YBa$_2$Cu$_3$O$_7$ THIN FILMS GROWN BY HIGH PRESSURE REACTIVE EVAPORATION AND HIGH PRESSURE REACTIVE SPUTTERING

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Abstract

A high pressure reactive evaporation process and a high pressure reactive sputtering process have been developed for the growth of high quality thin films of YBa$_2$Cu$_3$O$_7$. Both techniques, when used with heated substrates, are effective in the formation of the 123 phase in-situ during the film growth. With reactive evaporation only a cooldown anneal in a higher pressure oxygen ambient is necessary to obtain good superconducting properties. For the reactive sputtering process, a brief, post growth, rapid thermal anneal step is required for best results. Fully epitaxial growth has been achieved with single crystal MgO substrates. The resultant films, which can be quite smooth and uniform, have been patterned to micron and submicron dimensions and the transport properties of these microstructures have been examined.

Introduction

Since the discovery of high temperature superconductivity (HTS) in layered copper-oxide based systems there has been widespread strenuous efforts to produce thin films of these materials. Essentially all known techniques of thin film synthesis have been applied to this very challenging problem with varying, but generally increasingly higher, degrees of success. In this paper we describe recent results on the growth of YBa$_2$Cu$_3$O$_7$ thin films that we have obtained with two such techniques, high pressure reactive evaporation (HPRE) and high pressure reactive sputtering (HPRS). We have found that both methods when used with carefully heated substrates in the range of 400 to 700°C can result in the in-situ formation during the deposition process of the 123 phase of this material. For the HPRE films a simple "cooldown" anneal in 20 Torr O$_2$ gives fully oxygenated material with good superconducting properties. For HPRS we have found that a post-deposition rapid thermal oxygen anneal, typically at 750 - 850°C, for 2 min. is generally required to obtain good superconductive transitions.

For (100) single crystal MgO substrates in the higher temperature range both techniques result in the growth of HTS films with a very high degree of c-axis orientation normal to the plane of the film. For the HPRS process the degree of orientation is particularly high with x-ray data showing complete epitaxy between film and substrate.

The best HPRE films show sharp resistive transitions with zero resistance between 60 - 77 K. At 77 K the films on yttria stabilized zirconia (YSZ) have critical current densities $J_c > 2 \times 10^5$ A/cm$^2$. Films on MgO have lower critical current densities at 77K yet still have $J_c$ values between $2 \times 10^6$ A/cm$^2$ and $5 \times 10^5$ A/cm$^2$ at 4.2K, values similar to those obtained with YSZ. The best HPRS films on MgO have a depressed $T_c$ with zero resistance between 70 - 75 K. This lower $T_c$ is due to imperfect stoichiometry and large strain in the sputtered films.

The HPRE and HPRS films are comparably smooth and can be readily patterned by conventional photolithography and dry etching techniques to micrometer and submicrometer dimensions. Ohmic contacts ($\leq 3 \times 10^{-8}$ Ω cm$^2$) can be readily made to the films.

In this paper we review the basic HPRE and HPRS processes and discuss the properties of the resultant films as revealed by various analytical and transport measurements. Emphasis is given to the results of X-ray and transmission electron microscopy studies of film orientation, epitaxy and film-substrate interactions. We also discuss the patterning of the films and describe the transport and "Josephson-like" properties of the resultant microstructures.

Thin Film Growth: High Pressure Reactive Evaporation

The high pressure reactive evaporation process has been described in some detail elsewhere. Briefly, in our current implementation of this technique metallic Y and Ba are evaporated from two electron beam evaporation sources, while metallic Cu is evaporated from a resistively heated thermal source. The three individual
deposition rates (Y, Ba, and Cu) are monitored and controlled by three separate quartz crystal monitors, each with line of sight exposure to only one of the evaporation sources. The total film growth rate is ~5 Å/sec, yielding a 0.5 µm thick film in 15 minutes, and the individual rates were controlled to yield as well as possible the desired 1:2:3 stoichiometry. As discussed below this is the most difficult aspect of the HPRE process.

