

IN SITU GROWTH OF SUPERCONDUCTING YBaCuO USING REACTIVE ELECTRON-BEAM COEVAPORATION[†]

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Abstract

Conditions required for *in situ* growth of YBaCuO thin films by reactive electron-beam evaporation have been explored. Three sources of activated oxygen (atomic oxygen from microwave discharge, a plasma generated by electron beams, and an ion beam) were compared. The best results so far were obtained with atomic oxygen. Epitaxial films with high critical currents were grown on SrTiO₃ <100> and <110>, Al₂O₃ <1102> and MgO <100> at 600°C. Evaporation rates were controlled with a rate monitor using atomic absorption.

Introduction

Since the discovery of the new high-temperature superconducting oxides, considerable progress has been made in developing procedures for depositing thin films of these materials. The first successful, broadly-applicable approach involved depositing the constituents in an amorphous or disordered form with enough oxygen to stabilize the deposit and then to form the desired material subsequently by means of an oxygen anneal at high temperature.¹ On a suitable substrate, such as SrTiO₃, such films can be highly oriented and have quite good physical properties compared with ceramic samples. This is now a standard procedure for making thin films of the oxide superconductors.

It is widely recognized, however, that for both scientific and technological purposes it is necessary to be able to grow thin films of these superconductors *in situ* at lower temperatures and on a wider variety of substrates. Epitaxial growth is also desired. Some success along these lines has been reported. Various approaches have been tried, including sputtering of a composite target,^{2,3,4} electron beam sources in a high background oxygen pressure,^{5,6,7} ion beam sputtering of a composite target together with a molecular oxygen beam directed at the substrate,⁸ and laser ablation of a composite target (requiring in one case the addition of an oxygen plasma at the substrate).^{9,10} *In situ* films with good T_c's and increasingly respectable critical current densities have been reported in some cases.^{3,5,6,9,10}

In all of the above cases activated oxygen may have played an essential role in achieving the *in situ* YBCO growth. In each case some sort of plasma was present, either intentionally or as a byproduct of the conditions of deposition. By contrast, researchers using all thermal sources (MBE), in which case no plasma is present, have found that molecular oxygen at ~10⁻⁴ Torr is not sufficient even to oxidize copper deposits, whereas the addition of an oxygen discharge permits the *in situ* growth of "123-like" perovskite phases.^{11,12} The critical temperatures were low

presumably because of the insufficient flux of activated O₂. In addition to the apparent need for activated oxygen during growth, some kind of low temperature annealing protocol in a plasma or at a high oxygen pressure seems to be required in order to get the best results. The results to date do not provide much quantitative information regarding the precise conditions (e.g., the minimum oxygen pressure or the composition of the plasma) required for successful growth. Also, the presence of high oxygen pressure during growth introduces a number of technical problems for physical vapor deposition. These include oxidation of the sources during deposition and the control of deposition rates in the presence of a high background oxygen pressure, particularly in the case of electron-beam evaporation.

In this paper we describe our attempts to achieve *in situ* growth of the high-temperature oxide superconductors. We are exploring various approaches to produce activated oxygen, including the use of a microwave cavity discharge source of atomic oxygen, the plasma produced by the electron-beam sources themselves in the presence of a high background oxygen pressure, and an ion beam source. In each case we have attempted to quantify the actual flux of active species impinging on the substrates. Superconducting films of YBaCuO have been grown using all three approaches, although their properties are not yet optimized. To date, the best results have been obtained using the atomic oxygen source. We also are exploring the use of atomic absorption as a means of rate control of our electron beam sources. The atomic selectivity inherent in this approach holds the promise of a general approach to deposition rate control in the presence of large background gas pressures.

Atomic Absorption Rate Monitoring

Monitoring the evaporation rate of the various metal constituents in the high-temperature oxide superconductors presents problems at the high oxygen pressure required for *in situ* growth. Ion gauge detectors and mass spectrometers cannot be operated above 10⁻⁵ Torr; quartz crystal monitors are affected by the oxidation of the metals. In an attempt to circumvent these problems, we are exploring a newly available rate monitoring approach, developed by XINIX Inc., that uses the atomic absorption (AA) of light to detect the density of a particular atomic species in an evaporant beam. The method is intrinsically material specific and is capable of detecting the presence of evaporated atoms even at high partial pressures of reactive gases.

