-quality films.

For both ceramic and film high-temperature superconductors, there are still technological difficulties to be overcome in the production of materials with highly uni-

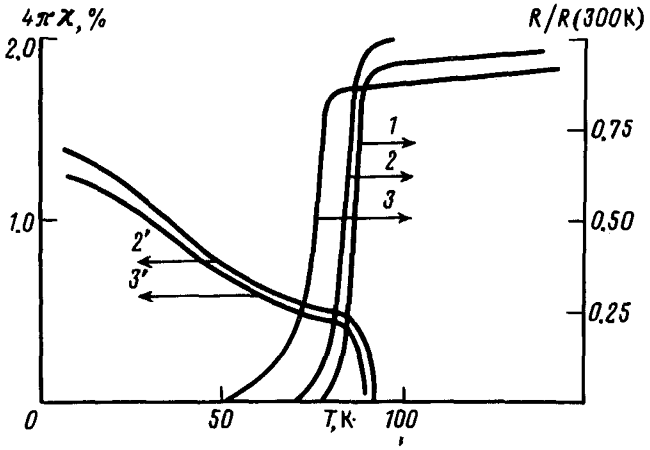

FIG. 1. Temperature dependence of the resistance (1–3) and the diamagnetic susceptibility (2',3') of the films. Annealing conditions: 1—20 h in oxygen; 2,2'—24 h in oxygen; 3,3'—14 h in air, followed by 10 h in oxygen.

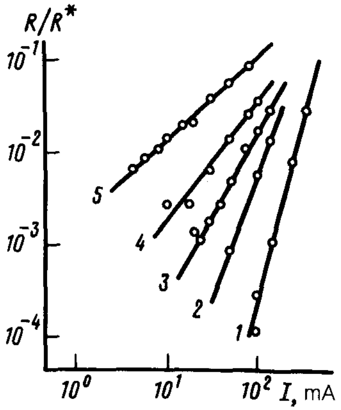

FIG. 2. Current dependence of the film resistance. T, K: 1—4.3; 2—42; 3—54; 4—61; 5—71.

form critical properties. The difficulties lead to a broadening of the phase–transition curve. The system has a set or distribution of local critical current densities, which depend on the temperature. An important point is that in this case the measured width of such a "macroscopic" transition may depend highly on the current I at which the measurements are taken. These arguments are confirmed by measurements of the current dependence of the resistance of the films at various temperatures $T < T_c$ and at various currents I above the critical currents at the given temperature. The results of these measurements are shown in Fig. 2 for conditions corresponding to a coexistence of normal and superconducting phases in one of the samples (line 1 in Fig. 1). The results have been normalized to the value of R^* near the transition on the side of the normal phase; here $R(I, T) \ll R^*$. We see that over the current range studied we have $R(I) \sim I^n$; the exponent n increases with decreasing temperature.

Using the results in Fig. 2 along with linear dependences interpolating the experi-

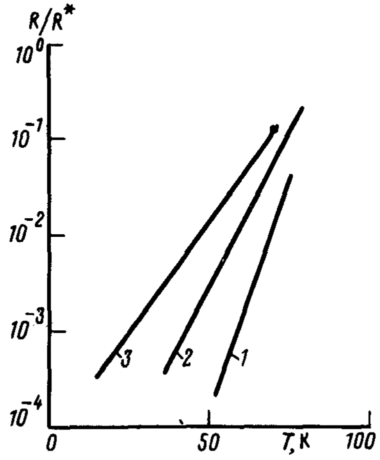

FIG. 3. Change in the temperature dependence of the resistance of a film with increasing current. I, mA: 1—10; 2—50; 3—100.

nental points, we can construct a “low-resistance” tail of the curve of the superconlucting transition of the sample for various values of I (Fig. 3). The broadening of the ransition tail with increasing I serves as an illustration of the effect of the current on he transition width.

In order to find direct proof of the existence of a superconducting phase in the esulting films and also to determine more precisely the temperature at which the hase transition begins in the nonuniform film material, we studied the magnetic roperties of the films. We measured the diamagnetic susceptibility by a mutual-inducion method in an alternating magnetic field no stronger than 4.5 G at a frequency of 19 Hz. Since the sensitivity of this method for plane, nearly two-dimensional films is ow, we used as samples in these measurements an envelope of the superconducting ilm around a substrate, to simulate the superconductivity of a bulk sample.

Figure 1 shows the temperature dependence of the diamagnetic susceptibility χ of he samples for which resistance curves 2 and 3 were measured. For both films, the hase transition typically begins at $T \sim 90$ K. Despite the important differences in the emperature dependence $R(T)$, the curves of $\chi(T)$ are the same here, within the xperimental error. This agreement probably means that the annealing conditions inluence primarily the critical parameters of regions of a weak superconductivity (the oundaries of microcrystals) in the circuit of the leakage current. The apparent explaation for the low apparent fraction of the superconducting phase in the film enveopes synthesized in this manner is a significant penetration of the magnetic flux in arts of the film in a perpendicular field and at the film boundaries (through the edge f the sample). Another contributing factor is a hysteresis in the magnetization reveral in an alternating magnetic field due to the penetration of magnetic flux along a etwork of weak links and the trapping of this flux at inhomogeneities.[17]

In summary, the results of this study show that even in this preliminary learning tage the polycrystalline films of the high-temperature superconductor, which have een synthesized from the melt, exhibit a high superconducting transition temperaure, $T_c \approx 90$ K, and a fairly narrow region (5–10 K) for the superconducting transiion of regions of weak links between crystallites. The film-synthesis method is quite imple and holds promise both for practical applications of superconductors and for ynthesizing film samples for physical experiments. In particular, the current-voltage haracteristics of the films studied here have the characteristic power-law dependence s the current is varied over a wide range. We believe that this is the first observation f such a behavior for high-temperature superconductors; this behavior has been seen n research on disordered “classical” superconductors.[18]

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