HIGH T_c SUPERCONDUCTING THIN FILMS, DEVICES, AND APPLICATIONS

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PREFACE

This book contains the proceedings of the 1988 Topical Conference on High T_c Superconducting Thin Films, Devices, and Applications of the American Vacuum Society (AVS). This Topical Conference was held in Atlanta, Georgia, immediately preceding the annual symposium of the AVS. This high-T_c meeting is the continuation of the topical conference on Thin Film Processing and Characterization of High-Temperature Superconductors, organized by the AVS in 1987. A third topical conference is planned in conjunction with the 1989 AVS annual symposium in Boston. These meetings reflect the continuing interest of the members of the AVS for high-temperature superconductivity, and the specific, crucial role that their research plays in the exciting field of science and technology.

The subject of high-temperature superconductivity was launched in late 1986 by the paper of Bednorz and Müller announcing the observation of possible superconductivity at 35 K in a compound of La, Ba, Cu and O. The scientific activity since that time has been frenzied, and shows little sign of abatement. It has been driven by the achievement of ever-higher critical temperatures: 95 K in YBaCuO and up to 125 K in TlBaCaCuO, and the establishment of superconductivity in other oxides: BaBiO alloyed with K, and BiSrCaCuO. Attracted both by the intrinsic scientific interest of these materials and by the promise of new technologies, scientists have shifted the focus of materials research and solid state physics to a remarkable extent toward superconductivity.

This field intersects most strongly with the traditional interests of the American Vacuum Society in the area of thin films. The fabrication of high-quality superconducting films is of course an absolute prerequisite for all electronics applications. More surprisingly, the successful passage of very high supercurrent densities in films (much higher than has so far been achieved in bulk samples) has demonstrated the importance of thin films for the fundamental science of high-temperature superconductivity. This was already clear at the 1987 AVS topical conference, where those results were reported. At the 1988 topical conference, the relevance of thin films for the understanding of transport at the microscopic level was demonstrated by studies of current flow across single grain boundaries.

Spectroscopy is the other area in which vacuum science has contributed in an essential way to this new field. No theoretical understanding of the materials is possible until the electronic structure has been clarified. The main features of the bands had already been identified by the time of the 1987 topical conference, and the valency of copper reasonably well established. At the 1988 topical conference observations of a Fermi edge were reported in both YBaCuO and BiSrCaCuO, and the appearance of a superconducting gap in the latter system was also suggested by photoemission studies.

The 1988 topical conference was opened by the keynote speaker, C. W. (Paul) Chu, who reviewed the recent discoveries of new high-T_c materials. The first session was held jointly with the AVS Topical Conference on Probing the Nanometer Scale Properties of Surface and Interfaces, and was chaired by J. Murday. The second invited speaker of the session was A. J. Melmed, who presented the first results obtained with field-ion microscopy on high-T_c samples. The second session was moderated by G. Margaritondo, and was dedicated to photoemission spectroscopy experiments. The invited speakers in this session were W. E. Spicer and J. H. Weaver. The afternoon session was chaired by L. C. Feldman. The first invited speaker was D. E. Aspnes, who reviewed the recent work with optical techniques. The next two invited speakers, C. C. Tsuei and G. J. Fisanick, covered different aspects of the crucial problem of critical current densities. The session was concluded by the invited presentation of G. K. Wehner on a novel sputter deposition technique. The conference had a poster session, which included 59 contributed presentations. The attendance throughout the meeting was one of the highest ever recorded for an AVS topical conference.

