Turkish Journal of Physics

Volume 22 | Number 9 Article 6

1-1-1998

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Recommended Citation

GÜLDESTE, Ayhan (1998) "Effect of Deposition Conditions on Composition of rf-sputtered Bi-Sr-Ca-Cu-O Thin Films," *Turkish Journal of Physics*: Vol. 22: No. 9, Article 6. Available at: https://journals.tubitak.gov.tr/physics/vol22/iss9/6

Tr. J. of Physics
22 (1998) , 901 – 910.

Effect of Deposition Conditions on Composition of rf-sputtered Bi-Sr-Ca-Cu-O Thin Films

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Received 25.08.1997

Abstract

The effect of rf-magnetron sputtering conditions on as-deposited film composition using a stoichiometric $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) target was investigated in an on-axis configuration, as the stoichiometrical control of the film is the most important parameter for the proper study of film characteristics. It was found that substrate target distance up to 55-60 mm may provide a film composition close to the target composition. The sputtering chamber pressure effecting film composition, especially in respect of Bi, is an important parameter which needs very pracise control. Bi ratio in the deposited films increases with increasing Ar pressure while Sr and Ca are not much affected. After 12 hours presputtering, a target can have a steady state for long subsequent period of 60 hours or more. Target aging and increasing chamber pressure reduce the deposition rate of the film. Considerable variation of composition was not observed over large area of about 4 cm diameter circle. The peeling off of films during ex-situ annealing, even at rather low temperatures, such as below 500°C is also discussed.

1. Introduction

The development of reproducible and stable processes for homogeneous deposition of high quality and large area high T_c films is crucial for the fabrication of many superconducting devices. Since the discovery of high T_c superconductors, a great deal of effort world-wide has been put into the development of thin-film technologies. Plasma sputtering techniques have been widely employed and proved suitable for the deposition of high T_c thin films [1, 2]. It is relatively easy to stabilize the common process parameters, such as power at the cathode, substrate temperature, target-substrate distance, gas pressure etc. Even though the principle of sputtering is well understood, the main problem in the sputtering process is that in most cases it suffers from non-stoichiometric transfer of the elements from the target to the substrate. Also, spatial inhomogeneties and instabilities of the plasma lead to inhomogeneous film deposition. The difficulties apparent in the deposition of high T_c materials are related to the fact that they are complex, multicomponent materials, with a delicate sensitivity to film composition that significantly influences the electrical properties of the films.

Sputtering in a glow discharge environment is rather complicated [3]. It has been most pronounced for YBaCuO that negative oxygen ions produced in the sputtering plasma cause backsputtering effect on the substrate that attaches the growing film, depleting it of some elements (Cu, Ba) more than others [4, 5]. The same effect in Bi-Sr-Ca-Cu-O (BSCCO) for the loss of bismuth, when deposited on a hot substrate (700°C) was first reported by Grace et.al. [6]. They conclude that the oxidant, not a thermal effect, is responsible for the extreme bismuth loss. Therefore, it is known that control of the "global" parameters alone does not lead to stable and reproducible deposition [7]. One of the key issues concerning the proper study of film characteristics as a function of one growth variable is stoichiometrical control. An understanding of the influence of the growth variables on composition may lead to progress in overcoming these impediments to useful studies of BSCCO thin films.

The results presented here are an attempt to give an insight into the effect of rf-magnetron sputtering conditions on the as deposited film composition using a stoichiometric Bi-2212 target.

2. Experimental

The target used throughout these experiments was prepared from Bi-2212 powder of nominal composition supplied by BDH and sputtering was conducted in Ar atmosphere. The discharge was run at a rf power level of 50 watt over the 2 in. disk target. Rf power more than 50 watts reduces the life time of the target as the localised heating in the "race track" area destroys the initial composition of the target. The substrates were not intentionally heated to gain a near-unity sticking coefficient for all incoming particles. The temperature during deposition was in the range of 110-120°C. These sputtering conditions, including substrate to target distance of 55 mm and gas pressure 10^{-2}mbar are called "standard deposition conditions" and used throughout these experiment 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 Camebox electron probe microanalyzer (EPMA). The $\mathrm{Bi}_{M\alpha}$, $\mathrm{Sr}_{L\alpha}$, $\mathrm{Ca}_{K\alpha}$, $\mathrm{Cu}_{K\alpha}$, lines were analyzed at 15 kV accelerating voltage with a 62° X-ray takeoff angle, and using standards for the ZAF routine calling for 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 1 μm to ensure that the primary electron beam did not penetrate the films and generate X-rays at the substrates.

