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Characterization of magnetron sputter deposited YBCO thin films by Rutherford backscattering spectrometry

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Abstract : Rutherford Backscattering spectrometry (RBS) has been employed to study the composition, thickness and inter-diffusion of high-T_c superconducting YBCO thin films prepared by the dc magnetron sputtering technique. The effect of various experimental parameters such as sputtering power, gas pressure, nature of substrate, buffer layer (on the reactive substrate) and spatial position of the substrate on the composition, thickness and superconducting properties of the YBCO films have been studied and correlated. RBS has also been used to investigate the inter-diffusion of film and substrate elements.

Keywords : YBCO Thin Films, RBS

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1. Introduction

Although extensive efforts have been going on in the synthesis of oriented thin films of high-T_c Perovskite materials, the effect of experimental parameters and the nature of substrate on the superconducting properties of the films are still of interest [1–4]. $SrTiO_3$ has a smaller lattice mismatch with YBCO as compared to MgO substrate. However, the dielectric constant of $SrTiO_3$ is largest among all the substrates being used currently for the deposition of YBCO thin films. Microwave devices such as resonators, delay lines and filters exhibit superior performance on low dielectric constant substrates such as α-Al_2O_3, but it reacts with YBCO material. On the other hand, MgO is relatively inexpensive, offers high mechanical strength and has demonstrated heteroepitaxy, and high-T_c films deposited on it show excellent superconducting properties [5].

Among the various film deposition techniques currently being used for the deposition of YBCO films, the high pressure dc magnetron sputtering technique offers a clear advantage due to its simplicity and fast deposition rate. High quality YBCO thin films are obtained only, when the key experimental parameters in the sputtering process are optimized. Also, the superconducting and structural properties have been found to be quite sensitive to the composition of the Perovskite thin films.

The Rutherford backscattering spectrometry (RBS) is a very useful non-destructive technique for elemental analysis as well as film-substrate inter-diffusion. In this paper, we report the results of RBS studies on Y-Ba-Cu-O thin films prepared *in-situ* on various substrates by the dc magnetron sputtering technique under various experimental conditions. The composition, thickness and diffusion coefficient have been obtained from the RBS studies and has been correlated with the superconducting properties of the films. We have studied the effects of sputtering power, gas pressure, nature of the substrate and effect of a buffer layer on the composition of the YBCO thin films deposited on various substrates. The spatial homogeneity of the thin films deposited by the sputtering process has also been studied. We have investigated the effect of long time sputtering (of the order of 40 hours) on the composition of the sputtering target which is crucial for the reliability of the sputtering process.

2. Principles of composition analysis by RBS

The RBS technique is very useful for the characterization of thin solid films. The various types of possible analysis include identification of elements, composition, thickness and depth profiles of thin solid films. The technique is based on the interaction of incident monoenergetic ions with the films. Most of the ions lose their momentum by collisions with target atoms (thin film and substrate), and finally stop at a certain depth below the surface depending upon energy of the ions. During the interaction with target, a small portion of incident ions comes close to target nuclei and gets backscattered. These backscattered ions are collected and their energies are analyzed to carry out the composition analysis'of the thin films.

The mass analysis of different atoms by RBS is based on the principal of conservation of energy and momentum in a two body elastic collision process. The energies of the ions backscattered from target nuclei contain the signature of the different types of atoms in the target and hence, masses of different elements can be sorted out and recognised. The scattering probability is proportional to the square of the atomic number of the element. The composition of the thin film is then obtained from the observed peak areas. The determination of the composition of the thin film as a function of depth or thickness is possible because of the energy loss of the ions passing through the thin film. The energy width of the backscattering signal provides the thickness of the film.

3. Experimental

The YBCO films were prepared by the dc magnetron sputtering technique. The thin films were deposited on various substrates using a single stoichiometric target of $Y_1Ba_2Cu_3O_{7-x}$ in an mixture of argon and oxygen in the ratio of 2 : 1 (partial pressures). The experimental details of the film preparation are discussed elsewhere [6].

Several sets of samples were prepared by varying one of the following parameters, namely sputtering power, gas pressure (P), substrate temperature (T), buffer layer, substrate material and spatial position of the substrate. We have also studied the effect of long time sputtering (of the order of 40 hours) on the composition of the sputtering target which is crucial for the reliability of sputtering process. The details of the samples are described in Table 1.

Table 1. Details of samples.

