**MECHANISMS CONTROLLING THE IN-SITU FORMATION AND
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MECHANISMS CONTROLLING THE IN-SITU FORMATION AND SUPERCONDUCTING PROPERTIES OF BI-SR-CA-CU-O FILMS

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Abstract

We have previously shown^{3,6} that sputtered films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (BSCCO) deposited onto single crystal MgO substrates held at substrate temperatures, T_s , near 700°C and slowly cooled in oxygen, form High Temperature Superconducting (HTS) films with T_{CZERO} between 50 and 70K. The conditions necessary to achieve superconductivity include having close to stoichiometric composition at the T_s required to form the superconductor. Both T_{CZERO} and c-axis orientation increase with T_s while the relative bismuth content decreases. Bismuth film content is affected by the type and amount of oxidant, total system pressure, target-to-substrate spacing, and substrate bias. We suggest oxygen resputtering of the film may play a role similar to that reported for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). Oxygen partial pressure during and cooldown rate from T_s to $\approx 350^\circ\text{C}$ also affects the superconducting properties.

Introduction

Low-temperature, in-situ processing of HTS YBCO has received considerable attention recently with many researchers demonstrating that the best results are obtained from films grown epitaxially¹. Less attention has been paid to in-situ processing of thin films of the HTS cuprates based on Bi and Tl, in spite of their potential for higher T_c , fewer insulating impurity phases, and c-axis orientation without the requirement for epitaxy². Growth of HTS Tl-based films by in-situ processing has shown little progress presumably because of the extreme volatility of Tl at the growth temperatures needed. However several recent papers³⁻⁷ report progress on in-situ growth of BSCCO.

This paper reports on the in-situ formation of superconducting films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ using composite-target sputtering with substrate temperatures, T_s , significantly less than required for post-annealed films. We will also discuss Bi loss in our films relative to the target, and how it is affected by the type and amount of oxidant present, total system pressure, target-to-substrate spacing, substrate bias and T_s . Electron microscopy reveals that the films are polycrystalline with grains several microns in diameter, relatively free of internal defects such as intergrowths, are somewhat smoother than post-annealed films, and that some segregation into nonsuperconducting grains³ can occur.

Film Preparation and Characterization

All films were grown in a dc magnetron sputtering system equipped with a load-lock mechanism, and a variable speed turbo pump to control pressure during sputtering. Composite targets were formed by cold-pressing the appropriate amount of calcined powders of the carbonates and oxides into a 1.75 inch diameter by 0.125 inch thick disk. Further heat treating was necessary to lower the resistance sufficiently for dc sputtering. Prior to depositing films, targets were presputtered for several hours to establish equilibrium conditions. The chamber and target were not exposed to atmospheric conditions once presputtering had been completed; rather the system was brought to one atmosphere of nitrogen or oxygen between runs and further protected by the load lock during sample changes. This procedure was found necessary to keep the target resistance low enough to permit repeated dc sputtering. Films were sputtered at a rate of 5-10 nm/min. onto single crystal MgO substrates facing the target and located 25-50 mm from the target, and in an atmosphere of 4-300 mtorr research grade Ar with an O_2 partial pressure of 0.3-50 mtorr or pure oxygen at 300 mtorr.

Substrates were bonded to a stainless steel heater block using silver paint. Although this method worked well, there was still some evidence of non-uniform bonding with the possibility of small temperature gradients ($<10^\circ\text{C}$) across the sample surface. Substrate temperature T_s was measured and controlled over the range from 650-750°C using a type-K thermocouple embedded in the heater block. A second thermocouple, used to calibrate the block thermocouple against the substrate surface temperature, was bonded to the surface of a piece of substrate material which was bonded to the heater block. At $T_s=700^\circ\text{C}$, the surface thermocouple never read more than 20°C lower than T_s .

Film compositions were measured by electron-induced x-ray fluorescence (done in a scanning electron microscope) and photon-induced x-ray fluorescence, calibrated with a single-crystal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ standard and ICP-AES analysis of these films. The photon-induced method employs a Cr-target x-ray tube to excite atomic fluorescence lines in the films. A standard SiLi detector is used and the results obtained take into account x-ray absorption in the film, which for the energies, film thickness and geometries used, are small effects. The error is estimated to be $\approx 2\%$ of the amount present for a film of nominal 2212 composition.

