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Sequentially Evaporated Thin Y-Ba-Cu-O Superconductor Films: Composition and Processing Effects

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ABSTRACT

Thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been grown by sequential evaporation of Cu, Y, and BaF_2 on SrTiO_3 and MgO substrates. The onset temperatures were as high as 93K, while T_c was 85K. The Ba/Y ratio was varied from 1.9 to 4.0. The Cu/Y ratio was varied from 2.8 to 3.4. The films were then annealed at various times and temperatures. The times ranged from 15min to 3 hours, while the annealing temperatures used ranged from 850°C to 900°C. There was found a good correlation between transition temperature (T_c) and the annealing conditions; the films annealed at 900°C on SrTiO_3 had the best T_c 's. There was a weaker correlation between composition and T_c . Barium poor films exhibited semiconducting normal state resistance behavior while barium rich films were metallic. The films were analyzed by resistance versus temperature measurements and scanning electron microscopy. The analysis of the films and the correlations are reported.

INTRODUCTION

With the widespread effort to investigate and develop electronic applications of the superconducting oxides, a large variety of techniques have been used to form high temperature superconducting thin films. One such technique consists of the sequential evaporation of a multi-layer stack containing the constituents of the superconductor followed by annealing in an oxygen ambient. When performed by electron beam evaporation from a multi-hearth gun, this technique allows deposition of films with little spatial variation of stoichiometry as all components of the film are evaporated from the same point in space. The stoichiometry of the films is also easily adjusted by controlling the thickness of the individually deposited layers. This technique has been employed with a variety of starting materials; Y, Ba and Cu metals themselves¹⁻³, a combination of the metals and oxides^{2,4,5}, a combination of metals and BaF_2 ³ and a combination of oxides and BaF_2 ⁶.

In the work reported here, we have performed sequential evaporation of Cu, Y and BaF_2 to study the formation of superconducting films on SrTiO_3 and MgO substrates. We have varied the stoichiometry of the films by adjusting the thicknesses of the individual layers. Films of fixed composition have also been differently annealed to assess the influence of annealing conditions. The fabricated films were characterized through measurement

of their resistance as a function of temperature and through scanning electron microscopy. The results of these characterizations are presented here.

DEPOSITION OF FILMS

Deposition of the films was performed in a CHA Industries electron beam evaporator. The system is equipped with a four hearth gun, allowing deposition of the multi-layer stack without breaking vacuum. Thickness of the layers was controlled via an Inficon XTC thickness monitor and rate controller. The depositions were calibrated by measurements of step heights using a surface profilometer.

A cross sectional drawing of the structure of a typical as deposited film is shown in Figure 1. First approximately 510Å of copper was deposited on the substrate. This was followed by an approximately 480Å thick layer of yttrium which was followed by an approximately 1920Å thick layer of barium fluoride. For most of our depositions, this multi-layered sequence was repeated four times for a total of twelve layers. For the thicknesses listed above, the film is characterized by a barium/yttrium atomic ratio of 2.25 and a copper/yttrium atomic ratio of 3.01, which has produced our best results on SrTiO_3 substrates. We have investigated the properties of films with barium/yttrium ratios ranging from 1.9 to 4.0 and copper/yttrium ratios ranging from 2.8 to 3.5. We have used barium fluoride rather than elemental barium since barium fluoride is less reactive.

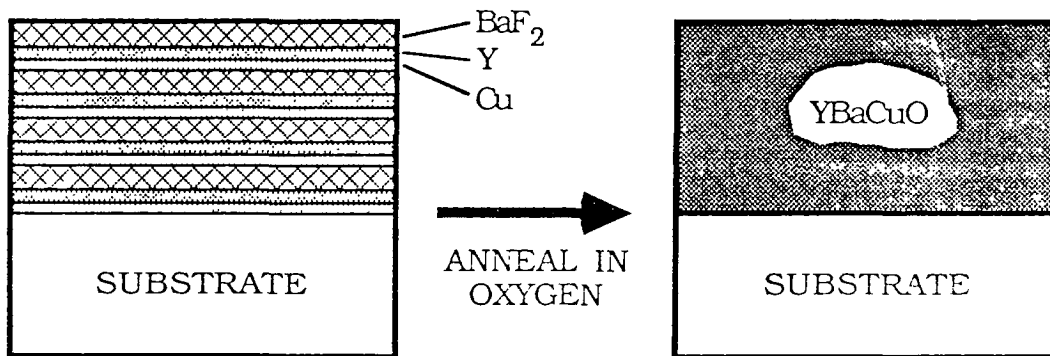


Fig. 1. On the left: Typical twelve layer structure of the as deposited film. On the right: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ formed after annealing in oxygen.