As in 1987, all divisions of the AVS sponsored the topical conference. This general interest was reflected by the composition of the Program Committee, chaired by G. Margaritondo, whose members were M. D. Boeckmann, Donald Carmichael, Susan Cohen, H. F. Dylla, L. C. Feldman, Richard J. Gambino, and John T. Grant. We enjoyed many constructive interactions with the AVS Program Committee, and in particular with its Chairman, John Noonan. The organization of the conference was impeccable, thanks to the excellent preparation work done by the AVS Meetings Manager, Marion Churchill, and by Marcia Schlissel. We are also grateful to the Local Arrangements Committee, chaired by John Wendelken with the assistance of Don Santeler. Due to the rapid evolving of high-T_c research, we again adopted a quick publication schedule for these proceedings. The timely processing of the papers would not have been possible without the help of Gerry Lucovsky, Rita Lerner, and of many other people, to whom we are deeply indebted. We would like to mention all members of the Program Committee, who also served as monitors for the reviewing process, and the many anonymous referees who provided accurate reviews in a very short time. We thank Kathleen Strum for supervising the operation of the Editorial Office in Atlanta. The office was run by many volunteers, including several members of the Program Committee, and Doreene Berger, Yeh Chang, Michael Hennelly, Ming Tang, and Tom von Foerster. We are much indebted to Lois Blackbourn for her organization of the final reviewing process, and to Lori Johnson for her assistance.

The work of the authors and of all the people mentioned above has produced a timely review of this exciting area of research. We trust that the book will be as successful as the proceedings of the 1987 topical conference [*Thin Film Processing and Characterization of High-Temperature Superconductors*, edited by J. M. Harper, R. J. Colton and L. C. Feldman, AIP Conference Proceedings no. 165 (American Institute of Physics, New York, 1988)]. Besides conveying information in a timely fashion, it is our hope that this book will provide a permanent record to one of the most exciting periods in the lives of the members of the American Vacuum Society.

Proceedings Editors

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Robert Joynt
Marshall Onellion

University of Wisconsin-Madison

November 23, 1988

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REACTIVE SPUTTERING OF SUPERCONDUCTING THIN FILMS

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ABSTRACT

We report a simple, versatile method for fabrication of superconducting thin films of $Y_1Ba_2Cu_3O_{7-x}$ using reactive RF sputtering from three targets in vacuum and a subsequent anneal in oxygen.

The structure and composition of the films were verified using Rutherford backscattering spectroscopy and x-ray diffraction studies. Measurements of resistivity and susceptibility vs. temperature established the superconducting transition temperatures for the films. Comparison of the susceptibility and resistance transitions demonstrates heterogeneity in the superconducting character of the films.

INTRODUCTION

The new high temperature superconductors present exciting prospects for high performance microwave circuits. As part of a program for the development of high temperature, superconducting, passive microwave devices we have developed techniques for the preparation and characterization of thin films of $Y_1Ba_2Cu_3O_7$.

METHOD OF PREPARATION

We have used sapphire, ceramic alumina, and 9.5 mole % Y-stabilized cubic zirconia substrates in our experiments. The substrate dimensions were 0.300"x0.420". All substrates were ultrasonically cleaned using Microcleaner detergent[1] for 15 minutes. The substrates were then rinsed in deionized water, dipped in Chromerge[2] and rinsed again in deionized water and then in boiling deionized water. The substrates were then boiled in isopropanol and finally baked for 60 minutes at 250 C.

The sapphire and ceramic alumina substrates were then coated with 100 nm of either reactive sputtered ZrO_2 or thermally grown ZrO_2. The thermally grown films were prepared by sputtering Zr and subsequently oxidizing at 500 C in air.

The substrates were transferred into a Perkin Elmer 4400 series sputtering system via a load lock. The $Y_1Ba_2Cu_3O_{7-x}$ was then deposited by reactive sputtering from three targets of yttrium , copper and barium under an atmosphere of 80% argon, 20% oxygen at 12-15 microns

pressure. The deposition is carried out at room temperature. The substrate rotates under the three targets in succession, at 15 rpm. The sputtering yield from each target is controlled individually by varying the sputtering power. Hence, the stoichiometry of the film can be varied at will. The total sputtering yield at the nominal $Y_1Ba_2Cu_3O_{7-x}$ composition is 0.03 nm/sec. The films prepared for these experiments were about 2μ thick. The sputtered samples were stored either in vacuum or a nitrogen dry box after preparation.

