SUPERCONDUCTING ELECTRONIC FILM STRUCTURES

A. I. Braginski, J. R. Gavaler, and J. Talvacchio
Superconductor Materials & Electronics

Annual Report for the Period
January 1 to December 31, 1987

AFOSR Contract No. F49620-85-C-0043
Research sponsored by the
Air Force Office of Scientific Research
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SUPERCONDUCTORS, YTTRIUM, BARIUM, COPPER, OXIDES, HIGH CRITICAL TEMPERATURE, THIN FILMS, TUNNELING, BARRIERS, YTTRIUM BARIUM COPPER OXIDE.

Bulk samples of the new oxide superconductors were prepared and some of their properties measured. Thin films of Y-Ba-Cu-O, completely superconducting below 85K, were prepared by both sputtering and evaporation. The sputtered films on (100) and (110) Sr-Ti-O substrates were epitaxial. A correlation between oxygen content in as-deposited films and the formation of non-superconducting surface layers was established. The thickness of these layers was greatly reduced by sputtering in argon and oxygen gas mixtures. The presence of fluorine in the evaporated films was also found effective in minimizing the barium segregation which produces such layers. Zero resistance gold contact layers were obtained on Y-Ba-Cu-O-sputtered films which were processed entirely in situ. Tunneling data using a low-temperature tunneling microscope were obtained on both evaporated and sputtered Y-Ba-Cu-O films. A new surface characterization capability based on the analysis of LEED or RHEED diffraction spot intensity was developed.
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1. ANNUAL REPORT, SUPERCONDUCTING ELECTRONIC FILM STRUCTURES

January 1, 1987 to December 31, 1987
AFOSR Contract No. F49620-85-C-0043
A. I. Braginski, J. R. Gavalec, and J. Talvacchio
2. ABSTRACT

Bulk samples of the new oxide superconductors were prepared and some of their properties measured. Thin films of Y-Ba-Cu-O,
completely superconducting below 85K, were prepared by both sputtering and evaporation. The sputtered films on (100) and (110) Sr-Ti-O substrates were epitaxial. A correlation between oxygen content in as-deposited films and the formation of non-superconducting surface layers was established. The thickness of these layers was greatly reduced by sputtering in argon and oxygen gas mixtures. The presence of fluorine in the evaporated films was also found effective in minimizing the barium segregation which produces such layers. Zero resistance gold contact layers were obtained on Y-Ba-Cu-O-sputtered films which were processed entirely in situ. Tunneling data using a low-temperature tunneling microscope were obtained on both evaporated and sputtered Y-Ba-Cu-O films. A new surface characterization capability based on the analysis of LEED or RHEED diffraction spot intensity was developed.
3. OBJECTIVES

The objectives of the Westinghouse-AFOSR Program are:

1. Investigate the low-temperature synthesis of high-critical-temperature superconducting films.
2. Fabricate and evaluate films of very high-critical-temperature superconductors. (This task was added in spring of 1987.)
3. Grow epitaxially single-crystal superconducting films and coherent layered structures.
4. Characterize the near-boundary crystalline and phase perfection of superconducting layer surfaces and interfaces, mostly by in-situ methods.
5. Study tunneling into high-critical-temperature ($T_c$) superconducting films.
6. Investigate artificial tunnel barriers.
4. ACCOMPLISHMENTS

4.1 PREAMBLE

This five-year research program, initiated in January 1983, is aimed at understanding and improving the superconducting and normal state properties of layered, epitaxial, thin-film structures incorporating high-critical-temperature superconductors. Anticipated results are intended to form a materials science base for a future technology of high-operating-temperature superconducting electronics. The initial work in this program was performed under a contract covering the period from January 1, 1983 to December 31, 1984. In 1985 the level of effort was augmented to include an additional objective (No. 6). During 1986 the level of effort was reduced, and work toward one of the original objectives (the study of rf surface losses in high-\textit{T}_c superconducting films) was discontinued.

In late 1986, the discovery of very high \textit{T}_c's in a new class of oxide superconductors caused an additional redirection in the program. During the first six months of this reporting period following consultation with AFOSR, the level of effort toward the objectives listed in Section 3 was temporarily reduced so that studies on the preparation of bulk samples of the new high-\textit{T}_c oxide superconductors could be performed. These studies, together with work that was done during 1987 on all listed objectives, are described in this report. The research reported here is continuing under a new Westinghouse-AFOSR contract beginning in January 1988.