3. Results and Discussion

3.1. Substrate-Target Distance

In order to investigate the effect of substrate to target distance on film composition, this distance was changed between 35 and 95 mm by using a substrate holder with different lengths. The substrate holder was made from 1.5 mm thick copper plate bent into a right angle for on-axis configuration, where the substrate faces the target for maximum deposition rate. All sputtering parameters except for substrate-target distance and sputtering time have been kept constant. Sputtering time has been increased with increasing substrate-target distance to obtain approximately the same film thickness above 1 μm, since the deposition rate decreases with increasing substrate-target distance. At least two spots from representative area of each of the 5×10 mm^2 films were analysed for five samples placed on an Al disk of 40 mm diameter (Figure 1) for each substrate-target distance to provide an average film composition over ten points from the large Al disk area of 9.62 cm^2. The variation of metallic composition (normalized to Cu:2) with substrate to target distance is shown in Figure 2.

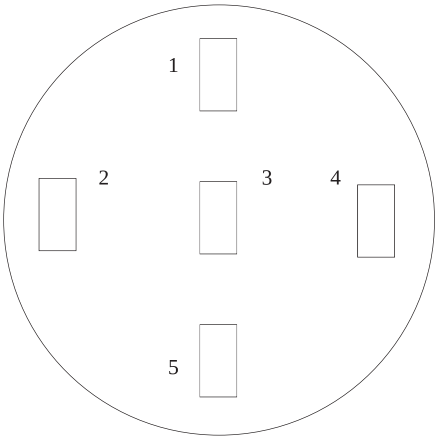


Figure 1. The position of the substrates on the Al disk holder.

As can be seen from Figure 2 for distances between 35 and 55 mm the film composition is close to the target composition; with the Ca, Sr and Bi ratios decreasing with increasing substrate-target distance above 55 mm. In this work 55 mm has been used as a near optimum substrate-target distance.

3.2. Ar Pressure

The effect of the gas pressure on the cation ratio of metallic elements has also been investigated by changing Ar gas pressure through 10^{-2} to 10^{-1}mbar. Figure 3 shows the dependence of Ca, Sr and Bi ratios (normalized to Cu:2) in films deposited at 55 mm substrate to target distance. It was found that the Bi ratio in the deposited films is very sensitive to sputtering gas pressure while Sr and Ca are not much affected. The Bi ratio of the deposited film is very close to that of the target for a pressure of 10^{-2}mbar, increasing with increasing Ar pressure. Therefore 10^{-2}mbar was used as an optimum pressure value providing a film composition which is very close to the target composition.

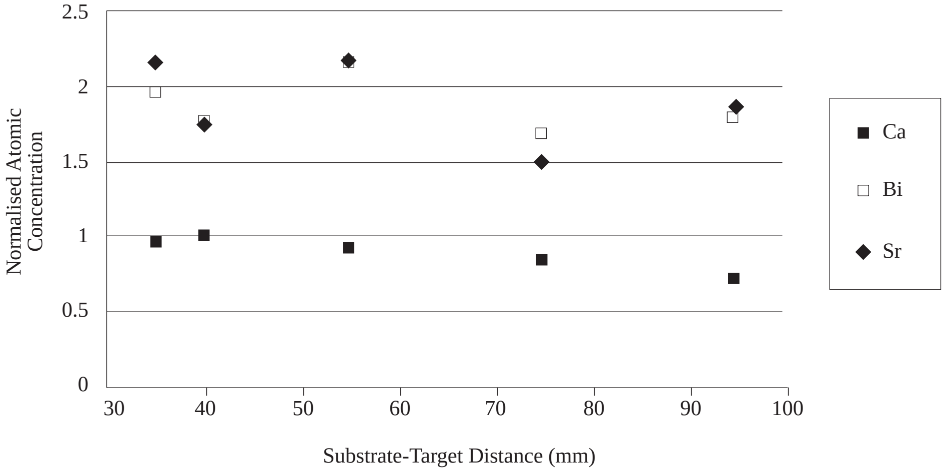


Figure 2. The variation of film composition deposited from the Bi-2212 target of nominal composition, with substrate to target distance.

