ANSTO Heavy Ion ToF for Analysis of Light Elements in Thin Films

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Abstract

Thin films have various potential applications in electronic devices, and their performance is intricately linked with the electric and magnetic properties of the film, in which an important role is played by the presence of light elements, in particular Hydrogen, Oxygen and Nitrogen. The source of light elements, the form in which they are incorporated into the thin film, and how this is influencing the MgB_2 thin film properties is currently under scrutiny by various research groups. Typically these films are grown on oxide ceramic substrates, such as Al_2O_3-C and it is possible that the source of Oxygen is the substrate itself or the growth atmosphere. Here we report on a study of light elements in MgB_2 thin films grown on various substrates, using heavy ions recoil and a time-of-flight detector. A series of MgB_2 thin film samples produced by PLD (pulsed laser deposition) were analyzed, including films produced in-situ on Al_2O_3-C substrates with an on-axis and off-axis geometry, one film produced in-situ with an off-axis geometry, and one film produced ex-situ, with a bulk-like T_c. We also analyzed one film produced with on-axis geometry under the same conditions on Si (001) substrate. The amount of Oxygen detected by ToF, appears to be correlated with the T_c of the films, the higher the T_c the lower the oxygen content. Also, the superconducting properties of the examined thin films are discussed in the context of the results.

Keywords—Heavy ions ERDA, MgB_2 thin films

Introduction

Thin films characterization by heavy ions time-of-flight ERDA spectrometry is an attractive technique due to its capacity to detect elements over a wide range of Z, and to extract from the recoiled particles both mass and depth information. Over the last 15 years ANSTO has developed and constantly improved such a system [1], used routinely to characterize complex thin film architectures, and optimized for multi-layered, multi-element configurations found in the areas of semiconductor and superconductor device development. One such thin film with device application potential is MgB_2, in which Oxygen has been gradually revealed as playing an important role in its electric and magnetic properties. As early as 2001, it was reported that the exposure to low levels oxygen during fabrication of MgB_2 thin films could "alloy" the *ex situ* annealed MgB_2 films to form a $Mg(B\text{-}O)_2$ alloy, resulting in a much improved critical current J_c but a slightly lower transition temperature T_c of 35 K [2] than the bulk. A study of grain boundaries in Oxygen-alloyed bulk samples by selected area electron diffraction (SAED), suggests that Oxygen was incorporated in the form of MgO phase with a size of about 10nm [3], where periodical Mg-B-O layers were found at the grain boundaries. These studies suggest that oxygen-rich precipitates could provide pinning centers as the precipitates and oxygen-incorporated grain boundaries are of favorable dimensions, between 5-100nm, which is comparable with the coherence length ξ of MgB_2 which is around 5nm [4,5]. However, the decrease of the transition temperature with the incorporation of Oxygen observed in bulk and thin films is undesirable, and it is more pronounced in thin films. The cause

appears to be the influence of Oxygen precipitates on the electron-phonon coupling parameters, as suggested by calculation for two possible oxygen-ordered MgB_2 compounds of composition Mg_2B_3O and $Mg_2B_3O_2$ [6]. The results show that the calculated T_c values of Mg_2B_3O and $Mg_2B_3O_2$ are 18.3K and 1.6K, respectively. This result is in accordance with the reported decrease of T_c in some oxygen enriched MgB_2 samples, especially in the *in situ* prepared thin films [7,8]. There is enough evidence to suggest that in device applications based on MgB_2 thin films, the presence of Oxygen and its distribution will strongly influence the device performance, and therefore detailed information of Oxygen form and its distribution in MgB_2 films is necessary. In this paper, we report the results of Oxygen distribution measured by heavy ion ERDA in different types of MgB_2 films prepared by the pulsed laser deposition (PLD) method.

Experimental details

The ERDA experiment was carried out in a vacuum better than $1x10^{-6}$Pa, using Iodine ions of 82.5MeV. A schematics of the experimental apparatus used here is shown in Fig.1. The beam was shaped in a rectangular form, 3mm high and 1mm wide, and directed onto the sample at an incident angle of 67.5°, between the beam direction and sample normal. The energy of recoils was measured with a time-of-flight detector placed at an exit angle of 45° relative to the sample normal, resulting in a scattering angle of 45°. The two electrostatic mirrors were placed 0.5m apart, and each contained a $25\mu g/cm^2$ C foil to measure the flight time of the recoils. The final rest energy of the recoils was measured with a surface barrier detector, placed at the end of the flight path. The samples are placed on a 2-axis goniometer, and placed in the beam path at the required position. In this experiment, the total charge collected on each sample during the measurement was 12μC.