4.2 PREPARATION AND PROPERTIES OF BULK SAMPLES OF THE HIGH-\textit{T}_c OXIDES

Although the successful performance of this program requires the growth of superconducting films, initial effort involving the newly discovered high-\textit{T}_c oxide superconductors was done exclusively on bulk
samples. This initial work was necessary to gain some understanding of these new materials so that eventually they could be prepared in thin-film form. Preparation of bulk samples was done by the now standard ceramic technique starting from the oxides or the carbonates of the constituent elements. The first superconductor prepared was La$_{1.8}$Sr$_{0.2}$CuO$_4$. A description of the preparation and some properties of this compound was published in *Applied Physics Letters*. Following announcement of the very high T$_c$'s in Y$_1$Ba$_2$Cu$_3$O$_{7-x}$, bulk samples of this compound were prepared and some of their properties measured. These data were reported in *Phys. Rev. B*. Collaborative work with three other groups (at the National Bureau of Standards, the University of Texas, and Boeing Research Laboratory) also produced data on the properties of the bulk samples made here at the R&D Center. The data from these collaborations have been published in *Cryogenics, Materials Research Society Extended Abstracts, Japanese Journal of Applied Physics (Proceedings of LT-12)* and *Applied Physics Letters*. A summary of all the work on high-T$_c$ oxide superconductors done at Westinghouse was presented at the "International Workshop on Novel Mechanisms of Superconductivity" and has been published in the Proceedings.

At present no further work on the preparation of bulk samples is planned as part of the AFOSR program. All material preparation work is now being focussed on the deposition of thin films. The status of the thin-film work is discussed below.

4.3 LOW-TEMPERATURE SYNTHESIS OF HIGH-T$_c$ FILMS

During the course of this program, work toward this objective has been centered on the low-temperature growth of films of the A15 and B1 structure superconductors since these materials were the highest temperature superconductors known. With the advent of the new high-T$_c$ oxides, the emphasis has now been totally shifted toward these new materials. Until now, no work has been specifically directed toward finding means to synthesize these oxides at lower temperatures than are now being used.
4.4 FABRICATION AND EVALUATION OF VERY HIGH-\(T_c\) SUPERCONDUCTOR FILMS

During the course of the current Westinghouse-AFOSR program the primary equipment used for film deposition and characterization has been the Superlattice Deposition and Analytical Facility (SDAF) which was specifically purchased for this program. Early in 1987, however, it was decided to use another system for the oxide superconductor film work because of concerns about contaminating the ultra-high-purity environment of the SDAF. The system used was a standard high-vacuum apparatus (background pressure \(\sim 10^{-7}\) Torr) equipped with an e-beam gun and resistively heated tungsten and tantalum boats. The initial superconductor which was prepared as a thin film was \(\text{YBa}_2\text{Cu}_3\text{O}_7\). Y-Ba-Cu films were first deposited at ambient temperatures with no deliberate addition of oxygen. The deposition rates were controlled manually. These metallic films were then ex-situ annealed in oxygen at 850°C to form the superconducting compound. The substrates were sapphire, \(\text{ZrO}_2\), and \(\text{SrTiO}_3\). The results and conclusions from these initial experiments were as follows: Films were grown that were close to the desired \(\text{YBa}_2\text{Cu}_3\text{O}_7\) composition. In the best case, they became completely superconducting at \(\sim 70\)K. The relatively low \(T_c\)'s, compared to the bulk material, were attributed primarily to insufficiently precise control of deposition rates, which resulted in films that were slightly off ideal "1,2,3" stoichiometry. The films had poor surface quality due to the reaction of the essentially metallic as-deposited films with room air, during their transfer from the deposition system to the annealing furnace. A significant dependence of \(T_c\) on substrates was also observed. The Sr and Ti from the \(\text{SrTiO}_3\) substrates which diffused into the deposited films had the least deleterious effect on critical temperatures, while the Al from the sapphire had the most. These latter results, documenting the dependence of \(T_c\) on substrates, are reported in more detail in the Proceedings of the International Workshop on Novel Mechanisms of Superconductivity.

Following an evaluation of these initial data, it was concluded that the various problems that were encountered could be best resolved
using the capabilities of the SDAF. Therefore, starting at mid-year, all of the thin-film experiments were transferred to this facility. The first $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films made in the SDAF were evaporated from the pure metals in a UHV environment, again without the deliberate addition of any oxygen during deposition. After annealing in oxygen, films on SrTiO$_3$ substrates were obtained which were completely superconducting at 83K. The higher $T_c$'s of these compared to the earlier films were due mainly to improved rate control and thus better stoichiometry. The films showed no indication of epitaxy. It was found that in-situ annealing in one atmosphere of $\text{O}_2$ at temperatures as low as $\sim 500^\circ\text{C}$ was sufficient to stabilize the film surface, making it essentially inert to room air. However, it was also found that films 10,000 Å thick contained a $\gtrsim$ 1,000 Å thick non-superconducting barium-rich surface layer. Apparently, during oxidation of the as-deposited metallic films, barium diffused toward the surface. These results suggested that to minimize barium segregation, the films should be deposited as oxides rather than as metals. Because sputtering equipment is generally more tolerant to the presence of high levels of oxygen compared to evaporation equipment, the effort to deposit oxide films was and is still being made in the sputtering system of the SDAF.