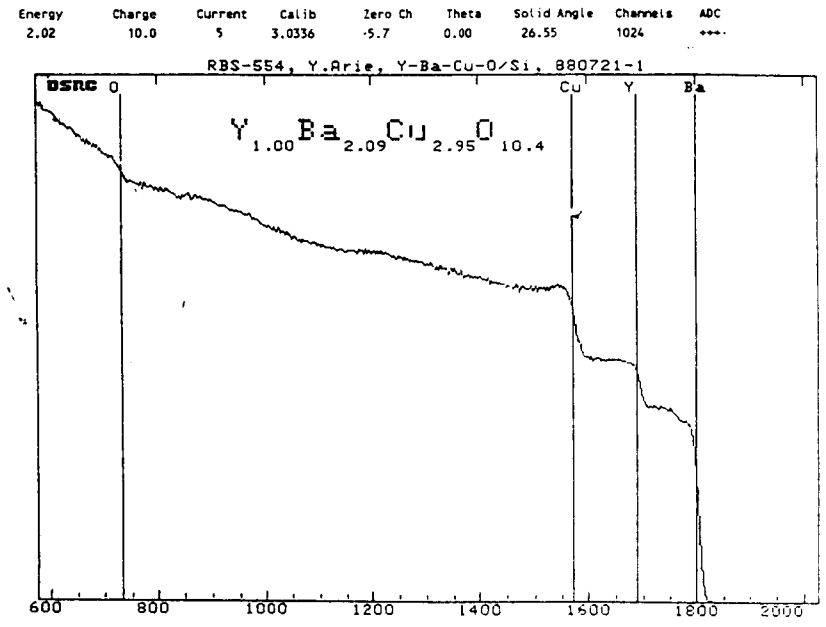
The annealing furnace used in these experiments is a programmable Lindberg furnace[3]. Our basic annealing procedure is:

- The furnace is ramped up to 900 C over 30 minutes. At this time the samples are in the furnace tube, but outside the heated region.
- After the furnace reaches 900 C, the samples are moved into the heated region at the rate of 2.5 cm/minute.
- The samples remain in the heated region for annealing for a variable length of time.
- At the end of the anneal time the furnace is ramped down to 650 C at the rate of 8 C/minute.
- The sample is then soaked at 650 C for 10 hours.
- The temperature is then ramped down to 400 C at 8 C/minute.
- The sample is soaked at 400 C for 4 hours.
- The furnace is then turned off and allowed to cool to room temperature over about 2 hours.
- The entire procedure is carried out in a flowing stream of dry oxygen.

The annealed samples were stored either in vacuum or a nitrogen dry box after preparation.

MATERIALS CHARACTERIZATION

Films of $Y_1Ba_2Cu_3O_{7-x}$ were deposited on silicon wafers at the same time as the preparation of the sapphire, alumina and zirconia samples. Rutherford backscattering spectra (RBS) of as prepared films on these silicon substrates show a composition of $Y_1Ba_2Cu_3O_8$ with 10% accuracy. Figure 1 shows a typical RBS spectrum. X-ray diffraction studies of as prepared films on strontium titanate substrates indicate that the films are amorphous.



A portion of an annealed sample was scraped from a cubic zirconia substrate and characterized using x-ray powder diffraction. The diffraction pattern indicates that the sample is almost entirely the orthorhombic form of $Y_1Ba_2Cu_3O_{7-x}$. One extra "weak" line may indicate the presence of a small amount (<5%) of $Y_1Ba_2Cu_3O_5$. It was not possible to make a definite identification on the basis of one line.

SUPERCONDUCTING PROPERTIES

We test the superconducting properties of our films using four-terminal, low frequency AC resistance measurements; four-terminal, DC resistance measurements; and low frequency AC susceptibility measurements. The AC resistance measurements are made with a low frequency impedance analyzer[4]. The DC resistance measurements are made with a programmable current source and a nanovoltmeter[5] using standard current reversing procedures to eliminate thermal EMF's. Connections to the samples are made using InHg amalgam.

The susceptibility measurements are made using the thin film susceptometer sketched in figure 2. The mutual inductance and the equivalent series resistance of the coil pair are measured using our low frequency impedance analyzer.

