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AFOSR-TR- 93 02 64

HIGH TEMPERATURE SUPERCONDUCTING FILMS AND MULTILAYERS FOR ELECTRONICS

John R. Gavaler and John Talvacchio
Cryogenic Electronics

Annual Report for the Period
February 21, 1992 to February 20, 1993

AFOSR Contract No. F49620-91-C-0034
Research Sponsored by the
Air Force Office of Scientific Research
Air Force Systems Command
United States Air Force

February 20, 1993

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Westinghouse STC
1310 Beulah Road
Pittsburgh, Pennsylvania 15235-5098

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified			3. DISTRIBUTION / AVAILABILITY OF REPORT 1993-01-01		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE N/A			4. PERFORMING ORGANIZATION REPORT NUMBER(S) 93-9SL2-SUPER-R1		
5. MONITORING ORGANIZATION REPORT NUMBER(S)			6a. NAME OF PERFORMING ORGANIZATION Westinghouse Science & Technology Center		
6b. OFFICE SYMBOL (If applicable)			7a. NAME OF MONITORING ORGANIZATION DCASMA Pittsburgh 53111A		
6c. ADDRESS (City, State, and ZIP Code) 1310 Beulah Road Pittsburgh, PA 15235-5098			7b. ADDRESS (City, State, and ZIP Code) 1626 William S. Moorhead Federal Building 1000 Liberty Avenue Pittsburgh, PA 15222		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Air Force Office of Scientific Research			8b. OFFICE SYMBOL (If applicable) DE		
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-91-C-0034			8c. ADDRESS (City, State, and ZIP Code) 110 Duncanson Ave Suite B15 Bolling AFB DC 20332-0001		
10. SOURCE OF FUNDING NUMBERS			11. TITLE (Include Security Classification) HIGH TEMPERATURE SUPERCONDUCTING FILMS AND MULTILAYERS FOR ELECTRONICS		
PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2305	TASK NO. GS	12. PERSONAL AUTHOR(S) Gavaler, J. R. and Talvacchio, J.		
13a. TYPE OF REPORT Annual			13b. TIME COVERED FROM 2-21-92 TO 2-20-93		
14. DATE OF REPORT (Year, Month, Day) 1993 February 20			15. PAGE COUNT 27		
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	superconductors, yttrium, barium, copper, oxides, high, critical, temperature, thin films, tunneling, barriers, sputtering		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Progress is reported on four tasks which address problems fundamental to the understanding of the superconducting state in HTS films, the application of HTS films in passive microwave circuits, the realization of HTS digital electronics, and the development of new superconducting devices. An anti-correlation between critical temperature and normal state resistivity was observed at certain compositions in the YBCO, LSCO, and BKBO systems. The criticality of optimizing both oxidation steps involved in YBCO growth to obtain low rf surface resistances was demonstrated. A new insulating material, Sr-Al-Ta-O (SAT), was developed as an epitaxial insulator in multilayer YBCO circuits to replace Sr-Ti-O. The dc resistivity and surface morphology were as good as those of Sr-Ti-O while the real and imaginary parts of the dielectric constant were greatly superior. Systematic studies were made of the processing parameters for step-edge S-N-S YBCO Josephson junctions. The critical parameters for junction reproducibility were found to be a step angle of approximately 15° and a high-conductivity normal-metal barrier. All-BKBO tunnel junctions were demonstrated with Sr-Ti-O tunnel barriers which exhibited a superconducting gap structure to within 2K of the transition temperature of the BKBO electrodes. Epitaxial Sr-Ti-O films were also used as buffer layers to permit single-orientation BKBO films to be grown on practical La-Al-O or Nd-Ga-O substrates. The two critical materials issues in the development of HTS multi-chip modules were addressed through demonstrations of epitaxial growth of 1.5 micron thick MgO insulators, and patterning of 6 cm-long, 4 micron-wide YBCO lines without degraded properties.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL W. J. Stock			22b. TELEPHONE (Include Area Code) 202-767-4933		
			22c. OFFICE SYMBOL NE		

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

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Unannounced	☐
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Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

**1. ANNUAL REPORT: HIGH TEMPERATURE
SUPERCONDUCTING FILMS AND
MULTILAYERS FOR ELECTRONICS**

February 21, 1992 to February 20, 1993

AFOSR Contract No. F49620-91-C-0034

J. R. Gavaler and J. Talvacchio

2. ABSTRACT

Progress is reported on four tasks which address problems fundamental to the understanding of the superconducting state in HTS films, the application of HTS films in passive microwave circuits, the realization of HTS digital electronics, and the development of new superconducting devices. An anti-correlation between critical temperature and normal state resistivity was observed at certain compositions in the YBCO, LSCO, and BKBO systems. The criticality of optimizing both oxidation steps involved in YBCO growth to obtain low rf surface resistances was demonstrated. A new insulating material, Sr-Al-Ta-O (SAT), was developed as an epitaxial insulator in multilayer YBCO circuits to replace Sr-Ti-O. The dc resistivity and surface morphology were as good as those of Sr-Ti-O while the real and imaginary parts of the dielectric constant were greatly superior. Systematic studies were made of the processing parameters for step-edge S-N-S YBCO Josephson junctions. The critical parameters for junction reproducibility were found to be a step angle of approximately 15° and a high-conductivity normal-metal barrier. All-BKBO tunnel junctions were demonstrated with Sr-Ti-O tunnel barriers which exhibited a superconducting gap structure to within 2K of the transition temperature of the BKBO electrodes. Epitaxial Sr-Ti-O films were also used as buffer layers to permit single-orientation BKBO films to be grown on practical La-Al-O or Nd-Ga-O substrates. The two critical materials issues in the development of HTS multi-chip modules were addressed through demonstrations of epitaxial growth of 1.5 micron thick MgO insulators, and patterning of 6 cm-long, 4 micron-wide YBCO lines without degraded properties.