The initial $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{x}}$-sputtered films were deposited in a partial pressure of oxygen of $10^{-5}$ Torr at a deposition rate of 30 Å/min. The films on SrTiO$_3$ were found, in the best case, to be completely superconducting at 85K. Similar to the evaporated films the early sputtered films, even when deposited on SrTiO$_3$, were polycrystalline with little or no indication of epitaxial growth. These initial results were reported in *Applied Physics Letters*. Subsequent sputtering experiments under nominally similar conditions have since produced $\text{YBa}_2\text{Cu}_3\text{O}_{7}$ films on SrTiO$_3$ which are clearly epitaxial. These are described in the next section of this report. The reason for the lack of epitaxy in the first films is not known, although it may have been associated with a poorer surface quality of the original SrTiO$_3$ substrates. In the sputtering experiments performed thus far, films
have been deposited in partial pressures of oxygen of up to $3 \times 10^{-4}$ Torr. Depth profiling of films sputtered in oxygen indicate that the non-superconducting surface layer has been reduced to a thickness of about 100 Å. The effort to determine whether this layer is due to a remaining slight oxygen deficiency in the as-deposited films is still in progress. Data on sputtered films were presented at the October 1987 TMS meeting in Cincinnati. The most recent results will be presented at the March APS meeting and in a contributed paper at the "International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity" (HTSC-M2S) in Interlaken, Switzerland.

Following reports in the literature which described the high $T_c$'s when using BaF$_2$ as the source for Ba in the evaporation of YBa$_2$Cu$_3$O$_7$ films, some additional evaporated films were prepared. These films showed minimal segregation of Ba during the annealing process. The use of a BaF$_2$ source thus potentially presents an alternative method for minimizing Ba diffusion and the resulting growth of a non-superconducting surface layer. These data will also be presented at the March APS meeting.

4.5 EPITAXIAL GROWTH OF SUPERCONDUCTING FILMS

Epitaxial films of YBa$_2$Cu$_3$O$_7$ have been grown on SrTiO$_3(100)$ and SrTiO$_3(110)$ substrates. X-ray diffraction measurements of films grown on SrTiO$_3(100)$ indicated that each grain grew epitaxially, but the films were not single crystals. The films grew mostly in the [100] direction with a minor [001] component. Transmission electron microscopy of the films showed that grains were oriented in two possible [010] directions, 90° apart, in the plane of the film. This "a-axis" growth is desirable for tunneling because the coherence length is larger for the [100] direction than for [001]. However, the "a-axis" growth and "checker-board" microstructure limited the critical current density to $5 \times 10^5$ A/cm$^2$ at 4.2K because the direction of current flow was perpendicular to Cu-O planes regardless of which way the current bridge
was patterned. An analogous structure has been observed for growth on SrTiO$_3$ (110) substrates where there were two in-plane directions in which the [013] axes of epitaxial grains could align. The data on epitaxial growth and microstructure will be presented at the March meeting of the APS.

A separate report at the March APS meeting on the preparation of SrTiO$_3$ substrate surfaces and its effect on the nucleation of epitaxial films will also be presented. If complete control over the growth orientation could be achieved, "a-axis" growth would be chosen for tunneling and "c-axis" growth for carrying current.

Epitaxial and single-crystal NbN films have been used in a collaboration with a group from MIT to study the effect of Ar ion-beam irradiation on NbN. Results from single-crystal samples showed that the reputed insensitivity of NbN to radiation damage is related to the microstructure rather than the fundamental mechanism of superconductivity in NbN. Grain boundaries in fine-grained samples acted as sinks for ion-induced defects that significantly lowered $T_c$ in single-crystal samples. This work is described in a paper submitted to *Phys. Rev. B*. Another aspect of this work, the influence of ion irradiation on the critical current of NbN, will be discussed at the March APS meeting.

