Abstract

The interface between thin films of the YBa$_2$Cu$_3$O$_{7-x}$ superconductor and metallic and insulating overlayers is studied using films prepared in-situ by coevaporation employing ozone vapor oxidation. Thin layers of Y, Y$_2$O$_3$, and BaF$_2$ can be evaporated at various stages of the YBa$_2$Cu$_3$O$_{7-x}$ cool-down process. The effect of the overlayers on the oxidation state of the superconductor copper signal can be assessed using X-ray photoelectron spectroscopy (XPS).

Introduction

The character of the interface between thin films of YBa$_2$Cu$_3$O$_{7-x}$ and ultrathin metallic and insulating overlayers grown on the surface is of considerable importance to those interested in fabricating tunnel junctions and devices. The difficulties encountered in producing high quality junctions using artificial barriers with these materials are well known. The small coherence length of YBa$_2$Cu$_3$O$_{7-x}$ makes it difficult to couple to the superconducting order parameter, since one must prepare a clean, fully oxidized film to within a coherence length of the surface. We are interested in barrier materials which may be applied smoothly in ultrathin layers without disrupting the oxidation state and, therefore, the pairing strength of electrons at the film surface. The in-situ process employed here provides a unique opportunity to maximize the oxidation state of the surface and arriving evaporants with a highly reactive flux of pure ozone.

In order to understand the effect of evaporated overlayers on the integrity of the superconductor surface, the interface between the superconductor and various overlayers is studied using X-ray Photoelectron Spectroscopy (XPS). Similar experiments have been performed using cleaved YBa$_2$Cu$_3$O$_{7-x}$ single crystals and noble metal overlayers. The materials are applied immediately after the deposition of the superconductor and the bilayer is transported into an adjacent analysis chamber without breaking vacuum. We have employed an in-situ technique using evaporation and ozone oxidation in order to prepare YBa$_2$Cu$_3$O$_{7-x}$ films under high vacuum conditions. To date, Y, Y$_2$O$_3$, and BaF$_2$ have been applied to the superconductor surface and their effect on the oxidation state of Cu in the film is used to gauge their suitability as insulating barriers or proximity layers in the preparation of tunnel junctions.

Preparation of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films

Thin films of the superconductor were deposited onto heated MgO, yttria stabilized zirconia (YSZ), and SrTiO$_3$ substrates in a Vacuum Generators Model 80 MBE system by coevaporation in the presence of a flux of pure ozone gas. The base pressure of this system is $10^{-9}$ mbar. The Y and Cu were evaporated using electron beam guns while the Ba was deposited from a highly stable, low temperature Knudsen cell manufactured by EPI, Inc. The Cu evaporation rate was controlled by an Airco controller using a Quartz Crystal Monitor (QCM) to measure the evaporation rate. The yttrium rate was controlled by a Sentinel III controller. The Ba evaporation rate was monitored before the deposition of each film using a moveable QCM rate monitor and the temperature of the Knudsen cell was carefully controlled to maintain the desired rate throughout the typical 10 minute evaporation time. Total evaporation rates were nominally 3 A/sec, producing films with thicknesses of about 2000 A.

Pure ozone was obtained by distilling a mixture of O$_2$ and O$_3$ obtained by passing oxygen through a silent discharge generator, as has been described in previous publications. The pure gas was applied to the substrate during evaporation from a nozzle formed by a 12 mm I.D. stainless steel tube with a taper into a 25 mm glass capillary array. The array is 0.5 mm thick consisting of 50 μm dia. holes. This serves to direct the gas into a focused beam which is directed at the substrate. The flow rate of the gas was adjusted by controlling the pressure above the ozone distillate using a heater wrapped around the still tube. During the deposition, the system pressure was $5 \times 10^{-7}$ mbar, with the pressure above the ozone still at 350 mTorr, and an ozone flow rate of $1.4 \times 10^{17}$ molecules/sec. After deposition, the films are allowed to cool to below 200 °C in the same flow rate of ozone. The system pressure during the cool-down rises to $10^{-3}$ mbar, due to the lack of gettering.

