The research program described here was designed to contribute to the evaluation of high Tc superconducting materials for usefulness in electronic circuitry. The experimental techniques emphasized in this plan included electron tunneling and the use of intense magnetic fields to obtain information about the electronic properties of thin films of these materials. The superconductors studied included BiSrCaCuO, NdCeCuO, and BaKB10. Thin films were formed by pulsed laser ablation, magnetron sputtering, and molecular beam epitaxy. In addition to obtaining electronic transport and tunneling data on these materials, a technique was found to make high-quality superconductor-insulator-superconductor tunnel junctions using artificial grain boundaries. This technique is the only one thus far discovered for making all-thin-film quasiparticle tunnel junctions reliably from high Tc materials.
Synthesis and Study of High-\(T_c\) Superconducting Electronic Materials

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Paul M. Tedrow, Principal Investigator

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Abstract

The research program described here was designed to contribute to the evaluation of high $T_c$ superconducting materials for usefulness in electronic circuitry. The experimental techniques emphasized in this plan included electron tunneling and the use of intense magnetic fields to obtain information about the electronic properties of thin films of these materials. The superconductors studied included BiSrCaCuO, NdCeCuO, and BaKBiO. Thin films were formed by pulsed laser ablation, magnetron sputtering, and molecular beam epitaxy. In addition to obtaining electronic transport and tunneling data on these materials, a technique was found to make high-quality superconductor-insulator-superconductor tunnel junctions using artificial grain boundaries. This technique is the only one thus far discovered for making all-thin-film quasiparticle tunnel junctions reliably from high $T_c$ materials.

Introduction

From our point of view, the most important characteristic of a superconducting material and its fabrication processing for use in electronic circuitry is the ease with which tunnel junctions can be formed. The oxide superconductors have proved to be notoriously resistant to the development of reliable and high-quality tunnel junctions. The pursuit of good junctions largely motivated our changes of experimental course from BiSrCaCuO (BSCCO) to NdCeCuO (NCCO) to BaKBiO (BKBO). Although modestly good junctions were obtained with all three materials, the best junctions by far were fabricated using BKBO. The results of our work on BSCCO and NCCO have been described in the previous two annual reports and have been published in scientific journals. This report will focus, therefore, on the BKBO results. The first two sections summarize the results on BSCCO and NCCO.
Study of BSCCO

The high transition temperature ($T_c$) material BSCCO was attractive for electronic applications for two reasons. First, the 2223 phase has a $T_c$ of about 110 K, considerably above that of YBaCuO (YBCO). Second, the surface of BSCCO is less subject to degradation by exposure to air than YBCO. Unfortunately, the existence of three phases, denoted by 2201, 2212 and 2223, make the problem of forming epitaxial thin films very difficult. The requirements for thermal and compositional control are extremely stringent. Thus, fabricating tunnel junctions proved to be very difficult. We initially used magnetron sputtering and laser ablation to make films, eventually settling on the latter technique. Considerable effort was expended measuring transport properties of the films as a function of deposition conditions [1]. The best tunneling results were obtained on a multiphase film in which structure corresponding to the energy gaps of the phases present was observed [2]. The magnetic field dependence of the transport properties was measured and demonstrated the extreme anisotropy of this material and the importance of flux motion in its magnetic field behavior.

Studies of NCCO

The principal motivation for studying NCCO is that it is the only one of the high $T_c$ materials that is electron doped, the others being hole doped. Its $T_c$ of about 20 K is probably too low to be of practical interest. On the other hand, we found that its surface quality degraded at a rate a hundred times slower than that of YBCO, so there was some promise of good tunneling capabilities. The films we studied were made by laser ablation. This material is very anisotropic, and many of its transport properties could be described in terms of an assembly of nearly independent two-dimensional conductors (the Cu-O planes), both in the normal and the superconducting state [3].
Two important results were obtained from this work. First, because of the modest \( T_c \) of this material, the magnetic fields available at the Magnet Laboratory were sufficient to exceed the critical field at all temperatures. This capability allowed us to study the magnetic response of this material far more completely than can be done for the higher transition materials. As a result, by applying the appropriate theory to the magnetoresistance as a function of field and temperature, we were able to deduce for the first time the true critical magnetic field curve of an oxide superconductor [4], free from the distorting effects of flux motion.

The second result of importance, more related to electronic applications, was the first observation of quasiparticle tunneling at a grain boundary [5]. It has been known for some time that there is Josephson coupling across grain boundaries of oxide superconductors. The strength of this coupling decreases sharply with the angle of the boundary. These characteristics have been established by the use of bicrystal substrates and epitaxial films. In NCCO, the Josephson coupling becomes unobservably small for angles above about ten degrees. We were interested in the conduction mechanism for larger angles; when we measured the current voltage relationship for a 24 degree boundary, we found it looked like a superconductor-superconductor tunnel junction. Thus we found a way to make such junctions using only thin films. At this time, this is the only all thin film technique known. As we will describe in the next section, this technique works extremely well with the other material we have studied, BKBO.