Sample	Substrate	Deposition geometry	Mg cap layer	Surface etching	T_c [K]
1	Si (001)	On-axis	No	No	18.7
2	Al_2O_3-c	On-axis	No	No	25.8
3	Al_2O_3-c	Off-axis	Yes	No	26
4	Al_2O_3-c	Off-axis	Yes	No	28
5	Al_2O_3-c	Off-axis	No	Yes	33
6	Al_2O_3-c	Off-axis	Yes	No	33
7	Al_2O_3-c	Off-axis	Yes	No	34
8	Al_2O_3-c	Off-axis	No	Yes	34.5

Table 1.Summary of sample characteristics used in this study. The T_c's were determined by dc magnetization method

A number of MgB_2 films were grown by PLD, as detailed in Table 1, where the T_c of each sample was measured by SQUID magnetometer between 300K and 5K. The details of the PLD apparatus were described previously [8,9]. Two deposition geometries were applied. For "on-axis" deposition, the substrate normal was perpendicular to the target, and for "off-axis" deposition, the substrate normal was parallel to the target surface. For some films, after the deposition of the MgB_2 film, and before the *in situ* annealing process, pure Mg was deposited by PLD from a

separate Mg target, as the final "cap" layer, in order to compensate for the Mg loss during annealing. The thickness of the Mg cap layer was around 100nm. For some samples, the surface was etched away before the Oxygen and the T_c measurements using the ion beam.

Results and Discussion

The raw spectrum of sample 1 is presented in Fig. 2-a, in (Energy-time) space. This data was projected onto the time axis and converted into depth profile (Fig. 2-b) from first principle calculations, using previously published information on the stopping power of ions in matter [10]. The calculations show that at this energy of Iodine, the variation in the stopping power of elements of interest (Oxygen, Boron, Magnesium and Silicon) is only a few percentages between the top and the bottom of MgB_2 films. A close inspection of this figure shows a significant presence of Oxygen throughout the entire thickness of MgB_2 film, with a slightly higher concentration at the surface. Also, the Oxygen as well as Magnesium appears to have diffused into the Si substrate over a significant depth. As Oxygen was not present in the MgB_2 target used to grow the film, the most probable source for it remains the growth atmospheres. This is supported by the fact that, if the base pressure in the deposition chamber prior to the deposition is higher than approximately $1x10^{-5}$Torr, then the resulted film is not superconducting, and presumably all Mg is oxidized before the stable, MgB_2 phase is formed.

Fig 3 shows the same result for sample 2, which had the lowest T_c amongst the films grown on Al_2O_3. The depth profile of elements in the film also shows the presence of Oxygen wit a distinct peak at the surface. If we define the film-substrate interface as the depth where Oxygen and Al increase together, we can distinguish the Oxygen present only in the film. In this case, the amount of Oxygen is slightly smaller as compared with the film grown on Si substrate, but there is still a significant diffusion of Mg in the Alumina substrate. Surprisingly, this result also suggests a small diffusion of Boron into the substrate.

The ERDA result for sample 3 is shown in Fig. 4. This sample was also grown on Al_2O_3 (see Table 1), but with an off-axis deposition geometry, and additionally, an Mg cap layer was used. The depth profile of elements shows that, compared to the sample 2, Oxygen and Magnesium have a similar depth profile, but no diffusion of Boron into the substrate occurs.

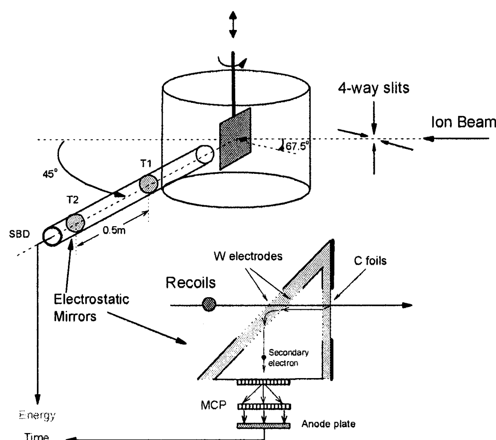
The ERDA results for the sample with the highest T_c (sample 8) are presented in Fig. 5-a. In this case the depth profile show a much lower Oxygen content in the film, and also no significant diffusion of Boron into the substrate. However, the same significant diffusion of Mg into the substrate is apparent for this sample.