Hollow-cathode lamps of each species to be detected are used as the light sources. The light from each source is transmitted into the chamber by means of an optical fiber. For detection of multiple species, the fibers from each channel can be bundled into a single unit. Using a lens, a parallel beam of light is formed that crosses through the stream of evaporants and is refocused onto a set of detector fibers. Each detector fiber leads to a monochromator acting as a bandpass filter tuned to the wavelength of the absorbed

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light of the particular species being detected. A photomultiplier detects the resultant light intensity. Each lamp is chopped electronically, and a lock-in amplifier is used to separate further the signals from different channels. For the deposition of YBaCuO films, three separate channels were used (Y, Ba and Cu), each containing its own light source, fiber, monochromator and chopping frequency.

In actual operation, the lamp current and photomultiplier gain are first adjusted to define the zero-rate level. During deposition, the light intensity at the detector is attenuated due to absorption by the evaporated metals. Since the relation between vapor density and detector output is nonlinear, higher sensitivities are obtained at lower vapor densities. We note that because the atomic vapor density rather than the flux is measured, the relationship between the detector output and deposition rate (vapor density times the velocity component towards the substrates) is influenced by the presence of oxygen or other gases, presumably in a reproducible way.

We calibrate the AA monitors by comparison with quartz crystal monitors in high vacuum and use them in feedback control during deposition in oxygen. In our present set up, some problems were encountered with thermal induced drifts. There is no evidence that this is a fundamental limitation. In any event, atomic absorption was used successfully for evaporation rate control, and we consider it to be a very promising approach for rate control at low rates in the presence of high background pressure levels.

Atomic Oxygen Source

A beam of atomic oxygen was obtained by flowing 99.99% pure O_2 through a quartz tube, along a short section of which a microwave discharge was created using an Evanson microwave cavity operating at 2.45 GHz.¹³ The microwave input power was 100 to 300 W. The entire tube was 1 m long with an outside diameter of 10 mm and an inside diameter of 8 mm. In the deposition chamber, the end of the tube was positioned 70 mm from the substrates and directed toward them. During operation the pressure at the discharge was 1–2 Torr, while the pressure inside the chamber was 2×10^{-4} Torr. The quartz tube was treated internally with a concentrated solution of boric acid in order to minimize recombination of atomic oxygen at the walls. We measured the ion current coming out of the tube by means of a Faraday cup and found it to be negligible ($< 10^{-9}$ A or 1×10^{10} ions/cm²-sec). The flux of atomic oxygen was measured as described below. We conclude that there are only neutral species (i.e., atomic and molecular oxygen) present in the beam.

A measure of the atomic oxygen flux was obtained by means of a thin film Ag sensor. Ag is known to react rapidly and specifically with atomic oxygen to produce a silver oxide.¹⁴ Monitoring the weight change of the Ag film by means of a quartz crystal-monitor permits a determination of the flux of atomic oxygen in the beam. Initially the mass increases linearly with time, crossing over eventually to a square root dependence. The initial linear increase corresponds to a constant oxygen absorption rate, which is limited by the flux of atomic oxygen impinging on the film. Since the absorption coefficient is less than one, only a lower limit to the flux can be established by this means. Repeating the experiment with the cavity discharge off showed negligible absorption, demonstrating the insensitivity of the detector to molecular oxygen. The long-time square root dependence arises when the absorption becomes diffusion limited. Using this technique, we established a lower limit of approximately 5×10^{15} atoms/cm² sec for the flux of atomic oxygen from the tube arriving at the position of the substrates during deposition.

