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Study of Oxygen Incorporation in PLD MgB_2 Films by Rutherford Backscattering Spectroscopy

Yue Zhao, M. Ionescu, S. X. Dou, and H. K. Liu

***Abstract*—The Rutherford backscattering (RBS) method has been employed to study the incorporation of oxygen into MgB_2 films during their fabrication by pulsed-laser deposition (PLD). A series of MgB_2 thin film samples were analyzed, including two films produced *in situ* on Al_2O_3 – c substrates (with higher T_c and lower T_c) with an on-axis geometry, one film produced *in situ* with an off-axis geometry, and one film produced *ex situ*, with a bulk-like T_c. The amount of oxygen detected by RBS, which is stable in the form of MgO, appears to be correlated with the T_c of the films, the higher the T_c the lower the oxygen content. The superconducting properties of the thin films are discussed in the context of the RBS results.**

***Index Terms*—MgB_2 thin films, Rutherford backscatter.**

I. Introduction

OXYGEN has been gradually revealed as playing an important role in MgB_2 superconductors. As early as 2001, Eom *et al.* reported that the exposure of an MgB_2 sample to a low level of oxygen could "alloy" the *ex situ* annealed MgB_2 film to form a $Mg(B-O)_2$ alloy, resulting in a much improved J_c and a slightly suppressed T_c of 35 K [1]. MgO phase with a grain size of about 10 nm was also observed in the oxygen "alloyed" film by selected area electron diffraction (SAED). Klie *et al.* studied the grain boundaries of MgB_2 bulk samples prepared by a sintering process with z-contrast STEM scans [2]. Periodical Mg-B-O layers were found at the grain boundaries. Furthermore, intra-grain Mg-B-O precipitates were reported later on by the same group [3]. Liao *et al.* observed precipitates inside the MgB_2 grains of solid state sintered MgB_2 samples with high-resolution transmission electron microscopy (HRTEM) [4]. Two types of precipitations were determined. One type has a coherent $Mg(B-O)_2$ structure with small sizes of about 5–30 nm, while the other type is f.c.c. MgO precipitates with much larger sizes of 15–100 nm. The MgO precipitates were also observed by Zhu *et al.* [5]. These studies suggest that oxygen-rich precipitates could provide pinning centers, as the precipitates and oxygen-incorporated grain boundaries are of favorable dimensions, between 5–100 nm, which is comparable with the coherence length ($\xi = 5$ nm [6], [7]) of MgB_2.

Idrobo *et al.* calculated the electron-phonon coupling parameters for two possible oxygen-ordered MgB_2 compounds with the composition Mg_2B_3O and $Mg_2B_3O_2$ [8]. The calculation suggests that the incorporation of oxygen reduces the transition temperature. The calculated T_c values of Mg_2B_3O and $Mg_2B_3O_2$ are 18.3 and 1.6 K, respectively. This result is in accordance with the reported suppression of T_c in some oxygen enriched MgB_2 samples, especially *in situ* prepared thin films [9]–[11].

In MgB_2 device applications, the existing form of oxygen and its distribution will strongly influence the device performance. Therefore, a comprehensive knowledge of the existence of oxygen in MgB_2 films is necessary. In this paper, we report a RBS study on the microscopic oxygen distribution in different kinds of MgB_2 films prepared by the PLD method.

II. Experimental Details

The MgB_2 target used in this experiment was produced from Mg and B commercial powders by hot isostatic pressing in Ar. The density of the target was around 84%. The X-ray phase purity of the target was high, with all peaks assigned to the MgB_2 phase. For *ex situ* MgB_2 film, the precursor film was deposited from a 40% density boron compact made from 99%-purity powder.

A number of MgB_2 films were grown by PLD on single crystal Si substrate with (001) orientation and Al_2O_3 – c substrates. The pulsed laser (248 nm) was focused to an elliptical spot with dimensions of 7 mm × 1.5 mm on the target. Two deposition geometries were applied. For on-axis deposition, the substrate normal was perpendicular to the target, and for the off-axis geometry, the substrate normal was parallel to the target surface. For *in situ* films, a Mg cap layer was deposited on the film surface after the deposition to compensate for the Mg loss during the *in situ* annealing. After the annealing, the Mg cap layer was fully evaporated away. In the preparation of the *ex situ* film, a boron precursor film was first deposited by PLD and then the sample was wrapped in Ta foil, sealed in a stainless steel tube, together with Mg pellets, and annealed in a tube furnace. For more details on preparation, see [12], [13]. Table I shows the preparation parameters and properties of these samples. The thicknesses of the films are similar, about 350 nm.

For the RBS experiment we used He^{+1} ions of 2 MeV. Around this energy, the scattering cross sections of He with Mg, O and Si do not present steep variations. Also, at this energy there are no specific nuclear reactions between He and the target atoms.