3. OBJECTIVES

The objectives of the Westinghouse-AFOSR program are:

1. Search for thin film superconductors with enhanced T_c 's and other superconducting properties.
2. Determine the fundamental lower limit of HTS rf surface resistance.
3. Investigate epitaxial multilayers, including Josephson junctions, incorporating deposited insulators and normal conductors with HTS films.
4. Develop materials and processing for alternative HTS devices.

4. ACCOMPLISHMENTS

4.1 PREAMBLE

The research reported here was performed under a Westinghouse-AFOSR Program which began February 20, 1991. The specific objectives of this program are listed in Section 3 of this report. These objectives are identical to the Tasks of the Work Statement. The overall objective is to investigate the fundamental physics and materials science of superconductors to enhance their properties for application in passive devices based on transmission line structures, active devices based on Josephson junctions, and novel active device structures based on the unique properties of superconductors.

4.2 ENHANCED SUPERCONDUCTING FILM PROPERTIES

The work on this task has been focussed on two distinct areas. In the first of these, the research is more speculative in that it is motivated by the hoped-for but unproven possibility that there exist even higher- T_c superconductors than those presently known. Using thin film growth methods the effort is being made to find some of these unknown materials. The research in the second area has a more modest but also a more immediately practical goal. In this case the effort is being directed toward improving properties of already existing superconducting materials thereby making them more useful in practical device applications.

The rationale in searching for higher- T_c superconductors using thin film methods is based on the apparent correlation between high critical temperatures and crystalline instabilities. This correlation suggests enhanced T_c 's might be obtainable if one could stabilize an otherwise unstable, potentially high- T_c superconductor, by preparing it as a thin film. The capability of forming normally unstable materials by thin film techniques is well documented in a variety of metallurgical systems. This has been accomplished as a result of

one or a combination of factors which are operative in the growth of films and which are not present when using bulk methods. These include very low crystallization temperatures, very high quench rates, and the potential for uniformly incorporating low levels of a stabilizing element into the film's crystal structure (i.e. "doping").

During this reporting period the effect of using very low crystallization temperatures and also doping known superconductors with various elements have been studied. Although no enhancements in T_c 's above those presently known were achieved, some important new data were obtained on three of the most widely studied of the oxide-superconductor systems, namely, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ (YBCO), and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (BKBO).

Considering YBCO first, a set of experiments was done in which this material was sputtered at incrementally lower temperatures starting at 750°C down to 500°C . At a temperature as low as 590°C , films were grown which, according to x-ray diffraction analyses, were single phase c-axis oriented and which had critical temperatures of $>92\text{K}$. Using ordinary methods, growth temperatures of approximately 700°C are required to sputter films with these properties. The successful growth of such films at much lower temperatures was made possible by using a procedure which was developed and patented under the present AFOSR-Westinghouse program. The most important novel ingredient of the process is the addition of water vapor to the standard argon-oxygen sputtering gas mixture.

Although the capability of sputtering 92K YBCO films at very low temperatures could eventually have practical implications, perhaps the most significant result obtained in these experiments was the finding that these films had unexpectedly low normal state resistivities. Until the present, all of the published data on YBCO films have all indicated the correlation that as normal state resistivity decreases and the resistivity ratio, $R_{300\text{K}}/R_{100\text{K}}$, increases, critical temperatures increase. It was found, however, that when the films grown at $\sim 600^\circ\text{C}$ were post-growth annealed (cooled down) in oxygen pressures of 20 Torr or higher, they had abnormally low room temperature dc resistivities of $\leq 150 \mu\Omega\text{-cm}$ and $R_{300\text{K}}/R_{100\text{K}}$ ratios of close to 4. Despite these very low

resistivities, their T_c 's were only $\sim 86\text{K}$. YBCO films deposited at higher (standard) temperatures typically have T_c 's of $>90\text{K}$, room temperature resistivities of $\sim 200\ \mu\Omega\text{-cm}$, and $R_{300\text{K}}/R_{100\text{K}}$ ratios very close to 3 when oxygen-annealed under these conditions. This result appears to suggest that it is possible to "over-dope" the "chain" sites in the YBCO structure with excess oxygen and thus degrade T_c .

To confirm that the abnormally low normal state resistivities and the low- T_c 's of the 86K films were directly related to the oxygen content in the chains, oxygen was removed from the chains by heating the films at 600°C in vacuum. The films were then reoxidized using standard temperature conditions but an oxygen pressure of only 10 Torr. After this procedure the films showed an increased room temperature resistivity of $200\ \mu\Omega\text{-cm}$, a decrease in $R_{300\text{K}}/R_{100\text{K}}$ to 3, and T_c 's of $\sim 92\text{K}$. These data and their possible interpretation were presented in a paper given at the 1992 Applied Superconductivity Conference.