To obtain the desired 123 phase during evaporation the oxygen pressure is maintained at a constant 0.65 mTorr, which is near the highest pressure at which the electron beam sources will operate reliably. At this elevated oxygen pressure the atomic mean free path is ~8 cm, so material is deposited on surfaces without line of sight exposure to the evaporation sources. Thus the quartz crystal monitors are not completely independent, the worst case being that 25% of the measured Cu rate is due to Y and Ba. This effect is predictable, however, and can be accommodated. After the deposition is completed, the chamber was backfilled with oxygen to ~20 Torr while the film cooled. Typical elapsed time in cooling from 650 C to below 200 C is about 20 minutes.

Since in this HPRE process we find that the sticking coefficient of the metallic vapor varies strongly with substrate temperature, to achieve the best reproducibility, the temperature is measured by a thermocouple attached directly to the surface of the substrate. The differences between the temperature measured in this way and the temperature measured on the heater assembly is found to vary widely, depending on the substrate material, the condition of the back surface of the substrate, and how tightly the substrate is clamped to the heater. For MgO substrates with the back surface polished a difference of 10 - 30 C is typical.

Examples of the resistive transitions that we have obtained with the HPRE process are shown in Figure 1. With the use of a cool-down anneal immediately after the deposition good results have been obtained with oriented SrTiO3, YSZ and MgO substrates without a post deposition anneal. The best films produced on YSZ have typical Tc's of 83-86 K, ΔTc of 2.4 K, and room temperature resistivities (ρRT) of 0.5-3 mΩ-cm. On SrTiO3 a film with Tc = 81 K, ΔTc = 4 K, and ρRT = 2.5 mΩ-cm is obtained, and on MgO Tc's of 81-83 K are typical.

Generally the HPRE process is used with substrate temperatures in the 625-650 C range. This has yielded our best results, such as those illustrated in Fig. 1. We have explored the effects of alternative growth temperatures. Films grown at temperatures as low as 560 C exhibit the 123 phase and superconducting properties, in that a resistive transition is observed, but this transition is broad, not reaching zero resistance until below 30 K.

![Figure 1: Resistivity vs. temperature for HTS films deposited in-situ on YSZ, SrTiO3, and MgO substrates.](image)

Films grown at substrate temperatures of 580 C are somewhat improved, but not until the substrate temperature during deposition was raised to 600 - 625 C could well oriented films be obtained with sharp resistive transitions.

We find that variation of the substrate temperature for HPRE is a considerable problem since as indicated above we find that the composition of the resultant film changes rapidly if T is varied while the evaporation rates are held constant. This fact is illustrated by the X-ray microprobe data in Figure 2 which is taken from a film that was grown at a nominal substrate temperature of 625 C on a YSZ substrate. As mentioned previously, temperature gradients of about 20 C can exist across the 1 cm width of the substrate. As shown in the figure the Cu/Y ratio for this film varied from 2.86 to 3.07 over 4 mm in the direction of the expected temperature gradient, showing that the sticking coefficient of Cu is a sensitive function of the substrate temperature. This observation is consistent with our general observation that for films grown at lower substrate temperatures, the Cu deposition rate must be decreased to produce a film with a stoichiometry close to the desired 3:1 Cu:Y ratio.

**Thin Film Growth: High Pressure Reactive Sputtering**

Reactive sputtering is a technique that has already seen widespread application and success in HTS thin film research. Recently Geerk et al. have demonstrated that a comparably high pressure variation of this technique is effective in the in-situ formation of the superconducting 123 phase thus eliminating the requirement for a lengthy post-growth oxygen anneal cycle which had previously been required for reactively sputtered HTS films. We have pursued investigations into
the effectiveness of a similar high pressure reactive sputtering technique. Details of this work will be presented elsewhere, but the basic process is implemented as follows: A standard 2 inch rf magnetron sputter source is employed with a sintered target of $\text{YBa}_2\text{Cu}_4\text{O}_{8-x}$ composition. During the plasma discharge the system pressure is regulated to a value somewhere in the 200 - 300 mTorr range with a $\text{O}_2$/Ar ambient. Typical discharge parameters that have proven successful are $\text{O}_2$/Ar ratios: 0.1 - 0.23, flow rates: $\sim$ 10 sccm, and rf power density: $\sim$ 5 W/cm$^2$. This results in a typical deposition rate of 9 nm/min for a target to substrate distance of 45 - 55 mm. During deposition the substrate temperature is typically held at 625 to 645 °C, although lower temperatures have been investigated. As is typical in the sputtering of HTS films we find the deposited film stoichiometry to be a strong function of gas composition, pressure and substrate temperature. Indeed it is by the slight variation of the gas mixture that we vary the film composition in our attempts to obtain the desired 1:2:3 stoichiometry.