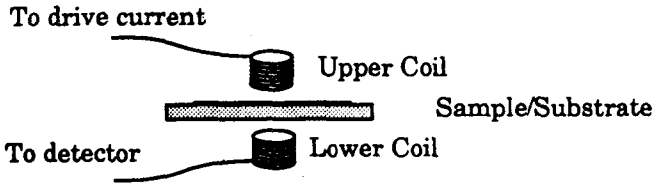


Figure 2

The experiments are carried out in a cryostat of conventional design. The experiments are supported by a thermal resistance at the end of a cold finger within the vacuum chamber of the cryostat. The temperature is measured and controlled using a calibrated silicon diode thermometer and a commercial controller[6]. The cryostat is cooled using liquid nitrogen or liquid helium. For temperatures between 45K and 77K we pump on the nitrogen.

The measurements are made under computer control and the instruments can be switched between samples by the computer. Four thin film susceptibility samples and two resistance samples can be measured during each run. Figure 3 shows the results on a typical sample on cubic zirconia. The four terminal resistance, inductance and equivalent series resistance have been normalized to their values at 300 K for easy comparison. The measurements were carried out at 10 kHz and an applied field of about 10^{-5} tesla.

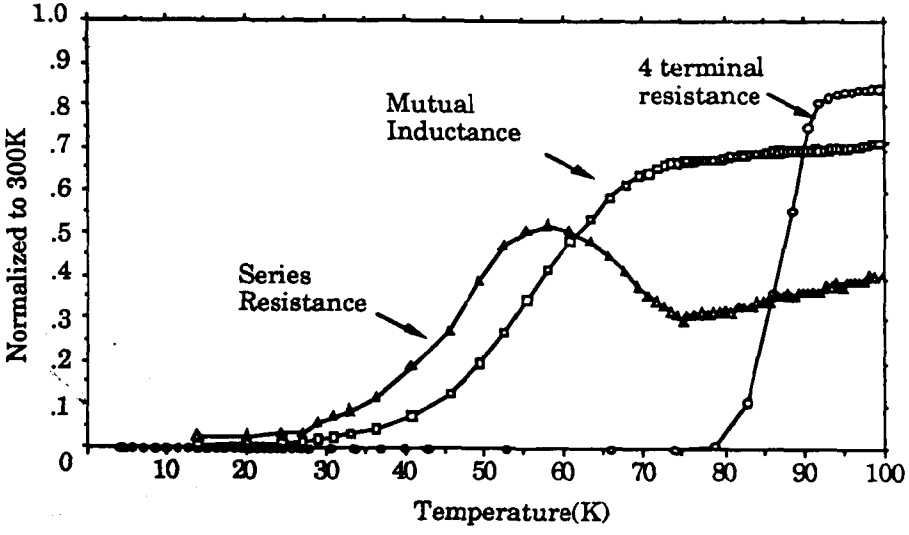


Figure 3

The width of the resistance transition is broad, 10-15 degrees, but comparable with those seen in the literature. We interpret this as a heterogeneous sample, with different parts of the sample undergoing the superconducting transition at different temperatures. Using the Bruggeman effective medium approximation for three dimensions[7] we expect that zero resistance will be reached at the percolation transition, when 33% of the material is superconductive.

Above the percolation transition there are no complete paths of superconductor. Flux lines can move freely across the sample and we expect no change in the mutual inductance. Below the percolation transition flux motion is impeded and the mutual inductance should begin to drop. Percolation paths of non-superconducting material, along which flux may move, will remain until the superconductor fraction exceeds 66%. Naively, we expect that this is the point at which the magnetic shielding should be complete and the mutual inductance should go to zero[8].

In figure 3, we see that the inductance signal varies slowly between 70K and 100K due to temperature dependent shielding of the mutual inductance coils by the copper sample holder. Below the zero resistance transition, we see a strong drop in the mutual inductance signal, going to zero at about 25K.

The series resistance plot shows an interesting peak. Below the percolation transition flux lines may break through the superconducting paths at weak points. This contributes a new source of loss in the film, which is seen in the peak in the series resistance. As the temperature is lowered, more of the sample becomes a superconductor and the strength of the weak points improves.

