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Study of microstructural changes in MgB_2 thin film superconductors irradiated with 200 MeV ^{107}Ag ions

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Abstract

MgB_2 superconductor thin films, prepared by pulsed laser deposition (PLD) and electron beam evaporation (EBE), have been investigated by scanning electron microscopy (SEM) before and after 200 MeV ^{107}Ag ion irradiation. The severe degradation of superconducting properties in irradiated PLD film and the absence of the same in EBE film correlates with the observed changes in their microstructures. The micrographs of the PLD film show an overall smoothing, flow pattern and reduction in size of the bigger agglomerates after irradiation. On the other hand, the microstructure of the EBE film does not show any significant change after irradiation. The flow pattern observed in the PLD film can be understood on the basis of the viscoelastic model for irradiation induced shear flow in amorphous solids. The observed degradation of the PLD film may thus be attributed primarily to its disordered nature under irradiation, whereas the radiation hardness of the EBE film may be due to its higher crystallinity.

1. Introduction

About two years ago, the discovery of superconductivity at 39 K in magnesium diboride (MgB_2) intermetallic binary compound [1] emerged as a surprise to the scientific community. Since then, a number of groups all over the world have been involved in studies determining physical properties of the compound as well as in finding out ways for its technical exploitation. Enhancement of critical current density is one of the most important requirements for useful application of a superconducting material. In this direction, irradiation with swift heavy ions (SHI) is a well-proven technique for the case of high temperature superconducting cuprates (HTSC) [2]. Following the same line, irradiation of MgB_2 with neutrons [3], protons [4, 5] and gold [5, 6] beams have been carried out by various groups. The results so far have been mixed. Initially promising in terms of J_c enhancement [4], the results turned out to show that MgB_2 is a radiation hard material [5, 6]. The differences in results, at first sight, seem to be due to the difference in microstructure of the samples and irradiation conditions.

SHI irradiation may lead to a number of structural modifications in solids. Ion-beam induced plastic deformation (IBID), observed primarily in amorphous alloys [7, 8], is one of the most common modifications. Attributed to the viscoelastic-fluid like behaviour of the solids subjected to irradiation [9, 10], IBID manifests itself as flow patterns that result in modification of the irradiated surface [11–15]. It is now widely accepted that IBID, as well as other structural modifications arise due to the transient mobility of the target atoms, induced by the electronic excitation, as the fast heavy

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ions slow down in the bulk of the material. However, the nature of structural modifications by SHI irradiation depends on the underlying microstructure of the samples.

Thin films deposited by different methods under different conditions may possess different microstructures. The effect of irradiation, with 200 MeV ^{107}Ag ions, on the superconducting properties of MgB_2 thin films deposited by pulsed laser deposition (PLD) and by electron-beam evaporation (EBE) is indeed different [16]. In order to show it arises from different microstructural changes after irradiation, we examined the same thin films as used in [16] by scanning electron microscopy (SEM). The SEM results show, for the first time, the evidence of SHI irradiation induced shear-flow on the PLD film surface and the absence of the same in the EBE film. In this paper, we discuss the possible reasons for the occurrence of shear flow patterns on the surface of one of the films, as well as its absence in the other film. This observation consolidates the assertion that irradiation effects on the superconducting properties of MgB_2 are microstructure dependent.

2. Experimental details

Two thin films of MgB_2, deposited by PLD and EBE, used for the present studies are the same as in [16]. Preparation and characterization details of these films are reported elsewhere [17, 18]. Both the films were *c*-axis oriented with randomly oriented grains in the *ab*-plane. Two pieces of each of the films, with dimensions of 4–5 mm × 4–6 mm × 250/550 nm, were cut from a single bigger piece or selected from the same batch of films. One piece of each type of the films was used as a pristine sample. Irradiation of the films was carried out using the pelletron accelerator facility at the Nuclear Science Centre (NSC), New Delhi, India, with a 200 MeV ^{107}Ag ion beam. The irradiation temperature was maintained at around 80 K using liquid nitrogen, and the final dose was 10^{11} ions cm^{-2}. SEM was carried out to study the microstructure of both the irradiated and the pristine samples using a Leo 440 (Oxford Microscopy, UK) instrument.