Electron-Beam Source

At high oxygen pressure during deposition we observe plasmas near the sources, which may act as a significant source of activated oxygen. In an attempt to quantify the resulting flux of neutral atomic oxygen, we have used the Ag sensor near the substrates. The e-beams were focused on empty water-cooled hearths, so that no evaporant flux would interfere with the mass change due to oxidation. No flux was detected. Nor were any plasmas observed, suggesting that the evaporant flux is important along with high oxygen pressure.

Ion Source

In order to generate a beam of low-energy ions, a modified Kaufman ion source was used. This source contained a single stainless steel mesh extraction grid, which provided a high flux of O_2^+ ions at the substrates, measured to be typically 0.3mA/cm² (or 2×10^{15} ions/cm²-sec) by a Faraday cup. The energy of the ions was less than 50 eV. Since atomic oxygen is also generated in a discharge of this sort, we used the silver thin film sensor to determine the amount of neutral atomic oxygen reaching the substrates. This measurement was performed in two modes, one with the source biased so that ions could not escape the gun, and one in the usual configuration, with the high ion flux present. In both cases the silver sensor measured 3×10^{14} atoms/cm²-sec showing the insensitivity of the Ag sensor to O_2^+ ions, and indicating an order of magnitude lower flux of neutral atomic species than that obtained from the microwave cavity discharge source.

Deposition Conditions

The primary objective of our work at this stage was to determine both the amount and species of activated oxygen needed to grow the 123 superconducting phase of YBaCuO *in situ*. We discuss here our results obtained using three sources of activated oxygen: neutral atomic flux from the microwave cavity source in high background pressures, electron-beam activated in high background pressures, and ion beam in low background pressures. In each case we have attempted to keep constant the metal stoichiometry (123), total deposition rate (2Å/sec), film thickness (3500Å), and substrate temperature (near 600°C). The films grown in high background pressures were deposited, then quickly cooled to 400°C and maintained at this temperature for 30 minutes in the atomic oxygen beam. The furnace was then turned off and the samples cooled to 100°C in 10 minutes while still in the beam. The films grown with the ion source received a quick "cool-down" anneal in 10 torr of oxygen to 200°C in 10 minutes. We note that the cooling after growth may play an important role in the resulting film properties, although we have not tried to optimize this procedure.

A schematic of the deposition system is shown in Figure 1. The metals were evaporated from three individual electron beam guns. The evaporation rate was controlled by chopped ion gauge

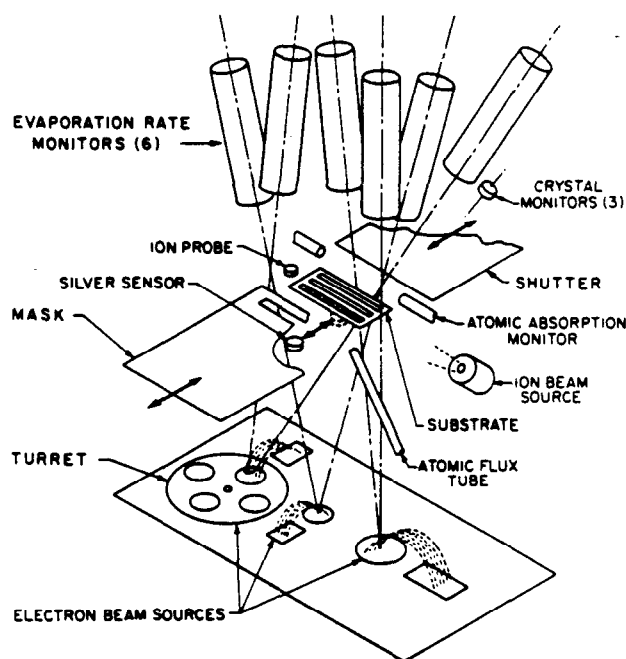


Figure 1 : Schematic of the deposition chamber.

rate monitors in low background pressures, and by AA in high background pressures. Both the ion source and neutral atomic source were aimed directly at the substrate block and the Ag sensor could be moved in front of the substrate position for atomic flux measurements. In addition, a cross shutter allowed the exposure of one row of substrates at a time, permitting sequential depositions using the different activated oxygen sources.

