Characterization of Superconducting Magnesium-Diboride Films on Glassy Carbon and Sapphire Substrates

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Recibido el 14 de mayo de 2007; aceptado el 26 de octubre de 2007

IBA methods were applied to measure elemental depth profiles of precursors and superconducting MgB_2 thin films deposited on glassy carbon (Good Fellows) and sapphire (Al_2O_3) substrates. For each type of substrates we obtained a pair of samples i.e. one amorphous precursor and one superconducting film which were then characterized. A $^3He^+$ beam was used to bombard both, precursors and superconducting films in order to obtain the samples elemental composition profiles. The zero resistance $T_{co}$and the middle of transition T_{cm} values were 26.0K and 29.7K for the MgB_2 film deposited on glassy carbon substrate. In the case of sapphire substrate the T_{co} and T_{cm} values were 25.0K and 27.9K, respectively.

Keywords: Superconducting MgB_2 films; IBA methods; RBS/NRA analyses.

Bombardeo de materiales con haces de iones producidos por un acelerador de partículas fueron usados para medir la composición elemental y su perfil en profundidad de películas delgadas superconductoras de MgB_2depositadas sobre sustratos de carbón vidriado (Good Fellows) y zafiro (Al_2O_3). Para cada tipo de sustrato, obtuvimos un par de muestras, es decir, película precursora amorfa y película superconductora, las cuales fueron caracterizadas. Un haz de $^3He^+$fue usado para bombardear tanto las películas precursoras y superconductoras para obtener su composición elemental. Los valores de la resistencia nula T_{co}y la resistencia media de transición T_{cm}fueron 26.0 K y 29.7 K para las películas superconductoras de MgB_2depositadas sobre los sustratos de carbón vidriado. En el caso cuando se uso zafiro como sustrato los valores deT_{co} y T_{cm} fueron 25.0 K y 27.9 K.

Descriptores: Películas superconductoras MgB_2; Análisis materiales por bombardeo de iones.

PACS: 29.30.Ep; 74.72.Fq; 74.76.Bz

1. Introduction

Due to its remarkably high transition temperature T_c=39−40K as well as a simplicity in the chemical composition and the crystal structure, the recently discovered superconducting MgB_2 compound [1] already attracted relatively large interest of researchers from both points of view i.e. basic research as well as practical applications. Both types of applications, i.e. the high-current magnet and power applications [2] as well as the low-current applications for superconducting electronics devices may utilize this simple superconductor.

For the superconducting electronics it is of importance to prepare MgB_2 in the form of thin films usually less than 1μm thick having the required properties. Josephson junctions [3], superconducting bolometers [4] and integrated circuits [5] were already fabricated with possibility to operate in compact cry coolers [6] at temperatures above 15-20K.

Although superconducting MgB_2 powder is available from major chemical suppliers, the preparation of high quality thin films samples is still a technical challenge. Various methods are used to deposit the Mg and/or B films as PLD [7], magnetron sputtering [8], e-beam evaporation [9], etc.

Because of presence of light elements in MgB_2 films as boron and eventually oxygen, not many methods are suitable to investigate these films from the point of view of their chemical composition, elemental depth profiles and the film-substrate interaction. Auger electron spectroscopy (AES) has been used to investigate surface chemical composition and to some extent (not for very thick films) also depth profiles [10]. Very elegant and non-destructive investigations of MgB_2 thin films may be performed by ion beam analysis (IBA) namely by Rutherford back scattering (RBS) as well as by the appropriate nuclear reactions (NRA). In our previous work [11] we studied superconducting MgB_2 thin films deposited on Si substrates by IBA methods which were applied to measure the elemental atomic composition and the MgB_2 film-substrate interface. In the present work we applied IBA methods to investigate properties of similar superconducting MgB_2 thin films deposited in this case on glassy carbon and sapphire substrates. Study of a possible substrate influence on T_c values of the superconducting MgB_2 films was also one of aims of this work.

2. Experimental details

The detailed description of the MgB_2 film sample preparation was presented in [12] and therefore only brief outline will be given here. First, three amorphous B/Mg bilayers were

deposited successively by e-beam evaporation at room temperature on glassy carbon (Goodfellow) and sapphire (alumina Al_2O_3) substrates in the vacuum background of 10^{-4} Pa starting with B and ending with Mg on the top of the film precursor. The total deposited film thickness was about 900 to 1000 nm. One half of deposited precursors were then converted to superconducting films by an annealing in an Ar atmosphere of 16 Pa for 10 minutes at 700°C and subsequently cooled down to room temperature in an Ar atmosphere of 300 Pa. In such a way, for each type of substrate we obtained a pair of samples i.e. one deposited amorphus and one annealed superconducting film which were then characterized.