Sample set	Fixed parameters	Variable parameters
Set 1	Substrate : MgO, d = 30 mm P = 800 mTorr, T = 730°C	Sputtering power or, gas pressure
Set 2	P = 800 mTorr, T = 730°C, d = 30 mm	Buffer layer on α-Al_2O_3 and substrate material
Set 3	P = 800 mTorr, T = 730°C, d = 30 mm	Spatial position of substrate
Set 4	–	Fresh or sputtered target

The depth *versus* concentration profiles of the YBCO films have been determined by the use of the RBS technique [7]. The RBS measurements were carried out using a 1.6 MeV $^4He^+$ beam obtained from a 2 MeV Van-de-Graaff accelerator. A beam current of ≈ 8–10 nA was used and the $^4He^+$ ions were detected at a scattering angle of 150° with the incident beam. The RBS spectra were analyzed using the RUMP code [8]. This simulation program requires as input the experimental parameters, sample configuration and composition. The simulated spectrum is then compared with the experimental spectrum and the parameters readjusted. The simulation is repeated until a sample configuration giving the best fit is obtained. In order to study the diffusion of the film material into the substrate, the program allows the use of various solutions of the diffusion equations in the simulation. In the present study, the YBCO film thickness is large as compared to the diffusion length, hence the error function (erfc) solution [9] of the diffusion equation has been utilized, *i.e.*,

$$C(x,t) = C_0/2 \ \mathrm{erfc}\left[x/(4Dt)^{1/2}\right],$$

where x is the distance, t the diffusion time, C_0 the initial concentration and D the diffusion constant.

4. Results and discussion

The sputtering process requires the optimization of various interdependent experimental parameters such as sputtering power and gas pressure. These parameters have varying effects on the composition and superconducting properties of the thin films. We have studied the effect of an independent variation of each of these parameters on the superconducting properties of the films.

4.1. *Effect of sputtering power and gas pressure :*

Figure 1(a) shows a typical RBS spectrum of a YBCO thin film (set 1) deposited on a (100) MgO substrate at a sputtering power of 40 W. The backscattered signal from the heaviest element barium with atomic number 56, appears at the energy of 1.55 MeV (surface edge).

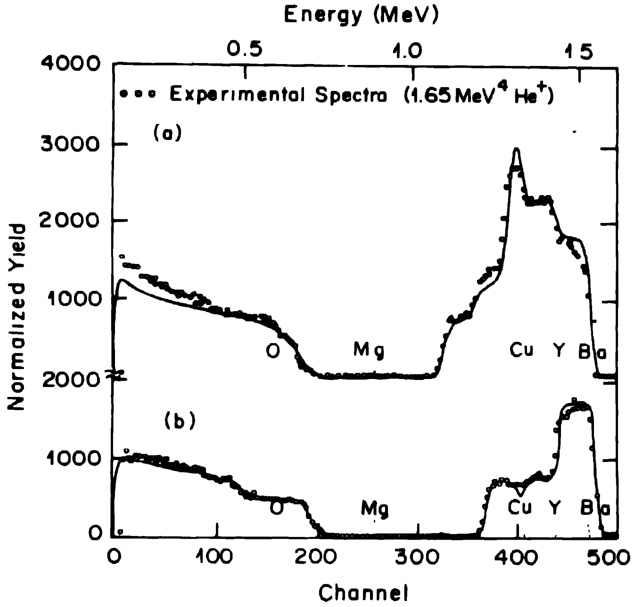

Figure 1. RBS spectra of YBCO thin films deposited on a MgO substrate at (a) 40 W and (b) 5 W of sputtering power. Simulated spectra are shown by continuous line. The dotted lines indicate the surface position of Y, Ba, Cu, O and Mg elements.

The He^+ ions scattered by atoms below the surface are observed at energies below 1.55 MeV. The signal drops off at the rear end of the sample. The next heavy element yttrium with atomic number 39, appears at 1.46 MeV *i.e.* below the barium signal. The next element copper with atomic number 29, appears at 1.35 MeV. The theoretical spectrum for a particular element ratio is simulated using the computer program RUMP, and is normalized for scattering cross section. The Y : Ba : Cu cation ratio of the above spectrum is found to be 1 : 2 : 3.

The sputtering power was then changed from 40 W to 5 W in order to decrease the deposition rate. Figure 1(b) shows the RBS spectrum of YBCO thin film deposited on a MgO substrate. The films deposited at low power, were found to have non-stoichiometric cation ratios of Y : Ba : Cu as 1 : 1.2 : 1.7 *i.e.* are deficient in barium and copper elements.