Results

These techniques were applied to films grown on Al_2O_3 $\langle 1\bar{1}02 \rangle$, SrTiO_3 $\langle 100 \rangle$, $\langle 110 \rangle$ and $\text{MgO} \langle 100 \rangle$. Figure 2 shows the resistive transitions obtained for the samples grown on each substrate in a background pressure of 2×10^{-4} Torr with an additional flux of 3×10^{15} atoms/cm²-sec from the atomic oxygen source. We have also observed similar transitions on these substrates for films grown with twice this flux.

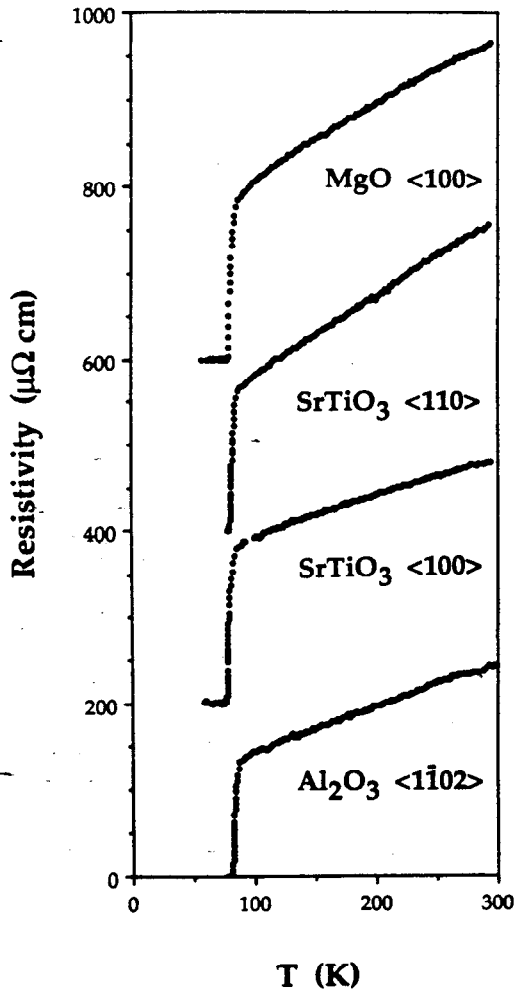


Figure 2 : Resistive transitions on each substrate.

Critical current measurements were performed on samples grown using the additional atomic oxygen flux, in a vibrating sample magnetometer with a perpendicular field up to 8 kG. According to the Bean formula¹⁵, we calculate a critical current density at 4.2K of 2×10^5 A/cm² on Al_2O_3 , 5×10^5 A/cm² on SrTiO_3 $\langle 110 \rangle$, and 1×10^6 A/cm² on MgO .

The samples grown in high background pressures with only electron beam activated species show resistive transitions which are quite broad for films grown on Al_2O_3 and SrTiO_3 $\langle 100 \rangle$ substrates. Those on MgO and SrTiO_3 $\langle 110 \rangle$ show transitions

similar to those observed when the additional atomic flux is used during growth.

In the case where the ion beam is used in low background pressures, we obtain nonmetallic films on Al_2O_3 , and MgO . On SrTiO_3 $\langle 100 \rangle$ we typically observe nonmetallic films, although we have observed a broad transition when the films were Cu-rich. Broad transitions are observed on SrTiO_3 $\langle 110 \rangle$.

Table 1 indicates both the onset and zero resistance temperature in the resistive transitions using each source of activated oxygen. It is clear that the films grown in higher background pressures show transitions on each substrate which have higher onset temperatures and are much sharper than any observed with the ion source growth. This leads us to conclude that a high flux of low energy ions is not necessary to form the 123 superconducting phase. The more important conclusion from Table 1, is that the 123 superconducting phase can be grown *in situ* using all three sources of activated oxygen. However, for any given specific species of activated oxygen it is necessary to provide a sufficient effective partial pressure.

Table 1 : Summary by substrate of onset, zero resistance temperature and phase believed to dominate the transition for each oxygen source.

