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THE DISTRIBUTION OF ELEMENTS IN MgB_2 SUPERCONDUCTING FILMS PREPARED BY SEQUENTIAL E-BEAM EVAPORATION

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The preparation of MgB_2 superconducting films is often linked with difficulties to obtain the film stoichiometry due to the different melting points of deposited materials (magnesium and boron) and the escape of Mg during in-situ annealing. The interaction of the MgB_2 films with an incident ion beam of the analytical technique applied can also be a problem, because it can cause distortion of the composition of the prepared films. Superconducting MgB_2 thin films have been prepared on carbon substrates using sequential e-beam evaporation of boron and magnesium to create a multi-layer structure with a total thickness of 500 nm. After deposition, an in situ annealing was performed at 700 °C at various partial pressures of Ar. We studied the composition of the as-prepared and annealed films by ion beam analysis. The distribution of boron was measured by resonance nuclear reaction $^{11}B(p,\gamma)^{12}C$ and the obtained results were confronted with Rutherford backscattering analysis and measurements of electrical properties. A possible influence of incident ion beam on the examined film is discussed. We showed that process of a sequential deposition of B and Mg followed by in-situ annealing is suitable for preparation of superconducting MgB_2 film.

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1 Introduction

Recently discovered MgB_2 superconductor seems to be a promising material for superconducting electronics. MgB_2 superconducting thin films have properties more similar to classical low-T_c superconductors (Nb) with the highest critical temperature where granular boundaries are more transparent to current flow, films have lower anisotropy and coherence length is larger compared to high-T_c copper-oxides [1]. However, the preparation of MgB_2 films is often linked with difficulties to obtain the film stoichiometry and to incorporate the film into multilayer cryoelectronic structure. Typical most frequently used methods of film fabrication are pulsed laser deposition, co-evaporation, Mg diffusion, and magnetron sputtering. In all cases the main problem is an

Mg volatility due to which unheated substrates and Mg-enriched targets are used in deposition process. There are two principal annealing procedures in preparation of MgB_2 films. The first, in-situ annealing [2,3] at 600-700 °C often under vacuum conditions and the second, ex-situ annealing of Mg-B or B precursor films at 900 °C [4]. The MgB_2 films prepared by in-situ annealing have usually lower zero resistance T_{c0} value (25-30 K) and offer nanocrystalline MgB_2 structure. On the other hand, MgB_2 films prepared by ex-situ process where Mg powder and boron film is sealed in Nb tube exhibit T_{c0} values up to 39 K but grain size is of the order of 0.1 to 1 μm with higher surface roughness compared to in-situ prepared films.

The study of phase and elemental composition of prepared MgB_2 films can efficiently help to solve the problems mentioned above (stoichiometry and homogeneity of MgB_2 films). However, the most of the standard techniques are not able to give this information due to a low sensitivity (energy dispersive X-ray microanalysis, microprobe analysis) or an escape of Mg during etching of MgB_2 film in order to obtain the concentration depth profile (Auger electron spectroscopy).

There are two aims of this work. The first, the preparation of MgB_2 film using non-traditional sequential e-beam evaporation of boron and magnesium to simplify the process of preparation. The second, the application Ion Beam Analysis (IBA) to study concentration profiles of the prepared films to obtain information about the depth distribution of elements in films after in-situ annealing and to demonstrate the possibilities of IBA methods in characterization of MgB_2 films.

2 Experimental

2.1 Sample preparation

The MgB_2 thin films were prepared by a multilayer processing technique and in-situ annealing. The magnesium and boron layers were deposited on glassy carbon C (Carbon Vitreous, Goodfellow) substrates by sequential electron-beam evaporation at the background vacuum of 10^{-4} Pa. The deposition performed at the room temperature was divided into 4 evaporation steps in which the boron and magnesium layers were alternated, with Mg at the top of the film precursor. An excess of about 100% of Mg has been used if compared with the stoichiometry composition. The total thickness of deposited multilayer film was $\sim$ 500 nm. The precursor films were then in-situ heated at the rate of 40 °C/minute to 280 °C and kept at this temperature for 30 minutes in an Ar atmosphere of 0.06 Pa. Subsequently, the Ar pressure was increased to 16 Pa and the temperature was increased at the rate of 40 °C/minute to 700 °C and kept there for 10 minutes. The samples were then cooled down to room temperature in the Ar atmosphere of 300 Pa.

