

# Reproducible technique for fabrication of thin films of high transition temperature superconductors

P. M. Mankiewich, J. H. Scofield, W. J. Skocpol, R. E. Howard, A. H. Dayem, and E. Good

Room 4D-335, AT&T Bell Laboratories, Holmdel, New Jersey 07733

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We report on a new process to make films of  $Y_1Ba_2Cu_3O_7$  using coevaporation of Y, Cu, and  $BaF_2$  on  $SrTiO_3$  substrates. The films have high transition temperatures (up to 91 K for a full resistive transition), high critical current densities ( $10^6$  A/cm<sup>2</sup> at 81 K), and a reduced sensitivity to fabrication and environmental conditions. Because of the lower reactivity of the films, we have been able to pattern them in both the pre-annealed and post-annealed states using conventional positive photoresist technology.

The recent discovery of a broad class of materials such as  $Y_1Ba_2Cu_3O_7$  with superconducting transition temperatures exceeding the boiling point of liquid nitrogen (77 K) has sparked wide interest in studying the physics and possible applications of these materials. The mechanical and electrical properties of the available bulk (ceramic) materials are not yet suitable for many of the traditional large-scale applications such as magnets or power transmission. Thin films of such materials can be made, however, that have much larger critical current densities (albeit on special substrates).<sup>1-3</sup> With further development, these might readily be integrated into either hybrid superconducting/semiconducting circuits (e.g., as interconnects) or developed into an all-superconducting electronics technology.

While there have been several reported successes in producing these films using *e*-beam evaporation<sup>1,3,4</sup> or sputtering,<sup>2,5</sup> the processes require extreme care and are difficult to reproduce on a routine basis. In addition, the bulk material is sensitive to environmental conditions, especially water,<sup>6</sup> indicating that the films may require special handling to ensure stability. In particular, we have found that films made by coevaporation using a Ba metal source quickly degrade in the presence of moisture. We report here a new process based on coevaporation of Y, Cu, and  $BaF_2$ . It reproducibly makes thin films that have greatly reduced sensitivity to moisture and full transitions (zero resistance) to the superconducting state in the range  $T_c = 85$ –92 K.

Barium metal is easily oxidized and reacts quickly, developing a white, shaggy surface in a few minutes upon exposure to air. This greatly complicates the operation and maintenance of a vacuum deposition system. The  $BaF_2$  source, in contrast, is relatively inert, does not require special handling, and does not significantly contribute to outgassing in the deposition system. Films made with  $BaF_2$  survive direct immersion in water before annealing and we have not observed any degradation after exposure of the annealed films to air. This is in sharp contrast to films made with Ba metal which dissolve in water in their pre-annealed state. The films containing  $BaF_2$  can also be patterned using conventional photolithographic techniques either before or after annealing. This is a critical first step towards making test devices and studying the characteristics, such as rf surface loss, of importance to electronics applications. In addition, the low-field critical current density of these films is high. Using a

microbridge geometry defined by scratching, we have measured a critical current density of  $1 \times 10^6$  A/cm<sup>2</sup> at 82 K in our best film to date.

Our best results are obtained on (100) oriented  $SrTiO_3$  substrates.<sup>7,8</sup> These are solvent cleaned and then blown dry with dry nitrogen before insertion in the evaporation station.

The evaporator is a diffusion-pumped glass-bell-jar system with a base pressure before evaporation of  $2 \times 10^{-6}$  Torr and an oxygen pressure during deposition of  $1 \times 10^{-5}$  Torr. The substrate holder is ordinarily not heated, although we have obtained acceptable results by heating it to nominally 550 °C. We have also obtained  $T_c \approx 90$  K in films made without the addition of oxygen during evaporation.

We coevaporate Y, Cu, and  $BaF_2$  from separate sources, heating the Y in a 3-kW electron beam hearth, and the  $BaF_2$  and Cu in separate tungsten resistive boats. The  $BaF_2$  is in the form of 99.9% purity crystalline pieces.<sup>9</sup> Electron diffraction studies of  $BaF_2$  films evaporated from a similar source show that the material vaporizes and deposits as a molecule. The rates for all three sources were controlled using feedback from quartz crystal monitors. We were guided to appropriate rates by compositional depth profiling of as-deposited and annealed films using Auger analysis during ion milling, calibrated using bulk  $YBa_2Cu_3O_7$  as a standard. Total indicated  $BaF_2$  deposition thicknesses range from 1000 to 5000 Å. (The deposited  $BaF_2$  thickness corresponds roughly to the final thickness of the annealed films.)