The critical temperature T_{co} (zero resistence) and T_{cm} (a middle of superconducting transition) values were measured by a standard 4-point resistive method. The XRD patterns were measured by Siemens D-5000 diffractometer in Bragg-Brentano as well as in the grazing incidence geometries with the angle of incidence set to 1° and 1.5° in order to suppress the signal coming from the substrate. The film surface morphology was examined by a JEOL JSM - 35CF scanning microscope.

The IBA facilities of the Institute of Physics of the National Autonomous University of Mexico (UNAM) based on a single ended 5.5 MV Van de Graaff accelerator were used to obtain the atomic composition profiles of the MgB_2 films. A $^3He^+$ beam was used to bombard the targets positioned normal to the incoming beam and the energies of the produced particles were measured with a surface barrier detector set an angle 156°. The $^3He^+$backscattered elastically cross sections on B, O and Mg nuclei are not ready available in the literature and the RBS method may be not valid to analyze these films. $^3He^+$in the energy range of 1.5-2.7 MeV with 0.3 MeV steps were use to bombard thick reference targets (MgB_2 pellets and Al_2O_3) in the same conditions as the analyzed films. Our measurements of the 2000 keV $^3He^+$ elastic spectraof the reference thick samples were fitted with RBS cross-sections; therefore we could safely apply these cross-sections to analyze the Mg-B and MgB_2 films. The film elemental profiles were obtained by analyzing the particle energy spectra with the DataFurnace code [13]. This program uses the simulated annealing algorithm and its automatic fitting code generates its own layer structure i.e. the number of layers, layer thickness and the composition as well.

3. Results and discussion

The zero resistance $T_{co}$and the middle of transition T_{cm} values were 26.0K and 29.7K for the MgB_2 film deposited on glassy carbon substrate. In the case of sapphire substrate, the T_{co} value was 25K and T_{cm} was 27.9K. Similarly as in a previous case of MgB_2 superconducting films on silicon substrate [11] we were not able to identify the presence of superconducting MgB_2 crystalline phase from the XRD patterns. Apparently, in our case of *in situ* annealed MgB_2 samples, the size of crystallites of this phase is too small to be detected (they must be larger than 0.1 μm). As we mentioned already above, the size of MgB_2 grains in case of an *ex situ* annealing could reach up to 1.0 μm. The rather smooth surface of our samples has been confirmed also by the SEM morphology observations with visible fine granular structure and the grain size being around 100 nm.

Figure 1 shows the comparison of the RBS experimental energy spectra (dots) corresponding to the 2000 keV $^3He^+$bombardment of the Mg-B precursor (not-annealed) and the MgB_2 (annealed film sample) on the carbon substrate. Figure 2, shows similar energy spectra for the Mg-B precursor and the MgB_2 superconducting sample on the sapphire substrate.

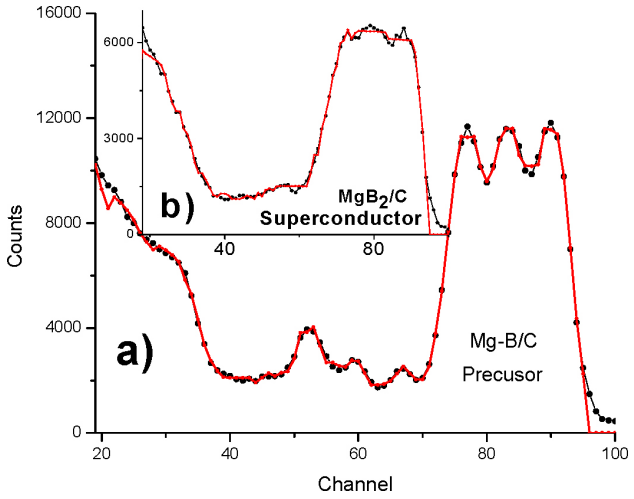

FIGURE 1. Comparison of the experimental RBS spectrum (dots) for a 2000 keV $^3He^+$beam bombardment of the films (a) Mg-B/ C precursor, (b) MgB_2/C superconductor. The RBS energy spectra were produced by the $^3He^+$ normal incidence sample bombardment. The surface barrier detector was set an angle θ = 156°. The solid line represents the DataFurnace fitting of the spectra.