2.2 Experimental details

The critical temperature values were measured by standard 4-point DC resistive methods. The elemental composition of the prepared layers was studied by ion beam analysis. Two independent methods were selected for determination of the depth profiles - Rutherford Backscattering Spectrometry (RBS) and Resonant Nuclear Reaction Analysis (RNRA). The RBS measurements were performed at IONAS accelerator at Universität Göttingen, Germany [5]. Normal incidence of the 0.9 MeV He^{++} ion beam and two surface barrier detectors at a scattering angle of 165° were used for the analysis of all samples. RBS spectra were evaluated using a RUMP code [6].

In evaluation also the molecular $H_2{}^+$ fraction of the beam was taken into account [7]. RNRA analysis was performed in Ion Beam Laboratory of Slovak University of Technology, Bratislava, Slovakia [8]. Two resonant (p,γ) reactions with closely laying reaction energies were chosen to determine the depth profiles of boron and magnesium, see Tab. 1. The detection electronics was set to enable simultaneous registration of γ-rays escaping from the both reactions. For boron, only a peak at 4.43 MeV was taken into account due to its high emission ratio.

Tab. 1. Nuclear reactions used for Mg-B depth profiles.

REACTION	E_{H^+} **[keV]**	E_γ **[MeV]**	σ **[mb]**	Γ **[keV]**	ϵ **[%]**
$^{11}B(p, \gamma)^{12}C$	163	16.11	0.157	7	3.5
—	—	11.68	—	—	96.5
—	—	4.43	—	—	96.3
$^{24}Mg(p, \gamma)^{25}Al$	226	2.06	—	1	—
—	—	1.56	—	—	—
—	—	0.95	—	—	—

E_{H^+}-incident proton energy, E_γ-emitted γ energy, σ-cross section, Γ-resonance width, ϵ-emission ratio (from [10,11]).

To be sure that the desired reactions were induced, the reaction γ-rays were at first measured by a HPGe (High-Purity Germanium) detector. The depth profiling was then performed by a high sensitivity 4π NaI(Tl) detector [9].

3 Results and discussion

In Fig. 1 a typical resistance versus temperature dependence of annealed multilayer Mg-B-Mg-B deposited on glassy carbon substrate (Mg-B-Mg-B/C) is shown. The superconducting transition (see inset of Fig. 1) begins just above 30 K, midpoint of transition ($R = 0.5\ R_N$, R_N = normal state resistance) is near 30 K and zero resistance critical temperature T_{c0} ranges from 26 to 29 K depending on the length of low resistance tail.

In spite of the presence of superconducting MgB_2 phase indicated by the electrical measurements, this phase was not indicated the X-ray-diffraction pattern, which is in agreement with other authors and it is usually linked with a fine granular structure of MgB_2 film [4].

The aim of the selected IBA methods was to obtain very specific information about the elemental composition of the treated samples. RBS is very suitable method to measure the distribution of elements heavier than the substrate. It is therefore well applicable for the determination of the Mg profiles in Mg-B system on a light substrate, where C is of natural preference. On the other hand, due to a low mass, it is not very suitable for boron profiles. Here RNRA can provide better results. However, the both methods have their advantages, but also some drawbacks, as can be seen from comparison of the obtained results.

RBS was performed at relatively low energy of primary Ions. The two main reasons have led to the choice of the low energy region:

(1) to achieve a maximum depth resolution, that means in terms of RBS to analyze a sample at