The observation of a decrease in T_c coinciding with a decrease in normal state dc resistivity was also observed in a study of LSCO films. In this system, the critical temperature increases as a function of Sr doping for $0 \leq x \leq 0.17$. In bulk samples prepared at atmospheric pressure, Sr doping levels >0.17 are accompanied by a compensating loss of oxygen leading to T_c and normal-state resistivity values which are independent of Sr content. By processing bulk samples with $x > 0.17$ under high oxygen pressures, it has been found (by other laboratories) that the hole concentration was proportional to the Sr doping level for x as large as 0.40.

For this program, LSCO films were prepared by off-axis sputtering from targets with various values of Sr composition, x . The optimum Sr content for superconductivity was determined to be at $x = 0.17$. These films are now being used for fundamental studies of the pairing mechanism in this compound. During this reporting period, their optical properties and Raman spectra were measured and published (in collaborations involving the University of Florida and Virginia Tech). Films with $x > 0.17$ were found to have the same properties as bulk samples which had been annealed in 100 atm O_2 .

Although the normal-state resistivity decreased as x was increased, T_c also decreased. The resistivity in the a-b plane for films with $x = 0.30$ had the lowest value for normal-state resistivity ever measured for a perovskite material.

An increase in normal-state conductivities with a corresponding decrease in critical temperature, observed in these two systems is a manifestation of the critical roles played by the chain layers in determining both the normal-state and superconducting properties of oxide superconductors. In a YBCO material that has a relatively low number of oxygen vacancies, i.e. when x is close to zero in the formulation $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, it has been suggested that ordering rather than reducing the number of vacancies in the chain layers, may be more important in determining the electrical properties of the material. This possibility is in accord with the phenomenological model of Kresin and Wolf in which it is proposed that the chain layer is a superconductor due to its proximity to the Cu-O planes. Chains that had interruptions because of vacancies would act as pair breakers.

A suggestion, first proposed by Feenstra, to explain abnormally low dc resistivities in YBCO, is that it is possible to over dope YBCO with excess oxygen, thereby raising the oxygen content to some value greater than seven atoms per molecule, i.e., $x < 0$. At present there is no direct evidence available to confirm that oxygen over-doping actually occurs in YBCO films. The only over-doping studies that have been performed systematically were in bulk samples. This was done by substituting Ba on La sites in the $\text{La}_{1-y}\text{Ba}_{2+y}\text{Cu}_3\text{O}_{7-x}$ system. For over-doping to have occurred in YBCO films grown at low temperature, anti-site disorder would have to have been present with Ba on some of the Y sites.

In addition to the fundamental insights the above data provide, they also have practical implications. With respect to the LSCO results, films with the lowest normal-state resistivities were used as barriers as part of efforts to increase the resistance of YBCO S-N-S junctions above that obtainable with noble-metal normal conducting barriers while maintaining a relatively long normal-metal coherence length. These data are discussed in Section 4.4 of this report.

In the case of the YBCO data, they clearly show that greater care in the post-growth oxygen annealing procedure is required to optimize superconducting properties than previously was believed to be necessary, particularly when the films were grown at relatively low temperatures. In addition to the negative effect on T_c from the use of an non-optimized oxygen anneal, data have been obtained indicating an adverse effect on rf surface resistance from improper post-growth annealing. These data are discussed in the next section of this report.

Unlike the above work on YBCO and LSCO, the study of BKBO films is not motivated by the goal of enhancing critical temperature. The interest in this material results from the fact that it has a significantly higher coherence length than the higher- T_c oxides and, because of its cubic crystal structure, its properties are isotropic. However, similar to the highest- T_c oxide superconductors with anisotropic properties, the necessity for growing epitaxial single crystal films still holds because of the intrinsic weak links that form in oxide films containing high-angle grain boundaries.

Strontium titanate is the only substrate found to date on which single-orientation, epitaxial BKBO films with high T_c 's, J_c 's, and small x-ray rocking curve widths can be grown, but it is one of the least practical substrate materials due to its poor dielectric properties, small area, and high cost. BKBO films grown directly on the preferred substrates, LaAlO_3 or NdGaO_3 , had a mixture of (001) and (110) orientations. However, by growing SrTiO_3 (001) buffer layers on LaAlO_3 or NdGaO_3 , single-orientation BKBO(001) films were grown with properties equal to those obtained for films grown directly on SrTiO_3 single crystals, $T_c > 26\text{K}$ and $\Delta w \approx 0.7^\circ$. This result, together with the description of the use of epitaxial SrTiO_3 tunnel barriers in all-BKBO junctions (Section 4.4), is included in a paper accepted for publication in Applied Physics Letters.

The superconducting phase of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ exists in the range, $0.4 \leq x \leq 0.5$, with the highest T_c occurring for $x \approx 0.4$. The lowest normal-state resistivity ($45 \mu\Omega\text{-cm}$ at 30K) and highest resistivity ratio ($\rho_{300\text{K}}/\rho_{30\text{K}} = 1.89$) ever reported for BKBO was found in K-rich films that were prepared for this

program. Although systematic data is not yet available for $\rho(T)$ versus K content, it appears that the BKBO system shares with LSCO and YBCO both a decreasing T_c and increased normal-state conductivity as cation doping is increased beyond the optimum for superconductivity.

