A Potential Integrated Low Temperature Approach for Superconducting MgB_2 Thin Film Growth and Electronics Device Fabrication by Ion Implantation

Nianhua Peng, Christopher Jeynes, Russell M. Gwilliam, Karen J. Kirkby, Roger P. Webb, Guosheng Shao, Douglas M. Astill, and W. Y. Liang

Abstract—By implanting high fluence B into Mg targets, we demonstrate clearly that superconducting MgB_2 thin films can be formed at a low process temperature. The superconducting transition temperature T_c values observed are dependent on the growth condition. The ion beam synthesis experimental data are discussed and compared with simulation results of the B implantation process in Mg target. We propose that ion beam synthesis of MgB_2 is a potential approach for the mass production of superconducting electronics devices.

Index Terms—Ion beam synthesis, MgB_2 , thin films.

I. INTRODUCTION

MgB_2 is considered to be an excellent superconductor with potential technical applications for its simple chemical composition and the relatively high superconducting transition temperature T_c of 39 K. Thin films of MgB_2 are important for superconducting electronics device fabrication, however, there are still some obvious problems associated with the preparation of high T_c superconducting MgB_2 thin films such as the disparity of thermodynamics properties of Mg and B, and low decomposition temperature of MgB_2 [1], [2]. In addition to these, MgB_2 also has a very low sticking coefficient at low temperature for most of the substrate materials [3]. These make the direct deposition of MgB_2 thin films from a stoichiometric single target very difficult. Current approaches for the thin film growth of superconducting MgB_2 involve depositions of MgB_2 or Mg/B mixtures with extra Mg onto a substrate at a high temperature, followed by an anneal at a temperature above 600°C after deposition [4], [5]. The high temperature deposition and anneal brings in a potential problem for the fabrication of multiple layered structures, which is the most convenient form for superconducting electronics device fabrication. Generally speaking, a well-defined sharp and narrow (restricted by the coherence length) superconductor and nonsuperconductor interface structure is very important if the tunneling of superconducting electrons is utilized, such

as Josephson junctions. Considering the fact that both Mg and MgB_2 have low melting temperature at about 650°C , obviously any process at temperatures above 600°C should be avoided for the electronics device fabrication, as such a high temperature would lead to serious Mg vapor diffusion and MgB_2 decomposition which are detrimental to the formation and maintenance of sharp interface structures. For many challenging applications in high speed devices, a large number of uniform Josephson junctions have to be built with high integration density [6]. For future applications of superconducting electronics, the ideal thin film deposition technique for MgB_2 should be a low temperature process with capability for multiple layer structure fabrication and compatibility with current microelectronics technology.

Though deposition of superconducting MgB_2 thin films has been reported recently at relatively low temperatures with new techniques [7], [8], there are still technical problems to meet the criteria set above. Furthermore, the quality of single layer thin film still needs improvement. Moreover an integrated low temperature process for both thin film growth and electronics device fabrication is still not available.

The common feature of all those reported low temperature deposition approaches is the direct deposition of both Mg and B simultaneously, so the MgB_2 phase is formed at low temperature during the deposition process by controlling the deposition conditions. We note the similarity of crystal structures between Mg and MgB_2 [9]: the crystal structure of MgB_2 looks like an intercalation of two-dimensional hexagonal B sheet in between the host Mg hexagonal structure, with an expansion and displacement of the neighboring Mg sheets in the Mg structure to accommodate the B sheet, which also leads to an increase in mass density in MgB_2 compared to that of pure Mg. In other words, the framework of Mg could provide a structural constraint for the formation of the flat B sheets that are believed to be critical for the high T_c . Therefore we anticipate that a low temperature process will be possible if sufficient B can be mixed with a solid Mg at atomic scale to form MgB_2 .

Effective thermal diffusion of B into a Mg solid target may be one approach to achieve atomic scale mixing of B with solid Mg, but it needs a high diffusion temperature. At temperatures below the melting point of Mg, equilibrium thermodynamics for the binary Mg-B system suggests that the process will be very slow, if it is indeed possible [1], [2]. Furthermore, the thermal diffusion process is not a good approach for sharp profile control.

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N. Peng, C. Jeynes, R. M. Gwilliam, K. J. Kirkby, and R. P. Webb are with the University of Surrey Ion Beam Centre, Guildford, GU2 7XH, U.K. (e-mail: n.peng@surrey.ac.uk).