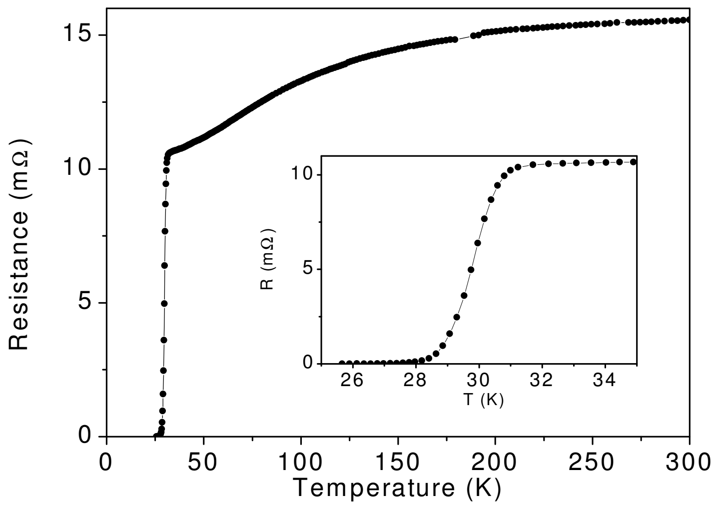

Fig. 1. A typical resistance vs. temperature dependence of MgB_2 thin film prepared on glassy carbon substrate.

a condition of maximum stopping power. For He ions it is around 600 keV at the sample surface

(2) to maximize the sensitivity in order to minimize the radiation damage of the samples, that could cause undesired redistribution of the studied elements. As the backscattering cross section varies with energy as $\sigma \sim f(E^{-4})$, lowering the energy from e.g. 2 MeV to 1 MeV results in a cross section increase by a factor of 16.

On the other hand, the chosen energy was not high enough to see more boron, than the first layer laying close to the surface. Nevertheless, the magnesium profiles, which were the goal of RBS analysis, are well resolved and also oxidation of Mg layers was clearly detected.

The typical experimental RBS spectra of as deposited and in-situ annealed multilayered films are shown in Fig. 2 and Fig. 3, respectively.

A very specific evaluation problem occurred due to the use of doubly- charged He ions for RBS analysis. As a rule of tomb hydrogen is always present as a rest gas in ion sources and molecular beam of ${H_2}^+$ is nearly impossible to filter out of the He^{++} beam. An accelerated ${H_2}^+$ molecule splits immediately after entering the sample into 2 protons, each carrying approximately half of the initial kinetic energy. As a consequence, acquisited RBS spectrum is a superposition of the He-RBS spectrum at a full energy and the H-RBS spectrum at a quarter energy. The low energy part of the spectrum is therefore distorted from the point of view of pure He RBS, as treated by the majority of available evaluation programs. The procedure how to deal with this problem is beyond the scope of this article and will be discussed in a separate study [7].

The theoretical spectra derived from a model of films divided into a few sub-layers fit experimental data reasonably well. The thicknesses in nm scale of the sub-layers used in the model were calculated from their mass density equal to bulk materials. The composition indicated in the model of Mg-B film is normalized to unity. The input to a RUMP code should be presented

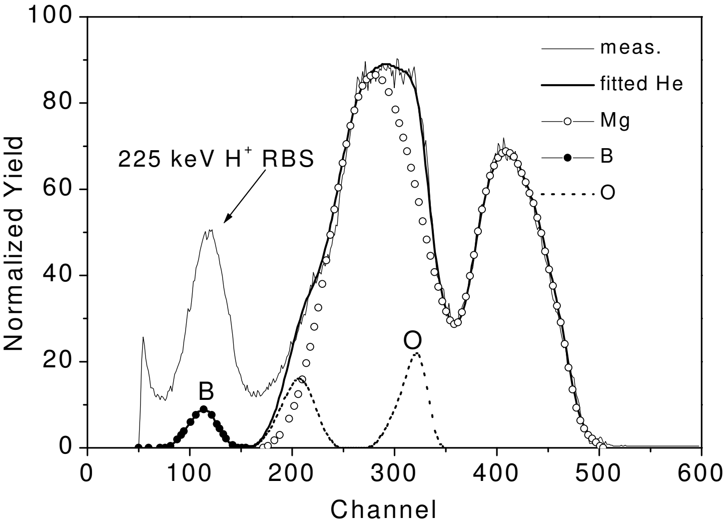

Fig. 2. 900 keV He^{++} RBS spectrum of as deposited Mg-B-Mg-B/C precursor sample. The spectrum was evaluated only with respect to He-beam, the H-part of the spectrum was not taken into account.

