Ion implantation followed by laser/pulsed plasma/ion beam annealing: a new approach to fabrication of superconducting MgB₂ thin films

Jerzy Piekoszewski,
Zbigniew Werner,
Marek Barlak,
Andreas Kolitsch,
Władysław Szymczyk

Abstract. The paper presents a new approach to formation of superconducting MgB₂ thin films: ion implantation followed by annealing in an unconventional second step treatment using pulsed laser, plasma, or ion beams. Merits and drawbacks of individual approaches are discussed.

Key words: MgB₂ • superconducting films • pulsed plasma annealing

J. Piekoszewski
Department of Material Studies,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock/Świerk, Poland
and Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-145 Warsaw, Poland

Z. Werner
Department of Material Studies,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock/Świerk, Poland
and Institute of Physical Chemistry PAS,
44/52 Kasprzaka Str., 01-224 Warsaw, Poland

M. Barlak
Department of Material Studies,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock/Świerk, Poland

A. Kolitsch
Forschungszentrum Rossendorf,
P. O. Box 510119, 01314 Dresden, Germany

W. Szymczyk✉
Department of Material Studies,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock/Świerk, Poland,
Tel.: +48 22 718 0562, Fax: +48 22 779 3481,
E-mail: szymczyk@ipj.gov.pl

Introduction

The number of papers on magnesium di-boride published since the discovery of superconductivity in MgB₂ in 2001 [6] exceeded the number of papers devoted to other metallic superconducting materials. That reflects some high expectations raised by this new material, since its advantages include the highest critical temperature of superconductivity (T_c) among metallic and inter-metallic compounds, as well as low-cost of its components. These expectations apply both to the bulk and to the thin film forms of the material.

Several PVD, CVD and ion beam techniques have been used to form thin superconducting MgB₂ films. A common feature of most of these techniques is *in situ* or *ex situ* conventional annealing of the Mg-B system, normally performed at some temperature between 600 and 950°C in Mg vapor or in some inert gas to prevent excessive loss of magnesium.

In the present concept we propose another two-step process. In the first step boron ions are implanted into magnesium substrate, or *vice versa*. By using multiple-energy implantations at appropriate fluencies, one is able to form a sufficiently thick layer of a stoichiometric mixture of both components. In the second step the structure is subjected to a pulsed energy deposition, which melts the near-surface layer of the structure. An expected advantage of transient process is that a plume of substrate material evaporated during the melting phase of the process can exert a pressure on the liquid surface, that would be sufficient to prevent any significant loss of magnesium from the irradiated Mg-B system. Below we are going to discuss some aspects of the issues mentioned above.

Ion implantation

The goal of the ion implantation process (B ions into Mg substrate or *vice versa*) is to form a layer in which the B:Mg atomic concentration ratio would correspond to stoichiometry of the MgB_2 compound. This layer should be sufficiently thick and preferably located at some depth beneath the surface to avoid its contamination, to diminish the sputtering effects [7], as well as to leave a sacrificial layer for vaporization. To obtain sufficient layer thickness one can employ multi-step implantation treatment performed successively at several different ion fluencies and energies. To bring the post-implantation B:Mg atomic concentration ratio as close to the MgB_2 compound stoichiometry as possible, superposition of several individual profiles simulated using the SRIM computer code [14] was optimized. Sample result of such optimization procedure is shown in Fig. 1 as the B depth profile produced in a Mg sample by implanting B^+ ions successively at 3 different fluency/energy combinations (1.6×10^{18} B^+ ions/cm^2 at 80 keV, 5×10^{17} B^+ ions/cm^2 at 60 keV, and 8×10^{17} B^+ ions/cm^2 at 40 keV). The simulated combined profile was in fairly good agreement with the one deduced from experimentally taken Rutherford Back Scattering (RBS) spectra analyzed using the SIMNRA computer code [12]. As can be seen in Fig. 1, even the lowest energy of 40 keV is sufficient to bury implanted layer some 200 nm below the surface. The 200 nm wide stoichiometric region reaches the depth of about 400 nm. The implanted layer width falls into the range of MgB_2 thin films prepared by some more conventional techniques.

