Rutherford Backscattering analysis of Bi-based superconducting films

J.C. Cheang-Wong
Instituto de Física, UNAM, A.P. 20-364, México 01000 D.F., México.

E. Díaz-Valdés
Escuela Superior de Física y Matemáticas-IPN, Edif. 9 UPALM, México 07738 D.F., México.

M. Jergel, A. Morales
Departamento de Física, CINVESTAV-IPN, A.P. 14-740, México 07000 D.F., México.

R. Vargas
Escuela Superior de Ingeniería Química e Industrias Extractivas-IPN, Edif. 7 UPALM, México 07738 D.F., México.

The elemental composition, film thickness and concentration depth profiles of precursor and superconducting (Bi,Pb)-Sr-Ca-Cu-O films were studied by the Rutherford Backscattering Spectrometry (RBS) technique. The precursor films were deposited on MgO single-crystalline substrates from an aerosol atomized ultrasonically from an aqueous nitrate solution. Precursor films, about 5 to 5.5 μm thick, were then annealed in air at temperatures ranging from 835ºC to 855ºC during 10 h. XRD studies revealed mainly the presence of the 2212 phase (for bulk T_c is about 85 K). Films annealed at temperatures $T_a \geq 850$ºC were superconducting with T_c in the range of 60 to 71 K, showing a double T_c onset at 85 K and 110 K. The RBS study of the Bi-profile of precursors showed a maximum content of Bi at a depth around 1 to 2 μm from the film surface. After the film annealing, the Bi content was found to be constant from the surface to about 1 μm depth, decreasing then its value towards the film-substrate interface.

Keywords: Superconductors, Bi-based thin films, Rutherford Backscattering, spray pyrolysis.

1. Introduction

Ion Beam Analysis (IBA) techniques, such as Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA), have been largely used to study the composition and microstructure of HT_c superconducting thin films [1,2]. In particular, we have used recently RBS to determine the elemental composition and concentration depth profiles of Tl-based superconducting films prepared by spray pyrolysis [3,4]. In the present paper we study the basic properties of a series of Bi-based films deposited on MgO single-crystalline substrates from an aerosol atomized ultrasonically from an aqueous nitrate solution. Actually, the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$/Ag composite tapes belong currently to the most promising HT_c superconductors for large-scale applications, namely for energy transmission devices [5,6].

In particular, Pb doping in Bi-Sr-Ca-Cu-O superconductors has been widely reported to promote formation of the $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) phase [7]. On the other hand, it was found that the Bi concentration is often non-uniform (less in the surface). However, in our case, for films having a uniform Bi concentration no clear improvement of T_c was reached.

The purpose of the present paper is to report on results of an investigation of Bi-concentration depth profiles of Bi-based superconducting films by means of the RBS method. Results of this investigation will be correlated with the film superconducting properties.

2. Experimental

A series of superconducting Bi-based films (Bi-Pb-Sr-Ca-Cu-O) were prepared by spray pyrolysis according to the 2-step procedure described in detail elsewhere [8]. First, an aerosol atomized ultrasonically from an aqueous nitrate solution of the Bi, Pb, Sr, Ca and Cu components (with a cation ratio 2:0.6:2:2:3) was sprayed for 5 minutes onto single-crystalline MgO substrates heated to 250°C. Three to five of such cycles were applied, leading to a total film thickness of about 5-5.5 μm. These Bi-Pb-Sr-Ca-Cu-O as-deposited precursor films were then annealed in air at temperatures ranging from 835 to 855°C for 10 h to become superconducting. Under these conditions, the complete decomposition of nitrates and an improvement of the chemical homogeneity of the synthesized films take place.

The superconducting state of the samples was detected by the critical temperature T_c value measurements, the microstructure, the chemical composition and the phase identification. The resistivity was measured by using the standard four-point resistive method with the 1 μV/cm criteria. The X-ray diffraction patterns and the phase composition were examined with the CuK_α radiation using a D-500 Siemens diffractometer in the standard Bragg-Brentano (θ-2θ) geometry. The RBS measurements were carried out using the Instituto de Física 3 MV accelerator (NEC 9SDH-2 Pelletron).

Thus, we determined not only the elemental composition of the samples, but also the concentration depth profiles of the constituent atoms [1,9]. In the present work we used a 3.1 MeV $^4He^+$ beam to obtain the composition of both precursor and superconducting films. The concentration depth profiles were obtained by fitting the experimental spectra using the RUMP simulation program [10].

