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Compositional Dependence of Properties of rf-Sputtered Bi-Sr-Ca-Cu-O thin Films

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Abstract

Compositional dependence of superconducting transition temperature (T_c) of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+x}$ thin films grown by rf sputtering on single crystal MgO substrates has been investigated. Films have been assessed by considering their initial composition in terms of (Ca+Sr)/Bi ratio with their atomic concentration normalized to Cu:2. It was found that T_{c-zero} of around 80K is achievable for (Ca+Sr)/Bi ratio between 1.4 and 1.65, while $T_{c-onset}$ remains above 90K. Quenching from high temperature increased T_{c-zero}, but it may result in a deterioration in resistivity due to micro cracks induced by the thermal stress.

1. Introduction

The discovery of high T_c superconductivity in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ (BSCCO) system has stimulated great efforts owing to its high superconducting transition temperature T_c and better stability in external atmosphere when compared xith a YbaCuO superconductor. They not only have high superconducting transitions temperatures but also extremely high critical magnetic field (H_{c2}) [1]. Phases of different structures exist in this system, which can be characterized by the number of CuO planes (n=1,2 and 3) parallel to the (001) crystallographic plane and consist of BiO double layers sandwiching perovskite-type cuboids containing Sr, Ca, Cu, and O [2].

Because of its high critical current density, rapid phase formation and phase stability, n=2 (Bi-2212) phase has become one of the most promising high T_c superconductor candidates for practical high current applications. The transition temperature of Bi-2212 depends sensitively on its oxygen content which determines the charge-carrier concentration, or equivalently the nominal Cu valence. The maximum T_c requires removal of oxygen from the material [3].

Plasma sputtering technique using single composite oxide target have been widely employed and proved suitable for the fabrication of high T_c thin films [4,5]. However, chemical inhomogeneties caused by spatial inhomogeneties and instabilities of the plasma lead to the formation of lamellae of various BSCCO phases parallel to the (001) planes [6].

This paper describes the work performed in making superconducting thin films of Bi-2212 by rf magnetron sputtering technique. The superconducing properties of the high T_c superconducting Bi-Si-Ca-Cu-O compounds are a function of the chemical composition of the phases. Therefore film properties were assessed together with film composition.

2. Experimental

The target used throughout these experiment was prepared from powder of nominal composition of Bi-2212 supplied by BDH and sputtering was conducted in Ar atmosphere. The discharge was run at a rf power level of 50 watts over the 2 in. disk target. The substrates were not intentionally heated. The temperature during deposition was in the range of 110-120°C. These sputtering conditions, which include substrate to target distance of 55 mm and gas pressure 10^{-2}mbar, are called "standard deposition condition" and used throughout these experiments unless otherwise mentioned.

The as-deposited film metallic compositions were analyzed using wavelength dispersive X-ray spectroscopy (WDS) which was carried out in a Cameca Camebax electron probe microanalyzer (EPMA). The $Bi_{M\alpha}, Sr_{L\alpha}, Ca_{K\alpha}, Cu_{K\alpha}$, lines were analyzed at 15 kV accelerating voltage with an X-ray takeoff angle equal to 62°C, and using standards for the ZAF routine of pure Cu, wollastonite($CaSiO_3$), pbte(PbTe), srf(SrF) and pure Bi. A thin carbon layer was evaporated on the samples because the as deposited films were not conductive. All the analyzed films were of thicknesses greater than 1μm to ensure that the primary electron beam did not pentrate the films and generate X-rays from the substrates. The annealed films were characterized by X-ray diffraction (XRD) using a Cu target and by Scanning electron Microscopy (SEM). T_c were measured using the conventional four point contact technique with a measuring current of 100μA, and a lock-in amplifier as the voltage detector.