The total necessary boron fluence was almost 3×10^{18} ions/cm^2. At that high fluencies, one should verify whether concentration of atoms retained after implantation is high enough in view of the limitation imposed by the sputtering phenomenon. Fortunately, yield of sputtering of magnesium by boron ions turned out to be very low. Sputtering does not play any significant role even at very high fluencies, and the MgB_2 stoichiometry requirements may be met. This limitation is less severe for magnesium implantation into boron, sine the fluencies required in that case are significantly lower.
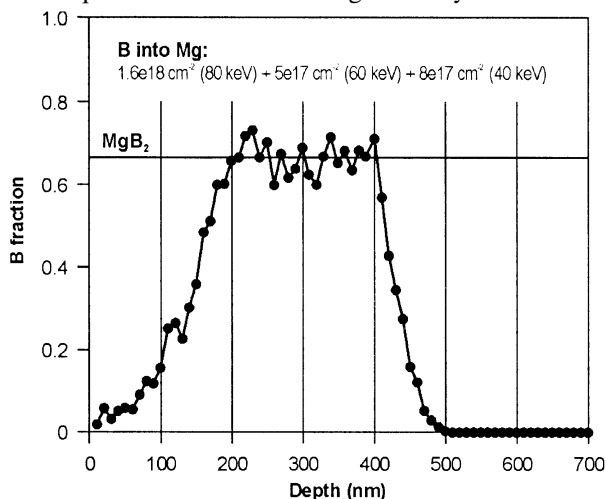
Systematic optimization of the multi-energy/fluence implantation process is still an open question to be solved by careful computer modeling.

Transient energy treatment

According to thermodynamical considerations presented by Liu Zi-Kui *et al*. [5] it is essential for MgB_2 stability that the pressure over the liquid phase is maintained at a sufficiently high level to prevent excessive transfer of Mg into the gas phase and transition of MgB_2 into other Mg-deficient compounds. For instance, the MgB_2 phase is stable up to 600°C at a pressure of 1 mTr, whereas at a pressure of 1 atm, the stability extends to 1545°C.

In the non-equilibrium regime (which is the case for every transient energy treatment), if a solid MgB_2 is to be formed in a Mg-B system heated to a high temperature, the system must be quenched from the appropriate pressure-temperature phase diagram "window". Generally speaking, the higher the pressure within the system, the higher the allowed temperature from which the system may be cooled down.

We modeled thermal effects of energy pulse treatment using the energy transfer in laser irradiated targets (ETLIT) computer code [15], which assumes surface absorption of the supplied energy. This assumption is valid both for plasma pulses containing low-energy ions, and for laser pulses. Figure 2 presents the results of such modeling performed for Mg target treated with Gaussian-shaped pulses of two different durations (100 and 1000 ns) depositing the energy with two different densities (0.5 and 1.7 J/cm^2). Materials parameters were adopted after [11]. Temperature evolution at 300 nm depth and melt depth vs. time are shown. The following conclusions may be drawn:
–   Short (100 ns) and low energy density (0.5 J/cm^2) pulses give rise to a shorter melting period and to a relatively rapid cooling rate.
–   Longer (1000 ns) and higher energy density (1.7 J/cm^2) pulses result in elongation of the melting time and slower cooling rate.
Since the slower cooling rate reduces the tendency for cracking of the solidified layer, whereas the longer melt duration favors formation of more homogeneous Mg-B system, the latter situation seems to be more advantageous.
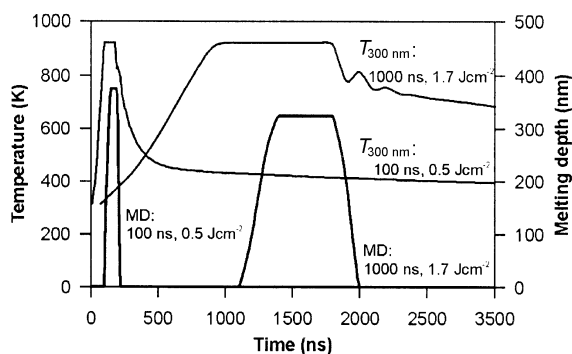

Fig. 1. The simulated B depth profiles in Mg obtained by a superposition of 3 different B^+ ion fluencies: 1.6×10^{18} B/cm^2 at 80 keV, 5×10^{17} B/cm^2 at 60 keV and 8×10^{17} B/cm^2 at 40 keV, respectively.

Fig. 2. The simulated temperature dependences at 300 nm and melt depth (MD) vs. time for Mg substrate treated with pulses of two different durations 100 ns and 1000 ns and two different energy densities 0.5 J/cm^2 and 1.7 J/cm^2, respectively, obtained with ETLIT code.