3. Results and discussion

The resistivity measurements were performed by the standard four-point method on Bi-based films annealed in air at five different temperatures (835, 840, 845, 850 and 855°C). All the films were superconductors, except the one annealed at 835°C. Fig. 1 shows the curves corresponding to the films annealed at 850 and 855°C. The main feature of resistivity curves of the superconducting films is the presence of a double T_c onset at 85 K and 110 K, which indicate the coexistence of two different Bi-based superconducting phases in the samples. Moreover, the critical temperature T_c(R=0) seems to depend mainly on the annealing temperature T_a Indeed, while the best T_c's, in the range of 60 to 71 K, were obtained for the films annealed at $T_a \geq 850$ºC, no superconducting properties could be observed for films annealed at $T_a \leq 835$ºC.

The X-ray diffraction pattern of the film annealed at 855°C, giving the highest T_c, may be seen in Fig. 2. The main diffraction lines assigned to the $Bi_2Sr_2Ca_1Cu_2O_8$ (Bi-2212) phase are indicated. However, it must be stressed that we are using the Bragg-Brentano configuration, and hence only diffractions from the planes parallel to the film surface can be observed. Therefore, other minor phases can be present, such as the Bi-2223, in agreement with the presence of a double T_c onset at 85 K and 110 K in the resistivity curves.

The tail observed in these curves may be due to the presence of the Bi-2201 phase, whose assigned lines are indicated in the diffraction pattern, since their intensities decrease with the increment of T_c, thus showing its influence. On the other hand, it is important to notice that the crystallographic phase composition and the elemental chemical composition may differ from each other, sometimes even substantially, as confirmed in our previous experiments [3].

The sample composition as well as the concentration depth profiles of the constituent elements were determined from the RBS measurements. Fig. 3 shows the RBS spectra obtained with a 3.1 MeV $^4He^+$ beam from two superconducting films annealed during 10 hours at 850°C (T_c = 59 K) and at 845°C ($T_c \approx 58$ K). The RBS results show that the superconducting films mainly have a $(Bi,Pb)_XSr_{1.4}Ca_1Cu_{1.5}O_{8+\delta}$ chemical composition, with x varying from $x = 2$ at the surface region and then decreasing with depth.

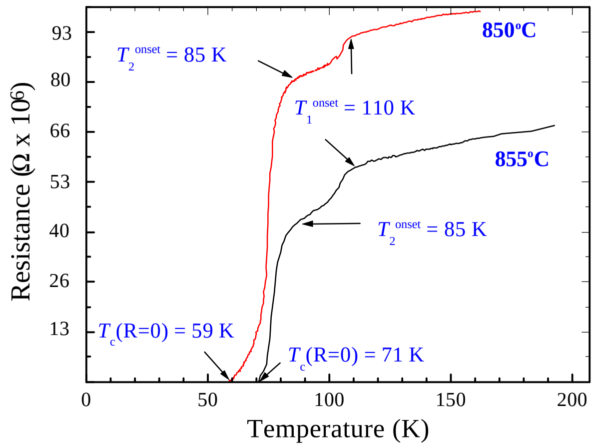

Fig. 1.Resistivity *vs* temperature curves corresponding to the Bi-based superconducting films annealed in air at 850 and 855°C.

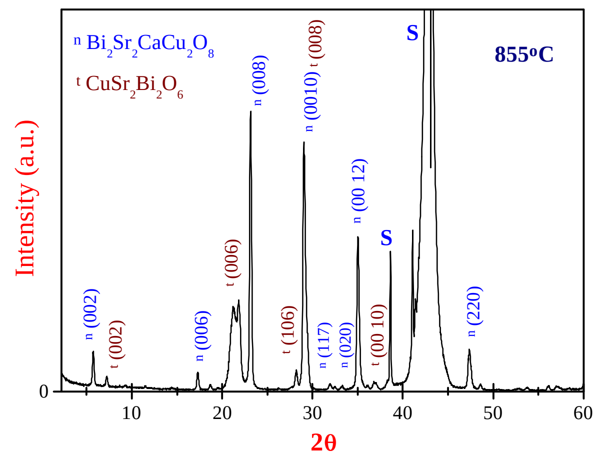

Fig. 2. XRD pattern of the Bi-based superconducting film annealed at 855°C. The identified diffraction peaks for the Bi-2212 (*n*) and Bi-2201 (*t*) phases are indicated, as well as for the MgO substrate (S).