After deposition the films are typically brown, translucent, and insulating. They then are placed in a 1-in. tube oven with a slow flow of dry oxygen and annealed at peak temperatures in the range 800–920 °C for times varying from 30 min to 6 h. By using spring-loaded electrical contacts, we have been able to measure the superconducting properties of annealed films, inspect the films optically, and then subject them to additional annealing cycles.

During annealing, nontransparent metallic regions nucleate and grow in two morphologies: irregular patches and mutually perpendicular needlelike structures in the plane of the surface. Metallic conduction and high transition temperatures are observed when the network of nontransparent regions is sufficiently dense to percolate across the film. From our observations we conclude that both the patches and the needles are high  $T_c$  materials in different crystal orientations. Thinner films subjected to lower annealing

temperatures have relatively fewer needles, and x-ray analysis shows a very high degree of fully oriented polycrystalline order, with  $c$  axis perpendicular to the plane of the substrate. This is the desired orientation for optimal transport in the plane of the film. The x-ray results will be presented elsewhere in conjunction with scanning Auger compositional analysis and Rutherford backscattering (RBS) channeling experiments.

Figure 1 is a scanning electron micrograph of the microstructure of a 2000-Å-thick film initially deposited on a room-temperature SrTiO<sub>3</sub> substrate and subsequently annealed for 3 h at a peak temperature of 850 °C. This film has a very high proportion of interconnected metallic patches, which have a somewhat pebbly texture at the surface. A few oriented needles are visible near the top of the picture. A pattern of occasional voids and bright (insulating) regions decorates the apparent interstices between the metallic patches. Despite these imperfections, the film had outstanding superconducting properties.

Four-terminal low-frequency ac measurements were made with spring-loaded contacts mounted on tenth-inch centers. The room-temperature resistivity of the film was  $\approx 130 \mu\Omega$  cm. To reduce the contact resistance for critical current measurements on the film of Fig. 1, 1 mm gold dots were evaporated through a shadow mask onto the film, and then aligned with the pressure contacts. The film was scratched with a carbide tool so that the current from one pair of contacts to the other was forced to flow through a 75- $\mu$ m-wide constriction. The substrate was pressed against a copper block with an embedded silicon diode thermometer and a heater on the backside. This assembly was mounted inside a phenolic shell with a small hole and suspended in a helium storage Dewar above the surface of the liquid. Reproducible measurements were obtained for both heating and cooling, as well as for different distances of the probe above the liquid level in the Dewar. The thermometer calibration and transition temperatures of other samples were checked using liquid nitrogen as a coolant.

Figure 2 shows the resistive-to-superconducting transi-

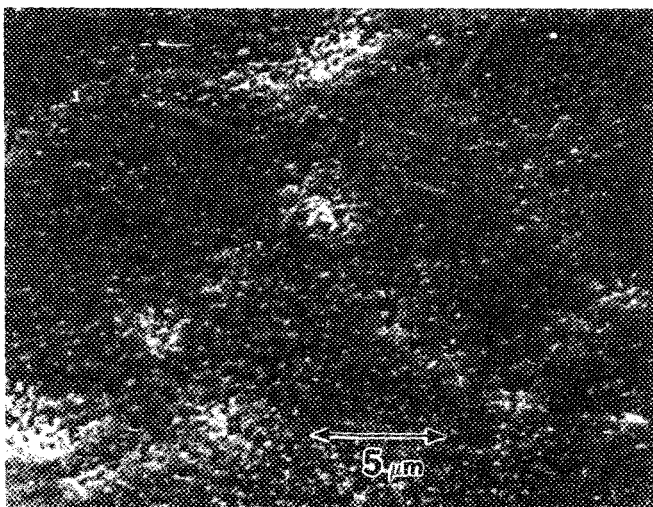


FIG. 1. Scanning electron micrograph of a 2000-Å-thick superconducting film of Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> made using BaF<sub>2</sub> as a source material.

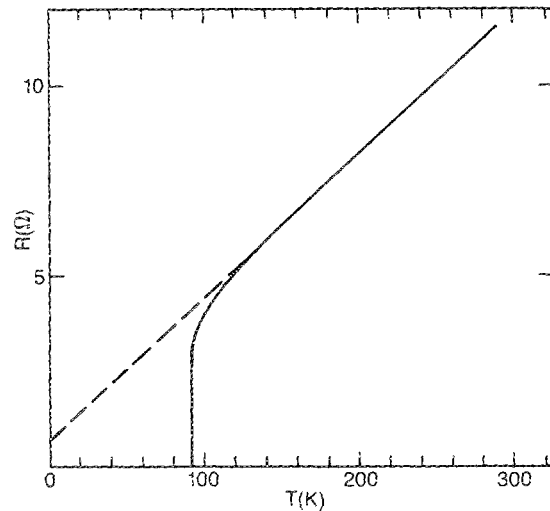


FIG. 2. Resistive transition of a 75- $\mu$ m-wide microbridge scratched in the film of Fig. 1.