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TABLE I
FABRICATION CONDITIONS FOR THE PLD FILMS USED IN THIS RBS STUDY. THE T_C's WERE DETERMINED BY dc MAGNETIZATION

#	Substrate	Deposition conditions	Annealing conditions	T_c
1	Si (001)	On-axis PLD MgB_2 target	*In situ*, 680°C, 1 min, in 1 atm Ar	25K
2	Al_2O_3-c	On-axis PLD MgB_2 target	*In situ*, 680°C, 1 min, in 1 atm Ar	29K
3	Al_2O_3-c	Off-axis PLD MgB_2 target	*In situ*, 650°C, 1min, in 1 atm Ar	29K
4	Al_2O_3-c	On-axis PLD Boron target	*Ex situ*, 900°C, 30 min, sealed with Mg	37K

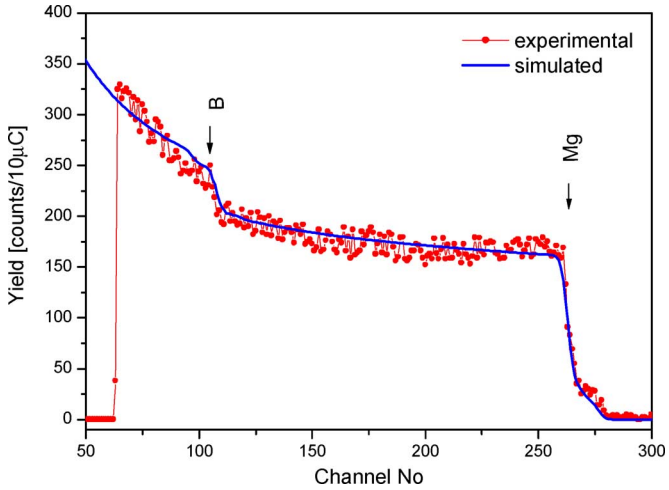

Fig. 1. RBS spectrum of the MgB_2 target.

The experiment was carried out at ANSTO on a 2MV Tandetron accelerator, and Si-surface barrier detectors with standard detection electronics were used. The incident angle (α) of the He ions was 0°, the exit angle (β) was 20°, and the scattering angle (θ) was 160°. The total charge measured on each sample was 10 μC. Simulation software SIMNRA was used for experimental data analysis and simulation purposes.

III. RESULTS AND DISCUSSIONS

The RBS spectrum of the 6 mm-thick MgB_2 target is presented in Fig. 1. The Channel No. represents the number of energy channels of the Multi Channel Analyzer, and it is equivalent to the energy of the He projectiles (4 keV/channel) scattered from the Mg and B atoms in the target. The yield represents the number of He projectiles scattered off the Mg and B atoms for 10 μC of charge.

At the applied energy of the He projectiles, the target can be considered infinitely thick. As the result, the RBS spectra of Mg and B appear like steps, with the front edges positioned at characteristic energies for Mg-He and B-He interaction. A close inspection of Fig. 1 reveal that only Mg and B atoms are present in the target, with no significant presence of oxygen.

In Fig. 2 is shown the RBS spectrum of an MgB_2 film grown by PLD on Si as described in the Experimental section. In this case the He ions fully penetrate the MgB_2 film, and as a result

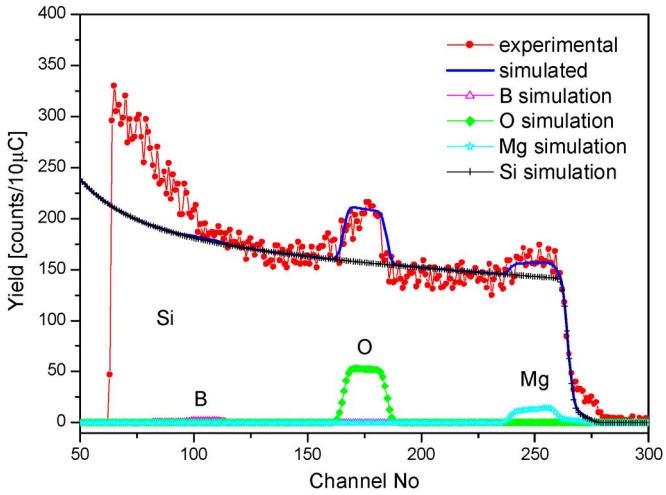

Fig. 2. RBS spectrum of MgB_2 film grown by PLD on Si (001) substrate and annealed *in situ*.

the signatures of the atoms present in the film appear like distinct peaks in the spectrum. The presence of oxygen and Mg is clearly visible, in the form of broadened peaks. The width of these peaks is similar, and both are an indication of the thickness of the MgB_2 film.