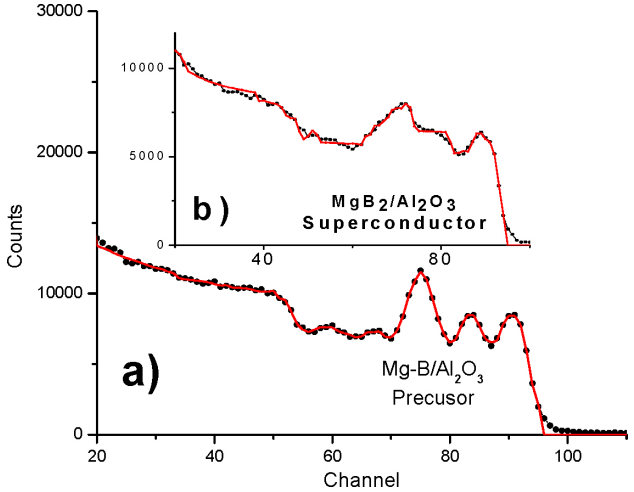

FIGURE 2. Comparison of the experimental RBS spectrum (dots) for a 2000 keV $^3He^+$beam bombardment of the films: (a) Mg-B/ Al_2O_3precursor, (b) MgB_2/ Al_2O_3 superconductor. The RBS energy spectra were produced by the $^3He^+$ normal incidence sample bombardment. The surface barrier detector was set an angle θ = 156°. The solid line represents the DataFurnace fitting of the spectra.

From the particle energy spectra of Mg-B precursors for both types of substrates, several peaks may be observed due to the multilayer process used to deposit these films. After the Mg-B precursors were annealed in order to obtain the MgB_2 superconducting phase, it may observe from the associated RBS spectra, that the multiple peak structure disappears. This is because the annealing of the Mg-B multi-layers enhances both, interdifusion of the Mg-B atoms as well as chemical reactions during sintering the material.

The solid lines in the Figs. 1 and 2 represent the DataFurnace fitting to RBS spectra. A multiple scattering correction has been introduced on the Mg signal to ensure a correct subtraction of the background to the B signal, using the procedure developed recently by Barradas, Jeynes, and Jackson [14]. Figure 3 shows as a 3-D plot the complex atomic profiles used to fit the RBS spectrum of the Mg-B precursor film on C substrate. A similar atomic profile, to fit the Mg-B precursor film on sapphire was obtained. It may be observed from Fig. 3, that the Mg-B sub-layers profiles show some degree of interdiffusion and unexpected thick film interfacial mixing structure with the carbon substrate. Important concentrations of oxygen in majority of the sub-layers may also be observed.

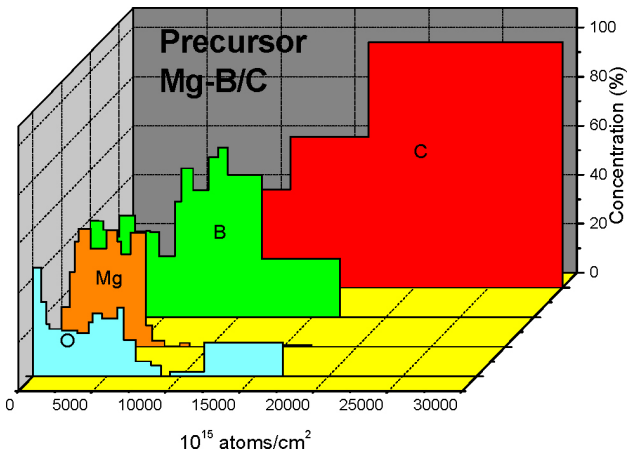

FIGURE 3. The DataFurnace Mg, B, O atomic profiles for fitting the RBS spectrum of Fig. 1a. The DataFurnace Mg-B/C film thickness was calculated as 616 nm and the interfacial mixing was 1144 nm. The precursor Mg-B/sapphire film thickness was calculated as 712 nm and the interfacial mixing was 1010 nm.