3. Results and discussion

The critical temperatures T_c of 29 and 32 K in PLD and EBE films, respectively, determined by the onset of zero field cooled (ZFC) diamagnetic signals, is found to be much less in comparison to the highest observed 39 K in bulk MgB_2 compounds. The lower T_c values can be due to either non-stochiometry introduced during *ex situ* processing or inter-band impurity scattering in these two-gap superconductors [19]. However, after irradiation, T_c of the PLD film was severely degraded from 29 to 25.5 K, whereas it increased slightly for the EBE film from 31 to 32 K. Similarly, the critical current density as a function of applied field $J_c(B)$ and irreversibility line $B^*(T)$ also degrade severely after irradiation in PLD film, but practically no change in these properties is observed in the EBE film [16]. For instance, after irradiation, in the case of the PLD film the J_c (4.2 K, 1 T) changes from 3.7×10^5 to 2.2×10^4 A cm^{-2} and B^* (4.2 K) changes from 8.3 to 3.8 T. By contrast, the same changes in the case of the EBE film are 1.2×10^6–1.1×10^6 A cm^{-2} and 3.6–3.5 T, respectively.

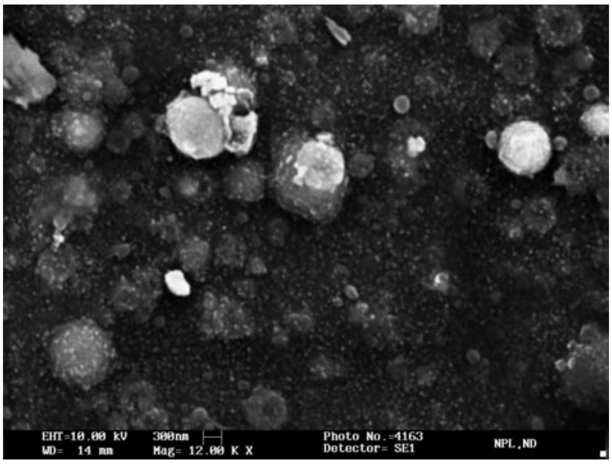

Figure 1. SEM image of pristine MgB_2 thin film deposited by PLD (at 12 000× magnification).

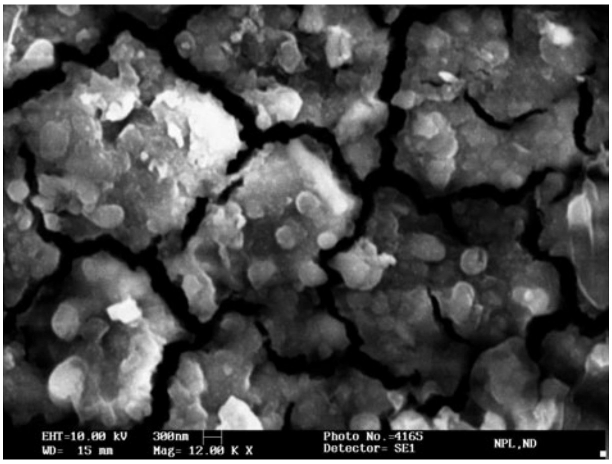

Figure 2. SEM image of pristine MgB_2 thin film deposited by EBE (at 12 000× magnification).

Figure 1 shows a typical SEM image of the pristine PLD film. It is evident that the film consists of granular structure. Small grains of typically about 80 nm size agglomerating into bigger particles make the most of the film. On the other hand, the SEM images of pristine EBE film show a 'tiled' structure with the size of 'tiles' ranging between 3 and 4 μm, and the gap between tiles extending up to about 200–300 nm (figure 2). The tiled structure seems to be an agglomeration of small flat grains of size around 500 nm. Moreover, at higher resolutions, the SEM images also show grain boundaries, which measure around 20 nm for both PLD (figure 3) and EBE films (figure 4). These measured values are in accordance with the typical values reported earlier in a bulk sample of MgB_2 [20].

The SEM images of the irradiated samples show interesting results. In the irradiated PLD film, a definite flow pattern is observed (figure 5) on the surface, marking significant mass movement. The observed flow pattern in irradiated PLD film is similar to the ion beam induced shear flow pattern observed in amorphous metallic alloys submitted to SHI irradiation [11–15]. In the amorphous solids, it has been attributed to the motion induced by electronic excitation of near surface atoms due to irradiation. In order to confirm our observations, we have used the viscoelastic model of

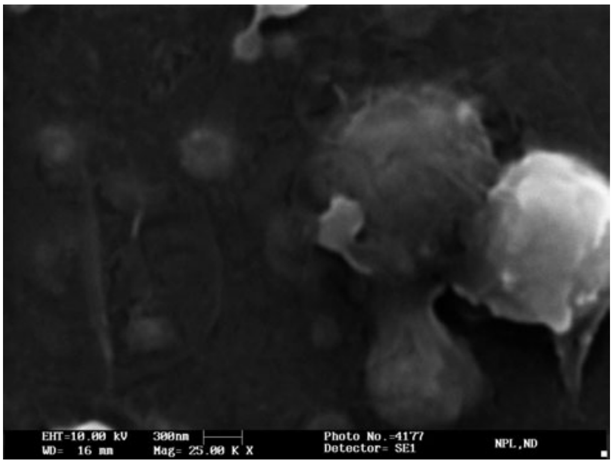

Figure 3. SEM image showing a grain boundary in MgB_2 thin film deposited by PLD (at 25 000× magnification).