3. Results and discussion

3.1. Annealing temperature

Films, from the stoichiometric Bi-2212 single target under the standard sputtering conditions, as deposited on cold substrates were uniform, shiny and insulating. The composition of a typical as-deposited film was $Bi_{1.96}Sr_{1.96}Ca_1Cu_{2.4}$ (normalised here to Ca:1). clearly the composition of the films differs from that of the target in that it is rich in Cu. However, this composition was not fixed, the ratio of (Ca+Sr)/Bi being changed between 1.41 and 1.56 for the films used to study the effect of annealing temperature on the as deposited films, but they were all rich in Cu. Crystallisation of the desired superconducting phase was achieved during high temperature annealing in air. films were slowly heated a with ramping rate of 2°C/min. from bellow 500°C to the desired annealing temperature and sintered at different temperatures for more than 6 h, then slowly cooled at a rate of 2°C/min. to 600°C. Below 820°C and above 845°C Bi 2212 formed together with the Bi-2201 phase. XRD patterns of these films revealed that almost single phase Bi-2212 can be obtained in a temperature range of width of at least 25°C. However, the best textured film was obtained for the annealing temperature regions of 830-835°C with a c-axis lattice parameter of 30.22 $\mathring{A}$, and with a narrow full width at half maximum. The width of the reflections indicates the presence of faults in samples annealed above or below this temperautre region. Nevertheless, (001) reflections of the phases Bi-2201 and Bi-2212 are difficult to resolve in a $\theta/2\theta$-scan, e.g. the positions of (0010) for Bi-2212 and (008) for Bi-2201 differ by less than 0.1°.

Figure 1 shows the temperature dependence of resistivity for the samples annealed at different temperatures for longer than 6 h in air. The highest temperatures of onset and zero resistance are 96K and 82K, respectively, for the sample annealed at 830°C, which has a (Ca+Sr)/Bi ratio of 1.41 (curve b). An increase of 0.5 in the (Ca+Sr)/Bi ratio did not affect the transition temperature. ($T_{c-zero} = 82K$) while it reduces the $T_{c-onset}$ by 3K (curve c). The sample annealed at 820°C showed poor superconducting properties with a long transition tail of 50K ($T_{c-zero} = 44K$). another sample, having the same (Ca+Sr)/Bi ratio of 1.55 to that of the sample annealed at 820°C, showed zero resistance at 71K with a $T_{c-onset}$ of 92K when it was annealed at 835°C.

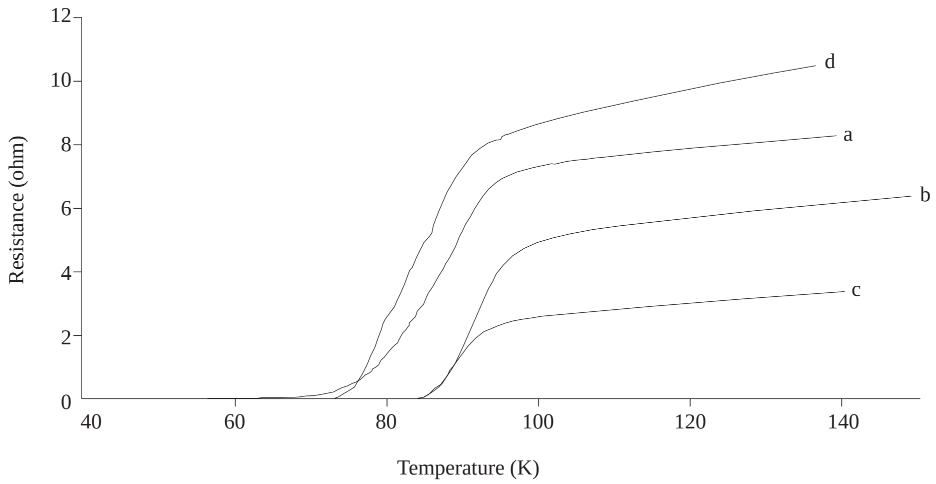

Figure 1. Temperature dependence of resistivity for samples annealed at different temperatures for longer than 6 h in air having slightly different (Ca+Sr)/Bi ratios: (a) at 820°C, (Ca+Sr)/Bi= 1.56 (b) at 830°C, (Ca+Sr)/Bi=1.41 (c) at 830°C, (Ca+Sr)/Bi=1.46 (d) at 835°C, (Ca+Sr)/Bi=1.55.