This technique produces shiny black films which are homogeneous over a rectangular area of 12x25 mm. No features can be distinguished in the films down to the 200 Å resolution of the scanning electron microscope. The composition of the films used in this study were measured using Rutherford Back Scattering (RBS). They are all within 5% of the nominal "123" composition with a typical film containing 51.1% Cu, 33.0% Ba, and 16.9% Y.

Figure 1 is a plot of resistance versus temperature for our best film, where the superconducting onset temperature is 85 K and the complete superconducting transition temperature occurs at 80 K. The critical current of this film was measured using a contactless inductive technique at 4.2 K. The value of $2.7 \times 10^7$ A/cm$^2$ obtained by this technique competes with the J$_c$'s of some of the best films described in the literature.

Preparation of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films

Figure 1. Resistance vs. temperature of a YBa$_2$Cu$_3$O$_{7-x}$ thin film grown on SrTiO$_3$ with 80 K transition temperature.

The x-ray diffraction pattern of the above film was obtained using a Philips 3010 powder diffractometer with Cu Kα radiation and is shown in Fig. 2. The x-ray scan shows only c-axis reflections, along with small peaks which have not yet been identified, but are not due to BaCuO$_2$, CuO, or the "211" phase. The reduced T$_c$ of the film may be due to an oxygen deficiency, and detailed x-ray analysis shows a slightly expanded c-axis, (= 11.73 Å) which would indicate such a deficiency. RBS analysis, on the other hand, indicates that the films are fully oxidized. Work is in progress to fully characterize the oxygen content of the films.

Experience with molybdenum contamination in the vacuum system used to develop the ozone oxidation process$^9$ compelled us to perform a thorough study of the contaminant levels in these films. Small levels of impurity elements which can sometimes find their...
way into vacuum chamber components are known to seriously affect the $T_c$ at very low concentrations. Sapphire substrates placed adjacent to the MgO and YSZ substrates used for these films were used to collect material which is analyzed using Induction Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). These films were placed into solution of weak acid and analyzed for Mo, Fe, Al, Y, Ba, and Cu. The analysis can detect impurities of less than 1 atomic percent of the Cu concentration. In one film prepared using our routine method the Mo concentration is 0.17%, Fe is 1.2%, and Al is 0.27% by weight. The value for Fe is worrisome and work is in progress to systematically confirm the existence of and eliminate any contaminants.

It should be emphasized, however, that neither an oxygen deficiency nor the presence of a small impurity element in the superconductor are likely to affect the conclusions offered in this work. This is because we are looking for gross disruptions to the bare YBa$_2$Cu$_3$O$_7$-x signal due to reaction with the overlayer.

**Effect of Overlayers on the YBa$_2$Cu$_3$O$_7$-x Surface**

*Yttrium and Y$_2$O$_3$ Overlayers*  

The effect of depositing clean Y metal onto the surface of an YBa$_2$Cu$_3$O$_7$-x film is investigated by observing any change in the XPS Cu 2p doublet due to Y disruption of the Cu oxidation state. For this measurement 10 Å of Y metal is evaporated at a system pressure of about 5x10^-9 Torr onto the just-prepared film at a substrate temperature of about 20 °C. Figure 3 is a comparison of the Cu 2p doublet of a YBa$_2$Cu$_3$O$_7$-x film immediately after preparation (a) and the same film after the Y evaporation (b). The XPS data was collected using Mg Kα radiation, and a Vacuum Generators CLAM detector. The smaller satellite peaks observed in Figure 3(a) are typical of fully oxidized copper and are not present in the spectrum of pure Cu metal. As seen in Figure 3(b) the application of the Y metal severely diminishes the intensity of these peaks as it robs the surface copper of its oxygen. This situation is unacceptable in the process of preparing tunnel junctions since the superconducting order parameter will be quenched at the surface.