To date the best films that we have produced by this HPRS process have a composition, as measured by electron microprobe, typically in the range of Y:Ba:Cu = 1:1.85 - 2.3 : 2.7 - 3.4. Further improvements in this stoichiometry appear likely. Films produced on MgO substrates by HPRS are smooth and quite uniform in composition over a 1 cm substrate, as measured both by electron microprobe and by resistance measurements on microfabricated test structures across the substrate (see below). As-deposited films, even after a cool-down anneal, are generally not superconducting or do not have good transitions through they generally are metallic and do exhibit the 123 phase when examined by X-ray diffraction, albeit with a considerably larger than normal c-axis lattice spacing, $c = 12.0$ Å. In general the c-axis spacing can be readily reduced and the films made to exhibit fairly sharp transitions by the application of a brief rapid thermal oxygen anneal (RTOA) step, which typically involves heating the film to 750 - 850 °C for 1 - 2 minutes. The pronounced change in lattice constant that results from such an RTOA process is illustrated in Figure 3. There the c axis lattice constant decreased from 12.0 Å to 11.80 Å during a 2 min RTOA at 850 °C. Also the resistivity of the annealed film decreased by a factor of 2 - 5 as result of the anneal. We note that the annealed film is still considerably strained since the lattice constant is still greater than the 11.72 Å value measured in the HPRE films and the 11.66 Å value measured in bulk material. Longer anneals such as 1 hr at 500 °C do not relax this lattice strain implying that it is not principally due to O deficiency.

In Figure 4 we show the resistive transition of a 123 film produced by HPRS as measured following an RTOA step. This film was deposited at a substrate temperature of 645 °C onto a (100) MgO substrate. The Y:Ba:Cu composition of the film was 1 : 2.2 : 3.13. The transition is fairly sharp and the normal state resistance shows the
Figure 4: Resistive behavior of a 10 μm constriction patterned into a HPRS film grown on (100) MgO at 645 C. The film received a RTOA treatment before the measurement. The Y:Ba:Cu composition of the film is 1:2.2:3.13.

desired strong metallic-like variation with T. But the transition is considerably depressed from the bulk value and, as discussed below, the critical current density of these films, particularly in the region just below Tc, is comparably low. We attribute this to the less than ideal stoichiometry and, perhaps in part, to the still slightly greater than typical c-axis lattice spacing, 11.80 Å, of these films, even after the RTOA step. The origin of this expanded lattice constant for the HPRS films is under investigation. It may be due to strain created by the very high pressure ambient during deposition, or by the strong epitaxy (see below) that we observe between the rather mismatched 123 film and MgO substrate (~10% lattice misfit).

With HPRS we have been able to form the 123 phase in-situ with substrate temperatures as low as 500 C. But for best results and particularly for best c-axis film orientation we have found that substrate temperatures between 635 and 650 C are required. This is quite close to the result that we have found with HPRE on MgO and YSZ substrates. However, due to the many important parameters in any 123 thin film growth process this may or may not be a general result.

**Thin Film Orientation and Epitaxy**

Orientation of both the HPRE and HPRS 123 thin films have been examined with a thin film x-ray diffractometer operating in a 2θ mode, by rocking curve and full pole figure X-ray measurements and by selected area electron diffraction and cross-section transmission electron microscopy studies. X-ray 2θ scans such as those shown in Figure 5 reveal that all of the films deposited on YSZ substrates exhibited some degree of mixing between c-axis normal grains and a-axis normal grains, varying from approximately equal amounts of the two growth habits to predominantly c-axis normal growth. Again this variation appears to be strongly correlated with the growth temperature. As Tsub is increased from ~625 to ~650 C (Figure 5b) the c-axis orientation begins to dominate. These results are confirmed by SAD patterns, which also give information about the orientation of the films in the plane of the substrate and whether the film growth is epitaxial to the substrate. For the films grown on YSZ, the areas exhibiting c-axis normal growth are found in most cases not to be well oriented in the plane of the substrate, i.e. the growth is not epitaxial. The regions of a-axis normal growth, however, are registered with the substrate.