Results

Making superconducting films of the Bi-Sr-Ca-Cu oxide using composite target sputtering and low temperature in-situ processing with results such as those shown in Fig. 1, require a careful balance between substrate temperature, film stoichiometry, target composition, total system pressure, oxygen partial pressure, and cooldown conditions. For example, films rapidly cooled at high oxygen pressure ($\approx 1\text{ atm}$) or slow-cooled at a lower oxygen pressure (1 torr) or cooled in nitrogen, argon or a vacuum showed either semiconducting or insulating rather than superconducting behavior. It was necessary to slow-cool (we use $6^\circ\text{C}/\text{min}$) the films in a high pressure (400 torr to 1 atm) of oxygen to obtain superconductivity.

Fig. 1. Resistive transition for in-situ processed BSCCO film. $T_{\text{CZERO}} \approx 64\text{K}$.

Bi loss

Films deposited at 20 mtorr Ar and $\approx 1\text{ mtorr O}_2$ show significant Bi loss with increasing T_s , without a similar loss of Sr, Ca, or Cu. To compensate for Bi-loss, the target Bi content was

increased to approximately twice the normal amount. The results, shown in Fig. 2 for a 3.6,2,2,3 target and a 4,2,1,2 target indicate that for $T_s \leq 720^\circ\text{C}$ doubling the target Bi content results in approximately the correct Bi in the film, whereas above 720°C a dramatic drop occurs. The loss of Bi may be due to a variety of causes such as the inability to completely oxidize Bi, improper amounts of the other constituents resulting in free Bi or Bi_2O_3 which may volatilize away. At 700°C , the loss rates for Bi, Sr, and Ca are orders of magnitude greater while Cu is much less than our deposition rate. The oxides of Sr, Ca, and Cu are very stable at this

Fig. 2. The effect of in situ processing on the Bi concentration as a function of substrate temperature T_s for a 4,2,1,2 target (open circles) and a 3.6,2,2,3 target (solid circles). At $T_s = T_{\text{amb}}$, the film Bi concentration is ≈ 44 At.% for the 4,2,1,2 target and ≈ 34 At.% for the 3.6,2,2,3 target.

temperature whereas Bi_2O_3 will evaporate faster than our deposition rate unless it is bound into a compound oxide such as the BSCCO crystal structure. One would expect that the binding energy of Bi_2O_3 is temperature dependent, therefore the temperature dependence shown in Fig. 2 could be explained as a thermally driven desorption process. Since the oxides of Ca and Sr are more readily formed than Bi_2O_3 incomplete oxidation could explain the preferential Bi loss.

To test the idea of incomplete oxidation of Bi, a series of experiments were performed using higher oxygen partial pressures and a stronger oxidizer namely ozone. Increasing the O_2 partial pressure from 1 to 10 mtorr while holding the total pressure constant at 20 mtorr produced a decrease in Bi by more than a factor of three. Ozone in concentrations considerably less than those used for O_2 , gave an even greater Bi loss. Since more oxygen or a stronger oxidizer should have reduced Bi loss if incomplete oxidation were the prime loss mechanism, it seems likely that another mechanism is at work. Researchers sputtering YBCO had observed selective Barium loss and explained it in terms of negative oxygen ion resputtering however no such observations have been reported for BSCCO. Negative oxygen ions can be formed if the energy from the plasma splits O_2 into O which can pick up an electron from the ample supply in the plasma. Similarly O_3 can split even more easily into O_2 and O with the O picking up an electron. The O^- is then repelled from the target with the sputtering voltage which in our case is ≈ 200 volts. These ions can lose energy as they interact with the system gas pressure, however because of the electric field between the negative target and the substrate, they can be re-accelerated with enough energy so that by the time they reach the substrate they exceed the $\approx 50\text{eV}$ sputtering threshold and resputter some film.