P O_2	5×10^{-6}	2×10^{-4}	2×10^{-4}
Substrate	+ (ion source)	(e-beam activated)	+ (atomic O source)
Al_2O_3 $\langle 1\bar{1}02 \rangle$	nonmetallic	88-10K unoriented 123	88-80K $\langle 001 \rangle$ oriented $c = 11.7\text{\AA}$
MgO $\langle 100 \rangle$	nonmetallic	85-75K unoriented 123	88-79K $\langle 001 \rangle$ oriented $c = 11.7\text{\AA}$
SrTiO_3 $\langle 100 \rangle$	nonmetallic 88-45K* unoriented 123	88-10K unoriented 123	88-77K $\langle 001 \rangle$ oriented $c = 11.7\text{\AA}$
SrTiO_3 $\langle 110 \rangle$	75-30K unoriented 123	88-80K $\langle 110 \rangle$ oriented $a = 3.82\text{\AA}$	87-80K $\langle 110 \rangle$ oriented $a = 3.82\text{\AA}$

*10% Cu rich

In addition to electrical characterization, x-ray diffraction was used to study the structure of the films. Scans were taken which revealed both highly oriented phases as well as randomly oriented phases.

On all substrates except SrTiO_3 $\langle 110 \rangle$, the samples grown with the additional neutral atomic flux contain an oriented phase having a c-lattice parameter of about 11.7Å. On SrTiO_3 $\langle 110 \rangle$ the a-axis has been found to be 3.82Å. The oriented phases were further found to be epitaxial. Such lattice parameters are within the range for which superconductivity is known to exist in YBCO "123"¹⁶.

The sharp transitions and low normal state resistivities are consistent with superconductivity in the epitaxial phase. For these reasons, we attribute the resistive transitions to oriented "123". In addition to the epitaxial material, unoriented crystalline phases were present in these samples. A weak peak at 2.73Å, corresponding to the strongest reflection for the randomly oriented 123 phase, was always present. Other weak peaks associated with impurity phases were present in varying degrees.

Diffraction patterns from samples on all substrates except SrTiO₃ <110> grown in high background pressures with e-beam activated species also indicate randomly oriented 123 phase. These peaks are sufficiently strong to account for the resistive transitions. Weak, somewhat broad peaks from an oriented phase with a c-axis of 11.7Å were also present. These peaks were strongest for the case of MgO which may account for the relatively sharp resistive transitions. We also observe peaks associated with impurity phases. The sample grown on SrTiO₃ <110> however, shows <110> orientation with an a-axis of 3.82Å. We note that the diffracted intensity is much lower than those grown using the additional atomic flux.

The films grown on Al₂O₃ and MgO using the ion source were composed of randomly oriented, insulating phases. No evidence of 123 was found. Those on SrTiO₃ <100> were typically nonmetallic, containing an epitaxial, tetragonal phase with an expanded c-axis of 11.8-12.2Å. Lattice parameters greater than 11.8Å are distinctly larger than those corresponding to superconducting YBaCuO "123". In cases where a resistive transition was observed, we found evidence of a randomly oriented 123 phase. Films on SrTiO₃ <110> were typically superconducting. Epitaxial phases with c-lattice parameters of 11.77 Å were found along with unoriented 123. Since 11.77 Å is not consistent with superconductivity in 123¹⁶ and the transitions were broad, we associate superconductivity in these samples with the randomly oriented 123.

We have summarized these results by indicating in Table 1 the characteristic of the phase which seems to dominate the resistive transition.

Conclusions

We have demonstrated that *in situ* growth of superconducting YBaCuO by electron beam coevaporation is possible with a flux of at least 10¹⁵ particles/cm²-sec of some activated species of oxygen. To date films grown with an atomic oxygen flux have sharper transitions and higher critical currents than those grown with an ion beam. Epitaxial growth has been achieved at temperatures of 600°C on SrTiO₃ <100>, <110>, Al₂O₃ <1102>, and MgO <100>. In addition, rate monitoring by atomic absorption has successfully been used for the metal evaporation rate control at pressures above 10⁻⁴ Torr.

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