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SPUTTERED SUPERCONDUCTING FILMS OF $Bi_2Sr_2CaCu_2O_x$ MADE BY LOW-TEMPERATURE, IN-SITU GROWTH*

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ABSTRACT

Composite target rf magnetron sputtering has previously been successfully employed to make superconducting films of $YBa_2Cu_3O_{7-x}$ in-situ at substrate temperatures T_s<700 °C. We report the successful growth of superconducting films of $Bi_2Sr_2CaCu_2O_x$ on single crystal MgO substrates by a low-temperature process using dc magnetron sputtering from a Bi-enriched composite target. Using a substrate temperature $T_s \approx 645°C$, metallic films with a superconducting onset of 90-100K and an extrapolated T_{c0}=56K have been obtained. X-ray diffraction shows the films to be c-axis oriented. Electron microscopy reveals that the films are not significantly smoother than films which were post-annealed at 865°C, and that some segregation into nonsuperconducting phases had occurred. The exact mechanism by which crystallization and superconductivity occurs at such low temperatures is not yet known, but it can be speculated that the surface atoms are less constrained and thus have a smaller energy barrier to overcome in forming a crystal structure.

INTRODUCTION

Low-temperature, in-situ processing of thin films of the high temperature superconductor $YBa_2Cu_3O_7$ (hereafter denoted YBCO) has received considerable attention recently[1]. It provides the smoothest films by discouraging grain growth, the highest current densities, provided the films are grown epitaxially on $SrTiO_3$ substrates, and allows for the potential compatibility with a variety of other substrates which would melt or severely react with YBCO at the customary annealing temperatures of about 900°C. Although laser ablation[2] has been most successful, other deposition techniques such as sputtering[3], molecular beam epitaxy[4], and electron beam coevaporation[5] have also been successful.

Less attention[6,7] has been paid to in-situ processing of thin films of the high temperature superconducting cuprates based on Bi and Tl, in spite of their higher T_c, fewer insulating impurity phases and the fact that they offer better compatibility with more substrates than YBCO. The latter advantage is partly because the Bi- and Tl-based films do not require expitaxial growth to obtain high-quality c-axis oriented films necessary e.g., to maximize critical current density, because they usually exhibit a high degree of c-axis orientation perpendicular to the substrate[8]. This paper reports the formation of superconducting films of $Bi_2Sr_2CaCu_2O_x$ with T_{c0} = 56K by sputtering using an in-situ process and a substrate temperature, T_s, of only ≈645°C. This compares with the best $Bi_2Sr_2CaCu_2O_x$ films deposited in amorphous form at ambient temperatures by a variety of techniques including elemental[8] and composite target[9] magnetron sputtering which have T_{c0}'s of 80 to 84 K after they have been post-annealed at temperatures of 865-890°C, are phase pure by x-ray analysis and show a high degree of c-axis orientation. Although these in-situ prepared films represent a considerable breakthrough, electron microscopy analysis indicates they were not dramatically smoother and that some segregation into nonsuperconducting grains occurred. Such segregation was less severe in films deposited at ambient temperature and post annealed at 865°C.

EXPERIMENTAL

All films were grown in a dc magnetron sputtering system equipped with a load-lock mechanism, a roughing pump to evacuate the chamber and a liquid nitrogen sorption 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 never exposed to atmosphere once presputtering had been completed, rather the system was brought to one atmosphere of nitrogen 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 onto single crystal MgO substrates in an atmosphere of 20 mtorr research grade Ar with an O_2 partial pressure of $3\text{-}10\times10^{-4}$ torr which is introduced before sputtering begins.

Initial experiments used a Bi-enriched 2223 target of actual composition $Bi_{2.9}Sr_2Ca_{1.7}Cu_3O_x$ to compensate for possible Bi loss at high T_s. The substrates were clamped to a boron nitride heater block along with a type-K thermocouple spot-welded to a stainless steel foil. The temperature was adjusted manually from ~200°C (the ambient temperature due to the sputtering plasma) to above 700°C. The resulting film composition, measured by energy dispersive x-rays (EDS) calibrated with a single-crystal $Bi_2Sr_2CaCu_2O_x$ standard, was very nearly constant and similar to that of the target as T_s was increased up to ~600°C. For T_s above ~600°C, however, the Bi concentration in the film decreased, going precipitiously to zero at T_s~675°C. Some samples made with T_s=650°C showed a finite semiconductor-like conductivity, a sharp drop in resistance below ~100 K, and x-rays diffraction peaks characteristic of oriented crystalline 2212 phase, i.e., $Bi_2Sr_2CaCu_2O_x$.