In contrast, the 2θ scans of HPRE films grown on MgO substrates, Figure 5c, were almost entirely composed of the (00k) peaks characteristic of the c-axis normal growth, with an almost, but not quite complete, absence of the (k00) peaks from a-axis normal grains. Furthermore, cross-sectional TEM micrographs of these films showed large areas of clear epitaxial growth with a very clean interface between the substrate and the Cu-O planes of the YBa2Cu3O7 lattice.

Figure 5: X-ray diffraction 2θ scans for films on YSZ and MgO. Insets are expanded views of the (006) and (200) peaks. a) Film on YSZ exhibiting about equal amounts of c-axis and a-axis normal crystalline growth. The film was deposited at 625 C. b) Film on YSZ grown at an approximately 20 C higher temperature than (a) a showing a predominantly c-axis orientation. c) Well oriented film on MgO. Here the (200) peak is only barely detectable.
Even stronger epitaxial growth was observed on MgO substrates with HPRS films. Even though X-ray diffraction reveals the existence of secondary phases in the films, full pole figure scans as illustrated in Figure 6 reveal complete epitaxy between the superconducting 123 phase and the MgO substrate. No evidence of any other orientation could be detected in this film. These observations lead us to suggest that the much lesser degree than typical of ionic bombardment of the substrate due to the high pressure nature of the HPRS sputtering process plays a major role both in the in-situ formation of the 123 phase and in the occurrence of the strong epitaxy that is observed in the thin film growth. SAD and high resolution cross section TEM studies of these films are now in process and will be reported elsewhere.

**Thin Film Uniformity and Substrate Reaction**

Auger depth profile and Rutherford backscattering spectroscopy (RBS) have been generally used to investigate the uniformity of the HPRE and HPRS deposited films and the possibility of substrate-film reaction. To the resolution of either technique no evidence for substrate reaction or film non-uniformity have been obtained. However cross-section TEM studies of HPRE films grown on YSZ substrates do reveal the existence of a ~5 nm amorphous layer between the substrate and the film. High resolution (~1 nm) energy dispersive STEM electron microprobe measurements of this interfacial layer reveals the presence of a significant amount of Zr in this amorphous layer and in a portion of the crystalline film immediately above the amorphous layer. Since the 123 film has a strong epitaxial relationship to the substrate we suspect that this amorphous layer is formed by out-diffusion from the substrate to the initially crystalline bottom portion of the film, with this out-diffusion occurring gradually during the growth process. Again cross section TEM studies show no such interfacial layer for films grown on MgO.

**HTS Thin Film Processing and Patterning**

The HPRE and HPRS YBa$_2$Cu$_3$O$_7$ films can be readily patterned using conventional photolithographic methods and then etched using argon ion milling. Extensive patterns of lines and constrictions with widths ranging from 0.5 μm to 100 μm have been fabricated to measure critical current densities, orientation dependence of epitaxial thin film resistance and critical current densities, thin film uniformity and weak link properties. A long 2.0 μm constriction fabricated in this manner is shown in Figure 7. We have also fabricated 5 mm long co-planar transmission lines to study the propagation of ultra fast pulses in high Tc materials.\(^\text{13}\)

The dense fine grain structure of these films allows for uniform etching and electrical properties down to micron line widths. We have found no degradation in critical current densities going from neighboring 100 μm to 1 μm lines. For HPRE films we find that while critical currents of adjacent lines are very uniform there is usually a large variation of critical current densities across the 12 mm substrates. The best films have critical current densities which vary by a factor of two across the wafer. As noted above uniformity results for the HPRS films deposited on MgO substrates are typically much better. Resistivity variations of less than 20% across a 5 mm sample is typical.

In a process similar to that reported by others\(^\text{14}\) low resistance contacts to the YBa$_2$Cu$_3$O$_7$ films and test structures are made by depositing Ag after a short argon-
oxygen ion mill cleaning of the film’s surface. Typically the ion energy is 500 eV. If no further processing is performed the resultant contacts are ohmic but fairly resistant \((\leq 5 \times 10^{-5} \ \Omega \cdot \text{cm}^2)\). If the contact is subsequently thermally annealed at 750°C in oxygen for two minutes the contact resistance typically drops to less than \(5 \times 10^{-8} \ \Omega \cdot \text{cm}^2\).