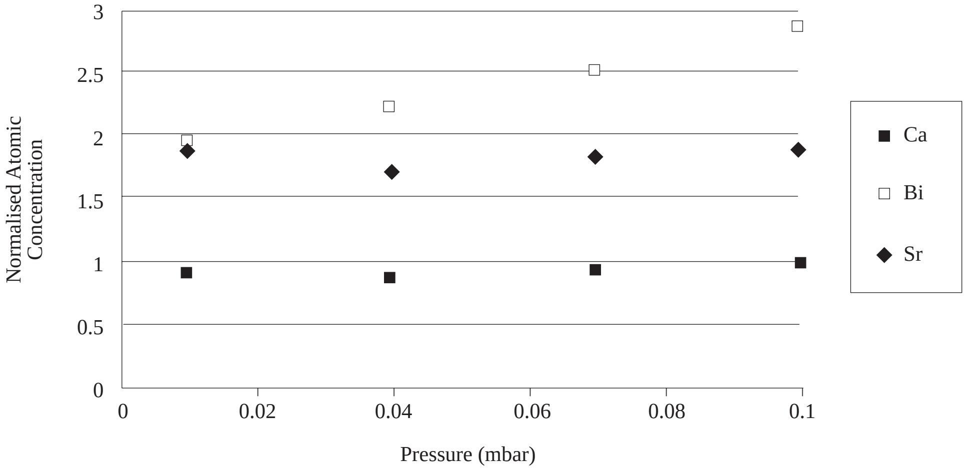


Figure 3. The dependence of as-deposited film composition on the sputtering chamber gas pressure for the target of nominal Bi-2212 composition.

3.3. Target Aging

The effect of time of target use on film composition was investigated over 72 hours. Before deposition a newly prepared target was presputtered for 15 minutes. For this experiment, one film, placed at the same position on the substrate holder for each run, was kept for metallic composition analysis. All films used for this purpose were deposited under the same sputtering conditions. At least two spots from representative areas of each film were analysed to provide the average film composition. Figure 4 shows the dependence of the metallic composition of films on the age of the target. This figure shows that over approximately 12 hours sputtering the Sr and Bi ratio in the deposited film decreases and becomes almost stable over a long period of 60 h. Therefore it is suggested that presputtering of a newly prepared target for at least 12 h is required to reach a steady state condition. Oxygen out-diffusion from the target surface, aided by ion impingement, is believed to be responsible for causing changes in the target and therefore a compositional variation of the sputtered films under the pure Ar atmosphere as the sputtering time increases. Introduction of oxygen into the vacuum chamber at a level of no less than 1.3×10^{-3}mbar might be an alternative to long presputtering [8].

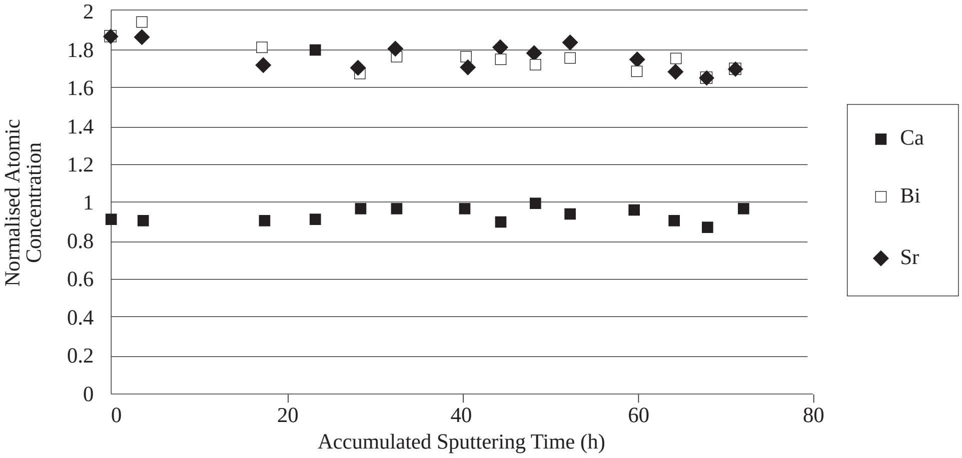


Figure 4. The dependence of as-deposited film composition on target aging.