4.3 RF SURFACE RESISTANCE

The rf surface resistance, R_s , of some of the YBCO films which had abnormally low dc resistivities, were measured at 10 GHz and 77K. High values in the range of 14-16 m Ω were obtained. Previous measurements of films sputtered under standard (higher temperature) conditions, which had normal dc resistivities, typically exhibited state-of-the-art R_s values in the 0.5-1 mohm range. As discussed above, the T_c 's of these low-dc resistivity films were only ~86K. The critical temperatures were raised to ~92K by removing oxygen from the films and then reoxidizing them under optimum temperature and pressure conditions. Unexpectedly, re-measurement of surface resistance of the now 92K films showed no improvement in R_s values. These data thus confirm previous results obtained during the course of this program that showed that high T_c 's do not necessarily guarantee low rf surface resistances.

X-ray analyses of a variety of films grown at relatively low (~600°C) temperatures, showed that regardless of what oxygen annealing procedure was used, they had x-ray rocking curve widths, $\Delta\omega \approx 0.5^\circ$. This could explain, at least in part, their inferior surface resistances compared to films grown under standard temperature conditions, which had $\Delta\omega = 0.3^\circ$. These data correlating rf surface resistance and crystalline perfection in YBCO films were also presented at the 1992 Applied Superconductivity Conference.

The use of a very low growth temperatures could also influence surface resistance in another manner (in addition to decreasing the crystalline perfection of the YBCO). At lower temperatures, it is also possible that YBCO formation in the film was incomplete and thus oxygen vacancies could be present in other layers besides those containing Cu-O chains. Experience obtained from this and previous AFOSR-Westinghouse programs showed that

such vacancies, deliberately produced by sputtering in insufficient oxygen, can result in the formation of non-superconducting Y-Ba-Cu-O single crystal films which are structurally closely related to YBCO. However, depending on other conditions the films can exhibit c-axis lattice constants either greater or smaller than that of YBCO. Because of this, a minor amount of an oxygen-deficient Y-Ba-Cu-O phase sufficient to adversely affect the R_s would be difficult to identify from x-ray data.

To investigate the possibility of an oxygen-deficient Y-Ba-Cu-O second phase being present in films grown at low temperatures, a series of YBCO films deposited at 600°C were heat treated in one atmosphere of oxygen at increasingly higher temperatures, starting at the growth temperature up to 800°C. The T_c 's and R_s 's were measured and the films were x-rayed after each heat treatment. In general no changes of any significance was observed in the critical temperature of the films after any of these experiments. The R_s values, on the other hand, began improving immediately. At 650°C they were down by a factor of two and at 750° by almost an order of magnitude and were approaching the values obtained in films which were sputtered at that temperature, i.e., ~0.5 mohm at 10 GHz and 77K. Treatment at higher temperatures produced no further improvements.

Although an observed improvement in the crystal perfection of films treated at the highest temperatures coincided with their greatly decreased R_s values, there was already a significant decrease in R_s in films treated at lower temperatures. These latter films showed no changes in their x-ray patterns. This indicates that at least part of the decrease in rf surface resistance was due to a more complete oxidation of the YBCO during the heat treatment in oxygen and was not solely due to an improvement in crystalline perfection. In either case, the results unambiguously show that the optimization of T_c in YBCO films is a necessary but not sufficient requirement for optimizing the rf surface resistance of these films. These most recent data on the R_s of YBCO films will be presented at the March 1993 meeting of the American Physical Society.

In addition to the observation of higher R_s values in films with larger rocking curve widths, mentioned above, another possible correlation between structural perfection and rf surface resistance was found. While measuring rocking curve widths of the (309) peaks of YBCO(001) films grown on LaAlO_3 , it was discovered that they were clearly split into two peaks due to a-b twinning for lower- R_s films but were single peaks with the same overall width for several higher- R_s films. The shape of YBCO(309) x-ray diffraction peaks and R_s measurements will continue to be compared for films grown under various conditions to determine the limits of this correlation. The only correlation in this general area, reported in the literature, is an x-ray diffraction study by the Stanford University group who found that R_s was proportional to the fraction of YBCO(001) grains misoriented by 45° in the plane of films grown on $\text{MgO}(100)$ substrates. However, for the technologically-important substrates which have a closer lattice match to YBCO, the fraction of misaligned grains is always zero.

It is worth noting that using the results of the present study on the rf surface resistance of YBCO films and also other procedures developed under this and previous AFOSR-Westinghouse programs, the microwave device programs currently in progress at Westinghouse are fabricating, on a routine basis, two-inch diameter YBCO films which have T_c 's $>90\text{K}$, R_s 's ~ 0.5 mohm (at 10 GHz and 77K) and no second phase Cu-O particles ("boulders") on their surfaces.

4.4 EPITAXIAL FILMS AND LAYERED STRUCTURES

Thick epitaxial insulating layers are required in the fabrication of a number of devices to permit integration of ground planes and crossovers in active circuits, fabrication of lumped-element capacitors, and implementation of flux transformers. Insulating film requirements were estimated for each of these applications. In 1991, under this program, epitaxial bilayers and trilayers of YBCO/insulator and YBCO/insulator/YBCO were fabricated with SrTiO_3 , LaAlO_3 , and MgO as the insulator. Vertical transport and capacitance measurements were made to obtain values for the resistivity and dielectric

constant of the insulator. The highest resistivity was found for SrTiO_3 insulators – higher than any value reported in the literature for an epitaxial insulator on an HTS film and sufficiently high for any application. The problem with SrTiO_3 is its high real and imaginary dielectric constants which slow and attenuate signals.