The effect of annealing temperature is clear for the later two samples having similar compositions, but it is really difficult to conclude for the first sample, which has different composition than the others, whether it is a composition effect or temperature effect. However, it is clear from resistivity curves b and c, normal state resistivity improved with increasing (Ca+Sr)/Bi ratio to the nominal value when they were annealed at 830°C.

3.2. Composition Effect

In order to understand the composition effect on T_c a series of samples having different (Ca+Sr)/Bi ratio between 1.4 and 1.65 were annealed at 830°C for more than 10 h. Figure 2 shows the T_{c-zero} and $T_{c-onset}$ dependence on (Ca+Sr)/Bi ratio. This figure suggests that T_{c-zero} of around 80Kis achievable for (Ca+Sr)/Bi ratio while $T_{c-onset}$ remains above 90K. However, T_{c-zero} is above 80K for the ratio below 1.54 while it is below 80K for higher values of the ratio. With respect to this result, the question of the low critical temperature value for the sample annealed at 835°C can be explained as a combined effect of composition and annealing temperature.

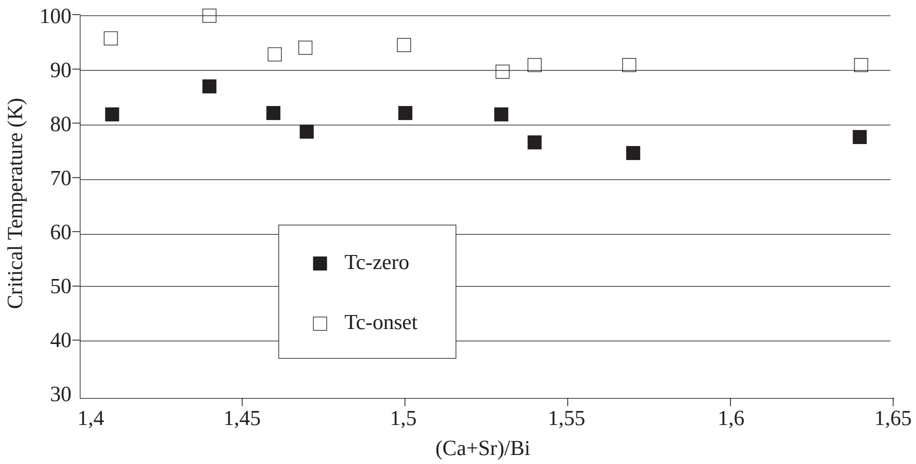

Figure 2. The dependence of critical temperatures on as deposited (Ca+Sr)/Bi ratio for samples annealed at 830°C for more than 10 h.

Figure 3 shows the resistivity dependence on temperature for samples having different (Ca+Sr)/Bi ratios annealed at 835°C for 3 h. The sample, with a high (Ca+Sr)/Bi ratio of 1.95 showed poor superconducting properties with low $T_{c-onset}$ and T_{c-zero} of 79K and 38K, respectively. The ratio of 1.59 has provided a norrow transition temperature of 10K with a T_{c-zero} temperature of 74K, supporting the above conclusion. SEM micrographs of these films showed that high (Ca+Sr)/Bi ratio resulted in a pure microstructure which is consistent with the resistivity curve. The transition curve corresponding the (Ca+Sr)/Bi ratio of 1.55 has already been described in previous section (Figure 1 curve d).