**Studies of BKBO**

Most of the final year of this program was devoted to studying BKBO. Although this material, like NCCO, has a modest transition temperature, 30 K, very good tunnel junctions were demonstrated soon after the discovery of the material. Unfortunately, these junctions were formed by pressing two superconductors together
mechanically. Making equivalently good junctions using thin film heterostructure techniques has proved to be essentially as difficult as with the cuprate materials. On the other hand, it is easy to make superconductor-normal metal junctions using the native surface layer of the material as a tunnel barrier and a counterelectrode of Au or Ag. These junctions are then very useful for doing fundamental physics investigations of the superconducting state of the oxide materials. We began this study by making films using the rf magnetron sputtering technique. We soon found it much more practical to obtain films from Dr. Eric Hellman of AT&T Bell Laboratories through the auspices of the Consortium for Superconducting Electronics. These films were made by molecular beam epitaxy. We then did surface treatment and annealing of the films in our laboratory and added the counterelectrodes.

**BKBO-Au junctions**

a. High-field studies

Analysis of the conductance of a superconductor-normal metal junction subjected to an intense magnetic field allows the determination of several materials parameters including electron mean free path, coherence length, and spin-orbit scattering rate. These parameters in turn are just those needed to calculate the critical magnetic field of the superconductor. This procedure is particularly interesting in the case of oxide superconductors because the motion of magnetic flux in these materials dominates the measurement of the resistive transition in a magnetic field, making it impossible to pick out a value for the critical field. Once the tunneling data are obtained and the critical field calculated, one can examine the magnetoresistance data and find which part of the transition corresponds to the critical field value. Since BKBO is the only high Tc material for which tunnel junctions are available, this study could have been completed only with this material [6].

Figure 1 shows typical conductance (dI/dV) data as a function of voltage for sev-
Figure 1: The differential conductance of a BKBO-Ag junction in applied fields of 0, 3.57, and 6.53 tesla. The dashed lines show the fit of the weak-coupling theory to the data.

eral values of applied magnetic field. From these curves we can obtain the parameters needed for the critical field calculation using the weak-coupling theory as adapted by Rainer to include applied magnetic fields. The dashed curves in fig. 1 represent the fit of that theory to the tunneling data. Notice that it is not necessary to apply magnetic fields as large as the critical field to obtain these data. This fact will be of great importance for similar studies of higher $T_c$ materials whose critical fields far exceed available magnet capabilities. The analysis of the curves of fig. 1 give values of 6.5 nm for the coherence length, $6.4 \times 10^{-5}$ m$^2$/s for the diffusion constant, and $7.2 \times 10^{-11}$ seconds for the spin-orbit lifetime. Figure 2 shows measured values of the resistance as a function of magnetic field for various temperatures. The transition to the normal state is quite broad for these materials because of the voltage arising from flux motion. We can use the data from the curves of fig. 1 to find the transition field for each temperature in fig. 2. These values are shown as squares on the curves in fig. 2. We see that the tunneling data agree very well with the magnetoresistance measurements in the sense that the calculated critical fields occur at points of the resistive transitions where the normal state resistance is nearly restored. This result
Figure 2: The resistance of a BKBO film vs applied magnetic field for temperatures of (a) 17.7 K; (b) 16.4 K; (c) 14.0 K; (d) 12.0 K; (e) 10.0 K; (f) 8.0 K; (g) 6.0 K; (h) 4.2 K.

is what would be expected if the breadth of the transition comes from flux flow. The other satisfying result of this technique is that a plot of the critical field vs temperature shows the proper curvature, in contrast to curves obtained by assuming that the critical field is represented by the field value at which a certain fraction of the normal state resistance is recovered.

b. High voltage measurements.

One of the powerful applications of the tunneling technique is the ability to gain information about the mechanism responsible for the superconducting interaction by measuring the tunneling conductance at voltages above the energy gap. The BKBO-Au junctions are well suited to this kind of investigation. A typical measurement of this type is shown in fig. 3. Here the incremental resistance, $dV/dI$, is plotted vs voltage [7]. The rapid decrease of the resistance with increasing voltage produces a curve similar to the zero bias anomaly well known in studies of conventional junctions with transition metal oxide barriers. In that case, the shape of the curve was
not believed to be related to the superconductivity, but instead to be an indication of scattering in the barrier [8]. In the case of BKBO, however, there has been observed a correlation between the strength of this background and the transition temperature of the material [9]. This very interesting question has yet to be resolved, and it is of great importance to the basic science of high T_c superconductivity.

Bicrystal junctions

As mentioned above, we found that grain boundary junctions in NCCO films acted like superconductor-superconductor quasiparticle tunnel junctions. We applied the same technique to BKBO films and found that very high quality junctions resulted [10]. Typical I-V and dI/dV curves for such a junction are shown in fig. 4. We believe that such junctions will find applications in superconducting electronics, especially if they can be realized with higher T_c materials.
Figure 4: I-V and $dI/dV$ characteristics of a bicrystal BKBO thin-film junction.

Summary

The ability to make good planar tunnel junctions is a demonstration of control of the materials problems associated with the superconducting films as well as being a necessary practical step for many electronic applications. This ability has not been achieved as yet with the oxide superconductors. In the course of this research program, we have examined three diverse materials from this point of view. Although interesting transport properties were observed, particularly in the case of NCCO, and marginal planar tunnel junctions were fabricated, we can reemphasize that the materials problems associated with the oxide superconductors are not yet under control, especially with respect to surface properties. The observation of quasiparticle tunneling at grain boundaries in NCCO and BKBO may be useful in electronic applications as well as for basic physics studies, and indeed has implications about the intergranular properties of these materials. To coin a phrase, more study is needed.
References