To further compensate for the Bi loss above T_s=600°C, a second target was made with composition $Bi_{3.6}Sr_2Ca_{1.66}Cu_{3.2}O_x$. Although Fig. 1 shows a similar drop in Bi concentration, some samples made near T_s=650°C showed considerably improved superconducting properties, presumably due to the higher Bi concentration, which in most cases was near the 28.5 atomic % required for the 2212 phase. It was found to be imperative to slow-cool (5 °C/min) the films in a high pressure (400 torr) of oxygen to obtain good superconducting properties. Films rapidly cooled at high oxygen pressure or slow-cooled at a lower oxygen pressure (1 torr) or cooled in nitrogen gas showed either semiconducting or insulating rather than superconducting behavior. Superconducting transitions ranged from less than 10 K to the best resistive transition which is shown in Fig. 2 and extrapolates to zero resistance at 56 K.

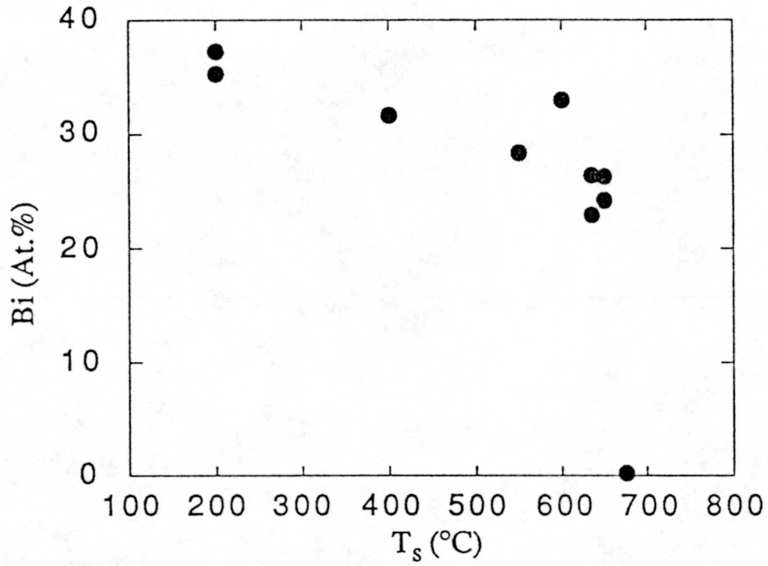

Fig. 1. The effect of substrate temperature, T_S, on the Bi concentration of the as-deposited films. The Sr, Ca, and Cu concentrations remained relatively constant with increasing T_S.