At this point, it is important to stress that with RBS we can not accomplish the accurate determination of the Bi and Pb concentrations independently, because the contribution of Bi and Pb atoms to the RBS spectrum can not be distinguished from each other. However, recent studies concerning the effect of Pb in Bi-based superconductors demonstrate that Pb doping promote not only the formation of the $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ phase [11], but does not affect the critical temperature [12]. Therefore, for convenience, the $(Bi,Pb)_X$ concentration will be referred to here after just as the Bi concentration. In order to accomplish the best RBS simulation for all the Bi-based films we assumed that the ratio of the Sr, Ca, Cu and O constituents does not change as a function of depth, i.e., Sr:Ca:Cu:O = 1.4:1:1.5:8, but only the Bi concentration does.This assumption is sustained on the fact that calcium and/or bismuth are the most likely diffusing

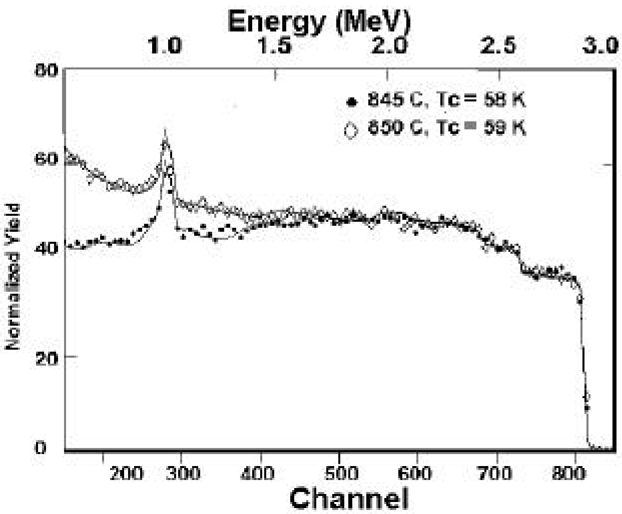

Fig. 3. 3.1 MeV $^4He^+$ RBS spectra obtained from two Bi-based superconducting films annealed at 850°C (T_c = 59 K) and at 845°C ($T_c \approx$ 58 K). The solid line represents the RUMP simulation.

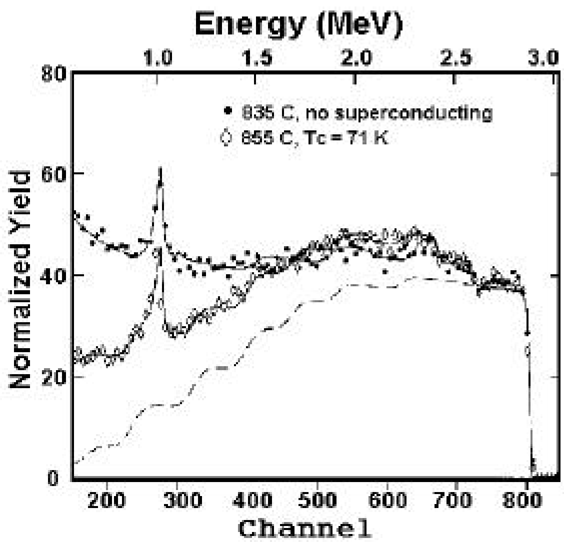

Fig. 4. 3.1 MeV $^4He^+$ RBS spectra obtained from a superconducting film annealed at 855°C (the highest T_c = 71 K) and from a Bi-based film annealed at 835°C (not superconducting). The RUMP simulation is included (——), together with the contribution of Bi atoms to the RBS spectrum of the superconducting film (----).

species in Bi-based films [13]. Moreover, the effect of a small change in Bi content has more significance on the RBS simulated spectrum than a similar or larger deviation in Ca content does, because the contribution of each element to the RBS spectrum depends on the square of the atomic number. According to the RUMP simulation (Fig. 3), the film annealed at 850°C exhibits the most homogeneous Bi concentration as a function of depth compared with the other studied samples. However, its critical temperature T_c is essentially the same that those of the film annealed at 845°C

Therefore, it seems that the behavior of the Bi-concentration depth profiles does not affect significantly the T_c. Actually, the Bi concentration is often non-uniform in Bi-based film, but for films having a uniform Bi concentration no clear improvement of T_c was attained [14].

We would like to insist on this fact by showing in Fig. 4 the RBS spectra obtained from a superconducting film annealed at 855°C (with the highest T_c = 71 K) and from a Bi-based film annealed at 835°C (not superconducting). It is clear that a more uniform Bi-concentration profile is observed for the non-superconducting film. The dashed line in Fig. 4 represents the contribution of Bi atoms to the RBS spectrum of the superconducting film.

Moreover, we investigated the content and depth profiles of bismuth for samples annealed at different temperatures, up to the depth of 5-6 μm from the film surface, using the 3.1 MeV $^4He^+$ RBS spectra. Fig. 5 shows the Bi-concentration depth profiles of the superconducting Bi-based films annealed at different temperatures, and no evident dependence of the physical properties, mainly T_c, on the Bi-concentration profiles can be asserted. Indeed, the Bi content of all the Bi-based superconductors was found to be constant ($Bi_{X=2}$) from the film surface up to a depth of about 3 μm, where the Bi-concentration depth profiles decreased towards the film-substrate interface.