In this reporting period, an additional series of candidate insulating films was evaluated. Since SrTiO_3 already met requirements for dc resistivity and film morphology, only materials with suitable dielectric constants and loss tangents were considered, including NdGaO_3 , CeO_2 , and $\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (SAT). SAT was discussed by several groups involved in bulk crystal growth at an ONR-sponsored Workshop on New Substrate Materials for High- T_c Superconductors in Williamsburg in February, 1992, as a candidate substrate material. Although single crystals could not be grown due to incongruent melting, a composite sputtering target was purchased to see if SAT could be stabilized in thin-film form. In the cases of NdGaO_3 or CeO_2 , suitable growth conditions were not found for high-resistivity films to grow at a reasonable rate. However, growth conditions were found for deposition of SAT films on YBCO which resulted in smooth films with very high resistivity. Resistivities in the 10^{10} ohm-cm range were measured at both room temperature and at 77K. SAT has been reported to have a dielectric constant of 25 and loss tangent of 1×10^{-4} so it should be suitable for the many applications where the group velocity in SrTiO_3 is too slow or SrTiO_3 is too lossy. The results of the survey of epitaxial insulators and success with SAT were reported at the Applied Superconductivity Conference.

A mask set was fabricated which enabled measurements to be made of the properties of epitaxial YBCO and insulator films under the same conditions as when they are incorporated into multilayer HTS circuits. In contrast to the Ar ion milling parameters used in fabricating step-edge grain-boundary or S-N-S Josephson junctions, the edges of each film layer were ion-milled at a shallow angle to avoid the formation of a weak link or a discontinuity in places where the YBCO or insulating film must cover a step. The only chips fabricated and tested to date used SrTiO_3 insulators. The dc

resistivity of the insulator was reduced to from $>10^9 \Omega\text{-cm}$ in planar structures to $10^7 \Omega\text{-cm}$ over a step. This is still adequate for digital circuit applications. The fabrication of a similar set of chips with SAT insulators will be performed under a DARPA-sponsored program in which crossovers are needed for Lange couplers.

For some applications, notably compact superconducting delay lines, thick epitaxial insulating films are desirable with thicknesses as large as $10 \mu\text{m}$. Neither sputtering or laser ablation is an appropriate technique for thick films. In collaboration with Northwestern University and Penn State University, MOCVD and LPE growth of thick epitaxial insulators are being pursued. Patterned and unpatterned YBCO films were sent to Northwestern University for MOCVD deposition of YAlO_3 and NdGaO_3 films. The insulating layers will be patterned at Westinghouse and a second YBCO layer deposited to permit complete evaluation of the insulators. The same experimental procedure will be followed with LaAlO_3 films grown by LPE at Penn State when their process is under better control.

Although conditions could not be found for the growth of smooth CeO_2 films on YBCO, CeO_2 was used successfully as a buffer layer which permitted low- R_s YBCO films to be grown on the R plane (1102) of sapphire. The CeO_2 deposition temperature had to be maintained at $630\text{-}650^\circ\text{C}$; much lower than the $740\text{-}760^\circ\text{C}$ necessary for growth of smooth SrTiO_3 or SAT on YBCO. Based on the R_s values of YBCO overlayers, CeO_2 buffer layers were superior to any of the other buffer layers for sapphire tested earlier in this program including MgO , La-Sr-Cu-O , SrTiO_3 , or LaAlO_3 .

The use of SrTiO_3 buffer layers for BKBO-based epitaxial film structures was described in Section 4.2. The structural and superconducting properties of BKBO films and successful demonstration of epitaxial BKBO/insulator/BKBO trilayers were reported at the Applied Superconductivity Conference and a paper has been accepted for the proceedings. The two insulators used were MgO and SrTiO_3 , the two substrate materials which have the closest lattice match to BKBO. The best results for all-BKBO junctions were obtained with SrTiO_3 barriers. These are included in the paper accepted

for publication in Applied Physics Letters. The magnitude of the gap voltage indicated that nearly equal contributions were made by the base and counterelectrodes.

A critical problem in the fabrication of these junctions was the occurrence of electrical shorts between electrodes for barrier thicknesses less than 20 nm, indicating that SrTiO_3 formed as islands which did not coalesce until their thickness reached that nominal value. An alternative perovskite barrier material, BaZrO_3 , has been selected for investigation since its better lattice match to BKBO provides a more energetically favorable opportunity for layer-by-layer growth instead of island growth. Scanning tunneling microscopy, in collaboration with NIST in Boulder, Colorado, is being used in parallel with junction measurements to monitor progress in obtaining smooth barrier layers.

X-ray photoelectron spectroscopy showed that a native insulating layer of carbonates formed upon exposure of BKBO films to air. This surface layer created a pervasive problem in making electrical contacts to BKBO films and junctions. The solution was to routinely deposit an in-situ Au layer on each BKBO film or trilayer.

4.5 MATERIALS AND PROCESSING FOR HTS DEVICES

Several different configurations for YBCO Josephson junctions are being developed at Westinghouse under various programs. One of the configurations which is being investigated under this program is a step-edge S-N-S junction in which a thin YBCO film is made discontinuous by covering a sharp step in the substrate which is high compared to the film thickness. The YBCO banks are then connected by a much thicker normal metal. The yield of these junctions has been remarkably high when gold, deposited in situ, was used as the normal metal layer. Modulation of the Josephson current was observed up to 82K. Two objectives during this reporting period were to investigate higher-resistivity normal-metal barriers for higher $I_c R_n$ products and to determine the effect of processing parameters on the reproducibility of Josephson critical currents in these junctions.