If resputtering due to negative oxygen ions is a factor in Bi loss then reducing or increasing the average energy of the ions striking the film should reduce or increase Bi loss. To test this, the substrate was biased at -40 volts relative to ground in order to reduce the energy of incoming particles or deflect them away from the substrate entirely. Results showed that the Bi loss could be reduced significantly. Decreasing or increasing the total pressure while keeping the oxygen partial pressure constant will reduce or increase the number of collisions thereby increasing or reducing the average

incident ion energy. Lowering the total pressure to 5 mtorr reduced the Bi content as might be expected while increasing the total pressure to as high as 300 mtorr brought the Bi pressure up to target concentrations. We also sputtered in pure oxygen at 300 mtorr (at half the target-to-substrate spacing of the 300 mtorr Ar/O_2 experiment) and found the Bi film content to be slightly less than that obtained from the 300 mtorr Ar/O_2 mixture, suggesting that high gas pressure is important to lowering negative oxygen ion energies to below the resputtering threshold. Bi loss at 300 mtorr O_2 might be explained as follows. The Bi flux at the substrate was less (the film was thinner than the 300 mtorr Ar/O_2 film even though it was much closer to the target) and the O^- flux was greater (6 times more oxygen than the 300 mtorr Ar/O_2 experiment), thus the probability of a resputtering event occurring was increased. A film made at 300 mtorr O_2 and 25% closer to the target than the previous 300 mtorr O_2 film showed even less Bi. The results of the Bi loss experiments are summarized in table 1.

Table 1. Bi loss as a function of total pressure, oxygen partial pressure, and substrate bias

Total Pressure mtorr	Oxy. part. pres mtorr	Substrate Bias volts	Bi in film % of target Bi
5	1	0	56
5	1	-40	61
20	1	0	76
20	4.5	0	65
20	10	0	23
75	12.5	0	77
150	25	0	100
300	50	0	100
300	300	0	86
20	0.1 (ozone)	0	16
20	0.1 (ozone)	-40	67

Substrate Temperature Effects

Substrate temperatures below 650°C generally produce semiconducting or insulating films presumably due to lack of sufficient thermal energy to form a well-ordered HTS phase. At higher substrate temperatures, there is more thermal energy available and film quality improves. But as we previously discussed, at temperatures above 730°C , severe Bi loss occurs and films are almost always insulating. Inbetween these extremes, it is possible to form superconducting films of varying quality with the best films made at temperatures near 700°C . Fig. 3 shows the effect of T_s on T_{czero} and $T_{\text{c midpoint}}$ while holding all other conditions constant. The trend of the T_{czero} data in Fig. 3 suggests it might be possible to achieve midpoint transitions above 80K and T_{czero} 's near 80K by raising T_s to ≈ 740 to 760°C . However, hope of actually accomplishing this depends on finding a way to reduce Bi loss at higher temperatures, such as substrate bias and higher pressure during deposition.

Fig. 3. Effect of substrate temperature on T_{czero} (circles) and $T_{\text{c midpoint}}$ (squares).

Although diffraction patterns of our in-situ processed 2212 films show a very high degree of c-axis orientation, films made between 685 and 695°C have rather broad rocking curves with a FWHM = 2-3 degrees, suggesting many c-axis planes are at orientations other than the plane of the film. However, for $T_s \geq 705^\circ\text{C}$ the FWHM drops abruptly to $< 1^\circ$, which is better than of our typical post-annealed films, and equal to high quality 2212 single crystals⁸ ($T_{czero} = 86\text{K}$) as can be seen in Fig. 4. Although the single crystal peaks appear sharper, the FWHM rocking curve values of 0.7 degrees for the film and 0.6 degrees for the single crystal are quite close. The broadened film diffraction peaks may be a consequence of phase inhomogeneities and the polycrystalline nature of the film.

Fig. 4. X-ray diffraction pattern of an in-situ processed BSCCO 2212 film (solid line) made at $T_s = 715^\circ\text{C}$, compared to a BSCCO 2212 single crystal with a $T_{czero} = 86\text{K}$. The film shown here had a $T_{czero} = 54\text{K}$.

Microstructure.