As illustrated in Figure 7, we have found that conventional microfabrication processing which includes solvent cleans, low temperature bakes, and/or thin film depositions in vacuum will not noticeably change the superconducting properties of the \(\text{YBa}_2\text{Cu}_3\text{O}_7\) films. The effects of such processing on the surface properties of the films are currently being studied. As discussed above rapid thermal anneals in oxygen at temperatures of 700°C to 850°C have slightly improved or slightly degraded the properties of the HPRE films depending on the sample, while RTOA anneals of the HPRS films is currently required for good results. Much longer anneals at 700°C to 900°C for either class of films cause degradation of the film properties. We have not found extended low temperature \((T \leq 550 \text{ °C})\) anneals to be efficacious.

**Critical Current and Weak-Link Behavior**

Critical current vs. temperature measurements made on 5 μm and 20 μm width constrictions on YSZ and MgO substrates for HPRE films are shown in Figure 8. For a film on YSZ with a zero resistance \(T_C\) of 86 K critical currents of \(2 \times 10^5 \ \text{A/cm}^2\) at 77 K are obtained, with values exceeding \(10^6 \ \text{A/cm}^2\) at 4.2 K. On MgO, measurements on both 5 μm and 20 μm width constrictions show that the critical current at 77 K is somewhat lower than that obtained on YSZ, down to 5 \times 10^4 \ \text{A/cm}^2, but it also rises to reach about \(10^6 \ \text{A/cm}^2\) at 4.2 K. This depression of \(J_C\) at 77 K is expected due to the lower value of \(T_C\) for the films on MgO substrates, 82 K vs. 86 K. In the temperature region near \(T_C\) the critical current is clearly limited by weak links between adjacent grains and thus rises slowly below \(T_C\). For the best HPRE films fabricated into 2 μm test structures, \(J_C\) values of \(5 \times 10^6 \ \text{A/cm}^2\) have been obtained at 4.2 K. \(J_C\) vs. \(T\) data generally could not be obtained for such films as the microstructure tends to fuse during the first excursion to the normal state when \(J_C\) is in this range.

While \(T_C\) is further suppressed and the transition is broader for the HPRS films grown on MgO the low temperature critical current density for the better films is still of the order of \(5 \times 10^5 \ \text{A/cm}^2\). At the higher temperatures, nearer \(T_C\), the reduced critical current densities are presumably caused by weak links between grains due to lack of stoichiometry. We have not observed any clear Josephson effects in the thin film microstructures down to the 1 μm size. Such Josephson effects have been observed in 1 μm lines with obvious structural defects as observed by SEM. These defects are caused by electrical stress during testing.

An example of such an effect is shown in Figure 9 where the I-V characteristic of a long 1.0 μm wide constriction is shown in the presence and absence of 10 GHz microwave radiation. The presence of the Josephson constant voltage steps in the irradiated I-V is clear. Of course the I-V characteristic of the constriction does not exhibit the form typical of a good Josephson weak link, and the effective \(J_C R_p\) product of the weak link, \(-20 \mu\text{V},\) is far below the value to be expected from a good high \(T_C\) weak link, \(>10 \text{ mV}\).

**Summary**

We have found HPRE to be a successful technique for the in-situ formation of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) thin films with good superconductive properties. For best results the technique does require precise control of substrate temperature and, of course, film stoichiometry. HPRS has also been demonstrated as being able to provide in-situ formation of the 123 phase although a post-growth rapid thermal
anneal step is currently required to obtain the best superconductive properties. When used with YSZ and MgO substrates heated above 625°C well oriented film growth is obtained, with (100) MgO substrates providing the best c-axis normal orientation results. HPRS has been found to be particularly effective in yielding complete epitaxy on MgO and in yielding very uniform films. Further improvements in HPRS film stoichiometry should make this a very attractive process.

The HPRE and HPRS thin films are relatively smooth and are readily patterned by photolithography and inert ion beam etching procedures to micrometer and sub-micrometer dimensions. In the less ideal HPRS films ac Josephson weak link effects have been observed in such micro-constrictions in a broad temperature range below $T_C$.

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