However, when selecting the process parameters it is important to keep in mind that higher temperature of the surface region enhances vaporization of the substrate material and thus prevents loss of excessive amount of magnesium.

Obviously, there is some upper limit for pulse energy imposed by the fact that a too high energy may lead to ablation (evaporation) of the entire layer.

Laser beams

Pioneering experiments on transient laser treatment of implanted silicon and other semiconductors date back to the mid-seventies of the last century. They were aimed mainly at annealing of implantation-induced defects and activation of donor and acceptor dopants. Laser annealing has been demonstrated using a variety of laser sources and a wide range of pulse durations/energies. In early period mostly Q-switched ruby ($\lambda = 0.694$ μm) and Nd:YAG ($\lambda = 1.06$ μm) lasers with pulse duration 20–110 ns and energy density between 0.3–2.0 J/cm^2 were used. At present, one observes a strong trend to use UV excimer lasers (λ from 157 to 351 nm, pulse duration from few nanoseconds to just over 100 ns, typical energy output from a few up to 1000 mJ) in industrial applications. For instance, in-line beam excimer laser annealing (ELA) treatment applied to manufacture low temperature poly-silicon (LTPS) for mass production of active matrix liquid crystal displays (AM-LCD) was performed using Lambda Physik XeCl laser operated at 300 Hz, 1050 mJ output, and pulse duration of 52.9 ns extended to 391 ns [13].

Experiments dealing with laser annealing of superconductors started in the 80 of the last century. For instance, transformation of an amorphous non-superconducting Nb-C-N film into superconducting one (T_c of about 12 K) by means of irradiating the system with a Q-switched Ruby laser at 15 ns pulse variation and energy density ranging from 0.1 to 10 J/cm^2 was demonstrated [2]. However, to our knowledge, experiments in this field are rather sparse.

Practically, any kind of high-power pulsed laser may be suitable to accomplish the annealing of metallic superconductors since light of any wavelength from ultraviolet to near infrared is absorbed in a similar way in metals [1]. However, it seems that lasers of the type mentioned in the first paragraph of this section [13] are most suitable for that purpose.

High intensity pulsed plasma beams

In the course of nuclear fusion research several plasma pulse generators have been developed. Rod plasma injector (RPI) type of generator [9] is of special interest in the present context. It is capable to produce pulses of any working gas plasma with duration in the range 0.1 to 1.0 μs and energy density between 1 and 7 J/cm^2. The ions produced in such pulses have a broad energy spectrum (from 0 to several tens of keV), depending on the kind of the working gas. Several experiments have been conducted on transient melting and doping various materials. In particular, the formation of p$^+$-n

and n$^+$-p junctions for silicon photovoltaic solar cells was successfully demonstrated [10]. The working gases were BF$_3$ and PF$_5$, respectively.

RPI machine seems to be well suited also for the purpose of annealing implanted Mg-B systems under the cap of magnesium vapor preventing any excessive loss of Mg from MgB$_2$ layers. This approach has been experimentally verified for both versions of ion implantation (B into Mg and Mg into B). Existence of superconducting regions in the temperature range 33–33.8 K after ion implantation and plasma pulse treatment has been demonstrated e.g. [8], although without percolation.

Considering an optimum choice of plasma pulse parameters, we may refer to the results of simulation presented in the introduction. Assuming a typical plasma pulse duration about 1 μs, the required density of energy deposited by the pulse would be about 2–3 J/cm^2. However, it should be pointed out that the plasma pulse generation technique suffers from a rather poor reproducibility in comparison to the ELA technique.

Pulsed ion beam

Advantages of mono-energetic pulsed ion beam treatment include capability to adjust ion energy in such a way that the energy losses are fairly uniform over the desired thickness, in particular over the thickness of the implanted region. This feature allows smaller temperature gradients to develop in the treated sample and potentially may lead to better quality of the produced layers, e.g. due to reduced tendency to cracking.

Pioneering research on application of pulsed ion beams to material processing was performed on pulse annealing of ion-implanted Si [4]. The existing machines capable of producing the suitable ion beams were recently reviewed in [16].