3.4. Deposition Rate

The effective parameters on the deposition rate are substrate to target distance, rf power, sputtering gas pressure and, specially for multicomponent high T_c superconductors, the aging of the target. The effect of the first two parameters is well known, being that deposition rate increases with decreasing substrate to target distance and increasing rf power. The effect of target aging on the deposition rate of over 60 h accumulated sputtering time and gas pressure for a narrow pressure range around 10^{-1}mbar were investigated in this study and it was found that with increasing gas pressure and aging of the target the deposition rate gradually decreased. The deposition rate of Bi-2212 films as a function of accumulated sputtering time and gas pressure is given in Figure 5 and 6, respectively.

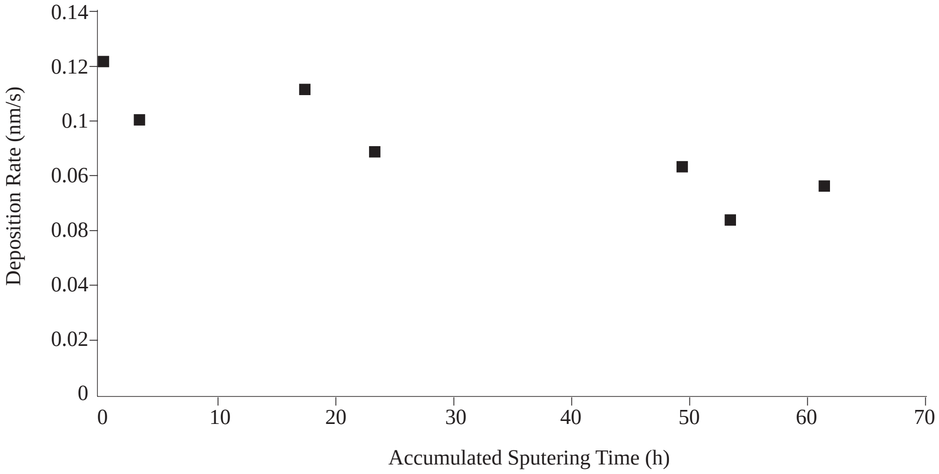


Figure 5. The dependence of deposition rate on accumulated sputtering time.

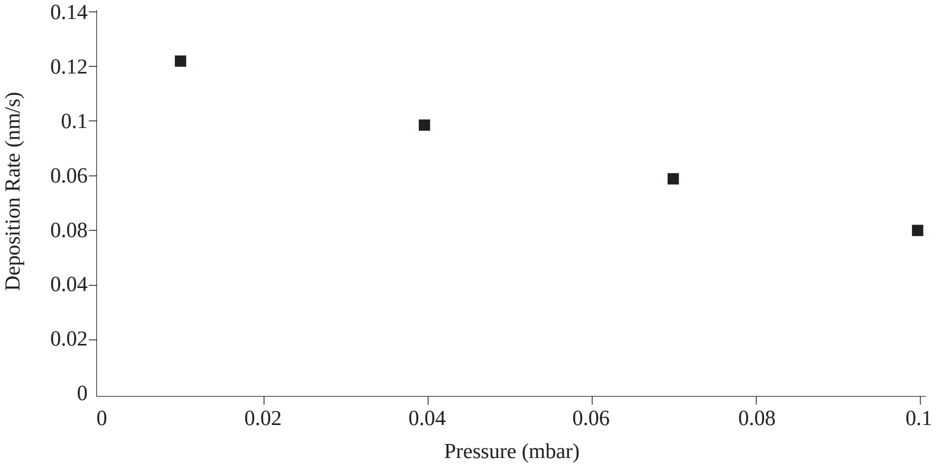


Figure 6. The dependence of deposition rate on sputtering chamber gas pressure.

3.5. The Variation of Composition Over the Large Area

To investigate the variation of composition, substrates were widly placed over an aluminum disk of 40 mm diameter, in the positions shown in Figure 1. The distance between the center of the outer substrates and the center of the disk is 1.5 cm. The analysis from two points for each position was taken. The variation of the atomic concentration of metallic cations with substrate position for a substrate target distance of 55 mm is shown in Figure 7. This result revealed that there is no significant change of film composition from position to position in the range studied.