From these measurements, we infer that the actual widths of the transitions of these films are > 65K -- the onset is seen in four terminal resistance at 90K, the 33% complete point is at 75K, and the 66% complete point is at about 25K.

We have seen similar results on samples on cubic zirconia annealed for times ranging from 12 minutes to 3 hours. We have also seen this behavior on samples prepared using the ceramic alumina and sapphire substrates described above.

DISCUSSION

The resistance and susceptibility data demonstrate that we can prepare thin films of $Y_1Ba_2Cu_3O_{7-x}$ material on a variety of substrates using reactive RF sputtering. The same technique can be easily adapted to more complex materials by the addition of a fourth or fifth target and the associated power control systems.

Our results support the idea that these films are heterogeneous, with a broad range of transition temperatures. Such heterogeneity can have important consequences. Gittleman and Matey[9] have shown that the microwave surface resistance of superconductor/normal composites is a function of the volume fraction of the superconducting phase.

Our results show that characterization of the superconducting properties of HTSC thin film by four terminal resistance measurements alone neglects important aspects of the film.

ACKNOWLEDGEMENTS

Our thanks to R. Paff for the x-ray diffraction study, to L. Hewitt for the RBS measurements, to V. Pendrick for help in preparing the substrates, to J. Gittleman for helpful discussions, and to A. Schujko for technical assistance.

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1 International Products, Trenton, NJ.

2 Fisher Scientific, Fairlawn, NJ.

3 55000 series with 55114P temperature control console. Lindberg Co., Watertown, WI.

4 Model 4192, Hewlett Packard, Palo Alto, CA.

5 Models 181 and 220, Keithley, Cleveland, OH.

6 DT-470 and Model 805, Lake Shore, Westerville, OH.

7 R. Landauer, " Electrical Conductivity in Inhomogeneous Media" in *Electrical Transport and Optical Properties of Inhomogeneous Media*, J. C. Garland and D. B. Tanner, Ed., AIP Conference Proceedings No. 40 (American Institute of Physics, 1978).

8 There are cases in which the Bruggeman theory needs more attention to the details than we have taken here. For example, if the superconductor was present in the form of thin shells surrounding a normal material, with the shells imbedded in a matrix of normal material, the normal material inside the shells would not participate.

9 J. I. Gittleman and J. R. Matey, "Modeling the Microwave Properties of the $Y_1Ba_2Cu_3O_7$ Superconductors", J. Appl. Phys., to be published.

PREPARATION AND CHARACTERIZATION OF HIGH T_c $YBa_2Cu_3O_{7-x}$ THIN FILMS ON SILICON BY DC MAGNETRON SPUTTERING FROM A STOICHIOMETRIC OXIDE TARGET

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ABSTRACT

The effects of deposition temperature and O_2 pressure during cool down on the superconducting properties of $YBa_2Cu_3O_{7-x}$ thin films on Si substrates by DC magnetron sputtering from a stoichiometric oxide target are reported. Results form X-ray diffraction analysis indicate that the films deposited at 400°C or lower, at 650°C and cooled down in $< 4 \times 10^{-4}$ O_2, and at 650°C and cooled down in > 0.16 Torr O_2 have, respectively, amorphous, tetragonal, and orthorhombic structure. Superconducting orthorhombic films with a zero resistance T_c of as high as 76 K have been thus prepared on Si directly, without further heat treatments. The deposition of these films on Si is possible because of the minimal film-substrate interaction at the relatively low deposition temperature used, as indicated by the depth profiles obtained for these films using secondary ion mass spectrometry. Results of cross-sectional transmission electron microscopic studies of some of these films with different T_c and X-ray photoemission spectroscopic studies of the amorphous, tetragonal, and orthorhombic films are also reported.