By the way of an example, Figure 3 presents the depth energy loss profile for 350 keV Ar ions implanted into Mg, as calculated using SUSPRE code (University of Surrey). In this case ions loose most of their energy in a near-surface layer of a thickness corresponding roughly to the thickness of implantation simulated in Fig. 1. Ar ions beams can be produced in the so-called magnetically insulated ion diodes (MID) generators with gas pre-fill (machines of that type have been developed
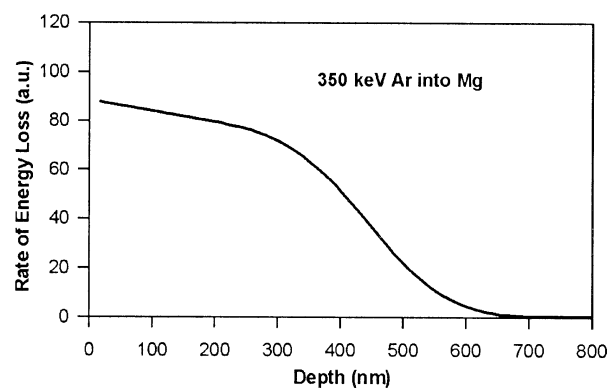

Fig. 3. The rate of energy deposition in Mg for Ar ions of 350 keV energy calculated using SUSPRE code.

at Los Alamos National Laboratory [3]). Such generators seem to be well suited for the present purpose in view of their ability to produce beams of any type of noble-gas ions. Most of MID-type machines produce beams of H and C ions with energies within the 100–300 keV range, i.e. much in excess of the implanted layer thickness.

Conclusions

Thin superconducting MgB_2 films may be produced using a number of ion implantation/annealing treatments. Further development will have to concentrate on experimental validation of various possible approaches. Physical aspects of interaction of beams of various types with the processed Mg-B structures must be carefully considered to choose the optimal technique. Of great importance is the possibility to control the beam parameters.

References

1. Allmen M (1987) Laser-beam interactions with materials, physical principles and applications. Springer-Verlag, Berlin, p 17
2. Appleton BR, White CW, Stritzker B, Meyer O (1980) Laser annealing of superconductors. In: White CW, Peercy PS (eds) Laser and electron beam processing of materials. Academic Press, New York, p 714
3. Davis HA, Wood BP, Munson CP *et al*. (1998) Ion beam and plasma technology development for surface modification at Los Alamos National Laboratory. Mater Chem Phys 54:213–218
4. Hodgson RT, Baglin JEE, Pal R, Neri JM, Hammer DA (1980) Ion beam annealing of semiconductors. Appl Phys Lett 37;2:187–189
5. Liu ZK, Schlom DG, Li Qi, Xi XX (2001) Thermodynamics of the Mg-B system: Implications for the deposition of MgB_2 thin films. Appl Phys Lett 78:3678–3681
6. Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y, Akimitsu J (2001) Superconductivity at 39 K in magnesium diboride. Nature 410:63–65
7. Peng N, Jeynes Ch, William RM *et al*. (2005) A potential integrated low temperature approach for superconducting MgB_2 thin film growth and electronics device fabrication by ion implantation. IEEE Trans Appl Supercond 15;2/3:3265–3268
8. Piekoszewski J, Kempiński W, Andrzejewski B *et al*. (2005) Superconductivity of MgB_2 thin films prepared by ion implantation and pulsed plasma treatment. Vacuum 78:123–129
9. Piekoszewski J, Langner L (1991) High intensity pulsed ion beams in material processing: equipment and applications. Nucl Instrum Methods B 53:148–160
10. Piekoszewski J, Werner Z, Szymczyk W (2001) Application of high intensity pulsed ion and plasma beams in modification of materials. Vacuum 63:475–481
11. Qian M (2006) Creation of semisolid slurries containing fine and spherical particles by grain refinement based on the Mullins-Sekerka stability criterion. Acta Mater 54:2241–2252
12. SIMNRA code, http://www.rzg.mpg.de/~mam/
13. Simon F, Brune J, Herbst L (2006) Advanced excimer-based crystallization systems for production solutions. Appl Surf Sci 252:4402–4405
14. SRIM 2006 code, http://www/srim/org
15. Szyszko W, Vega F, Afonso CN (1995) Shifting of the thermal properties of amorphous germanium films upon relaxation and crystallization. Appl Phys A 61:141–147
16. Werner Z, Piekoszewski J, Szymczyk W (2001) Generation of high-intensity pulsed ion and plasma beams for material processing. Vacuum 63:701–708