If we assume a uniform distribution of oxygen inside the MgB_2 film, the modeling result shows a symmetric peak. On the other hand, the experimental curve shows that the peak of oxygen is skewed. This suggests that oxygen is not uniformly distributed in the film, but a higher amount is present near the surface of the film.

It is interesting to know the origin of this rather large amount of oxygen present in the film. Quantitative analysis of the result shows that the film stoichiometry is close to MgB_2 $(MgO)_{5.7}$. As the oxygen is not present in the target, the only remaining possibilities for its provenance are the deposition atmosphere or an oxidation of the film after it was exposed to ambient atmosphere. Although there is slightly more oxygen present at the surface of the film, it appears less likely that the oxidation of the film could take place by exposing to the ambient atmosphere, because once the MgB_2 film is formed it is stable in air. If, however, during the deposition and *in situ* annealing not all Mg is used up to form the MgB_2 phase or evaporated, then the excess Mg could easily be oxidized by exposing it to air. So the protective Mg cap layer on top of the film before annealing could also be a cause of the higher level of oxygen near the film surface. On the other hand, a strong argument in support of the deposition atmosphere being the source of the oxygen in the film is the fact that, if the base pressure in the deposition chamber prior to the deposition is higher than approximately 1×10^{-6} Torr, then the resultant film is not superconducting, and presumably all Mg is oxidized before the MgB_2 phase is formed.

When the MgB_2 film was grown on Al_2O_3, the presence of oxygen in the film is again visible, as shown in Fig. 3, as a distinct peak. This is clearly separate from the oxygen signal coming from the substrate, which appears as a step at a slightly lower energy. The sharp front edge of the O step is an indication that the oxygen in the substrate is not diffusing into the MgB_2

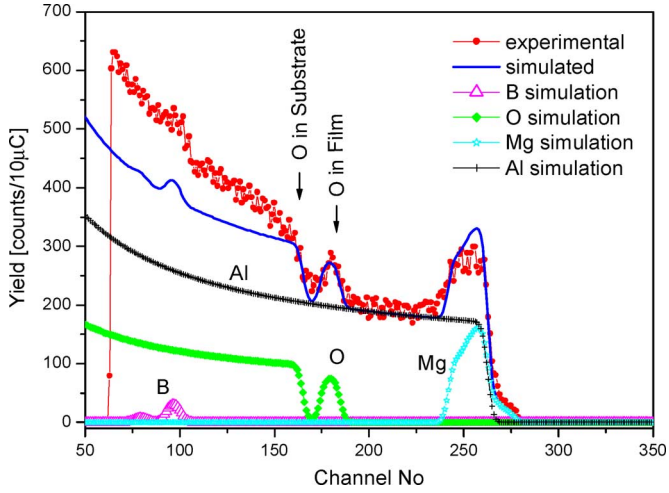

Fig. 3. RBS spectrum of an MgB_2 film grown by on-axis PLD on Al_2O_3 and annealed *in situ*.

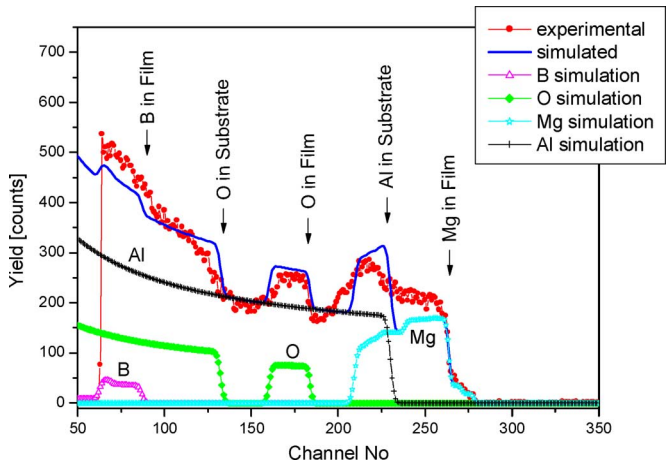

Fig. 4. RBS spectrum of an MgB_2 film grown by off-axis PLD on Al_2O_3 and annealed *in situ*.

film. In addition, the amount of oxygen is smaller as compared with the film grown on the Si substrate, and the amount of Mg is larger, in spite of the two films having approximately the same thickness, which suggests that a larger amount of MgB_2 phase was formed.

In Fig. 4 is presented the RBS spectrum of an MgB_2 film grown by off-axis PLD on Al_2O_3 and annealed *in situ*. As in the case of the previous films grown on Si and on Al_2O_3, oxygen is present in the film, but the amount of Mg is larger still, suggesting better conditions for the formation of MgB_2 phase.