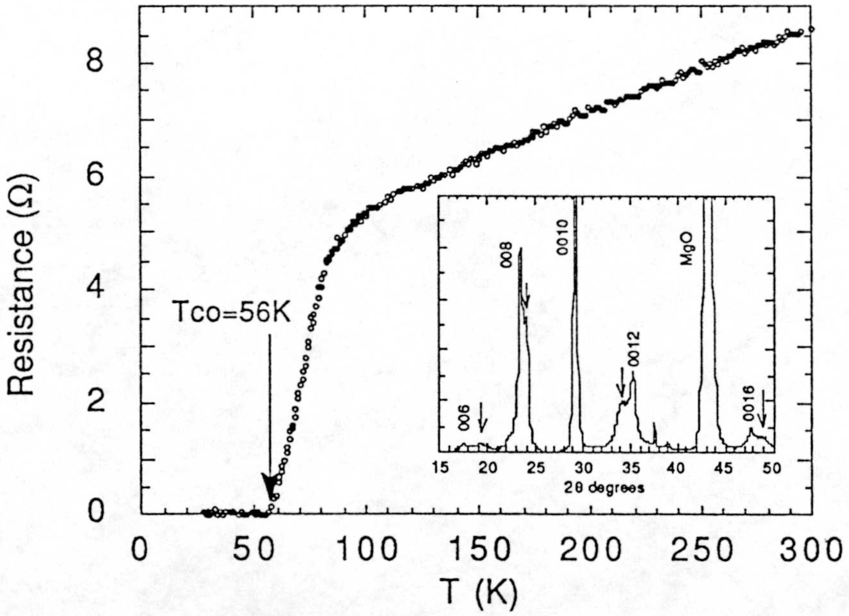

Fig. 2. The best resistive transition for an in-situ processed film is shown. The inset shows X-ray diffraction data for the sample, with the θ–2θ scan normal to the film surface. Note the strongly c-axis oriented peaks of the $Bi_2Sr_2CaCu_2O_x$ phase along with several weak 2223 peaks (denoted by arrows).

There is a narrow temperature window for formation of the 2212 phase in-situ: for $T_S < 630^\circ$C films are disordered and semiconducting; while for $T_S > 660^\circ$C they are insulating with severe Bi deficiency. Because the temperature window for forming the superconducting phase is so narrow, it is imperative that substrates be thermally linked to the heater block surface exactly the same way each time, otherwise run to run reproducibility is poor. Varying the O_2 partial pressure during deposition between ~0.1 and 1 mtorr had little effect, but in a few films made above 1 mtorr the resistance goes up, exhibiting either semiconducting or insulating behavior. This was accompanied by a decrease in Bi concentration, presumably due to a lower sputtering rate while the Bi loss rate from the film remained unchanged. Substituting the more reactive N_2O for O_2 did not improve the films.

X-ray diffraction results, shown in the insert of Fig. 2 with the θ-2θ scan normal to the film surface, are consistent with peaks of the 2212 phase with the c-axis oriented perpendicular to the substrate as in our post-annealed films[8]. Examination of the x-ray pattern also reveals weaker peaks which can be indexed to the 2223 phase (designated by arrows). By increasing the calcium content relative to bismuth, it is possible to make films which exhibit an x-ray spectrum showing only the 2223 phase as shown by the solid line spectrum in the Fig. 3 insert . Unfortunately these in-situ formed films in their as-sputtered form have not shown any evidence of the 110 K resistive transition associated with the 2223 phase, but rather show evidence for a low temperature transition as shown in Fig. 3, which is qualitatively similar to that found in the in-situ formed 2212 phase. Subsequent post-annealing at 800°C for 3hrs. does improve T_{c0}, and suggests the onset of the 110 K phase as also shown in Fig. 3.