INTRODUCTION

Thin films of the newly discovered high T_c Y-Ba-Cu oxide superconductors have been successfully deposited on various substrates. Most of these films were deposited on e.g., $SrTiO_3$, and MgO, because of the strong interaction of these films with other substrates (e.g., Al_2O_3 and Si) during the high temperature (~900 °C) post annealing step required to achieve high T_c superconducting state[1]. For microelectronic applications such as interconnects and hybrid semiconductor/superconductor devices, it would be more desirable to deposit these films on Si substrates. It is well recognized that to deposit these films on Si a diffusion barrier[2] or a low temperature process is required to minimize this film-substrate interaction. We reported previously[3] the deposition of these films at 600-700°C on Si wafers with a zero resistance temperature (T_c) as high as 76 K using DC magnetron sputtering from a stoichiometric oxide target. Recently, deposition of these films on Si at the similar temperature range has been reported using activated reactive evaporation[4,5] and laser ablation[6,7]. In this paper, the effect of deposition temperature and oxygen pressure during the cool-down period after sputter deposition is reported. Results of cross-sectional transmission electron microscopic (TEM) and X-ray photoemission spectroscopic (XPS) studies of some of these films are also reported.

EXPERIMENTAL PROCEDURES

The preparation of the 2" $YBa_2Cu_3O_{7-x}$ sputtering target, and the substrate-cathode configuration used to achieve stoichiometric film composition were described previously[1]. Briefly, this configuration utilizes an off-centered substrate holder and a positively biased counter electrode (anode) to minimize the preferential resputtering effect due to the presence of negative ions during sputtering[1,8,9]. The sputtering target used typically has a T_c of ~ 90 K and consists dominantly of the $YBa_2Cu_3O_{7-x}$ phase although minor secondary phases such as Y_2BaCuO_x, and $CuBaO_2$ or CuO are detected occasionally, according to X-ray diffraction analysis. Results of electron microprobe analysis show that the target used has mostly a Y:Ba:Cu ratio of (1):(2.1±0.1):(3.0±0.1) with isolated impurity phases.

These films (1-2μm thick) are deposited onto (100) Si substrates at ambient temperature to 700 °C and cooled to room temperature in ~2 hours in the presence of up to 200 Torr O_2. The Si substrates are mechanically clamped to a Cu substrate holder during deposition. The temperature of the Cu holder is controlled to within 1 °C of the desired temperature with an Omega CN9000 or CN2010 temperature controller, and is measured with a mechanically attached chromel-alumel thermocouple. The substrate temperature is taken as the temperature of the Cu holder, and no attempt is made to measure the temperature of the Si substrate directly. The film deposition rate is typically 40 Å/min. at 100W DC input power and 4 mTorr Ar-10% O_2 total pressure.

The technique for measuring the temperature dependence of the resistance of these films was also described previously[1]. In addition, several techniques including electron microprobe, scanning electron microscopy (SEM), TEM, XPS, Secondary Ion Mass Spectrometry (SIMS) and x-ray diffraction techniques are used to characterize these films. Transmission electron microscopic studies are carried out using a JEOL JEM-200CX TEM microscope, operated at 200 KeV. Cross-sectional view samples, prepared with conventional methods, are used to obtain the bright or dark field images and selective area diffraction patterns. X-ray photoemission spectroscopic studies are made with a SSI model 501 small spot ESCA system equipped with a monochromatic Al Kα X-ray source. The reported binding energies were referenced to C 1S at 284.6 eV.

RESULTS AND DISCUSSION

1. The Effect of Deposition Temperature

The superconducting properties of these films are studied as a function of substrate temperature under different cool-down conditions. The films deposited at temperatures between 600 to 700 °C and cooled down in 1-200 Torr of O_2 are superconducting without further heat treatments. As reported previously[1], the films with the highest T_c (76 K) are deposited at 650°C. Results of electron microprobe analysis show that the films deposited at 650 °C have a Y:Ba:Cu ratio of (1):(2.2):(3.05), compared to the ratio of (1):(2.1±0.1):(3.0±0.1) for the sputtering target used. A ratio of (1):(2.4):(3.1) and (1):(2.4):(3.8) is observed for the films deposited at 600 °C and 700 °C, respectively. The films deposited at less than 600°C generally are not superconducting regardless of the cool-down conditions, although the compositions of these films are close to that of the sputtering target. Figure 1 shows the X-ray diffraction patterns for the films deposited at ambient temperature (~ 80°C), 485°C, and 650°C (T_c = 76 K). The film deposited at