ANNEALING

The deposited films were annealed in a hot wall, programmable, quartz tube furnace. The furnace was preheated to the annealing temperature and purged with oxygen prior to inserting the samples. Temperatures ranged from 850°C to 900°C. The samples were pushed into the furnace with either a fast push of approximately 30sec or a slow 5min push. The duration of the anneals ranged from 15min to

3hr. The temperature was then ramped to 450°C at a rate of -2°C/min. The samples were held at 450°C for 6hr and then the temperature was ramped to room temperature at -1°C/min. During the high temperature portion of the anneal the ambient consisted of ultra high purity oxygen bubbled through room temperature water to assist in removal of fluorine from the films. Dry oxygen was used during all other portions of the annealing process.

CHARACTERIZATION

Ohmic contacts were formed on the films to allow measurement of their resistance as a function of temperature. Most of the samples were rectangular in shape with widths of approximately 5mm and lengths of approximately 1cm. The contacts for these samples were deposited by evaporation of 1 μ m of silver through shadow masks to produce four stripes across the width of the samples. For some irregularly shaped samples, shadow masks which produced four dots were used. The contacts were annealed in dry oxygen at 500°C for 1hr. The temperature was ramped to 250°C at a rate of -2°C/min and then to room temperature at -1°C/min.

The samples were mounted to a sample holder and gold ribbon bonds were made between the silver contacts and bonding posts. A four probe DC measurement was employed to determine the resistance. The samples were cooled in a closed cycle helium refrigerator. Measurements were performed from room temperature to well below the transition temperature for superconducting films or to approximately 10K for non-superconducting films.

Scanning electron microscopy (SEM) was employed to observe the morphology of the films. In addition, several of the films on SrTiO₃ substrates were analyzed by x-ray diffraction spectroscopy (XDS) to observe orientation and the presence of other phases.

RESULTS

Figure 2 is a plot of the distribution of composition for several films. Each point on the plot represents the combination of Cu/Y ratio and Ba/Y ratio used for a deposition. Each of these films was made with a 12 layer deposition and was between 1.0 and 1.2 μ m thick before annealing. All of the samples shown in this plot were annealed with the procedure described above for 45min at 900°C. A few films with composition well outside the range plotted here (larger Ba/Y ratios) were also deposited. They are not plotted since they had a small residual resistance below the "transition" temperature even though they showed a fairly sharp onset of superconductivity and transition. Films of many other compositions were also deposited but were not annealed at the same conditions and are thus not plotted here.

Associated with each point on the plot are two numbers and a letter. The first number is the onset temperature in Kelvin. The second number is the temperature below which the resistance of the sample was zero. The letter "m" refers to a metallic behavior of the normal state resistance with temperature while the letter "s"

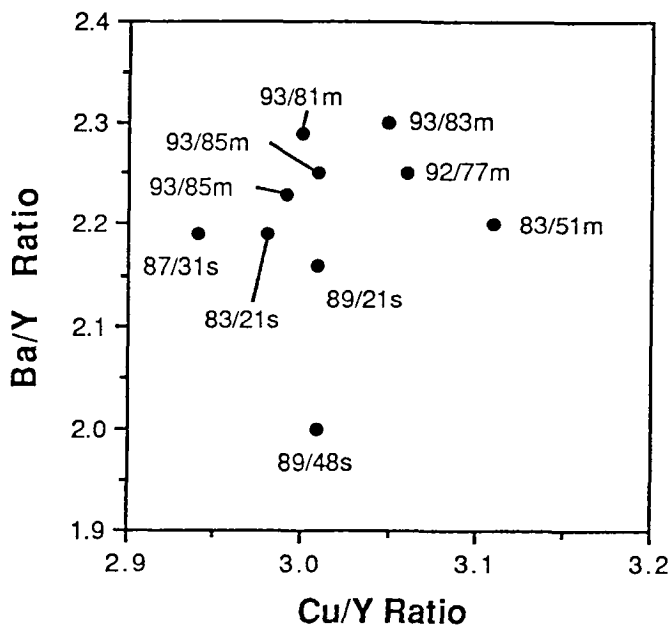


Fig. 2. Composition of several films annealed at 900°C for 45min. The numbers give onset/ T_c . m: metallic normal state, s: semiconducting normal state.

indicates that the normal state resistance of that sample showed a semiconducting behavior with temperature.

The data in this plot show that there is a minimum Ba/Y ratio below which the samples have a semiconducting normal state resistance-temperature (R-T) characteristic. Those films deposited with a Ba/Y ratio of greater than approximately 2.2 have a metallic normal state R-T characteristic. This was also true of the films, mentioned above, with the large Ba/Y ratios (≈ 3.0 and ≈ 4.0).

Over the ranges studied, the Cu/Y ratio does not affect the qualitative character of the normal state resistance. As would be expected, adjusting the thicknesses of the individual layers to make the films copper rich or poor does degrade the onset temperature and critical temperature of the resulting films.