Two normal-metal alternatives to Au were investigated: Ag-Au alloys and epitaxial layers of over-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Films of LSCO with $x = 0.3$ were developed as part of Task 1 which were not superconducting but which have a lower normal-state resistivity at 40-80K than superconducting LSCO ($x = 0.17$). A disadvantage of using higher-resistivity normal-metal barriers is that the barrier length must be shorter to maintain the same Josephson current since the normal-metal coherence length is proportional to the inverse square root of the resistivity. In the step-edge junctions, it was not clear whether the length scale of the separation between YBCO banks was approximately the step height or some smaller distance. Since typical step heights were 10 times the LSCO coherence lengths and no Josephson coupling was observed for these junctions, the height of the step was apparently a good approximation for the separation between YBCO banks. Alloys of Ag and Au represented an intermediate resistivity. The resistivity of these junctions were higher than for Au barriers but the junctions were less reproducible. Since reproducibility is a greater concern than $I_c R_n$ product, Au barriers were used for subsequent junction experiments. These results were presented at the March Meeting of the American Physical Society.

A systematic study was performed on the effects of step heights and step angles on junction characteristics and reproducibility. Steps were made in either NdGaO_3 substrates or SrTiO_3 insulating films. All steps were made by Ar ion milling using a deposited Nb milling mask. Cross-sectional SEM micrographs were obtained both for uncoated steps and steps covered with a YBCO/Au bilayer. The milling angle was found to be the critical variable affecting junction performance. Using a new 15 cm ion miller with a cold rf discharge operated at 150 eV, step angles were well-controlled and measured to be 10° greater than the milling angles in a range of angles from normal incidence. When samples were not rotated during milling, the range was 0° to 45° . With rotation, the range was 0° to 20° . Outside these ranges, the step profiles were pathological.

The optimum milling angle for junction reproducibility was approximately 15° . Junctions made on such steps had RSJ-like characteristics.

Although the junction resistance, R_n , was independent of angle, the Josephson critical current, I_c , increased as the angle increased. At high angles, I_c and $I_c R_n$ were large but the I-V curves were indicative of flux flow and the other indicators of Josephson coupling, Shapiro steps and SQUID voltage modulation, were less pronounced. The 15° junctions had a spread in critical current of $\pm 30\%$ across a wafer. Much broader distributions were obtained if YBCO films contained CuO precipitates which nucleated preferentially at the step. These results were presented at the Applied Superconductivity Conference.

A second junction configuration under investigation as part of this program requires a-axis-oriented YBCO films in a traditional (with respect to low- T_c superconductors) sandwich structure. The a-axis orientation permits the maximum value of the anisotropic coherence length to determine junction properties. Growth conditions were found for preparing a-axis films by off-axis sputtering. The optimum deposition temperature was 580°C for a-axis films. As discussed in Section 4.1 of this report, the presence of water vapor in the sputtering gas promoted c-axis instead of a-axis growth and therefore was left out of the sputter gas mixture.

The $\text{LaAlO}_3(001)$ wafers used for the growth of a-axis films were cut and polished to $\pm 1^\circ$ of the $[001]$ direction. The a-axis films which were grown on the particular wafers which were cut to within 0.5° of the $[001]$ direction, grew epitaxially with four in-plane directions for the c-axis, each separated from the next by 90° . A-axis films deposited on LaAlO_3 wafers miscut by $>0.5^\circ$, also grew epitaxially but with a single in-plane direction for the c-axis either parallel to the $[100]$ or $[010]$ direction of the substrate. The preferred direction of these two was the one closer to the gradient of the miscut. Bridges were patterned in several films with a preferred in-plane direction for the c axis. The resistivity measured for currents flowing in the c direction was semiconductor-like (negative temperature coefficient) with a value comparable to measurements made in this direction in YBCO single crystals. The resistivity for currents flowing in a bridge perpendicular to the c-axis on the same sample had the metallic temperature dependence characteristic of current flow in the a-b plane.

Trilayers of YBCO/PrBCO/YBCO were grown under the same conditions used for single-layer a-axis films. The trilayers grew epitaxially with a preferred in-plane direction for the c-axis in each layer. Previous work under this program and in other laboratories either used c-axis films for these trilayers or used a-axis films containing high-angle (90°) grain boundaries arising from the four directions for the c-axis. The objective of this effort is to determine whether the use of the favorable-coherence-length direction and elimination of high-angle grain boundaries in the junction barrier will improve junction characteristics.

The epitaxial insulators developed under Task 3 have dielectric constants which are satisfactory for digital circuits or SQUID sensor circuits but too high for some other applications. In the case of multi-chip modules, low dielectric constants, $\epsilon \leq 6$, are required. In the case of crossovers in analog microwave circuits, the crosstalk between lines due to capacitive coupling is minimized by reducing ϵ . The lowest dielectric constant obtainable requires the development of air-bridge crossovers. Some efforts reported by other laboratories used Au air bridges deposited on polyimide supports but the rf surface resistance is too high in Au. In this program, a mask set has been fabricated to permit YBCO film layers to cross using air bridges. The design uses an epitaxial SrTiO_3 insulating layer to support the growth of the top YBCO film. A highly differential wet-chemical etch for SrTiO_3 will be used to remove the insulator. If the SrTiO_3 etch is not sufficiently differential, thin layers of more-inert epitaxial insulators such as SAT can be deposited at each YBCO/ SrTiO_3 interface using the same mask set.