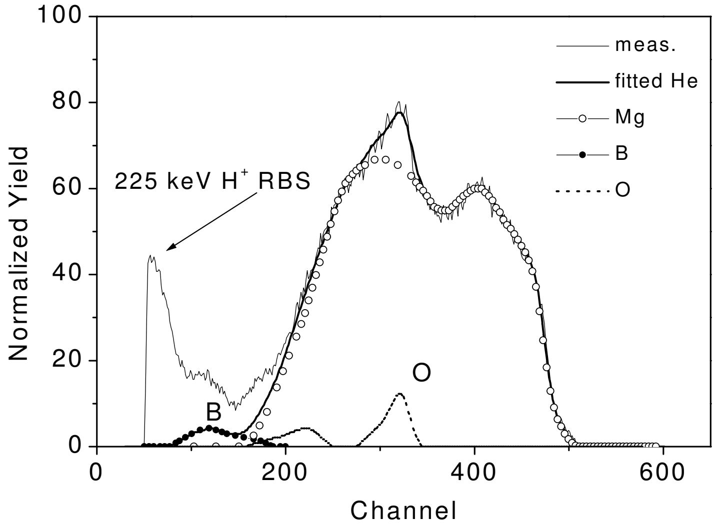

Fig. 3. 900 keV He^{++} RBS spectrum of annealed Mg-B-Mg-B/C superconducting sample. The spectrum was evaluated only with respect to He-beam, the H-part of the spectrum was not taken into account.

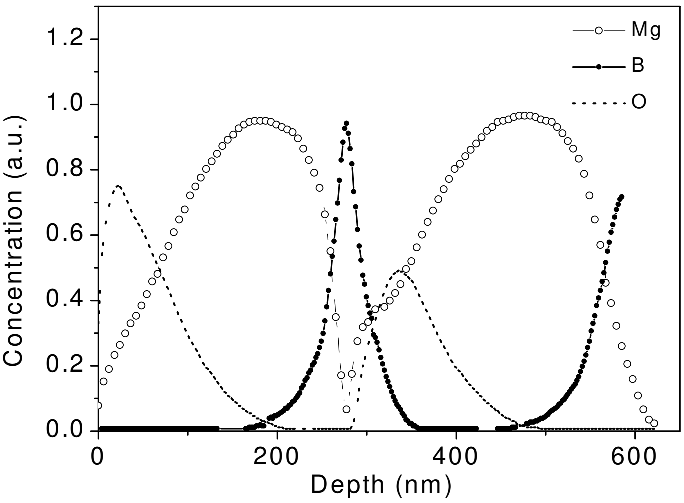

Fig. 4. Concentration profiles of as deposited Mg-B-Mg-B/C precursor sample derived from RBS spectrum in Fig. 2.

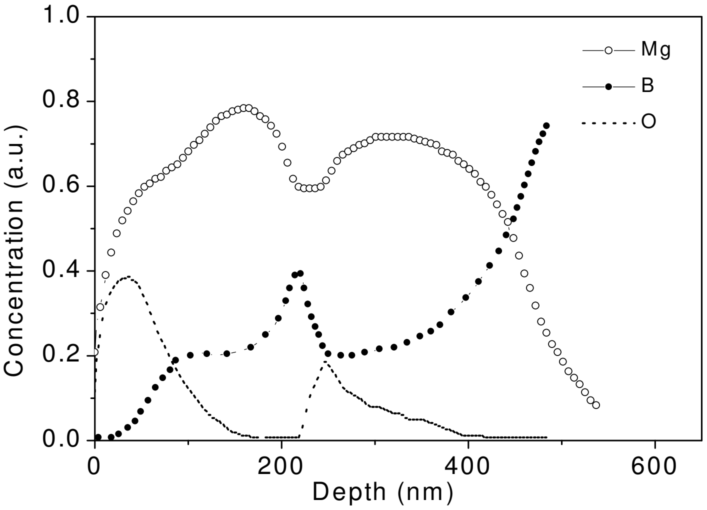

Fig. 5. Concentration profiles of annealed Mg-B-Mg-B/C superconducting sample derived from RBS spectrum in Fig. 3.