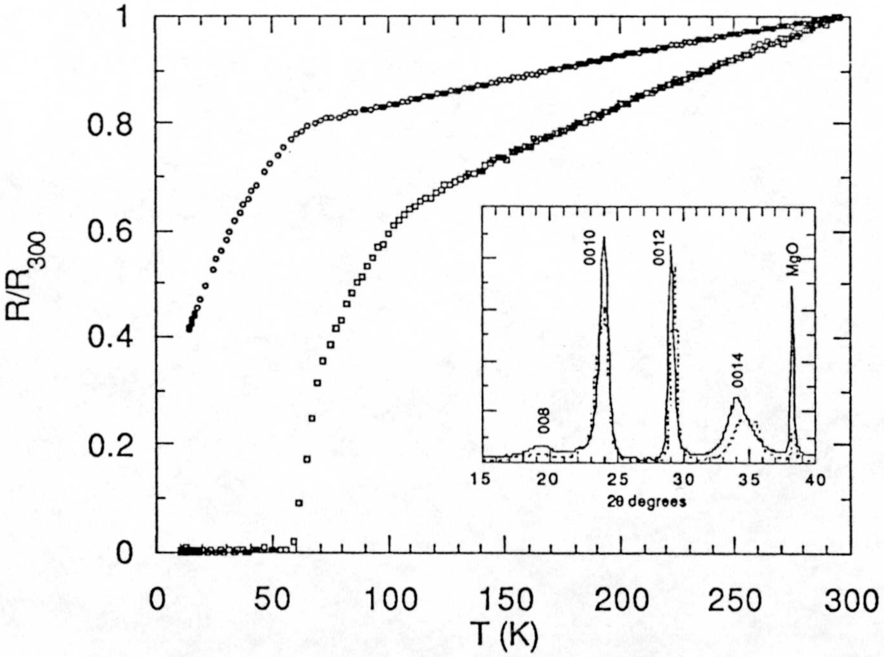

Fig. 3. In-situ formed BSCCO 2223 phase (circles) followed by post-anneal at 800°C for 3hrs. (squares). The insert shows the c-axis oriented 2223 phase (solid line) and the post-annealed spectrum (dotted line). Note the shift toward 2212 phase with annealing.

DISCUSSION

The exact mechanism by which crystallization occurs for the low-temperature, in-situ processing is not yet known, but we may speculate that for in-situ processing the atoms arriving at the surface can have thermal energies higher than the substrate temperature, are less constrained due to the two-dimensional nature of the surface layer and thus have a smaller barrier to overcome in forming crystal structure. Atoms in the amorphous films formed at low deposition temperatures (≈200°C) and post annealed must overcome the barrier associated with the three-dimensional lattice of interconnected bonds as suggested by the considerably higher post annealing temperatures needed to form the superconducting phase.

Unfortunately, these in-situ films exhibit a significant degree of segregation. This segregation was examined using EDS, backscattered electron imaging in a scanning electron microscope (SEM), and x-ray diffraction. EDS analyses revealed Bi-rich regions and Cu-rich regions in addition to regions close to the target composition. Backscatter images allowed estimates of grain size and the average electron density with a higher spatial resolution than EDS. X-ray diffraction revealed other oriented phases such as the Ca-poor 2201 phase of Bi-Sr-Ca-Cu-O, some unoriented grains of both 2201 and 2212 phases, and additional crystalline material as of yet not identified. The results of these measurements are summarized in Table I, which shows the measured range in composition for a given film and includes data for the in-situ films as well as data for some films deposited at ambient temperature and post-annealed. Clearly the extent of segregation increases with higher substrate temperature. It can also be seen in Table I that films prepared by ambient temperature deposition followed by annealing exhibit much less segregation than the corresponding in-situ films.

Table I. The effect of in-situ processing temperature, T_s, and subsequent post-annealing temperature, T_a, on the composition variations (ranges refer to atomic % of individual, identifiable grains or regions) and the occurrence of impurity phases in Bi-Sr-Ca-Cu-O films.

T_s (°C)	200	645	200-550	600	635-645	650-675
T_a (°C)	865	865	none	none	none	none
Bi range	6	38	<1.9	15	20	37
Sr range	1.3	16	<1.2	0.9	19	31
Ca range	2.1	10	<1.4	1	20	29
Cu range	9	86	<3	17	59	96
$Bi_2Sr_2CuO_x$	yes	yes	no	no	yes	yes
CuO	no	yes	no	no	yes	yes
CaO	no	no	no	no	yes	?

A series of films deposited from a $Bi_2Sr_2Ca_{0.9}Cu_2O_x$ target at T_s=200°C and annealed at 700°-865°C also revealed increasing segregation with annealing temperature. For annealing temperatures below ≈800°C, no segregation or well-developed granular structure was apparent, with the exception of a few surface particles. For annealing temperatures of 800°C and above, a more developed structure was observed, and evidence of segregation was apparent in backscattered electron images. In the case of the sample annealed at 800°C, the grains observed were sub-micron in size and thus below the resolution of EDS. The sample annealed at 850°C exhibited segregation on a spatial scale comparable to that observed in the in-situ films which were prepared at a much lower temperature and were also Ca deficient showing the 2201 phase and other impurities. Comparisons of ranges for segregation between in-situ processing and post annealing indicates that segregation is likely a surface phenomenon. We speculate that the surface mobility at 600-675°C allows nonsuperconducting compounds to nucleate and grow preferentially during in-situ growth. It is also possible that the existence of surface energies relevant to in-situ processing can change the relative stability of the various possible phases in this complex five-component chemical/metallurgical system. However for both in-situ processing and post-deposition annealing, segregation is observed on a scale of ≈1 μm.

