

MgB₂ superconducting films prepared by e-beam evaporation and *in-situ* annealing

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Superconducting MgB₂ thin films have been prepared on R-plane sapphire and Si(100) substrates using sequential e-beam evaporation of boron and magnesium. The deposition at room temperature was divided into 6 steps alternating boron and magnesium films up to the thickness of about 300 nm. The background vacuum was 10⁻⁴ Pa. After the deposition, an *in-situ* annealing was performed at 620°C at various partial pressures of Ar. The best zero resistance critical temperature value was 28K with the onset of transition being 35K.

The structure and the phase composition of the prepared superconducting films were measured by the X-ray diffraction (XRD). The elemental composition has been investigated by Rutherford back scattering (RBS) technique. In order to detect possible incorporation of oxygen into the films, the ⁴He-beam has been applied using the advantage of the elastic ¹⁶O(α,α)¹⁶O scattering resonance at 3.045 MeV.

Keywords: MgB₂ superconducting films; e-beam evaporation; Al₂O₃ and Si substrates; *In-situ* annealing properties

1. Introduction

Although the MgB₂ compound is known since early 1950's, it has been discovered only recently (in January 2001) to be superconducting [1]. As many authors have already mentioned, the discovery of this property aroused a great interest in the applications as well as in the fundamental aspects and properties of the MgB₂ compound. One of its most interesting properties is the highest T_c among non-oxide binary compounds, being close to 40K (before Nb₃Ge = 23.2 K [2], Nb₃Sn = 18.1K [3], etc). This material has a relatively simple crystal structure and, which is very important, grain boundaries do not influence the critical current density J_c values so dramatically as it is in the case of oxide high critical temperature (HT_c) superconductors. Both initial components Mg and B are also commercially easily available.

During the last months, MgB₂ has been fabricated in various forms as polycrystalline bulk and single crystals [1,4-8], thin films [9-13] and wires [14]. On the basis of the obtained results, two main types of applications are foreseen namely the low current microelectronics as well as large scale power applications.

For microelectronic applications it is of primary importance to prepare MgB₂ superconductor in the form of thin films usually less than 1 μm thick with preferably texturized epitaxial-like structure which allows for high current densities. Vacuum methods such as pulsed laser deposition (PLD) or e-beam evaporation are usually used to prepare Mg-B or B-precursors which must be subsequently annealed at high temperatures in order to build the appropriate structure. During the whole

preparation procedure it is necessary to keep in mind that magnesium is a very volatile material with the melting point of 650°C, and it is also very reactive with oxygen creating thus rather easily MgO compound which is actually an insulating material. The presence of oxygen may lead also to B₂O₃ formation. In other words, some traces of oxygen during the vacuum processing of MgB₂ films may decrease substantially the portion of MgB₂ content in the Mg-B film.

Two main annealing procedures of Mg-B or B precursor films are known today, namely an *in-situ* annealing of Mg-B precursor at about 600°C, and an *ex-situ* annealing of Mg-B or B precursors in Mg vapour at about 900°C. There are substantial differences between the properties of the films obtained by an *in-situ* and/or *ex-situ* annealings. The MgB₂ films prepared by an *in-situ* annealing [9,13] have usually a lower T_c being of the order of 25 to 30 K, and nanocrystalline perhaps even texturized MgB₂ structure with very small grain sizes. These films usually contain some amount of oxygen, especially in the form of also texturized MgO coming from an insufficient vacuum background. On the other hand, Mg-B or B precursors annealed *ex-situ* in the Mg vapour [10-12] exhibits T_c around 39K with a lower amount of oxygen but the grain size in this case is of the order of 0.1-1.0 μm. Non-connected MgB₂ grains are created at the film surface which means that this kind of processing may not be suitable to grow smooth MgB₂ films. It is also more difficult to grow texturized films structurally coherent with the substrate because in this case, the Mg vapour has to penetrate from the film surface up to the substrate interface which reacts as a last.