Figure 4. SEM image showing a grain boundary in MgB_2 thin film deposited by EBE (at 25 000× magnification).

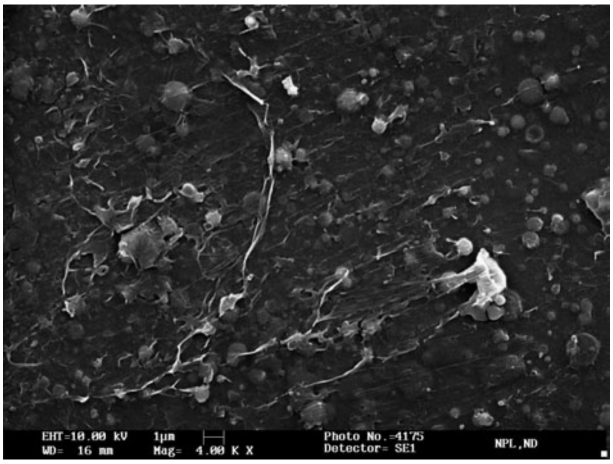

Figure 5. SEM image of a 200 MeV ^{107}Ag ion irradiated MgB_2 thin film deposited by PLD (at 4000× magnification).

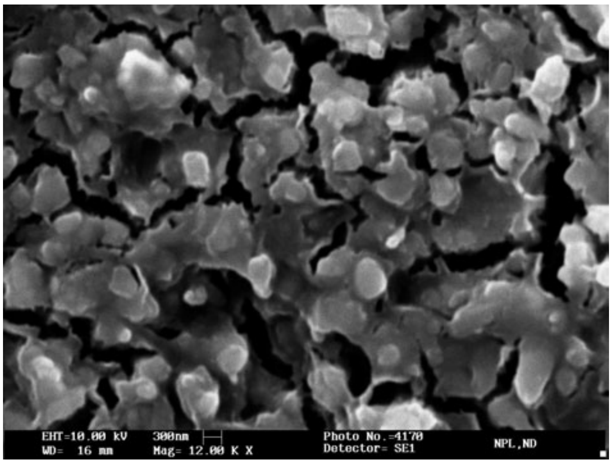

Figure 6. SEM image of a 200 MeV ^{107}Ag ion irradiated MgB_2 thin film deposited by EBE (at 12 000× magnification).

Trinkaus [9, 10] originally developed to explain the structural modifications of amorphous solids subjected to fast ions. Based on this model, the expression for shear shift of near surface atoms [9, 10] is given by,

$$\Delta x = 6R_p\phi\frac{1.16(1+\nu)\beta S_e}{3e(5-4\nu)\rho C}\sin\theta\cos\theta \qquad (1)$$

where R_p, ν, β, S_e, ρ and C are the range of the incident ions, Poisson number, thermal expansion coefficient, electronic energy loss, volume density and specific heat capacity of the material, respectively. θ is the tilt angle of the incident beam with respect to the target-surface [12, 13] and ϕ is the ion fluence (number of ions incident on the surface per unit area, i.e. the product of the ion flux and irradiation time). We have $S_e = 1.66$ keV Å^{-1} [21], $\phi = 10^{11}$ ions cm^{-2}, $\beta = 5.0\times10^{-7}$ K^{-1} at 100 K [22], and $\rho = 2.7$ g cm^{-3} [23]. Also, C (at room temperature) is approximately $3k_BN_A/M$, where k_B is the Boltzmann constant, N_A is the Avogadro number and M is the molar weight of the material. This gives $C = 543.09$ J kg^{-1} K^{-1}. Also, $\nu = 1/3$ for most of the solids. Putting these values and using thickness ($t = 0.55$ mm) of the film instead of the projected range R_p in equation (1) (since the ions pass only this distance through the material), we get $\Delta x = 0.53$ μm. Although, this calculated value of shear shift is lower than that obtained from the SEM images (1–2 mm) of irradiated PLD film, it essentially explains the flow-patterns. A more realistic value may be obtained if the value of C at about 100 K (irradiation temperature) is used. Thus, if $C = 190$ J kg^{-1} K^{-1} (at 100 K, the value obtained by extrapolating data in [24] using an exponential fit), we get $\Delta x = 1.52$ μm. This calculated value is in excellent agreement with that experimentally measured. On the other hand, the flow patterns were completely absent in the irradiated surface of EBE film (figure 6).