The microstructures of these films have been examined using scanning electron microscopy (SEM) and the composition has been determined using x-ray energy dispersive spectroscopy (XEDS). The microstructures consist of a smooth matrix phase with some second phase particles. When viewed at low magnifications, the films often exhibited a somewhat mottled appearance. Closer examination reveals that this mottling is an effect of variations in the number density and size of the second phase particles. Although there are some variations in microstructure from region to region within a given film, comparison between the films has shown that the microstructures are similar at all substrate temperatures, with the second phase particles growing in size as the substrate temperature increases. An example is shown in Fig. 5 for a films grown at 695°C and 710°C . The presence of the second phase particles does introduce some roughness to the surface since they are observed to grow out of the smooth matrix. In regions of the film where the particle-density is low, the matrix is very smooth over large distances. Transmission electron microscopy (TEM) of film cross sections has revealed some details of the nature of the matrix grains. An example of such a cross-section is shown in Fig. 6. The matrix grains can be identified as the 2212 phase through electron diffraction patterns and c-axis lattice fringe spacings. The grains are typically several microns in diameter, relatively free of internal defects such as intergrowths, and frequently meet at low angle boundaries. In the SEM images, some holes are typically observed in the film, and those holes seem to be associated with regions that have a high density of second phase particles. As the substrate temperature is increased, the microstructure is seen to coarsen somewhat, and the second phase particles begin to assume clearly identifiable crystallographic features. For example, many of the particles exhibit a square profile; and are often observed to possess growth ledges. XEDS analysis of these particles in the most coarse microstructures in which these particles may be isolated from the matrix phase has shown them to exhibit a composition close to $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{O}_x$.

Fig. 5. SEM backscattering images of films made at 695°C (left side) and 710°C (right side). The particles protruding from the surface grow in size and number-density as T_s increases, but have a composition similar to the underlying matrix.

Fig. 6. Cross-section TEM of superconducting BSCCO 2212 film made at $T_s = 705^\circ\text{C}$ from a 4,2,1,2,2 target composition. Note the individual grains and lattice planes relatively free of intergrowths and other defects.

Can the BSCCO 2223 phase be formed in-situ?

By using a Bi-enriched 4,2,2,3 target and depositing at a substrate temperatures from 675 – 720°C , films with approximately the 2223 stoichiometry can be formed. X-ray diffraction shows peaks associated only with the 2223 Bi-plane spacing (see solid curve in Fig. 7), whereas the $R(T)$ (upper curve in Fig. 8) shows metallic behavior with evidence for a transition beginning near 60K and no indication of any 2223 phase. Post-annealing these samples did produce films with a 110K partial transition and T_{czero} at $\approx 60\text{K}$ (lower curve in Fig. 8). The x-ray pattern (dashed line in Fig. 7) clearly indicates that the 2223 peaks have decreased in size and the 2212 structure has begun to form. Further post-annealing of this film causes more 2212 phase to appear at the expense of the 110K

phase. It is possible that what we have is the formation of Bi bilayers at about the right spacing for the 2223 structure but a disordered structure between the layers which may be deficient in one or more of the other three constituents. Post-annealing orders the structure somewhat but the deficient species (possibly calcium) prevents further ordering and instead drives the structure towards the 2212 phase because for that phase, there is more than enough calcium present.

Fig. 7. X-ray diffraction spectra for in-situ processed BSCCO 2223 film (solid line), and same film after post-annealing at 865°C for 1hr (dashed line). All 2223 peaks are designated by a solid circle, whereas the 2212 peaks are indicated by a cross.

Fig. 8. Resistive transitions for BSCCO 2223 in-situ processed film (upper curve) and the same film after post-annealing (lower curve).

Summary

Superconducting films of BSCCO 2212 and 2223 can be sputtered onto single crystal MgO substrates by an in-situ processing technique with T_{czero} 's as high as 64K, and a very pronounced c-axis orientation without the need for epitaxy. Bi loss in the films can be reduced by biasing the substrate negative or increasing the total system pressure. This should provide greater control over film properties and the possibility of sputter deposition at higher substrate temperatures to see if T_{czero} 's close to bulk can be achieved. The microstructure generally reveals a smooth matrix with submicron to micron sized particles protruding from it. These particles increase in size and frequency with increasing T_s and appear to be a Bi-Sr-Ca-oxide mixture.

The exact mechanism by which crystallization occurs during in-situ processing at temperatures $\approx 150^\circ\text{C}$ below post-annealing temperatures has not been established. Due to greater atomic

mobility amongst the surface atoms compared to that within a bulk film, there is a lower kinetic barrier for nucleation and crystal growth during in-situ processing. Thus the possibility exists that increases in surface energy relative to the underlying film could promote crystal growth at even lower substrate temperatures.

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8. Single crystal supplied by D. Shi, Materials Science Division, Argonne National Laboratory.

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