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From what we have mentioned above we can see the importance of growing thin MgB_2 films suitable for microelectronics applications, the importance of preparation procedure to grow films with suitable properties, and also the importance of the presence and control of the oxygen content in the Mg-B films. It is a purpose of the present paper to deal with these problems and, thus, to contribute to better understanding the properties and behaviour of this recently discovered superconductor.

2. Sample preparation and characterization.

The MgB_2 thin films were prepared by using a multilayer processing technique and *in-situ* annealing. The magnesium and boron layers were deposited on Al_2O_3 and/or Si substrates by sequential electron-beam evaporation at the background vacuum of 10^{-4} Pa. The deposition performed at the room temperature was divided into 6 evaporation steps in which the boron and magnesium layers were alternated. The total amount of deposited magnesium and boron enables us to prepare stoichiometric MgB_2 films about 300 nm thick after an annealing. The precursor films were then *in-situ* heated at the rate of $40^\circ\text{C}/\text{minute}$ to 280°C and kept there 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 $40^\circ\text{C}/\text{minute}$ to 620°C and kept there for 10 minutes. The samples were then cooled down to room temperature in the Ar atmosphere of 6.5 Pa.

The critical temperature was measured by a standard 4-point probe method. The X-ray measurements were performed at CuK_α wavelength (0.15418 nm) in grazing incidence geometry where the signal from the monocrystalline substrate is suppressed. A Siemens D5000 diffractometer with a grazing incidence attachment and LiF monochromator in the diffracted beam were used.

The Ion Beam Analysis facilities at the Institute of Physics of the University of Mexico [15] were used to analyse the MgB_2/Si and the $\text{MgB}_2/\text{Al}_2\text{O}_3$ samples. The ^4He RBS is often used to determine not only the elemental composition of the samples but also the concentration depth profiles of the constituent atoms. In order to detect a possible incorporation of oxygen into the MgB_2 films, a non Rutherford cross-section using a 3.100 MeV ^4He beam was used to take advantage of the elastic $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ scattering resonance at 3.045 MeV for the oxygen content measurements [16]. A solid state detector was set at $\theta = 170^\circ$ in order to measure the charge particle energy spectra. At this resonant energy the cross section for oxygen is 25 times larger than its corresponding Rutherford cross section. Therefore, an enhanced oxygen peak can be obtained enabling us a high sensitivity for the oxygen content determination. The ^4He elastically backscattered (BS) spectra allow also to determine the MgB_2 profile concentration and from the same particle spectra, allow also an over determination of the B content through the $^{10}\text{B}(\alpha,p_1)^{13}\text{C}^*$ nuclear reaction. The full concentration

depth profile of the samples was determined by fitting the BS experimental data using the SIMNRA code [17] and the boron concentration through the $^{10}\text{B}(\alpha,p_1)^{13}\text{C}^*$ nuclear reaction. For the boron determination, the detector angle was $\theta = 135^\circ$ in order to use the $^{10}\text{B}(\alpha,p_1)^{13}\text{C}^*$ nuclear cross-section data.

3. Results and discussion

The best zero resistance critical temperature T_{co} value was determined as 28K for the $\text{MgB}_2/\text{Al}_2\text{O}_3$ sample, Fig. 1, and 19K for the sample MgB_2/Si , Fig. 2. Metallic and semiconducting behaviour of the samples may be observed. The X-ray diffraction patterns were taken at different angles of incidence ranging from 0.5° to 2° . No peaks of the MgB_2 phase could be detected. This result implies that the grains of this phase are very small, far below $1 \mu\text{m}$, which is not surprising also in the view of the results of other authors [13]. These results were confirmed also by our SEM investigations of the surface morphology, i.e. no distinct grains were observed.