Combining the two parts, i.e. the changes in superconducting properties, and the occurrence of flow patterns, we may say that the PLD film was the one that got severely degraded by irradiation, whereas the EBE film behaved overall as a radiation hard target. In view of these facts, there seem to be four reasons responsible for the differences observed in irradiated surfaces of the two films:

(i) Microstructure

It is known that the symmetry of the microstructure of the target plays a significant role in the effects induced by irradiation. In crystalline materials, IBID, and hence the shear flow is negligibly small due to their highly symmetric structure [7]. Therefore, it could be assumed that under irradiation, the PLD film behaved like a disordered target, whereas the EBE film behaved as a crystalline one. This assumption is further supported by the fact that the PLD film has higher normal state resistivity (at room temperature, one order of magnitude higher than that of the EBE film) [17, 18]. Moreover, the relatively lower post-annealing temperature of 700 °C for the PLD film should have resulted in a more disordered film [17], which is also evident in the SEM image (figure 1). Further, the XRD measurements (θ–2θ scan) [17], done on the PLD film show 16.4° (001) and 33.2° (002) MgB_2 peaks. The other observed impurity peaks at 24.5° and 28.33° with corresponding d-spacings of 2.04 and 2.35 Å, respectively, were compared with those of several possible secondary phases Mg, MgO, MgO_2, MgB_6 and MgB_{12}. A very good match was found with the characteristic d-spacings of MgO and MgB_{12}, suggesting the presence of these compounds as secondary phases in the PLD film. The small peak at 27.2°, which may be a position that could be due to the (101) reflection of the MgB_2 also indicates that part of the film was disordered. On the other hand, the XRD carried out on EBE film post-annealed at 890 °C shows [18] the occurrence of bulk crystallization with the pronounced MgB_2 peaks for (001), (101) and (002). These observations also indicate towards the disordered nature of PLD and more crystalline nature of EBE films. Due to their disordered behaviour under irradiation, the mass movement (that leads to the IBID and shear flow) in PLD film due to irradiation was more significant than that in the EBE film. Thus the observed changes in the superconducting properties of the PLD film may be attributed to large-scale atomic rearrangements resulting in its chemical degradation.

(ii) Starting surface topography

The SEM images show nearly spherical agglomerates in PLD film as compared to nearly flat tile-like ones in the EBE film. This makes the former more damage prone by offering more variations in the effective tilt-angle θ of the incident beam. Line profiles taken at various places on the film-surfaces during electron microscopy also indicate that the starting surface topography of the PLD film is rougher than that of the EBE film. Large roughness of the surface makes the film more sensitive to fast ion beams [11–13, 15].

(iii) Grain size within the agglomerates

The SEM images clearly show that the agglomerates in the PLD film consist of much smaller grains as compared to those in the EBE film. With the same amount of available ion-deposited thermal energy, therefore, melting of an 80 nm-sized grain of PLD film is much easier and quicker than that of a 500 nm sized grain of EBE film. The grains in the PLD film seem to be better connected than that in the EBE film, thus better heat conduction in the former should further assist melting of its grains. However, we should remark here that the measurement of critical current density in both the films show an absence of weak links [16].

(iv) Thickness of the films

Since the PLD film is twice as thick as the EBE film, the incident ions spend twice the time in the former as that spent in the latter. Thus the thermal energy deposited, in the wake of incident ions, leads to a higher surface temperature of the PLD film in comparison to that of the EBE film. The higher surface temperature assists the shear flow of near surface atoms and they move comparatively larger distances in the PLD film before becoming finally quenched.

4. Summary

The difference in the effects of SHI irradiation on T_c, critical current density as a function of applied field, and the irreversibility line of superconducting MgB_2 films prepared by PLD and EBE can be correlated with different irradiation induced microstructural changes in them. The PLD film shows significant mass movement on the surface as evidenced by the observed flow pattern on the irradiated surface. This pattern is completely absent in the irradiated EBE film. The flow patterns can be explained on the basis of shear-flow mechanism within the framework of the viscoelastic model originally developed for amorphous solids subjected to fast ion irradiation. The occurrence of flow patterns in PLD film may thus be attributed to its disordered behaviour during irradiation. Consequently, significant mass flow, and hence atomic rearrangement results in this film, leads to the observed changes in its superconducting properties. On the other hand, the absence of such flow patterns in the EBE film may be due to its higher crystallinity. These results point towards an important fact that the radiation hardness of MgB_2 films may depend on their microstructure.

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