Our best films on SrTiO_3 are those deposited with a Ba/Y ratio of approximately 2.25 and a Cu/Y ratio of ≈ 3.0 . The R-T characteristic below room temperature for one of these films is plotted in Figure 3. This film had a room temperature resistivity of approximately $2\text{m}\Omega\text{-cm}$. The onset temperature of this film was 93K and the critical temperature was 85K. The 90% to 10% transition width for this sample was 3.6K. As can be seen from Figure 2, there is a range of ratios near these values which produce films with nearly the same onset and critical temperatures.

Films of several compositions were annealed at different temperatures or for different durations. Data for one of these experiments, involving four samples, is listed in Table I. These samples were annealed for 45min at three temperatures. Two samples were annealed at 850°C. One was quickly pushed into the furnace while the other was pushed into the furnace over a period of 5min. The other two samples were annealed at 875°C and 900°C, both with slow pushes. The last of these samples is included in Figure 2. The onset temperature, critical temperature, 90%-10% transition width and 99%-1% transition width are tabulated. The transition widths are referenced to the resistance just above the onset.

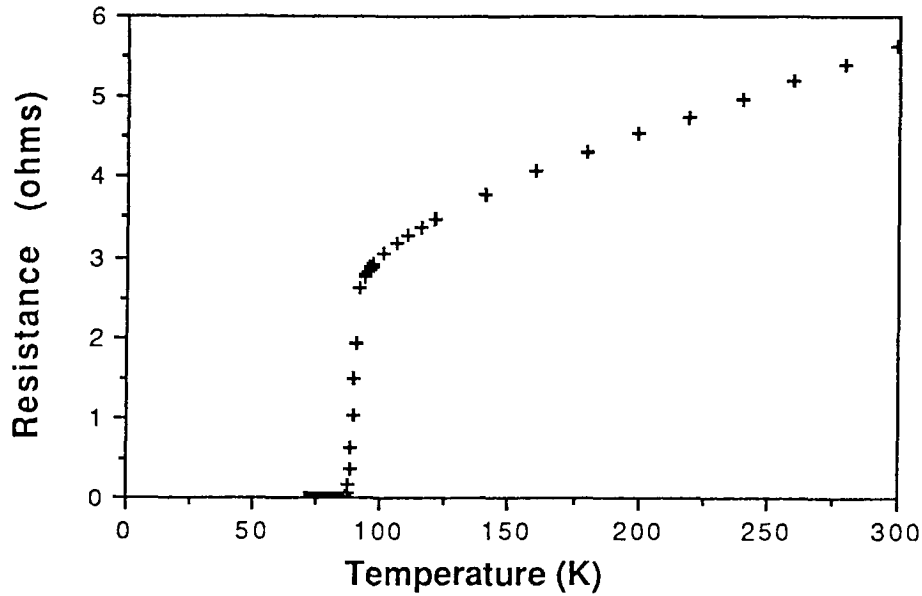


Fig. 3. Resistance as a function of temperature for a Y-Ba-Cu-O thin film with composition Ba/Y=2.25 and Cu/Y=3.01. Annealed at 900°C for 45min. Onset temperature=93K. T_c =85K.

Table I. Transition widths for three annealing temperatures.

Annealing Temperature (°C)	Onset (K)	T_c (K)	$\Delta T_{90\%-10\%}$ (K)	$\Delta T_{99\%-1\%}$ (K)
850 fast push	55	21	14.7	25.1
850 slow push	69	41	10.3	18.4
875 slow push	83	49	13.0	21.5
900 slow push	83	51	12.6	20.2

The tabulated data shows that both the onset temperature and critical temperature are improved with the higher temperature anneals. In addition, for the same onset temperature, a higher temperature anneal results in a slightly sharper transition. The push rate also has a dramatic effect on the R-T characteristic. The sample which was slowly pushed into the furnace had significantly higher onset and critical temperatures.

For several compositions of films on SrTiO_3 , two samples were annealed for 45min or 60min respectively at 850°C. No significant or consistent differences in their R-T characteristics were observed.

One of the films with a critical temperature of 85K was remeasured at two later times. The resistance as a function of temperature from 70K to 120K from these measurements is shown in Figure 4. The initial measurement is marked by the squares. The second measurement, plotted with crosses, was made 14 days later. The normal state resistance had increased by approximately $.8\Omega$ from the first measurement. The transition had degraded only slightly over this period. The sample was measured a third time 33 days after the first measurement, shown by the circles in Figure 4. The normal state resistance was seen to have increased very slightly from the second measurement. There was no additional change in the superconducting transition temperatures.