G. Shao is with the School of Engineering, University of Surrey, GU2 7XH, U.K.

D. M. Astill and W. Y. Liang are with the IRC in Superconductivity, Cambridge University, CB3 0HE, U.K.

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Energetic B ion implantation into Mg target is an ideal way to achieve this intercalation process, though post implantation annealing is necessary not only to remove the irradiation damage effects but also for the subsequent growth of superconducting MgB_2 grains. In contrast to the thermal diffusion process, ion implantation is not a thermodynamically equilibrium process, and high concentrations of B can be achieved in a Mg host by high fluence ion implantation. In fact, ion implantation is a well-established technology in today's microelectronics industry. A low annealing temperature should be sufficient for the MgB_2 phase growth as both Mg and B ions have been mixed thoroughly at atomic scale by the ion implantation process.

By implanting B into a Mg target, we have explored the fabrication of superconducting MgB_2 thin films at temperatures below 500°C . The formation of the superconducting MgB_2 phase has been confirmed by Rutherford backscattering spectroscopy (RBS), cross sectional transmission electron microscopy and DC magnetization observations. We reported a low T_c of 15 K previously [10]. Here we demonstrate an improvement in T_c to 21 K by increasing ion implantation fluences, and compare the implantation results with numerical simulations.

II. SIMULATION OF ION BEAM SYNTHESIS PROCESS

When energetic B ions are implanted into a solid Mg target, an embedded B rich thin layer will be formed inside the Mg target. The B distribution inside Mg can be described very well by using the classical binary collision approximation [11]. Our simulation code SUSPRE [12] has been developed for the numerical simulation of any ion implantation process. Fortunately, MgB_2 is the binary Mg boride with the lowest B concentration among all Mg borides and a very stable stoichiometry. Assuming that we can keep adding B into the target Mg host until that the critical ratio of B to Mg is 2:1 at which point it overflows into the neighboring target element, the simulated results using SUSPRE code reveal that the minimum implantation dose for a 80 keV B beam is 1.9×10^{18} ions/cm² to achieve a peak 2:1 ratio of B to Mg, as illustrated by curve a in Fig. 1. Further increase of implantation dose will lead to the overflow of extra B into surrounding area, so the MgB_2 thickness grows, as shown by curve b in Fig. 1. It is obvious that the minimum dose required for a MgB_2 stoichiometry depends directly on the beam energy. For example, the minimum fluence required to achieve a 2:1 B to Mg ratio for a 120 keV B beam is 2.25×10^{18} ions/cm². However, significant B overflow is expected for a 1.25×10^{18} ions/cm² B implantation at 30 keV, as shown by curve c in Fig. 1. The superposition of both 1.25×10^{18} ions/cm² B implantation at 30 keV and 2.25×10^{18} ions/cm² B implantation at 80 keV leads to the formation of a double layer structure as represented by curve d in Fig. 1. The B poor ditch in between the two B rich plateaus is of interest for planar SNS type sandwich structure fabrication if the B poor layer has a low T_c .

Apparently our simulation model is a very simple description for the real physical process of B implantation in Mg. For accurate profile and composition control, sputtering effect must be taken into account. The sputtering process is dependent on the

Fig. 1. The simulated B depth profiles in Mg target with different implantation fluences and energies: a, 1.9×10^{18} B/cm² at 80 keV; b, 2.15×10^{18} B/cm² at 80 keV; c, 1.25×10^{18} B/cm² at 30 keV; and d, the superposition of b and c.

beam implantation conditions such as relative ion mass, dose and beam energy etc. The sputtering effect is minimized by using B implantation into Mg target, as B is much lighter than Mg in mass.

The continuous growth of MgB_2 is possible only if extra B overflows into the neighboring "B poor" area. In theory, there is possibility that as more B introduced into the Mg target it becomes increasingly difficult to find a new place to incorporate the implant and the material "wanders off" to a neighboring element more frequently as the concentration approaches the saturation level. In this case it is possible for sputtering to affect the saturation limit, and consequently the composition profile never reaches a flat top with designed stoichiometry.

Obviously there are many factors that are believed to be important for the control of ion implantation process. As a pilot study on ion beam synthesis of MgB_2 , we will focus our current implantation experiments on the under-dose and close to MgB_2 stoichiometry implantations first.