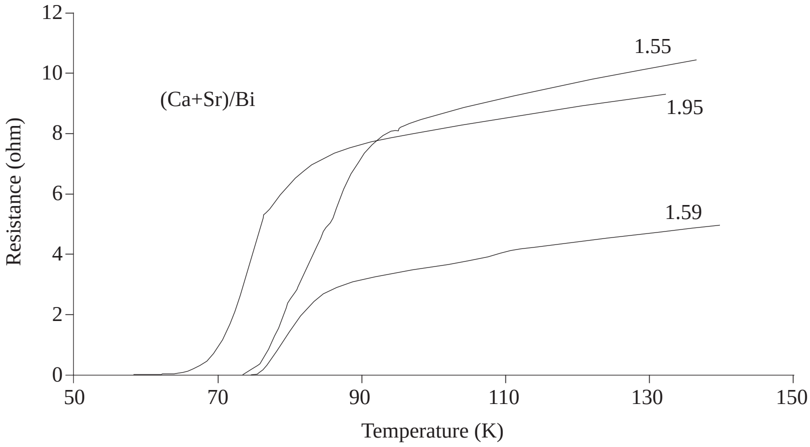

Figure 3. The temperature dependence of resistivity for samples having different (Ca+Sr)/Bi ratios annealed at 835°C for 3-6 hours in air.

3.3. The effect of quenching temperature

Two films taken from the same batch were annealed at 835°C for 6 h in air and then one of them quenched from the annealing temperature to room temperature in air. The other was cooled to 500°C with a ramping rate of 2°C/min. then air quenched. The crystal structure of the films was found to remain unaffected by quenching temperature (Figure 4). However there is a significant difference in the superconducting benaviors. T_{c-zero} and $T_{c-onset}$ for samples quenched from 835°C and 500°C are 77K, 90K and 71K, 92K, respectively (Figure 5). This variation of T_c is attributed to the oxygen content of the sample [7,8]. As samples air quenched from the annealing temperature contain less oxygen than those slowly cooled to low temperature before quenching, this result suggest that critical temperature increases with decreasing oxygen content for Bi-2212 phase [9]. However, the resistivity decreased with increasing oxygen content (the distance between voltage pick up leads was 1 cm for the low temperature quenched sample). The approximate resistivity values at $T_{c-onset}$ temperatures are 0.7 mΩ·cm and 0.2 mΩ·cm, respectively, for high and low temperature quenched samples. This result is consistent with that of Balestrino et al. [3], who reported that with increasing oxygen content both resistivity and T_c decrease.

3.4. Annealing time

The films have been annealed at 830°C for different periods of time from 10 min. to 22 h. Figure 6 shows the variation of T_{c-zero} and $T_{c-onset}$ with annealing period for some samples having (Ca+Sr)/Bi ratio between 1.41 and 1.64. It has been found that Bi-2212 films should be annealed for at least 1h to convert the Bi-2201 phase, CuO, CaO

(CaCuO) [10, 11] forming at relatively low temperature, into the Bi-2212 phase. Figure 7 shows XRD patterns of samples annealed at 830°C for 1h and 18 h. It seems from XRD patterns that prolonged annealing time can improve the structure of the film providing narrow and stronger peaks. microstructures of these films are similar with plate like grains, but the grain size of the 18 h annealed sample is almost 5 times large than that of the film annealed for 1 h.

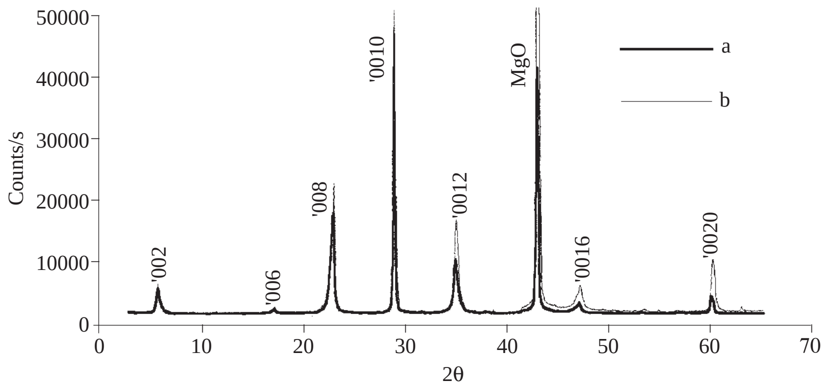

Figure 4. XRD pattern of samples annealed at 835°C for 6 h in air and quencehed from: (a) the annealing temperature (b) 500°C.

