CHARACTERIZATION OF THIN YBaCuO FILMS GROWN BY COEVAPORATION

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Abstract

Thin films of the $Y_1Ba_2Cu_3O_x$ superconductor have been grown by coevaporation and post annealing in oxygen on substrates of (100) SrTiO₃, (100) MgO, and (100) Yttria-stabilized Zirconia. Films grown on SrTiO₃ show evidence of both a- and c-axis growth normal to the substrate and strong in-plane order. Films on MgO show c-axis growth without any in-plane order, indicative of fiber texture. Transition temperatures of the films on MgO are depressed compared to those on SrTiO₃, but by using higher post-anneal temperatures we are able to improve the superconducting behavior of MgO samples.

Introduction

In this paper we discuss our attempts at growing films of $Y_1Ba_2Cu_3O_x$ by coevaporation on different substrates, primarily MgO. We concentrate on improving the superconducting properties of films grown on MgO by using different anneals and studying the effects of these changes with SEM and RBS. In addition, we look at the change in film properties for different compositions on different substrates.

Sample Preparation

The films were grown by coevaporation of Y, Cu and BaF₂ in the presence of oxygen. The substitution of BaF₂ for Ba was done following the results of Mankiewicz, et al.¹ The yttrium and copper were evaporated from electron beam sources, and the BaF₂ from an effusion cell. Rate control for the electron beam evaporators is provided by quartz crystal rate monitors, however there is no active rate control during the run for the effusion cell. Molecular oxygen was introduced by a 1/4 inch diameter tube aimed at the substrates. The background pressure in the chamber with the sources on is typically 10^{-8} Torr. Oxygen is bled in until the pressure is 10^{-6} Torr, although at the substrates the pressure is probably higher. The substrates were outgassed at 500 °C, and cooled to 50 °C in vacuum before deposition. Deposition rates were typically 1-10 Å/s, and film thicknesses are 5,000 - 10,000 Å after annealing. Our usual annealing procedure was to place the samples into a hot oven at 850 °C with a flowing gas mixture of O₂ and H₂O (formed by bubbling oxygen through water) for 30 minutes, followed by a 1 °C/min cool to room temperature in dry oxygen.

Film compositions are determined using elastic backscattering (EBS),² which is a variant of RBS but with 6.2 MeV alpha particles instead of the more typical 2 MeV energy. The use of higher energy alpha particles means that some of the lighter elements are no longer Rutherford-like in their

backscattering, such as oxygen and carbon. The higher energy does allow a clearer separation of the signals from the metallic elements, simplifying the composition analysis. The films were also characterized by x-ray diffraction using Cu K α radiation, SEM, and resistivity measurements.

Results on Strontium Titanate

Films grown on (100) SrTiO₃ and annealed in the manner described above have very good properties. X-ray analysis indicates that the films grow with both a- and c-axes normal to the substrate, and predominantly have the c-axis up, as seen in Fig. 1. Analysis of the reflections normal to the substrate give values for a and c of 3.832 ± 0.004 Å and 11.67 ± 0.02 Å, respectively. The rocking curve for the (005) reflection was measured to be $\approx 0.5^\circ$. The in-plane order for the c-axis grains was studied by examining the (018) reflection, which occurs at an angle of 20.6° away from the c-axis towards the b-axis. We found that the b-axis lines up with either the SrTiO₃ (010) or (001) axes, leading to a 4-fold degeneracy in the in-plane scans about the c-axis. The rocking curve for the (018) reflection was also $\approx 0.5^\circ$. As seen in Fig. 1, the sample also shows evidence for the "248" phase identified by Marshall and coworkers.³ The orientation of this second phase has (00L) along the sample normal, and we can identify the L=8, 10, 12, 16, 18, and 22 reflections with a lattice constant $c^* = 27.22 \pm 0.02$ Å. We have tentatively identified the remaining peaks as due to the "211" phase, Y_2BaCuO_x .

SEM studies of the microstructure of on-stoichiometric films show the presence of a "herring-bone" structure, with rectangular regions of size ≈ 0.5 μ m by 3 μ m. These regions keep their relative order over the entire area of the sample, and also show the 4-fold symmetry that is seen in the x-ray diffraction studies. The surface of the film contains regions of a second phase, probably BaCuO₂.

Resistivity measurements give a resistivity at 100 K of ≈ 200 $\mu\Omega$ -cm with a resistivity ratio between room temperature and 100 K of 2.9. The best samples have an onset temperature of 91 K with a complete transition occurring at 88 K. Critical current density measurements of these samples are being reported in a separate paper.⁴

An off stoichiometric composition affects samples on SrTiO₃ to a much less degree than other substrates. Figure 2 compares the resistivity of an on-stoichiometric film to one with composition Y(21)Ba(29)Cu(50), having a resistivity of ≈ 400 $\mu\Omega$ -cm at 100 K. Notice that the overall shape of R(T) is the same. The off-stoichiometric film has a complete T_c by 85 K. Films with composition as far off as Y(15)Ba(50)Cu(33) have been produced which still have relatively sharp transitions near 85-87 K.