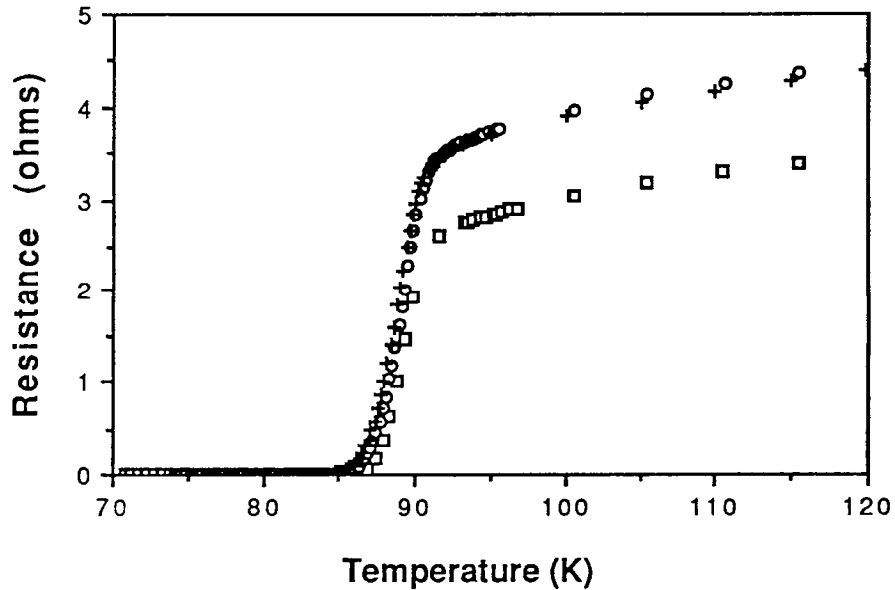


Fig. 4. Three measurements of the resistance as a function of temperature for a Y-Ba-Cu-O film. Squares: Initial measurement. Crosses: Second measurement, 14 days. Circles: Third measurement, 33 days.



Fig. 5. Scanning electron micrograph of a $1.2\mu\text{m}$ film deposited in 12 layers.

A scanning electron micrograph of the film of Figure 3 is shown in Figure 5. This film was deposited in twelve layers and had a thickness of approximately $1.2\mu\text{m}$ prior to annealing. The film is polycrystalline and can be seen to have both ordered and unordered grains. Observations of this and other areas of the film as well as other samples appear

to indicate that the film consists of a layer of ordered grains in contact with the substrate and an overlayer of unordered grains. The x-ray diffraction spectrum for this sample also shows incomplete ordering.

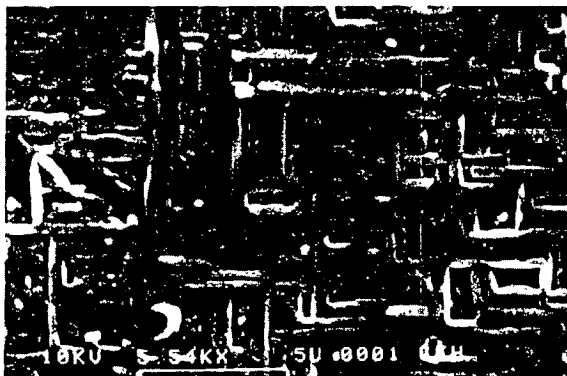


Fig. 6. Scanning electron micrograph of a $0.9\mu\text{m}$ film deposited in 18 layers.

In addition, superconducting films have been formed with depositions consisting of both more and less layers. Figure 6 shows a scanning electron micrograph of a film deposited in 18 layers which had a thickness of $0.9\mu\text{m}$ prior to annealing. This film appears to be more completely ordered than the thicker films formed with twelve layers.

Superconducting films on MgO substrates are not as readily formed. When the same annealing conditions used for SrTiO_3 are used for MgO, films with semiconducting normal state resistance temperature characteristics result. These films still show sharp onset temperatures in the vicinity of 90K, but the transitions have long resistive tails and zero resistance is achieved only below 15K, if at all. Better results are achieved by annealing at 850°C for times of two to three hours, yielding metallic normal state resistance characteristics, an onset of 93K and a critical temperature of 50K.

SUMMARY AND CONCLUSIONS

The technique of multi-layer sequential evaporation of BaF_2 , Y and Cu layers has been employed for the formation of high temperature superconducting films. The effects of varying the composition and annealing conditions have been studied. For films on SrTiO_3 annealed at 900°C for 45min, variation of the Ba/Y ratio significantly altered the resistance-temperature characteristics. Barium poor films exhibited semiconducting normal state resistance-temperature characteristics while barium rich films were metallic. The transition temperatures varied with both the Ba/Y and Cu/Y ratios. Films which were superconducting at 85K were formed with Ba/Y=2.25 and Cu/Y=3.0. For a given composition, films on SrTiO_3 had higher transition temperatures when annealed at 900°C than at 850°C . Conversely, films on MgO were better when annealed at 850°C for longer times. The normal state resistance of the films increased over a period of two weeks but the transition temperature degraded only slightly.

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