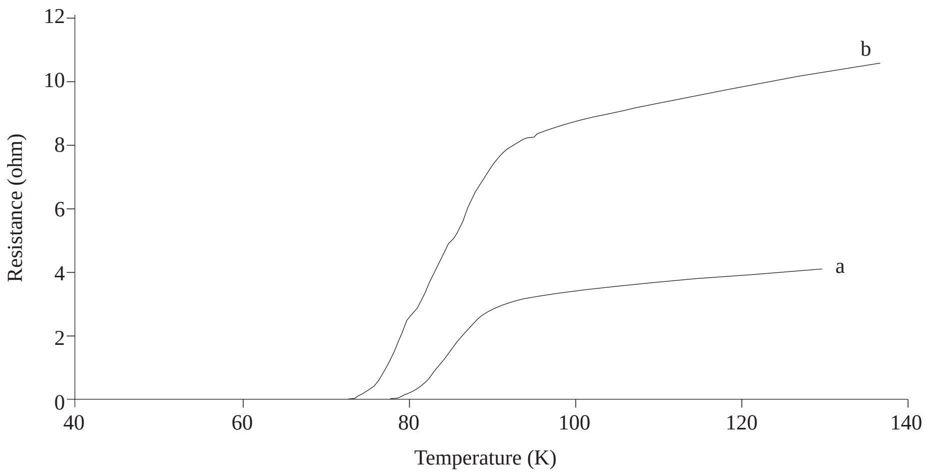

Figure 5. The temperature dependence of resistivity for the samples annealed at 835°C for 6 h in air and quenched from: (a) the annealing temperature (b) 500°C. The difference in the normal state resistance is caused principally by differences in the distances between the voltage contacts.

The temperature dependence of resistivity curves for these samples are consistent with XRD patterns and microstructure. $T_{c-onset}$ and T_{c-zero} (Figure 8) for 1h and 18h annealed films are 96K, 81K and 93K, 82K, respectively; resistivity is lower for prolonged annealing time. However, there is practically no difference between the transitions and XRD spectra of the films annealed for 10 h and 18 h.

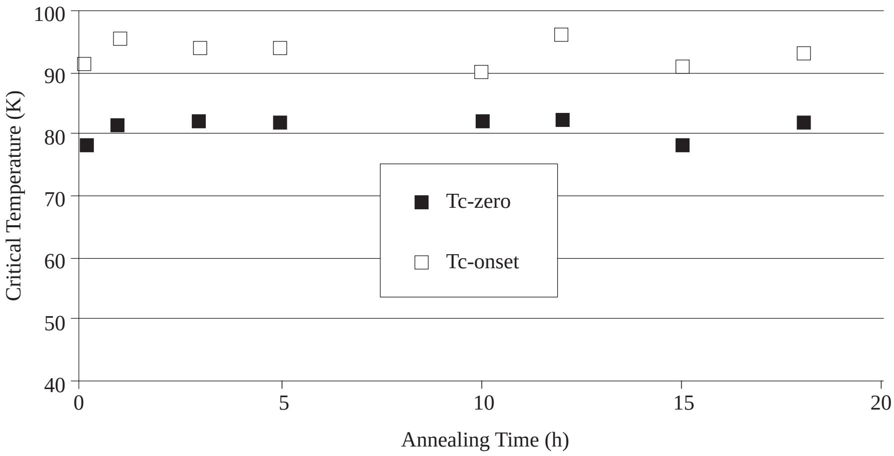

Figure 6. The dependence of critical teperature on annealing period for some samples annealed at 830°C in air.