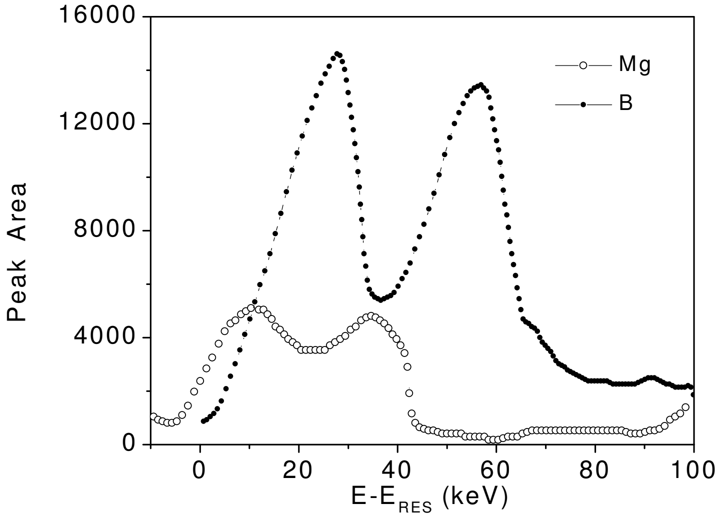

Fig. 6. RNRA analysis (γ-yield dependence on the beam energy) of as deposited Mg-B-Mg-B/C precursor sample. The value of E-E$_{RES}$ = 0 represents the sample surface. The peak area values were obtained as a sum of the three peaks indicated for Mg and B in Fig. 8.

as a histogram, however, to be closer to reality the concentration profiles are constructed as a curve smoothing the step-like raw input data.

Concentration profiles of as-deposited Mg-B multilayer film derived from RBS spectra (Fig. 4) clearly show the presence of oxygen in some parts of the film. Without introducing the proper amount of oxygen into the layer description in the RUMP code it was impossible to fit the experimental data. The maximum of oxygen at film surface is apparently a consequence of interaction of the film with the surrounding atmosphere. However, the maximum of oxygen between the second (B) and the third (Mg) layer can be linked to the reaction of oxygen from vacuum background and deposited Mg film before the next evaporation step.

The concentration profile after in-situ annealing of multilayer Mg-B film (Fig. 5) confirms a strong interdiffusion of Mg and B, where mainly a drop in concentration of Mg shows that the final film is not completely homogeneous. The oxygen observed at the Mg-B interface in the case of as-deposited multilayer film, was distributed towards the substrate after in-situ annealing. The presence of oxygen in MgB_2 film is usually linked with the creation of MgO which negatively influences superconducting properties.

A resonant nuclear reaction on boron (see Tab. 1) has the reaction width of 7 keV, that implies a relatively low depth-resolution. However, the accessible depth is much higher than that of RBS, so the whole boron profile can be determined. Concentration depth profiles derived from RNRA analysis for as-deposited and annealed films are shown in Fig. 6 and Fig. 7, respectively. The difference in the concentration profiles is clearly seen, however, the exact interpretation is due to a possible influence of the probing ion beam questionable.

In RBS analysis the whole depth profile can be calculated from a single energy-spectrum. The scattering cross-section is especially at lower energies sufficiently high to accumulate the spectrum in a few minutes. In contrast to this, in RNRA measurement, each point of the depth

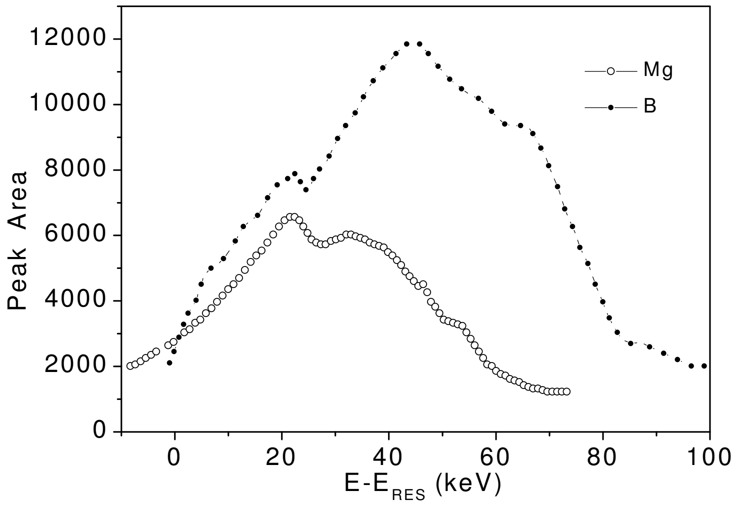

Fig. 7. RNRA analysis (γ-yield dependence on the beam energy) of annealed Mg-B-Mg-B/C sample. The value of E-E$_{RES}$ = 0 represents the sample surface. The peak area values were obtained as a sum of the three peaks indicated for Mg and B in Fig. 8.