The T_c ($R = 0$) values of the YBCO thin films deposited at the sputtering power of 40 and 5 W are found to be 90 and 78 K, respectively. The critical current density J_c of the thin film deposited at a sputtering power of 40 W, was of the order of 1×10^6 A/cm^2 at 77 K. The degraded superconducting properties of YBCO thin film synthesized at power of 5 W can be attributed to the increased proportion of yttrium in the composition of YBCO thin film.

It is difficult to obtain the concentration of oxygen by low energy RBS. This is due to the low scattering cross section of oxygen as compared to that of the heavy atoms in "123" materials. The scattering cross section of oxygen is by the factors of $(8/29)^2$, $(8/39)^2$ and $(8/56)^2$ smaller than those of copper, yttrium and barium respectively.

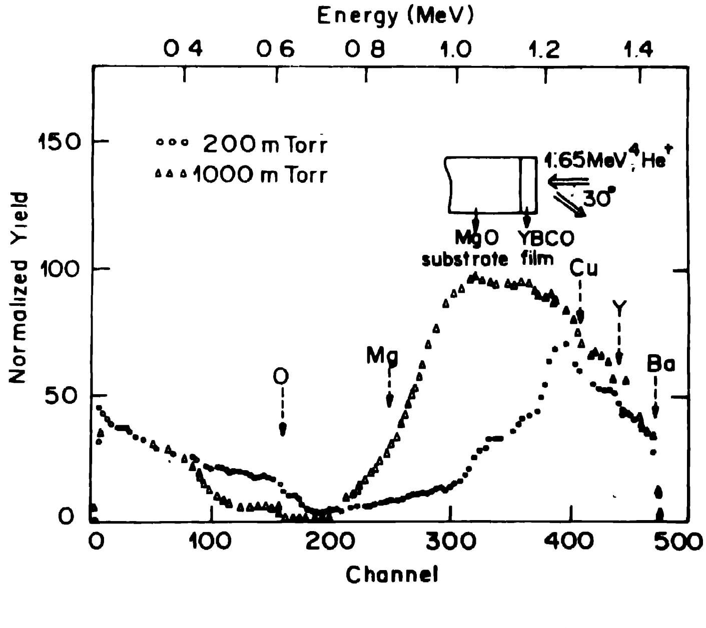

Figure 2. RBS spectra of YBCO thin films deposited on a MgO substrate at gas pressure of 200 mTorr and 1000 mTorr The simulated spectra are shown by the continuous line.

Figure 2 shows RBS spectra of YBCO films sputtered on (100) MgO substrates at gas pressures of 200 and 1000 mTorr respectively, for an interelectrode spacing of 30 mm and a substrate temperature of 730°C. From RBS analysis, it is observed that the cation ratio, Y : Ba : Cu of the YBCO film deposited at the gas pressure of 200 mTorr is 0.8 : 1.5 : 3, while the YBCO film deposited at 1000 mTorr gas pressure has been found to have a cation ratio of 1 : 2 : 3. The resputtering process occurring at low gas pressure is responsible for the observed yttrium and barium deficiency in the film deposited at low gas pressure. Generally, thin films deposited at low gas pressure are found to have non-stoichiometric chemical composition while films deposited at high gas pressure are found to be stoichiometric.

The thickness of the films as obtained from the RBS analysis, shows an increase from 4250 to 12200 Å with increase of the gas pressure from 200 to 1000 mTorr. The smaller thicknesses observed for the deposition at low gas pressure, is attributed due to resputtering during deposition.

The T_c ($R = 0$) of the YBCO thin film deposited at gas pressures of 200 and 1000 mTorr, has been found to be 71 and 88 K, respectively. The J_c of the thin films deposited at gas pressure of 1000 mTorr, has been found to be 9×10^5 A/cm^2 at 77 K. The deposition parameters and results are summarised in Table 2.

Table 2. Dependence of composition and superconducting properties on sputtering parameters.