4.6 CHARACTERIZATION OF NEAR-SURFACE LAYERS

4.6.1 YBa$_2$Cu$_{3}O_{7}$ Films

Both the epitaxial and polycrystalline films of superconducting YBa$_2$Cu$_{3}O_{7}$ that have been prepared thus far have a non-superconducting layer near their free surface. The thickness of this non-superconducting layer was found to be between $10^2$ and $10^3$ Å which exceeds the coherence length and in some cases is comparable to the penetration depth. The degraded surface layer is believed to be the cause of the measured high contact resistance and high rf surface resistance. The layer must be penetrated by the tip of a tunneling
microscope in order to obtain any tunneling characteristics. Attempts to tunnel between YBa$_2$Cu$_3$O$_{7}$ and a film counterelectrode have been, thus far, unsuccessful due to the presence of this degraded layer. Analogous results have been reported by others.

The results summarized in this section concern films deposited in oxygen pressures ranging from $p(O_2) < 10^{-9}$ to $3 \times 10^{-4}$ Torr at temperatures of 500°C or less. The analytical data on these films indicate that even the layers sputtered in the highest oxygen pressures were still oxygen deficient. All films were either in-situ or ex-situ preannealed in one atmosphere of oxygen at 500°C prior to a final reaction anneal, also in oxygen, at 850°C. In-situ reflection high-energy electron diffraction (RHEED) indicated that the surface of initial deposits was amorphous and remained so after preannealing. Ex-situ X-ray diffraction confirmed that the bulk of the film was also amorphous at this stage and crystallization (solid-state-epitaxial or random) occurred during the reaction annealing.

In addition to RHEED, the near-surface characterization of such films was performed by in-situ X-ray photoelectron spectroscopy (XPS), ex-situ Auger electron spectroscopy (AES) depth profiling, and ex-situ measurement of surface resistance between the film and a metallic (Au) overlayer deposited at room temperature on completely in-situ fabricated films.

Near-surface compositions were found to differ significantly from average bulk compositions in annealed films. In nearly stoichiometric epitaxial films deposited at $p(O_2) < 3 \times 10^{-6}$ Torr, copper was not even seen by XPS at the surface after annealing. Changes in near-surface compositions (atomic metal ratios) and their depth profiles were found to depend upon the partial pressure of oxygen during film deposition. In more oxygen-deficient deposits, the oxidation preannealing caused a stronger atomic segregation of Ba to the surface with correspondingly higher depletion in Cu and/or Y. The least amount of this segregation was found in films deposited at the highest pressure used, i.e., $p(O_2) = 3 \times 10^{-4}$ Torr. In films oxidized at 500°C the
surface composition remained stable upon reaction annealing at 850°C but could be changed by vacuum annealing at this temperature. The depth of segregation was on the order of 1500 Å in films deposited at the lowest pressures of O₂ but could be reduced to less than 900 Å by depositing at p(O₂) in the 10⁻⁶ Torr range and higher. In such films, processed entirely in-situ, the surface contact resistance to gold was unmeasurably low, with the sensitivity limit at 4 × 10⁻¹⁰ ohm-cm. This value is sufficiently low for interconnect application.

In films deposited as a mixture of BaF₂ and Cu and Y metal, in the absence of O₂, the surface segregation upon oxidation was much reduced, to 50 to 100 Å.

The results summarized above lead to the conclusion that oxidation of oxygen-deficient deposits, especially Ba, provides the driving force for the atomic segregation. To attain superconducting surfaces, the highly oxygen-reactive metallic film constituents must either be fully oxidized during deposition at low temperature or passivated, e.g., by binding Ba into the fluoride molecule. Alternatively, films deposited at high temperature must incorporate enough oxygen to permit the monolayer-by-monolayer formation of the desired crystal structure during deposition. This is the direction now pursued under this program. The data now in hand will be presented at the HTSC-M2S Conference in Interlaken (Switzerland) and the APS March meeting.

4.8.2 Analyses of Surface Layers from RHEED or LEED Diffraction Spot Intensity

An additional experimental capability, based on the analysis of LEED or RHEED diffraction spot intensity, was developed at no cost to AFOSR. The techniques are well established; however, they have never before been applied to superconducting films or multilayers. Familiarity with the hardware and software purchased from DataQuire, Inc., was established by collecting LEED diffracted beam intensity versus beam energy (LEED I-V curves) for each surface of NbN/MgO/NbN.
epitaxial tunnel junctions. Analysis of the LEED data supported several of the conclusions presented as part of a review of epitaxial NbN junction technology at the TMS-AIME Symposium on Metallic Multilayers: The first monolayer of MgO completely covered the NbN base electrode as expected for a Stranski-Krastanov growth morphology, and the initial layer of the NbN counterelectrode, 8 Å thick, was partly disordered even in junctions with 5 meV gap voltages.