III. THIN FILM GROWTH BY ION IMPLANTATION

Based on the numerical simulation results described above, we have carried out two sets of B implantation experiments into common commercial Mg ribbons, one is 10^{18} B/cm² at 80 keV and another is 2×10^{18} B/cm² at 120 keV using the 200 KV Danfsik implanter. As revealed from the RBS analysis, the surface of the Mg ribbon is more or less oxidized already. By changing the B ion energy, we may include a small amount of MgO in the implantation area with 80 keV B beam or exclude nearly all MgO at all with 120 keV B beam. All Mg ribbons were mounted on double sided conducting tapes with an embedded thermocouple to monitor the implantation temperature in-situ. The Mg targets were kept at a warm 230°C during implantations by using the beam heating effect in order to avoid the unwanted amorphization of Mg by the B irradiation. The exact target temperature is controlled by the beam current, and beam scanning frequency/area. X-ray diffraction on both virgin and as implanted Mg ribbons reveals that all Mg ribbons are in good crystallite status.

Fig. 2. Temperature dependent superconducting transitions from DC magnetization measurement for a sample implanted with 10^{18} B/cm² at 80 keV (curve a) and with 2×10^{18} B/cm² at 120 keV (curve b), both samples have been annealed at 500°C for 1 hour.

All as implanted samples do not show strong evidence of superconducting phase transition, but we do observe some weak antiferromagnetic signals at low temperatures (less than 10 K), implying the B in Mg host is not ordered. Post implant annealing is necessary for these implanted samples in order to enhance the growth of ordered MgB_2 grains. Annealing at 500°C for 1 hour leads to a clear evidence for the superconducting phase transition from DC magnetization measurements using a Quantum Design SQUID magnetometer, now matter whether it is in either flowing Ar, or N_2 , or in a sealed quartz tube under vacuum. RBS analysis of some of the annealed samples shows that the implant inhibits the growth of the surface oxides upon annealing.

It is interesting to note here that a higher T_c of 21 K is observed in samples implanted at 120 keV with 2×10^{18} B/cm², as shown in Fig. 2, while the T_c values for those samples subjected to implantation of 80 keV B with a fluence of 10^{18} B/cm² are only about 15 K, indicating high dose might help for the formation of MgB_2 grains. The peak B concentration in 80 keV implanted samples is just over 50% of the theoretical minimum value, but the average B concentration should be lower after thermal annealing as B may spread out to the neighboring area, this helps to understand the experimental fact that an extended anneal at 500°C cannot improve the T_c value. In contrast to this, the B concentration in 120 keV implanted samples is very close to the theoretical minimum value, it is very interesting to investigate further whether a longer anneal will improve the T_c or not. More information will be available soon by implanting Mg with B to an even higher concentration.

IV. PROSPECT FOR AN INTEGRATED LOW TEMPERATURE DEVICE FABRICATION ROUTE

We have demonstrated low temperature ion beam synthesis of MgB_2 . Low T_c values have been observed in samples with implantation fluences below the saturation level. With further optimization on the growth conditions, we expect to fabricate superconducting MgB_2 thin films with various T_c using the B ion implantation approach at high implantation fluences. We have demonstrated before that high quality Josephson junctions can be fabricated with polycrystalline thin films using the

masked proton beam damage method [13]. The thin film synthesis process described above can be easily extended to make more complex structures for the superconductor electronics device manufacture. This is an important advantage of ion beam synthesis process.

The low T_c observed in under-dose implanted samples suggests that a SNS or SIS type sandwich structure (possible Josephson junctions) can be fabricated by a sequential boron ion implantation process with two different ion energies, as shown in Fig. 1. Sequential implants can also produce thick films. An O implant could also be employed to turn the un-reacted Mg in B poor interface area into MgO , which is an insulator. Using a planar mask technology, other interesting interface structures can also be fabricated. Maskless device fabrication can be achieved as well if we use a pre-patterned Mg host for the B implantation.

It is very clear that any new fabrication process of superconducting MgB_2 device should be cost effective in order to make it economically viable, at least compared to other technologies either with MgB_2 or other high T_c superconductors. Compared to other thin film deposition methods, the primary extra cost for the ion beam synthesis process described above is because high fluences take a relatively long implantation time. Even in our research implanter with a B beam current of 0.5 mA, an implantation of 2×10^{18} B/cm² for a cross section of 25 cm² can be achieved in less than 5 hours. It should be emphasized here that industrial facilities for high fluence B implantation, about 10 mA in beam current, are readily available. This will cut the implantation time significantly. As the process is completely compatible with the microelectronics technology, the integration of many superconducting and nonsuperconducting interface structures will be straightforward. We believe this will enable affordable practical applications of superconducting electronics.

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