The amount of Oxygen measured by ERDA in these series of MgB_2 thin films was normalized to the thickness of the thickest film (sample 1) and to the maximum value of the Oxygen peak (also found in sample 1), with the result is shown in Fig. 5-b. A clear correlation between the transition temperature T_c and the relative amount of Oxygen is evident. This may explain the cause for some differences in the T_c between films produced under apparently "identical" conditions. This result also shows that Oxygen is higher when the deposition geometry was on-axis as compared to an off-axis deposition.

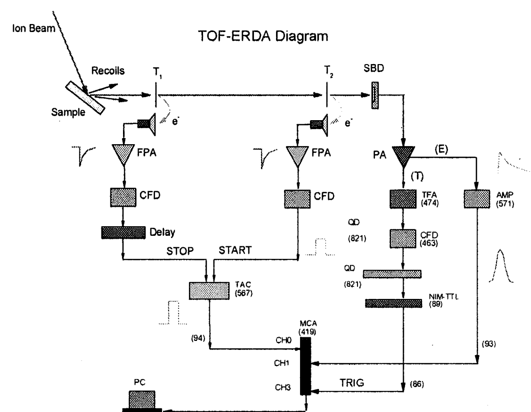
A surprising result is the presence of a significantly larger amount of Oxygen in the MgB_2 film grown on Si as compared to the film grown on Al_2O_3, but at this stage it is

not clear why this difference exist. The native SiO_2 layer on the Si substrate surface was not removed before deposition, but this is unlikely to be the main cause.

The diffusion of Mg into the substrate appears to be independent of the type of substrate (Si or Al_2O_3) and of the deposition geometry (on- or off-axis). This suggests a barrier against Mg diffusion may have to be created for the growth of these films. On the other hand, the diffusion of Boron appears to take place only when the substrate was Al_2O_3 and the deposition was on-axis.

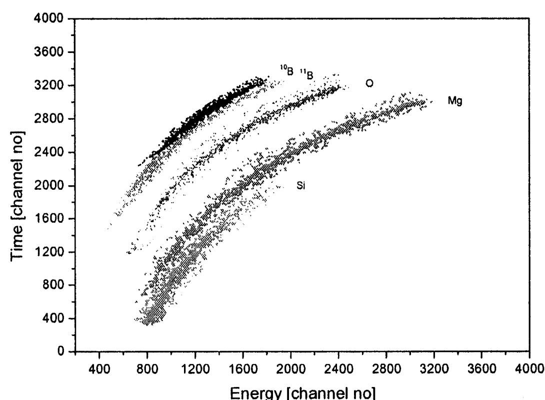


(a)

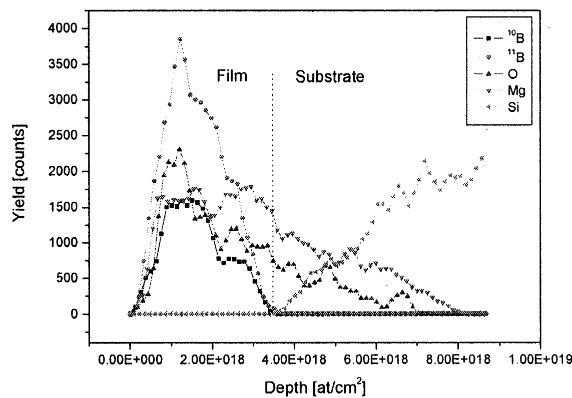


(b)

Fig. 1: Schematics of the ANSTO ERDA-ToF spectrometer: (a) hardware; (b) signal processing



(a)



(b)

Fig. 2: ERDA results for sample 1: (a) E-time spectra; (b) Depth profile of elements obtained from time-yield projection