Another unique requirement for insulators is presented by HTS multi-chip modules (MCMs). The major fabrication issues for HTS MCMs are deposition of a very thick ($1.5\text{--}2\ \mu\text{m}$) low- ϵ insulator, and patterning of very long, $2\ \mu\text{m}$ -wide, lines in YBCO films grown on top of the thick insulator. Both problems were addressed in this program. The best epitaxial insulator available at present for this particular application is MgO since it has the lowest dielectric constant. Films of MgO $1.5\ \mu\text{m}$ thick were grown by electron-beam evaporation on suitable substrates for epitaxial growth. Although

electron diffraction measurements confirmed that the MgO was epitaxial, x-ray rocking curve widths were much greater than for typical thin insulators ($\sim 0.3 \mu\text{m}$). Long and narrow lines, 6 cm x 4 μm wide, were patterned in YBCO films deposited on LaAlO_3 substrates with no degradation in film quality. The objective of this work is to reproduce such a result in YBCO films grown on electron-beam evaporated MgO.

4.6 OTHER ACCOMPLISHMENTS

In support of the work described above, a file of reprints and preprints on high- T_c superconductivity started in 1987 was maintained. The updated list of papers was entered into a computer and keywords were assigned to them to aid in retrieval. The entire database has been made available to the research community through the computer facilities at High- T_c Update. Annual updates to the database have been published in the Journal of Superconductivity. During 1992, the database was transferred to the University of South Carolina where it will be updated in the future.

The year 1992 marked the completion of a three-year, \$4M upgrade of facilities, funded by Westinghouse, which are dedicated to superconducting electronics. This program will have the benefit of new equipment for the deposition, patterning, and characterization of superconducting films and circuits. The number of vacuum deposition systems dedicated to HTS film structures has increased from two at the start of the program to seven by the end of 1992. The most recently installed system incorporates experience in growing YBCO-based structures gained in this program into a fully-automated production system capable of sequentially coating both sides of two 2-inch or one 4-inch substrate with multilayers composed of YBCO and appropriate epitaxial insulators or conductors. The most important new equipment in the superconducting electronics clean room (which has been doubled in area) is a dedicated ion miller with capability for up to a 6"-diameter wafer. The most significant new characterization tool is a state-of-the-art four-circle x-ray diffractometer.

To obtain optimum use of the unique material and measurement capabilities developed under the present and previous AFOSR-Westinghouse programs, collaborations with other research institutions have been continued and expanded. These collaborations are made with researchers whose work falls within the overall objectives of this program. A table of technical collaborations which were active in 1992 is shown in Section 7 of this report.

5. PUBLICATIONS

1. H.-J. Chen, S. Sridhar, and J. Talvacchio, "Dynamics of Vortex-Anti-vortex Pairs at Microwave Frequencies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ Films," submitted to Phys. Rev. Lett. (1993).
2. B. A. Baumert, J. Talvacchio, and M. G. Forrester "SrTiO₃ Buffer Layers and Tunnel Barriers for Ba-K-Bi-O Junctions," accepted for publication in Appl. Phys. Lett. (1993).
3. J. R. Gavaler and J. Talvacchio, "YBCO-Based Multilayer Structures on Large-Area Substrates," in Layered Superconductors: Fabrication, Properties, and Applications, ed. by D.T. Shaw, C. C. Tsuei, T. R. Schneider, and Y. Shihara (Materials Research Society, Vol. 275, 1992).
4. J. Owliaei, S. Sridhar, and J. Talvacchio, "Field-Dependent Crossover in the Vortex Response at Microwave Frequencies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ Films," Phys. Rev. Lett. 69(23), 3366 (1992).
5. F. Gao, D. B. Romero, D. B. Tanner, J. Talvacchio, and M. G. Forrester, "Infrared Properties of Epitaxial $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ Thin Films in the Normal and Superconducting States," Phys. Rev. B 47(2) (1992).
6. B. A. Baumert and J. Talvacchio, "Artificial Barriers for Ba-K-Bi-O Tunnel Junctions," accepted for publication in IEEE Trans. Appl. Supercond. (1993).
7. T. T. Braggins, J. R. Gavaler, and J. Talvacchio, "In-Situ Deposition of YBaCuO Films on Both Sides of Two-Inch-Diameter Wafers by Off-Axis Sputtering," Microwave Journal 35(8), 106 (1992).
8. D. B. Tanner, F. Gao, M. Quijada, D. B. Romero, J. P. Rice, D. M. Ginsberg, J. Talvacchio, M. G. Forrester, L. Forro, D. Mandrus, L. Mihaly, G. L. Carr, and G. P. Williams, "Optical Conductivity of the High-T_c's: Search for the Energy Gap," J. Phys. Chem. Solids 53(12), 1611 (1992).
9. T. Gong, L. X. Zheng, W. Xiong, W. Kula, R. Sobolewski, J. P. Zheng, H. S. Kwok, and J. R. Gavaler, "Femtosecond Spectroscopy of Y-Ba-Cu-O Thin Films," Proceedings of the Conference on Superconductivity and Its Applications, Buffalo, NY 1992, to be published.