Variable parameter	Cation ratio Y : Ba : Cu	Thickness (Å)	T_c (K)	J_c (77 K) (A/cm^2)
(a) Power				
5 W	1 : 1.2 : 1.8	1300	78	–
40 W	1 : 2 : 3	2500	90	1×10^6
(b) Gas pressure				
200 mTorr	0.8 : 1.5 : 3	4255	71	–
1000 mTorr	1 : 2 : 3	12200	90	9×10^5

4.2. *Effect of buffer layer and substrate material*

Figures 3(a) and 3(b) show the RBS spectra of YBCO thin films (set 2) deposited on α-Al_2O_3 and MgO/α-Al_2O_3 substrates, respectively, at a substrate temperature of 730°C, interelectrode distance of 30 mm and gas pressure of 800 mTorr. The RBS spectrum of the YBCO/α-Al_2O_3 sample shows an increase in the low energy tail of the element Cu in the thin film and the high energy edge of the substrate element Al. This indicates an inter-diffusion of Al atoms of the substrate and of Cu atoms of the thin film. This increase is however, considerably reduced when the film is deposited on a α-Al_2O_3 substrate with a MgO buffer layer (Figure 3(b)). The diffusivity of Cu in α-Al_2O_3 and MgO/α-Al_2O_3 has been found to be 6×10^{-19} and 2×10^{-19} m^2/sec, respectively. The sample having a buffer layer of MgO on the sapphire substrate shows a lesser amount of inter-diffusion at the substrate-film interface. The MgO thin film apparently acts as a diffusion barrier between YBCO and α-Al_2O_3.

The MgO buffer layer has been found helpful in improving the crystallographic structure of YBCO thin films deposited on an α-Al_2O_3 substrate by improving the c-axis orientation. Figures 4(a) and 4(b) show the XRD pattern of the YBCO films deposited on

α-Al_2O_3 and MgO/α-Al_2O_3 substrates respectively. One can notice that the random peak (103) present in the θ–2θ X-ray diffraction pattern of YBCO/α-Al_2O_3 has disappeared in the θ–2θ X-ray diffraction pattern of YBCO/MgO/α-Al_2O_3.

Also, the superconducting properties of the high-T_c YBCO films are very sensitive to the nature of the substrate. The critical temperature of the YBCO films deposited on α-Al_2O_3 and MgO/α-Al_2O_3 are 72 and 90 K respectively. The low T_c value of the film deposited on the α-Al_2O_3 substrate is probably due to strong inter-diffusion between the substrate and the thin film. The critical current density J_c of the thin film deposited on the MgO/α-Al_2O_3 substrate, is 2×10^4 A/cm^2 at 77 K. Similar results have been reported for YBCO films deposited on sapphire substrates using a buffer layer of CeO_2 to improve the superconducting properties [10].

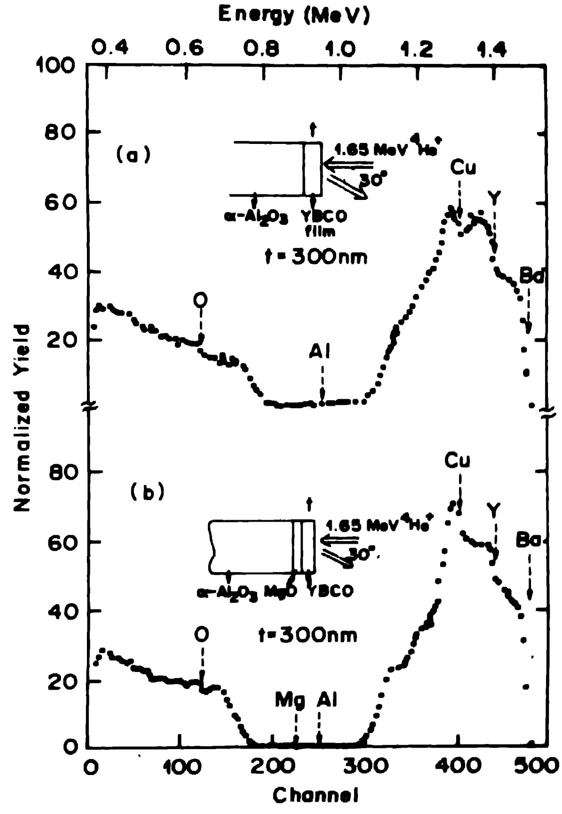

Figure 3. RBS spectra of YBCO thin films deposited on (a) α-Al_2O_3 and (b) MgO/α-Al_2O_3 substrates

Figures 5(a) and 5(b) show the RBS spectra of YBCO films (set 2) deposited on $SrTiO_3$ and YSZ substrates respectively. The spectrum of the film deposited on $SrTiO_3$ shows much smaller film-substrate inter-diffusion than for the film deposited on YSZ substrate. The Y : Ba : Cu cation ratios are 1 : 1.8 : 3 ($SrTiO_3$) and 1 : 1.5 : 2.5 (YSZ substrate). The latter composition is yttrium rich, as the *Y* from the substrate seems to have diffused in the film as detected by RBS. The T_c values for the films deposited on $SrTiO_3$ and YSZ were 90 and 87 K respectively. The J_c (77 K) of the YBCO thin films deposited on $SrTiO_3$ and YSZ substrates are 1×10^6 and 1.5×10^5 A/cm^2 respectively, indicating a better film formation on the $SrTiO_3$ substrate. The compositions and other properties of the YBCO thin films are summarized in Table 3.