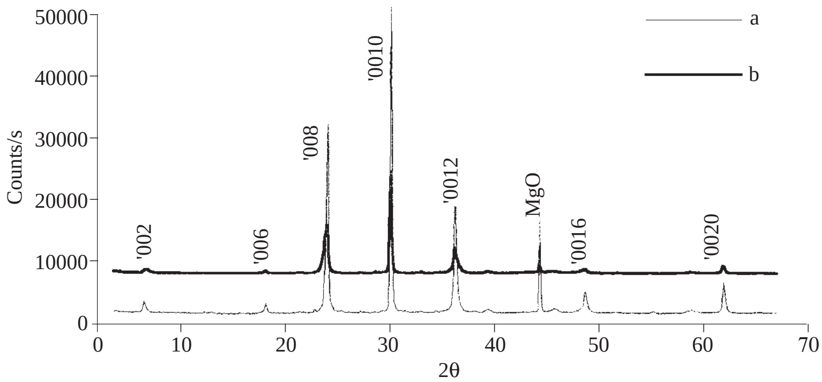

Figure 7. XRD pattern of samples annealed at 830°C in air: (a) 18 h (b) 1 h.

4. Conclusion

The investigation of optimum annealing conditions for ex-situ films such as anneaing temperature, annealing time, heating and cooling process for any high T_c material needs the same composition of the material, otherwise it will not be possible to find out a precise annealing condition which is suitable for the composition of interest. Bi-2212 thin films have been assessed by considering their initial composition in terms of (Ca+Sr)/Bi ratio with their atomic concentration normalized to Cu:2. The following conculusions can be darwn from the result of this assessment.

(1) T_{c-zero} of around 80K is achievable for (Ca+Sr)/Bi ratio between 1.4 and 1.65, while $T_{c-onset}$ remains above 90K. However, best superconducting properties can be obtained for the (Ca+Sr)/Bi ratio of 1.47, which is quite close to the nominal composition.

(2) an annealing temperature 830-835°C may provide highly oriented Bi-2212 films with the c-axis perpendicular to the substrate surface.

(3) Annealing time of 1 h may be adequate to reach a T_{c-zero} of above 80K. However, prolonged annealing for more than 10 h may improve the microstructure of Bi-2212 superconducting thin film.

(4) Quenching temperature affects the superconducting properties as it changes the oxygen content in the sample. Quenching from high temperature incerases T_{c-zero}, but it may result in a deterioration in J_c due to micro cracks induced by the thermal stress. Therefore slow cooling to or less than 700°C in reduced atmosphere may help to improve the film superconducting properties.

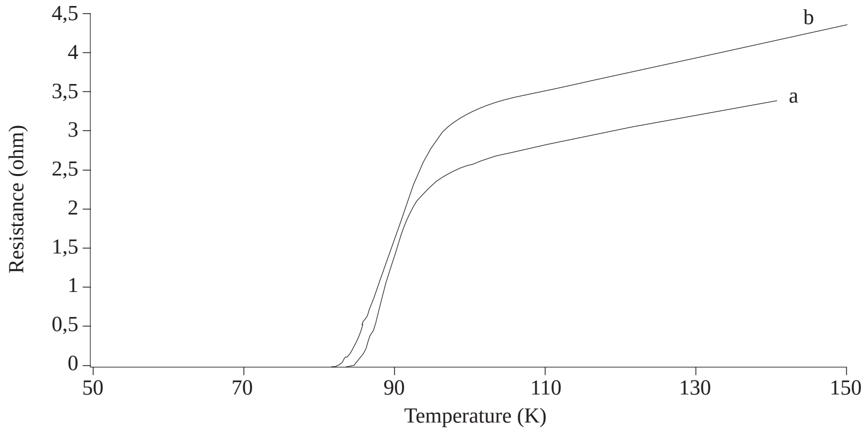

Figure 8. The temperature dependence of resistivity for samples annealed at 830°C for (a) 18 h (b) 1 h.

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