10. Wei Xiong, Witold Kula, Roman Sobolewski, and John R. Gavaler, "Superconducting Properties of Laser-Annealed Lines Fabricated in Oxygen Deficient Y-Ba-Cu-O Thin Films", *ibid.*, to be published.

6. PERSONNEL

J. R. Gavalier }
J. Talvacchio } Principal Co-Investigators

M. G. Forrester

R. L. Grassel

J. H. Kang

G. R. Wagner

B. A. Baumert (Carnegie Mellon University)

J. D. McCambridge (Yale University)

G. Skofronick (Penn State University)

7. COUPLING ACTIVITIES*

1. J. Talvacchio, "Requirements for Substrates and Deposited Insulators Used in Analog and Digital HTS Circuits," Invited presentation to the Workshop on Substrate Materials for High Temperature Superconductors, Williamsburg, February 1992.
2. J. Talvacchio and B. A. Baumert, "Barriers for Ba-K-Bi-O Tunnel Junctions," Contributed presentation to the APS March Meeting, Indianapolis, March 1992.
3. D. H. Kim, D. J. Miller, J. D. Hettinger, J. Sharping, R. A. Holoboff, R. T. Kampwirth, J. H. Kang, J. Talvacchio, and M. Eddy, "Effect of Substrate-Induced Microstructure on Transport Properties in Epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ Films," Contributed presentation to the APS March Meeting, Indianapolis, March 1992.
4. J. D. McCambridge, J. Talvacchio, and M. G. Forrester, "High- T_c Step-Edge SNS Junctions and SQUIDS," Contributed presentation to the APS March Meeting, Indianapolis, March 1992.
5. F. Gao, D. B. Tanner, J. Talvacchio, and M. G. Forrester, "Infrared conductivity of Epitaxial $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ Thin Films in the Normal and Superconducting States," Contributed presentation to the APS March Meeting, Indianapolis, March 1992.
6. J. R. Gavaler and J. Talvacchio, "YBCO-Based Multilayer Structures on Large-Area Substrates," Contributed presentation to the MRS Spring Meeting, San Francisco, April 1992.
7. M. G. Forrester, J. D. McCambridge, J. Talvacchio, J. H. Kang, J. X. Przybysz, D. L. Miller, and J. R. Gavaler, "Development of a Digital Integrated Circuit Process Based on Step-edge YBCO/Au S-N-S Junctions," Contributed presentation to the Applied Superconductivity Conference, Chicago, August 1992.
8. B. A. Baumert and J. Talvacchio, "Artificial Barriers for Ba-K-Bi-O Tunnel Junctions," Contributed presentation to the Applied Superconductivity Conference, Chicago, August 1992.

*Speaker's name is underlined.

9. J. Talvacchio, M. G. Forrester, J. R. Gvaler, and S. H. Talisa, "Epitaxial Insulating Thin films for High-Tc Superconducting Electronics," Contributed presentation to the Applied Superconductivity Conference, Chicago, August 1992.
10. J. R. Gvaler, J. Talvacchio, S. H. Talisa, and G. B. Draper, "Role of Oxygen in Optimizing Surface Resistance in YBCO Films," Contributed presentation to the Applied Superconductivity Conference, Chicago, August 1992.
11. J. D. McCambridge, M. G. Forrester, and J. Talvacchio, "Optimizing YBCO Step-Edge S-N-S Junctions for Digital Electronics," Contributed presentation to the Applied Superconductivity Conference, Chicago, August 1992.
12. J. Talvacchio, "Requirements for Thin Films Used in High-Speed Analog and Digital HTS Circuits," Invited presentation to the Workshop on MOCVD of High-Temperature Superconductors, Chicago, August 1992.

OUTSIDE COLLABORATIONS

Institution/Collaborator	Effort / Special Requirements
Penn State University Prof. A. M. Carim	Microstructure of a-axis YBCO structures - a-axis YBCO/PrBCO/YBCO trilayers
Carnegie Mellon University Prof. M. E. McHenry	Development of BKBO tunnel junctions - Epitaxial BKBO films and junctions
Yale University Prof. D. E. Prober	S-N-S Josephson junction development - in-situ S-N interface formation
Argonne National Laboratory Dr. D. H. Kim	Vortex dynamics in superconductors - epitaxial YBCO and NbN patterned films
University of Maryland Prof. C. J. Lobb	Strain effects in YBCO - patterned YBCO bridges
EMCORE Corp. Dr. C. Chern	rf surface resistance measurements - YBCO films grown by MOCVD
University of Florida Prof. D. Tanner	Infrared reflection and absorption - single crystal LSCO films
Northeastern University Prof. S. Sridhar	Magnetic field phase diagram mapped with R_s - YBCO with measured R_s
University of Alberta Prof. J. Jung	Mapping of critical current density - Patterned YBCO films
University of Maryland Prof. T. Venkatesan	Epitaxial insulator films - YBCO/insulator/YBCO structures
University of Rochester Dr. R. Sobolewski	Laser-patterning of YBCO films - Single-phase YBCO films
NIST, Boulder Dr. A. Roshko	STM investigation of BKBO films and barriers - Single-orientation BKBO films and bilayers
Purdue University Prof. M. W. McElfresh	Vortex dynamics in YBCO - Patterned a-axis YBCO films

8. PATENT

"Sputtering Method for Forming Superconductive Films Using Water Vapor Addition," J. R. Gavalier and T. T. Braggins, U. S. Patent #5,126,318, issued June 30, 1992.