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Figure 1. X-ray intensity vs $2\theta_B$ for a stoichiometric YBaCuO sample grown on (100) SrTiO₃ for diffraction along the sample normal. All peaks except those due to the substrate have been labeled.

Figure 2. Comparison of two samples deposited on SrTiO₃. The first, labeled "123", has the stoichiometric composition, while the one labeled "Y rich" has a composition of Y(21)Ba(29)Cu(50). Both plots are normalized to the resistance at room temperature.

Results on MgO

Films deposited on MgO and annealed in the usual manner have higher resistivities and depressed complete transitions as compared to films on SrTiO₃, as seen in Fig. 3. The resistivity curves show a significant low temperature tail, resistivities at 100 K are $\approx 750 \mu\Omega\text{-cm}$, and complete transitions are at ≈ 60 K. SEM analysis shows evidence for BaCuO₂ on the surface, and a superconductor grain size of $\approx 0.5 \mu\text{m}$. Going to progressively higher temperatures for the initial anneal and optimizing the time for best room temperature resistivity leads to improved film properties. Figure 3 shows that the resistivity has dropped by a factor of 2, and the superconducting transition has sharpened, but the onset temperature is still depressed to ≈ 85 K. The sample shows a complete transition by 80 K. X-ray diffraction (Figure 4) indicates that the films have c-axis growth, but without any in-plane order (fiber texture). There is also evidence for (013) and (026) reflections. Analysis of the (00L) peaks gives a value of $c = 11.69 \pm 0.01 \text{ \AA}$. The rocking curve for the (005) peak is $\approx 0.7^\circ$, larger than that for films on SrTiO₃. SEM shows that there are no longer regions of BaCuO₂ on the surface and the grain size is now $\approx 1 \mu\text{m}$.

Figure 3. Resistivity versus temperature for three stoichiometric samples of YBaCuO grown on MgO and annealed at different temperatures as shown on the graph.

The reason for the depressed transition temperature for films on MgO is still not understood. There is no strong evidence of interdiffusion from the EBS results, and the local composition as determined by EDACS shows that the metal composition is correct. There is certainly no evidence for gross interdiffusion up to the surface of any substrate species. EBS results are consistent with a fully oxidized film, but the uncertainty is easily $\pm 20\%$, so we cannot rule out the possibility of oxygen deficiency. The question would then remain, however, as to why the SrTiO₃ samples are fully oxidized, while MgO samples annealed concurrently are not.

Film compositions off the "123" ideal degrade the properties of samples on MgO very rapidly. A film on MgO with composition Y(21)Ba(29)Cu(50) has a substantially depressed transition temperature (45 K) with an onset at 80 K. The resistivity at 100 K is approximately 2.3 mΩ-cm, more than six times higher than for a stoichiometric film. Compositions towards the Cu rich side of "123" are affected to a lesser degree for films on MgO compared to other directions from the ideal phase.

Figure 4. X-ray intensity vs $2\theta_B$ for a stoichiometric YBaCuO sample grown on (100) MgO and annealed at 900 °C for 10 minutes for diffraction along the sample normal. All peaks except those due to the substrate have been labeled. The amorphous peaks at 22° and 68° are due to forbidden reflections in MgO.

Results on YSZ

Our results on cubic zirconia are limited to samples with compositions off the ideal. We have found that the superconducting properties for off-stoichiometric samples on YSZ are not as poor as those on MgO. Like films on MgO, varying the annealing parameters can improve the film qualities. Figure 5 shows the resistance trace for two films on YSZ with composition Y(21)Ba(29)Cu(50), but with different anneals. For the rapid ramp case, the sample was placed into a 850 °C furnace, while for the slow ramp case the sample was placed in a room temperature furnace and the furnace was ramped up at 20°C/min. These samples have transition temperatures of ≈ 60 K with onsets of 90 K. The resistivity at 100 K however is essentially the same as samples grown on MgO.

Figure 5. Comparison of YBaCuO with composition Y(21)Ba(29)Cu(50) grown on YSZ and using different methods to reach the high temperature anneal point.

Conclusions

We have grown superconducting films of YBaCuO on substrates of strontium titanate, magnesium oxide, and cubic zirconia using coevaporation with BaF₂ as the source of barium. We find that films on strontium titanate grow with a mixture of a- and c-axes oriented normal to the film, but with a high degree of in-plane order. Films on magnesium oxide grow with c-axis orientation, and require a higher temperature anneal in order to obtain the best resistivity and superconducting transition temperature. Films on cubic zirconia have not been extensively studied as of yet.

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