Fig. 3 shows the α backscattering energy spectrum (dots) from one of the MgB_2/Si samples. The full line represents the SIMNRA simulation to fit the spectrum. The following 4 layers were necessary to fit the spectrum (the number in parenthesis is the layer number, the layer number 1 being the front layer to the beam, followed by the layer thickness and its atomic composition): (1) 1000 Å : $\text{Mg}_1\text{B}_2\text{O}_{1.5}$; (2) 2000 Å : $\text{Mg}_{0.7}\text{O}_{0.2}\text{Si}$; (3) 4000 Å : $\text{Mg}_{0.05}\text{O}_{0.1}\text{Si}$; (4) substrate : Si. The layers 2 and 3 are considered as interface layers. The Mg peak signal can be seen overlapping with the Si substrate signals. However, the B contribution peak is too small and does not show up as a peak. The B contribution was deduced by fitting the Mg peak contribution through the ^4He energy loss factor of the MgB_2 films. The Si substrate signals can be considered as a background for the B and Mg signals and cause a relatively large error in the determination of the concentration of these elements. The error in the determination of B is 20% and for Mg it is 10%. The determination of B concentration through the $^{10}\text{B}(\alpha,p_1)^{13}\text{C}^*$ nuclear reaction proton yield

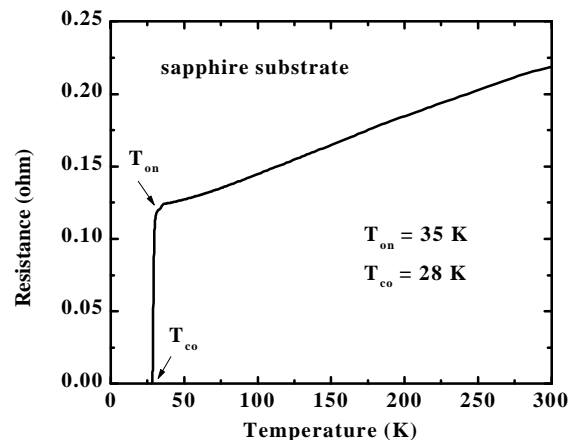


Figure 1. R vs. T dependence for $\text{MgB}_2/\text{Al}_2\text{O}_3$ sample. The $T_{\text{co}} = 28$ K, the onset transition value is $T_{\text{on}} = 35$ K.

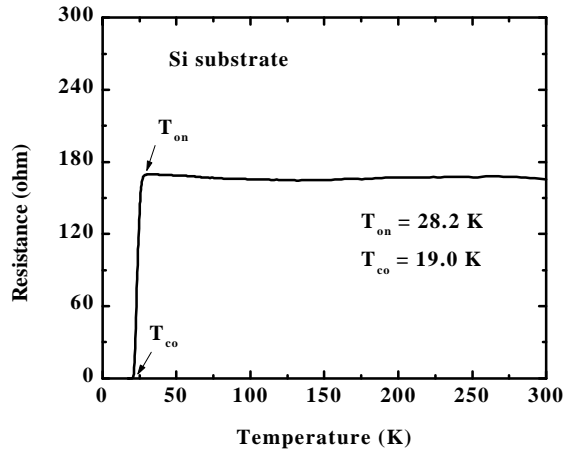


Figure 2. R vs. T dependence for MgB₂/Si sample. In this case T_{co} = 19 K and the onset value is T_{on} = 28.2 K.

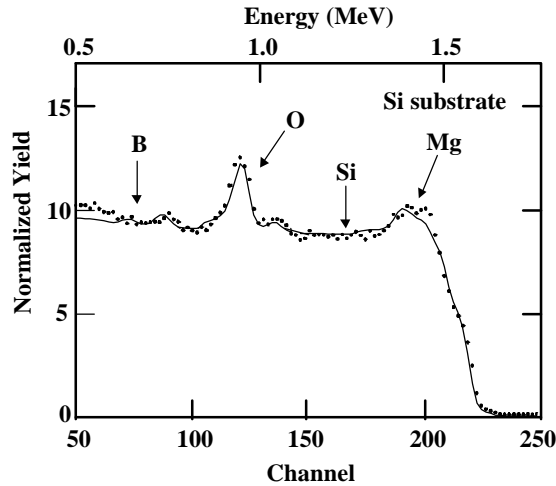


Figure 3. The BS spectrum (dots) obtained from MgB₂/Si sample by bombarding it with 3.100 MeV ⁴He⁺ beam. The detector was set at 170° as to measure the energy of all the particles produced by the bombardment. The solid line is the SIMNRA simulation.