Other capabilities of the new techniques are: the measurement of surface lattice constants to 1% accuracy, estimation of island size for films with a three-dimensional growth morphology, and modeling of surface atom positions and electronic structure. The last capability requires the use of extensive calculations similar to band structure calculations. Westinghouse has obtained a computer program from Dr. D. W. Jepsen of IBM Watson Research Center that represents the state of the art in these calculations. The program can be used to generate LEED I-V curves for comparison with experimental results. The inputs of surface structure and physics must be adjusted to obtain a good fit to experiment, resulting in a probable, although not unique, model of the surface. Some of the results in the NbN/MgO system were presented at the Superconductive Electronics Workshop.

4.7 TUNNELING INTO HIGH-T<sub>c</sub> SUPERCONDUCTORS

Tunneling data were obtained from bulk YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> samples in collaborative efforts with workers from the National Bureau of Standards (NBS) and the University of Texas. Tunneling experiments with YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> films were made at the University of Texas and here at the Westinghouse R&D Center. At NBS, the Josephson effect was observed in a "break" junction formed at the point contact between two halves of a fractured sample. The junction was susceptible to microwave radiation showing clearly visible Shapiro steps at temperatures up to 85K. The voltage/frequency ratio of the Shapiro steps showed that conduction was due to the tunneling of electron pairs. This work was published in Applied Physics Letters.
At the University of Texas, tunneling spectroscopy was performed with the aluminum tip of a scanning tunneling microscope on the surface of bulk YBa$_2$Cu$_3$O$_7$ samples cleaved at 77K in vacuum. Very high gap voltages were observed corresponding to $2\Delta/k_BT_C \approx 11$. The results were published in the *Japanese Journal of Applied Physics* (Proceedings of LT-18). More recently, epitaxial YBa$_2$Cu$_3$O$_7$ films deposited by sputtering or evaporation, and which crystallized in the [100] direction, were measured in the scanning tunneling microscope. Very low-leakage I-V curves were obtained. The straightforward interpretation of the curves would imply that $2\Delta/k_BT_C \approx 12$ along the a-axis direction, one of the directions that might be expected to have a larger gap. Other interpretations must still be considered such as tunneling among a network of series and parallel junctions. These preliminary results were presented at the fall meeting of the Materials Research Society.

Planar S-I-N structures were formed by depositing Pb or Nb cross-strips on YBa$_2$Cu$_3$O$_7$ films. The junctions had very high resistance and ohmic I-V curves that were attributed to the thick non-superconducting surface layer of the high-$T_c$ superconductor described in the previous section. These measurements will be included in the discussion of near-surface properties scheduled for the March meeting of the American Physical Society.

4.8 ARTIFICIAL TUNNEL BARRIERS

The advent of the high-$T_c$ oxide superconductors has, not surprisingly, caused a greatly decreased interest in Nb$_3$Sn and other A15 compounds. Studies involving these compounds, however, continue to have value if for no other reason that experience gained with these materials can eventually be applied to the new oxide superconductors. During the first two months of this reporting period experiments investigating a Sr-O artificial tunnel barrier were done in which both the base and counterelectrodes were Nb$_3$Sn. The Nb$_3$Sn base electrode was deposited by co-evaporation at 950°C on sapphire. The film as indicated by RHEED was
single crystalline. The barrier layer was formed by evaporating Sr-O at 300°C. XPS analysis showed a thickness of 24 Å. The structure of the Sr-O from RHEED analysis was textured showing that some epitaxy had occurred. The Nb$_3$Sn counterelectrode was then evaporated over the Sr-O at ambient temperature and then flash annealed at 650°C for two minutes. This Nb$_3$Sn layer was polycrystalline with no indication of texturing. Junctions were then made from these trilayers. Current-voltage measurements showed that a junction with an energy gap of over four millivolts had been formed. This first all-Nb$_3$Sn junction would have been a very important achievement if the A15 compounds had remained the highest $T_c$ superconductors. In the present context, however, the result is still significant in that it shows that a thin (~ 24 Å) Sr-O layer can experience relatively high-temperature processing and still survive as a junction barrier.

No effort has thus far been expended on investigating artificial tunnel barriers on the new oxide superconductors. Such an activity will become useful and meaningful only when the problems associated with the near-surface non-superconducting layers, discussed in Section 4.6.1, are resolved.
5. PUBLICATIONS


*Submitted for publication in 1986.


6. PERSONNEL

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7. COUPLING ACTIVITIES*


*Speaker's name is underlined.
8. PATENTS


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