The atomic sub-layer profiles generated to fit the superconducting MgB_2 films spectra of Figs. 1b and 2b are summarize in Table I and II, respectively. The complex depth profiles to fit these spectra are related to the great number of the sub-layers shown in these Tables. The depth resolution is optimal at the surface but it degrades quickly below the film surface due to the energy straggling and then, only the first four layers of the outermost sub-layers can be most effectively analyzed. It may be observed also, that the super-

TABLE I. The MgB2/C superconducting film atomic concentration (%) profile generated by the DataFurnance to fit the spectrum shown in Fig. 1b. The sub-layer thickness units are in 10^{15} at/cm^2. DataFurnace calculates the atomic density "r" (at/cm^3 $\times$ 10^{22}) for each of the sublayers in order to obtain the linear thickness t(nm) but this must not necessary correspond to a real film thickness. The sub-layers F,I and S means: film, interface and the substrate, respectively. The thickness for F and I -are 807 nm and 947 nm, respectively. The atomic concentration error was estimated as 10% for Mg, 15% for O and 20% for B.

Sub-layer No.	Position	t (at/cm2)	t (nm)	r(at/cm3)	Mg	B	O	C
1	F	451	76	6	19	18	62	0
2	F	369	59	6	27	22	51	0
3	F	2197	319	7	36	29	34	0
4	F	2546	318	8	36	44	20	0
5	F	298	34	9	30	51	19	0
6	I	596	54	11	9	67	14	11
7	I	906	82	11	13	59	7	21
8	I	1031	86	12	8	70	2	2
9	I	5316	418	13	0	78	0	22
10	I	1346	116	12	0	42	8	50
11	I	2032	189	11	0	16	12	71
12	S	9838	865	11	0	0	0	100

TABLE II. The MgB_2/Al_2O_3 superconducting film atomic concentration (%) profile generated by the DataFurnance to fit the spectrum shown in Fig. 2b. The thickness for F and I are 532 nm and 817 nm respectively.

Sub-layer No.	Position	t (at/cm2)	t (nm)	r(at/cm3)	Mg (%)	B (%)	O (%)	Al_2O_3 (%)
1	F	325	39	8	30	46	24	0
2	F	251	36	7	33	29	38	0
3	F	593	117	5	58	8	33	0
4	F	750	160	5	65	4	31	0
5	F	796	105	8	41	37	21	0
6	F	601	74	8	38	45	17	0
7	I	3396	506	7	54	26	7	12
8	I	1111	166	7	32	26	33	8
9	I	1317	144	9	0	52	16	31
10	S	21839	4376	5	0	0	0	100

conducting films are inhomogeneous and any of the sub-layers have not the ideal MgB_2 stoichiometry. Also oxidation of the sub-layers may be observed in the sample atomic profile structures.

4. Conclusions

IBA methods applied to obtain atomic profiles of the superconducting MgB_2 thin films deposited on glassy carbon and sapphire substrates show that the films were inhomogeneous and the presence of oxygen was detected apparently as formation of MgO and B_2O_3.Other important results were thick film interfacial mixing with the carbon and sapphire substrates were observed (see Table I and II) and they may be produce a high sticking coefficient of the MgB_2 films in both substrates.

The zero resistance $T_{co}$was 26.0K for the MgB_2 films deposited on glassy carbon substrate and in the case of sapphire substrate the T_{co} value was 25.0 K. For MgB_2 /Si films prepared with similar conditions as the films reported here [11], the T_{co} values were 29.3 K for MgB_2 films deposited on the Si (100) substrate and 28.0 K for the film grown on Si(111). From the variation of the measured T_{co} values, one may conclude some influence of the substrate used to grow the MgB_2 superconducting films. However, some researchers believed that the most important factors influencing the T_{co} value of polycrystalline MgB_2 thin films might be related to the deposition and annealing conditions but independent of the substrate materials.

One question could arise from IBA of the MgB_2 superconducting films, namely, how the IBA film analyses are consistent with the possibility to form superconducting films. Simple arithmetic calculations using the Table I and II show that in case of the MgB_2/C superconducting film, there are 3.4×10^{18} Mg atoms and 1.8×10^{18} B atoms. In the case of the MgB_2/sapphire superconducting film there are 2.2×10^{18}Mg atoms and 7.6×10^{18} B atoms. Then, in both cases, there are actually enough Mg and B atoms to form the superconducting MgB_2 phase.

Acknowledgments

The authors wish to thank Arcadio Huerta for his technical assisted.

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