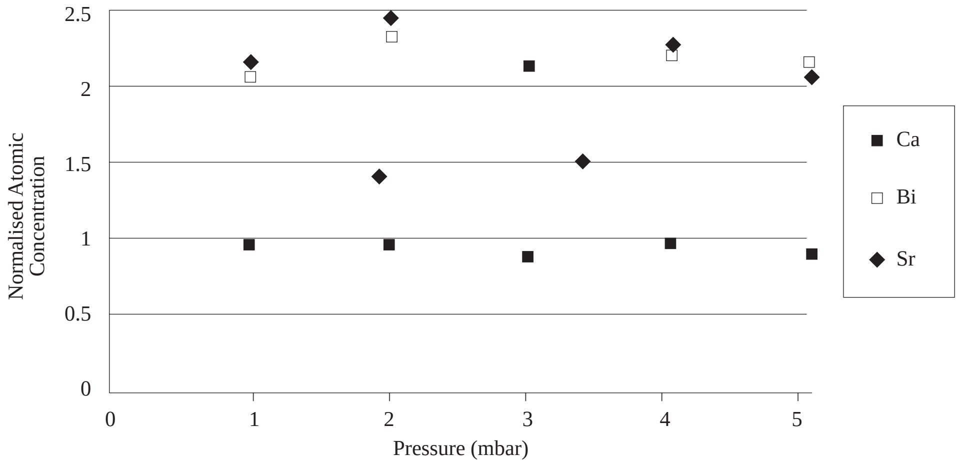
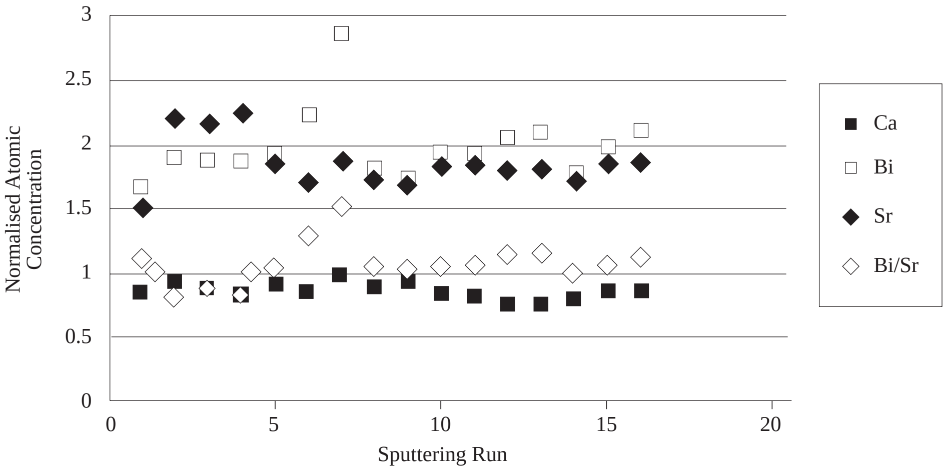


Figure 7. The variation of as-deposited film composition with respect to film position as shown in Figure 1.