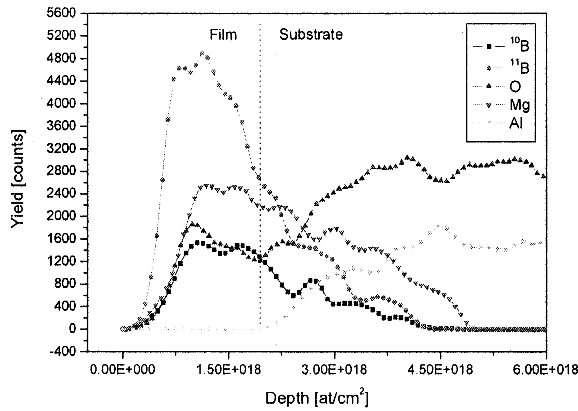


Fig.3: Depth profile of elements in sample 2

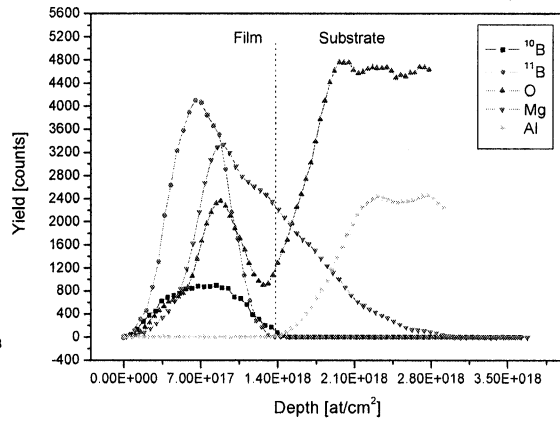
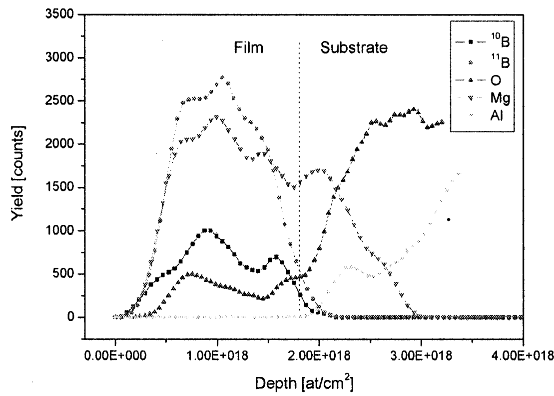
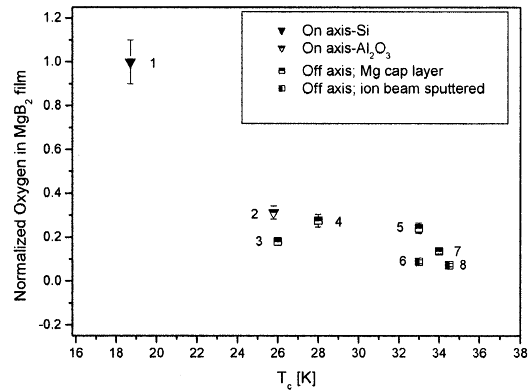


Fig. 4: Depth profile of elements in sample 3



(a)



(b)

Fig. 5: (a) Depth profile of elements in sample 8; (b) Oxygen vs T_c; the numbers represent the samples as described in Table 1

The use of a Mg cap layer, a common practice in the PLD fabrication process of MgB_2 thin films was investigated (comparison between samples 5 and 6), and a slightly larger amount of Oxygen was detected at the surface of the film 6, for which a Mg cap layer was used. As expected, this small redistribution of Oxygen did not affect the T_c of the film, and is possible that the use of the cap layer may not be as efficient as initially believed to be.

Conclusion

Using heavy ion ERDA analysis, we have shown in this work that a considerable amount of oxygen can be incorporated in the *in situ* PLD MgB_2 films. The Oxygen depth profile shows that it is present throughout the whole film, and even it diffuses into the substrate, in films deposited on Si. The results also show Mg is diffusing into both Si and Al_2O_3 substrates, and its diffusion into Al_2O_3 takes place for both on- and off-axis deposition geometries. Boron was found to have a limited diffusion into

Al_2O_3 when the deposition geometry was on-axis, and no diffusion when the film was deposited with off-axis geometry. The use of Mg cap layer appears to have little influence on the T_c, and the results suggest that the small variation of T_c between the films with and without the Mg cap layer may be associated with the small increase of Oxygen at the surface of the films when the cap layer was used.

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