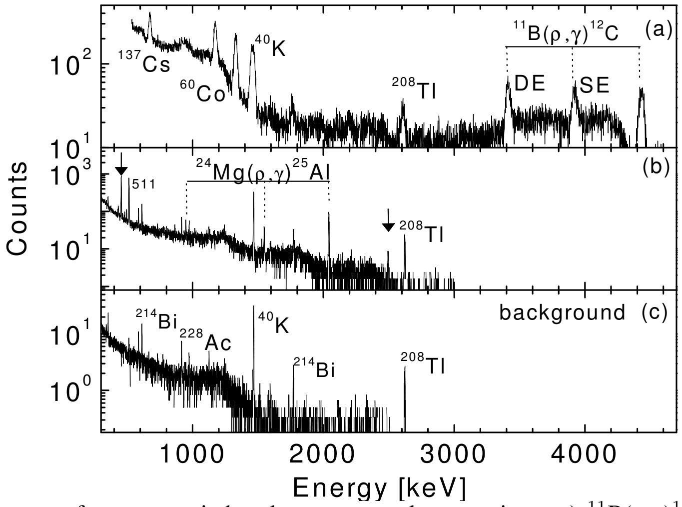

Fig. 8. HPGe-spectra from proton-induced resonant nuclear reactions: a) ^{11}B(p,γ)^{12}C nuclear reaction at E$_p$ = 163 keV. All three peaks (reaction, single escape (SE) and double escape(DE)) were taken into account when evaluating the boron quantity. The peaks from callibration standards (^{137}Cs, ^{60}Co) are also present in the spectrum. b) ^{24}Mg(p,γ)^{25}Al nuclear reaction at incident proton energy E$_p$ = 226 keV. The peak at 511 keV comes from subsequent decay of $^{25}\mathrm{Al} \xrightarrow{\beta^+} {}^{25}\mathrm{Mg}$. The peaks indicated by arrows were not identified satisfactorily. c) Laboratory background. The major constituents are ^{40}K, ^{214}Bi, ^{208}Tl and ^{228}Ac. The labelling of the single peaks is omitted for clarity.

profile is obtained from a separate energy spectrum accumulated at different energy of incident protons. This, together with very low reaction cross-section, implies enormous proton dose applied to the sample during measurement - the dose enhancement in our case as compared to RBS, was by a factor of 200. It can cause migration of the sample elements due to a radiation enhanced diffusion, temperature effects, etc. An indication of not negligible effect of the probing ion beam could be the observed loss of superconductivity of the samples after RNRA measurement. It is not clear, however, if this loss was caused by a structural change of the sample, or by a redistribution of the sample elements. This topic deserves a further study. Nevertheless, although only qualitative, the information provided by RNRA for boron precedes that of RBS. The RNRA determination of Mg needs some fundamental up-to-date studies of reaction parameters, as the ^{24}Mg (p,γ)^{25}Al reaction used in present work has unknown (at least for authors) cross-section and also uncertainty in γ emission [11,12], see Fig. 8.

4 Conclusions

MgB_2 superconducting films prepared by the sequential evaporation of B and Mg were examined by RBS and RNRA. We have shown the presence of oxygen in some parts of film, especially at the interface between the second (B) and the third (Mg) layer of the multilayer film as a consequence of a possible reaction of oxygen contained in a vacuum background and magnesium film before the next evaporation step. The oxygen at the interface was re-distributed towards the substrate after in-situ annealing. In spite of a strong inter-diffusion of magnesium and boron we observed a minimum in the concentration profile of Mg (maximum of boron) in annealed multilayer structure, which is the evidence of not completely homogeneous final film for given thickness of sub-layers. We compared two potential ion beam analyses - RBS and RNRA - and pointed out some obstacles connected with the analysis of Mg-B multilayer films.

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