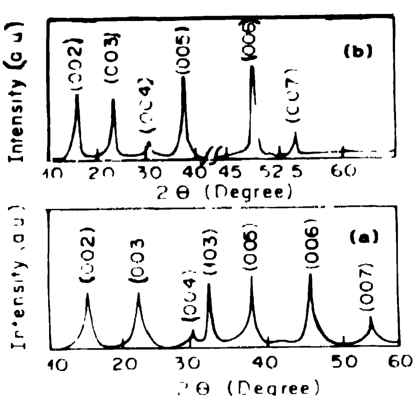

Figure 4. XRD pattern of YBCO thin films deposited on (a) α-Al_2O_3 and (b) MgO/α-Al_2O_3 substrates

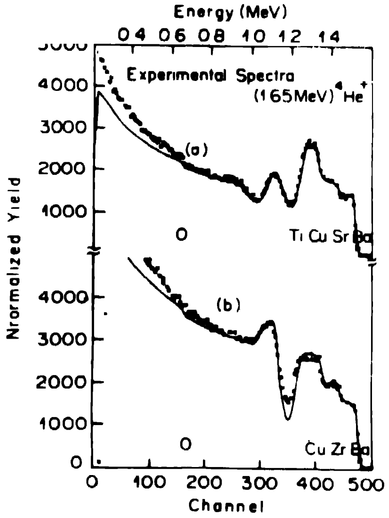

Figure 5. RBS spectra of YBCO thin films deposited on (a) $SrTiO_3$, (b) YSZ. The simulated spectra are shown by continuous line.

Table 3. Composition and superconducting properties of YBCO thin films on various substrates.

Substrate	Cation ratio Y Ba Cu	Thickness (Å)	T_c (K)	J_c (77 K) (A/cm^2)'
Sapphire	1.5 : 1.5 . 3.0	2450	72	
MgO/α-Al_2O_3	1 : 1.7 : 3	2700	90	2×10^4
YSZ	1 : 1.7 : 2.5	5200	87	1.5×10^5
$SrTiO_3$	1 : 1.8 : 3	4000	90	1×10^6

4.3. Spatial chemical homogeneity :

In the study of the homogeneity of the composition, samples were prepared by placing three (100) MgO substrates on the substrate holder within a diameter of 25 mm. Sputtering was performed at a substrate temperature of 730°C with an interelectrode spacing of 30 mm. The RBS results indicate that the cation ratios Y : Ba : Cu of the three films were 1 : 2 : 3, independent of position and that the thickness of the three samples varied within 10 percent only. The three samples showed a T_c of 90 K and a J_c(77K) of 1 × 10^6 A/cm^2.

4.4. *Aging of the sputtering target* :

It has been observed that the aging of the sputtering target during the sputtering process has a profound effect on the electrical and microstructural properties of the sputtered thin films [11]. In order to study this effect, a stoichiometric "123" sputtering target which has been used. for 40 hours, was studied by RBS for its composition. The RBS spectrum revealed a deficiency of the elements barium and copper; the cation ratio of Y : Ba : Cu amounted to 1 : 1.4 : 2.8. This indicates that prolonged sputtering affects severely the composition of the sputtering target. Hence, such targets can not be utilized to deposit stoichiometric 123 films.

5. Conclusion

The RBS studies have shown that the composition and thickness of magnetron sputter-deposited films are very much dependent on the deposition parameters in the sputtering process. Therefore, the superconducting properties are also affected by the variation of these parameters. Besides, RBS studies can give an idea of substrate-film inter-diffusion which is substantially present in case of a sapphire substrate, but is reduced considerably if a thin buffer layer of MgO is used. The studies have been used to optimize the thin film deposition and to obtain the optimized parameters for the deposition of YBCO thin films on (100) MgO and (100) $SrTiO_3$ substrates with critical temperature T_c of 90 K and critical current density J_c (77 K) of 1 × 10^6 A/cm^2.

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