Post annealing at ~865°C of the films processed in-situ at T_s=600 to 675°C did not homogenize them nor provide the good superconducting transitions found when starting with ambient T_s deposited films. Instead, the segregation is enhanced in the sense that the grains of both the superconducting phase as well as impurities increase in size as can be seen in Fig. 4.

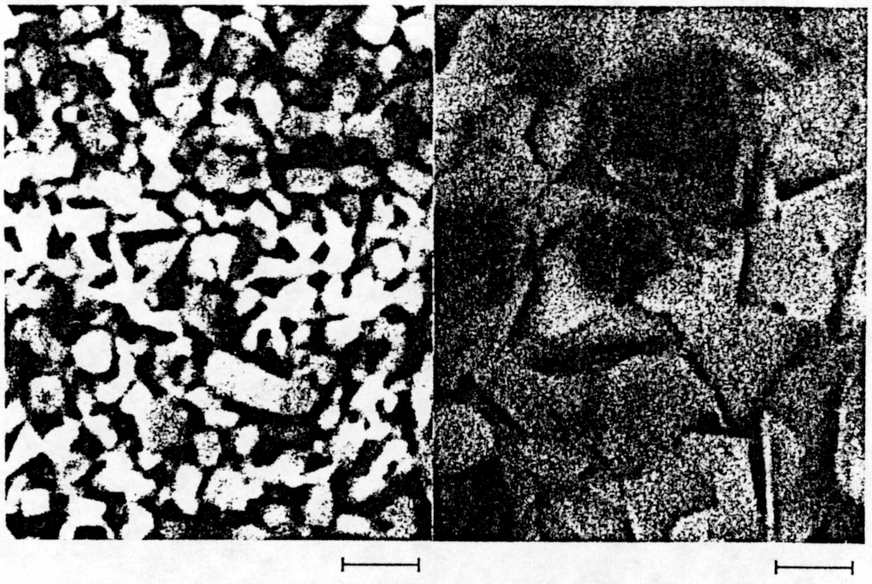

Fig. 4. Comparison of the backscattered electron images obtained with an SEM for an in-situ processed film at ~650°C, before (a) and after subsequent post-annealing at 865°C (b). The dark regions are not holes, but are Cu rich and Bi poor. The brightest regions have excess Bi.

Presumably, once segregation has occurred, films must be heated above the melting temperature to induce homogenization, as in the processing of bulk Bi-Sr-Ca-Cu-O. In one sample, however, where segregation yielded some nearly pure CaO regions large enough to be resolved in EDS, a subsequent anneal at 865°C caused the CaO regions to dissolve into the surrounding material. Except in cases where there is significant Bi loss, post-anneals have marginally improved the superconducting transitions, probably because of the increase in grain size and/or connectivity due to dissolving some of the insulating impurities.

SUMMARY

In summary, superconducting films of $Bi_2Sr_2CaCu_2O_x$ have been fabricated by a low-temperature, in-situ process with an extrapolated T_{c0} as high as 56 K. X-ray diffraction shows the film to be c-axis oriented, contain predominantly the 2212 phase with a small amount of the 2223 phase and in some in-situ films exhibit more randomly oriented grains implying a departure from the highly oriented films normally produced in the Bi-Sr-Ca-Cu-O system. A critical balance must be maintained between bismuth content and substrate temperature in order to obtain superconductivity; too low a temperature retains sufficient bismuth but produces a semiconductor, whereas too high a temperature drives bismuth out of the film and produces an insulator. More calcium in the film relative to bismuth encourages the formation of unit cells with a c-axis lattice constant similar to that found in the higher T_c 2223 phase although the T_c is similar to that of the lower T_c 2212 phase. Electron microscopy reveals that the films are not significantly smoother than films which were post-annealed at 865°C, and that some segregation into nonsuperconducting phases had occurred. The exact mechanism by which crystallization and superconductivity occurs at such low temperatures is not yet known, but it can be speculated that the surface atoms are less constrained and thus have a smaller energy barrier to overcome in forming a crystal structure.

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