TEM study has revealed the fine grain character of the *in situ* films, and the existence of oxygen is predominantly in the form of magnesium oxide, as indicated in the SAED pattern [14]. This is in accordance with the microscopic studies mentioned in the introduction section. The MgO phase, especially when concentrated at the surface layer of the MgB_2 film, will degrade the performance of the *in situ* MgB_2 film in a RF field, due to its negative effects on the surface impedance and non-linear response [15].

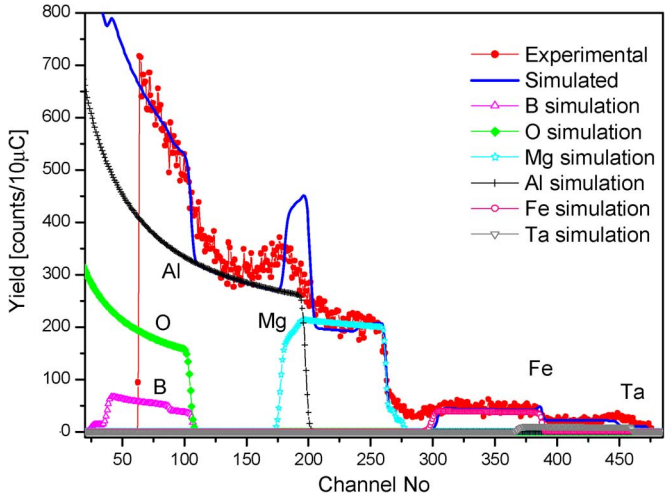

Fig. 5. RBS spectrum of an MgB_2 film deposited by PLD on Al_2O_3 and annealed *ex situ*.

The last sample analyzed was an MgB_2 film grown on Al_2O_3 and annealed *ex situ* as described in the experimental section. The RBS result is presented in Fig. 5.

In this case there is no oxygen present in the film, but small amounts of Fe (~1.5 at%) and Ta (~0.05 at%) are clearly visible. Their origins are most probably the Fe tube and the Ta foil used to protect the sample during the *ex situ* annealing. As described above, the fabrication process for this film involved the deposition of only B by PLD, and the reaction of the B film with Mg vapors *ex situ*. Taking into account all the results obtained in this study, it appears that the source of oxygen in the MgB_2 film fabricated by PLD is the oxygen present inside the deposition chamber. It is likely that once the Mg-B bond in the target is broken by the ~5 eV photons and the plume is formed, a large number of Mg ions in the plasma react with the oxygen present in the deposition atmosphere before they reach the substrate, forming MgO. This scenario is also consistent with the fact that the PLD-fabricated MgB_2 films are polycrystalline, with a small grain structure, as shown by X-ray diffraction.

A correlation between the T_c and the distribution of the constituents, especially for the oxygen in each film, is seen in this study. The film with the highest T_c of 37 K was achieved by *ex situ* annealing of the boron precursor film, and the RBS detection does not show any obvious oxygen signal in the film. The on-axis and off-axis *in situ* films on Al_2O_3 substrates have similar T_cs of 29 K, and they both show significant oxygen content. The magnesium and boron contents are much smaller in the lowest T_c sample, the *in situ* film on a Si substrate. One possible explanation of the lower amount of magnesium and boron is that Mg and boron diffused into the Si substrate, which probably results in an even poorer environment for MgB_2 phase formation. Thus Si substrate appears unsuitable for the high-temperature process due to the diffusion of Mg and B to Si.

Oxygen probably suppresses the T_c of the films by the formation of low-T_c phases such as Mg_2B_3O and $Mg_2B_3O_2$ [8]. The presence of oxygen in the *in situ* films is also a big barrier to applications of these films in microwave and RF related circumstances. Significant MgO diffraction signals were found in our

in situ films in a previous study [14]. The oxygen-enriched grain boundaries and MgO precipitates, especially those concentrated in the top layer of the film surface, are potential weak links in microwave fields. These weak links could be responsible for a sharp increase in the surface impedance with peak surface field in a 6 GHz RF field measured in our in situ films [16]. These oxygen-enriched phases would also present problems for an accurate thickness control of the insulator interlayer for Josephson Junctions. Further work to eliminate oxygen in the *in situ* films is necessary to achieve desirable performances in MgB_2-based microwave devices.

IV. Conclusion

Using RBS analysis, we have shown in this work that a considerable amount of oxygen was incorporated in the *in situ* PLD MgB_2 films. By contrast, no oxygen was detected in the *ex situ* film. The presence of oxygen in the MgB_2 films is independent of the substrate type (Si or Al_2O_3), or the deposition geometry (on-axis or off-axis). The distribution of oxygen in the *in situ* films is not homogeneous. The oxygen is concentrated in the near-surface region according to the skewed oxygen peak in the experimental RBS curves and is most likely in the form of MgO precipitates and inter-grain weak links judging form previous studies, which is not favorable for the RF applications.

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