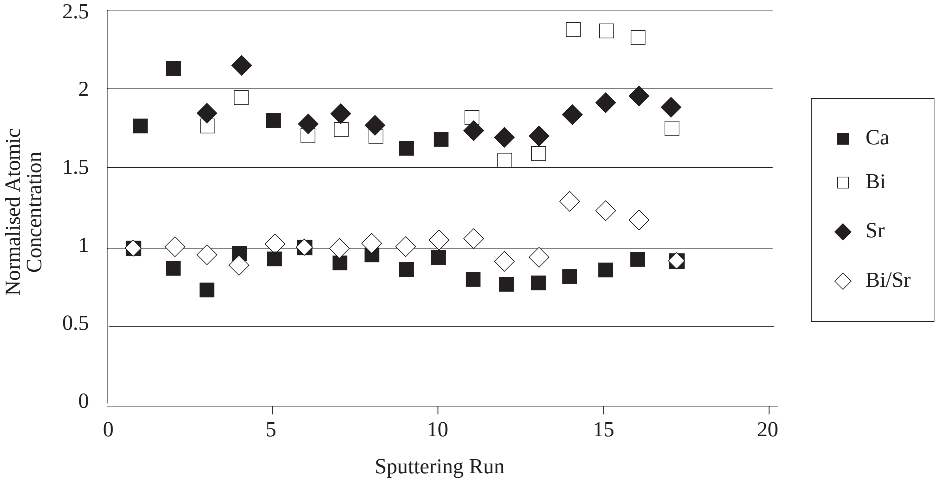
3.6. Peeling off of Thin Films

The main difficulty encountered in growing thin film by this process was the peeling off of films during ex-situ annealing, even at rather low temperatures, such as below 500°C. Initially, several reasons for the peeling off were considered, such as: (1) substrates not chemically well enough cleaned, (2) heating rate, (3) starting temperature of annealing, (4) film thickness and finally (5) thermal expansion between substrate and deposited film due to wrong composition of films.

In order to clean the polished substrates chemically they were washed first in acetone then in de-ionized (DI) water with ultrasonic vibration before loading into the furnace for high temperature annealing at above 1000°C. Substrates cleaned in this way were placed in the chamber without touching their surfaces. The as-deposited film thickness was less than 1 μm with a light brown color. The annealing process has been started from room temperature with a ramping rate of 1°C/minute. But again, films sometimes completely and sometimes partly peeled off from substrates above 400°C. Keeping this routine process the study has been focused on the thermal expansion mismatch between film and substrate due to wrong composition of the film. All films which had not peeled off, or which had partly stayed on the substrate, had the XRD pattern of the phase of interest when they were annealed at a suitable temperature.



(a)



(b)

Figure 8. During high temperature annealing process (a) Peeled off (b) Not peeled off as-deposited film composition.

To investigate the composition effect on the peeling off mechanism, EPMA analysis has been done for a film taken from each batch from the same position on the substrate holder. Figure 8a shows the ratio of atomic cations (Bi, Sr and Ca normalized to Cu:2) for the peeled off films. This figure also shows the Bi/Sr ratio. It can be seen from the figure that apart from runs 2-4, which have a Bi/Sr ratio less than 0.9, all the others have Bi rich composition. On the other hand, apart from runs 14-16, the Bi/Sr ratio is above 0.9 and not more than 1 for unpeeled films (Figure 8b). This analysis suggests that the peeling off mechanism may be related to the Bi/Sr ratio; if it is less than 0.9 or above 1 peeling off of the film during high temperature annealing may occur. However, the question of why when the Bi/Sr ratio is too high (runs 14-16, Figure 8b) or too low (not on the figure) the film did not peel off, is still open.

4. Conclusion

The composition of as-deposited Bi-2212 thin films has been investigated as a function of the rf magnetron sputtering variables, i.e. substrate to target distance, total sputtering gas pressure and aging of the target, in an on-axis configuration. Substrate-target distance greater than 60 mm resulted in a film composition considerably deviated from the target composition. However, it is not critical between 35-55 mm, giving a film composition close to target composition. It has been found that after 12 hours presputtering a target can have a steady state for a long subsequent period of 60 hours or over for an rf-power of 50 watt. Sputtering chamber Ar gas pressure has a strong effect on the Bi ratio of the as-deposited film composition, while other metallic cations, Sr and Ca are not much affected by chamber pressure. Bi ratio in the as-deposited film composition increases with increasing gas pressure in the chamber. Ar gas pressure of around 10^{-2}mbar was found to be suitable in our system but it is difficult to control precisely due to the spatial inhomogeneties and instabilities of the plasma. An homogeneous film composition at least over an area of a 4 cm diameter circle, which is the maximum area studied in this study, can be obtained.

The peeling off mechanism for ex-situ annealed thin films was investigated and found that the main reason is wrong composition within certain limits. Bi/Sr ratio should be kept between 0.9-1 (which is also essential for stoichiometry) to prevent the peeling off in as-deposited Bi-2212 thin films during the high temperature annealing process. For some extreme values of Bi/Sr ratio (too high or too low) the film may stay on the substrate. However as expected, this unstoichiometric composition does not allow good superconducting properties.

Acknowledgements

Financial support from Erciyes University (Turkey) is gratefully acknowledged. The author would like to thank to Prof. M.J. Goringe for his constant advice, Mr. C. Salter for the EPMA measurements and Prof. Sir Peter Hirsch for the provision of laboratory facilities at the Materials Department of Oxford University.

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