tion of the microbridge at 1  $\mu$ A current level. Zero resistance is obtained at about 91 K and the transition width is about 1–2 K. The extrapolation of the high-temperature resistance to a small intercept at zero temperature is consistent with a high proportion of crystallites with the  $c$  axis perpendicular to the substrate.<sup>10</sup> The ac measuring current was then increased to 1 mA, and an additional dc current through the sample was supplied. The beginnings of the resistive transition were then monitored as a function of temperature at several levels of applied dc current. The corresponding critical current density as a function of temperature is shown in Fig. 3. The solid symbols correspond to a flux flow resistance of approximately  $2 \times 10^{-4} R_N$  where  $R_N$  is the normal state resistance of the bridge. The open symbols show the temperature corresponding to a flux flow resistance about ten times higher. At the highest current level this coincided with a discontinuous transition. At  $1 \times 10^6$  A/cm<sup>2</sup> current density (150 mA), the first indications of flux flow occurred only above 77 K, and a discontinuous transition to the normal state did not occur until nearly 82 K. At 100 mA, the microbridge survived several such cycles, but at 150 mA it burned out, fracturing along a line between the narrowest points of

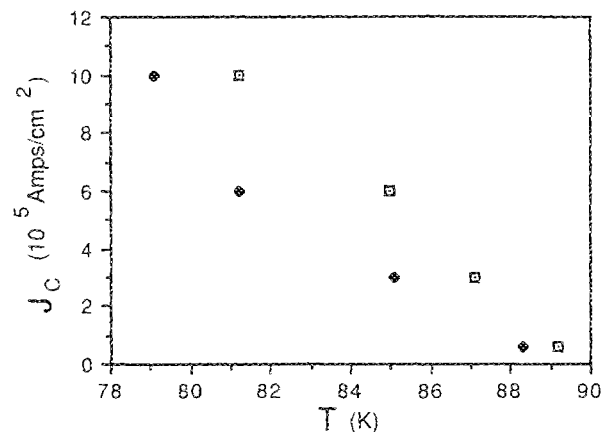


FIG. 3. Critical current density of the microbridge of Fig. 2. The solid symbols correspond to a flux flow resistance criterion of  $2 \times 10^{-4} R_N$  and the open symbols to  $2 \times 10^{-3} R_N$ .

the constriction, proving that the current was flowing through the microbridge.

Films made with BaF<sub>2</sub> on SrTiO<sub>3</sub> substrates are remarkably insensitive to fabrication and environmental parameters. Full resistive transitions above 80 K were obtained under a variety of conditions. For example, we have successfully changed the BaF<sub>2</sub> deposition rate by  $\pm 10\%$ , lowered the Cu deposition rate by 10%, and even deposited an initial underlayer of 600 Å of pure BaF<sub>2</sub>. We have successfully deposited films without the deliberate introduction of oxygen, and then allowed them to sit for 18 h in air before annealing. We find it possible to measure annealed films, subject them to water condensation from the air, and remeasure them without degradation of transition temperature or visible change. We have even successfully immersed as-deposited films in de-ionized water for 5 min before annealing.

We have also demonstrated a variety of patterning techniques using conventional positive resist. Liftoff was used to make 2 μm and larger features by depositing films on room-temperature SrTiO<sub>3</sub> substrates coated with a patterned positive photoresist layer, removing the photoresist with acetone, and then annealing the remaining patterned film. We have also patterned annealed films by coating them with positive photoresist, exposing the resist, and developing with standard aqueous developer. The pattern was transferred to the film by wet etching in dilute HCl (10 parts H<sub>2</sub>O to 1 part HCl).

Despite such treatments, to date 23 out of the 25 films made using BaF<sub>2</sub> on SrTiO<sub>3</sub> substrates have achieved transition temperatures  $T_c$  ( $R = 0$ ) between 80 and 92 K. (The two exceptions saw unusual thermal histories.) The microstructural properties of the films do vary, though, and this affects important parameters such as the critical current.

Nevertheless, the robust character of all our films deposited using BaF<sub>2</sub> as the deposition source is truly remarkable.

In contrast, the best  $T_c$  that we obtained in our deposition system using a Ba metal source (six attempts using SrTiO<sub>3</sub> substrates) was 60 K.

By replacing the metallic Ba source with BaF<sub>2</sub> for the coevaporation of Y, Ba, and Cu, we have been able to fabricate reproducibly thin films of superconductor with reduced sensitivity to fabrication conditions. We have also shown that these films can be patterned using conventional liftoff processing and should be suitable for conducting a wide range of research projects into the possible applications of these materials.

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