In order to study the effect of the annealing of the precursor films on the Bi-concentration profiles, RBS measurements were performed on Bi-based films before and after the annealing. Fig. 6 shows the Bi-concentration depth profiles of a Bi-based film before (not superconducting) and after an annealing at 855°C (T_c = 71 K). Before annealing, the Bi-profile presents a rounding shape with a maximum Bi content at around 1 μm from the film surface and a plateau in the region 2-4 μm. Moreover, the main feature observed on precursor films is a lacking of Bi atoms at the surface region (from the film surface up to ~ 1 μm). This Bi deficiency is overcome after the annealing treatment in air at different temperatures. Indeed, after the annealing, the Bi content is constant from the film surface up to a depth of about 2 μm, and then it decreases towards the film-substrate interface (see Fig. 5).

From the results shown in Fig. 1 and Fig. 2 we may observe that the highest T_c values and the best crystallographic orientations of Bi-based films are obtained after relatively high annealing temperatures $T_a \geq$ 850ºC.

Also, from the point of view of the Bi content, there is a well defined plateau up to about 2 μm from the film surface, giving apparently a relatively optimum Bi content ($Bi_{X=2}$) in the depth profile of superconducting films. From the presented results it seems that a correlation exists between the annealing temperature T_a and the critical temperature T_c(R=0), and that $T_a \geq$ 850ºC are required for synthesize Bi-based films with good

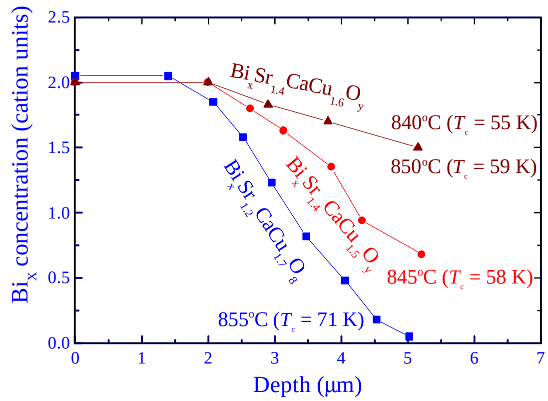

Fig. 5. Bi-concentration depth profiles of the superconducting Bi-based films annealed at different temperatures. Profiles were obtained from the RUMP simulation of the 3.1 MeV $^{4}He^{+}$ RBS spectra.

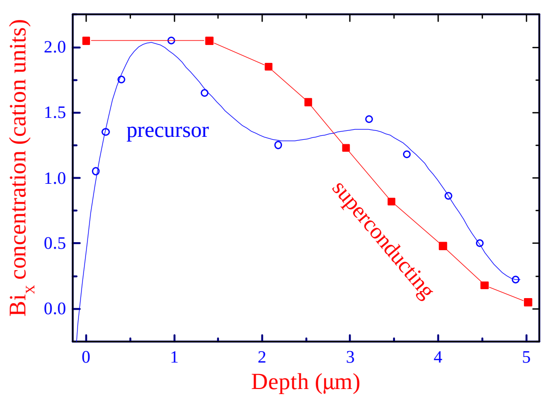

Fig. 6. Bi-concentration depth profiles of a Bi-based film before (not superconducting) and after an annealing at 855°C (T_c = 71 K).

superconducting and microstructural properties. However, at the moment we can not establish a clear relationship between the Bi-concentration depth profiles and the physical properties of Bi-based superconducting films. The only evidence we have is that good superconducting films are obtained, after annealing, when the Bi content seems to approach its stoichiometric value ($Bi_{X=2}$) at the near-surface region.

4. Conclusion

By means of RBS measurements we have determined the elemental composition and the concentration depth profiles of Bi-based superconducting films. By investigating also the reference precursor films we conclude that the Bi concentration varies as a function of depth and depends on the annealing temperature. Before the annealing, the Bi-concentration depth profiles showed a maximum at around 1 µm from the film surface, but there is a clear Bi deficiency at the surface region.

As a consequence of annealing, the mobility of Bi atoms in the film increases and therefore a uniform Bi content up to about 2 µm from the film surface is obtained, giving apparently a relatively optimum Bi content ($Bi_{X=2}$) in the depth profile of superconducting films.

Acknowledgments

The authors acknowledge K. López and F.J. Jaimes for accelerator operation, Dr. Matej Jergel for his helping in XRD measurements and the technical assistance on films deposition of J. García-Coronel. This work was supported by CONACyT under contracts G0010-E and F036-E9109.

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