The procedure described above is now modified to include an ozone flux directed at the substrate simultaneously to the application of a 10 Å Y metal overlayer. The flux rate is maintained at the nominal value employed in the preparation of the superconductor and the substrate temperature is about 20 °C. Again a plot of the Cu 2p doublet of the bare superconductor and the metal/ozone overlayer can be seen in Figs. 4(a) and 4(b), respectively. The relationship between the main and the satellite peak heights is unchanged by the application of the overlayer though the intensity of the entire signal is, of course, reduced by the Y$_2$O$_3$ overlayer. It is apparent that the highly reactive flux of ozone serves to oxidize and passivate the incoming Y atoms with respect to the valence state of the surface copper atoms.

In another test of the effect of Y on the superconductor surface a thin layer of Y was applied immediately after the deposition of the YBa$_2$Cu$_3$O$_7$-x film by closing the Ba and Cu source shutters and leaving the Y source shutter open to deposit another 10 Å. This was done while the ozone was flowing and the substrate temperature remained at the nominal value used during film growth, 650 °C. In this treatment there was no effect on the relative height or shape of the Cu XPS satellite peaks with respect to the main doublet except for the expected reduction in height of all of the peaks. This result is important for those applications where one wants to apply a highly crystalline barrier to the high $T_c$ surface with excellent electrical and mechanical properties. A high temperature, high mobility deposition may produce a smoother barrier with fewer pinholes than a "quench condensed" film.
Figure 3. XPS signal intensity vs. binding energy around the Cu 2p doublet (a) for a YBaCuO film, and (b) for the same film with a nominal 10 Å Y overlayer. The CuO satellites are at ~950 and 967 eV. The curves are offset for clarity.

BaF₂ Overlayers

Our interest in the effect of BaF₂ on the YBa₂Cu₃O₇₋ₓ surface is motivated by the potential applications of a highly inert insulator which may be deposited in a crystalline state for the preparation of tunnel junctions and field effect devices. In this study the BaF₂ is evaporated from a Knudsen cell using an evaporation rate of about 1 Å/s and is deposited onto the YBa₂Cu₃O₇₋ₓ surface in two different ways to test for an effect on the valence state of the Cu surface layers.

In the first case, 10 Å of BaF₂ is deposited onto a YBa₂Cu₃O₇₋ₓ film which had been prepared and cooled to approximately 20 °C in approximately an hour. No effect on the state of the Cu oxidation state is observed as the relative heights of the Cu 2p satellites and main peaks remain unaffected by the overlayer. The intensity of each of the peaks is, of course, reduced by the application of the overlayer.

The second case poses a more demanding test of the degree to which the BaF₂ overlayer remains inert with respect to the electronic environment of the surface copper. Here we apply a 10 Å BaF₂ overlayer immediately after the superconductor has been deposited at a substrate temperature of 650 °C. After the substrate is allowed to cool and moved into the analysis chamber the XPS spectrum shows no change with regard to the relationship of the CuO satellite peak heights and the bare Cu doublet intensities. Reflection High Energy Electron Diffraction (RHEED) of the surface indicates the BaF₂ overlayer has fiber texture-type growth.

Conclusions

Ultrathin Y overlayers are rendered inert with respect to an underlying YBa₂Cu₃O₇₋ₓ film surface by the application of a pure ozone flux at the surface during deposition. This is accomplished at ambient substrate temperatures and at the highest temperature used in the processing of the superconductor. The preparation of epitaxial or highly oriented Y₂O₃ barriers is thus possible without an apparent effect on the integrity of the high Tc surface and, perhaps, the superconducting order parameter. In addition the barrier can be applied at a high substrate temperature where the mobility of the evaporant is large and crystallinity and smoothness can be expected to be optimum. We expect that these results applied to high quality a-axis oriented films may enable the development of improved quality planar high Tc tunnel junctions.

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Figure 4. XPS signal intensity vs. binding energy around the Cu 2p doublet (a) for a YBaCuO film, and (b) for the same film with a nominal 11 Å Y2O3 overlayer. The curves are offset for clarity, and curve (b) is multiplied by 3.33 relative to curve (a).

References