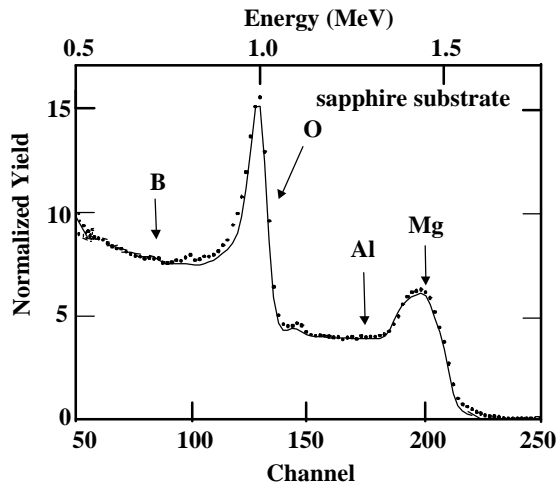


Figure 4. The BS spectrum (dots) obtained from MgB₂/Al₂O₃ sample. All experimental conditions were similar as those presented in Fig. 3

method are in a good agreement (15%) with the ⁴He BS determinations.

A plane silicon substrate was also irradiated under the same condition as MgB₂ films in order to discard the oxygen in the silicon wafer. This measurement does not show any oxygen present in the substrate and one can conclude that the oxygen is incorporated in the MgB₂ film only. The spectrum for the MgB₂/Al₂O₃ sample is shown in Fig. 4. Again, 4 layers were necessary to fit the spectrum. Results of this measurement are summarized in Table 1.

Currently, experiments are on the way in which we are using other beams and other nuclear reactions in order to increase the sensitivity of our method as to determine the content of individual components. By this procedure we will be able to distinguish increased intensity peaks coming from individual components without their overlapping.

4. Summary

We prepared MgB₂ superconducting films 300 nm thick by e-beam vacuum evaporation of Mg and B components followed by an *in-situ* annealing of the Mg-B precursors. Because of volatility of Mg, the precursor deposition was performed at a room temperature.

The zero resistance critical temperature values for the best samples were T_{co} = 28K for MgB₂/sapphire and T_{co} = 19K for MgB₂/Si films. The XRD diffraction patterns measured in the grazing incidence geometry did not show any intensity peaks which indicates a nanocrystalline structure of the synthesized films confirmed also by our SEM observations.

Results of the RBS analysis as well as those of elastic ¹⁶O(α,α)¹⁶O scattering resonance at 3.045 MeV for the determination of the oxygen content showed the elemental composition along the film thickness. It is of primary importance to determine especially the oxygen content inside the film as well as on the film/substrate interface and, eventually, also inside the substrate. In the case of Si substrate used, the highest oxygen content was found on the film surface decreasing towards the film thickness. In the case of sapphire substrate, the highest oxygen content is on the film/substrate interface bound probably to Mg and eventually also to B. We expect to obtain more information concerning the Mg-O and/or B-O binding from Auger and/or XPS spectroscopy. These experiments are currently on the way.

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Table 1. Atomic composition of the MgB₂/Al₂O₃ sample measured in sequential sublayers starting from the film surface.

Sublayer		Sublayer thickness (Å)	Composition				Remark
No	position		Mg	B	O	Al	
1	auto	2800	0.8	2.0	0.7	--	film
2	auto	1000	0.5	0.8	1.5	--	interface
3	auto	100	1.0	--	0.5	0.7	interface
4	auto	10000	--	--	3.0	2.0	substrate

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