200 MeV $^{107}$Ag ion irradiation induced mass transfer in MgB$_2$ thin film superconductors

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Abstract: We have investigated two MgB$_2$ superconductor thin films, prepared by two different methods, namely, pulsed laser deposition (PLD) and electron beam evaporation (EBE), by scanning electron microscopy (SEM) before and after 200 MeV $^{107}$Ag ions irradiation. Severe degradation of superconducting properties in irradiated PLD film and absence of the same in EBE film correlates well with the observed changes in their microstructures. It has been noted that the microstructural changes observed in the PLD film is due to significant irradiation induced mass-transfer at the film surface, which is evident from the SEM pictures (figure 1). This has been supported quantitatively using the viscoelastic model originally developed for amorphous solids subjected to irradiation.

Key words: Magnesium diboride, Superconductivity, Ion irradiation, Scanning electron microscopy, Mass transfer

1 Introduction

During an irradiation experiment involving swift (K.E. $\geq$ 1 MeV) heavy ions (SHI), a large number of target atoms are set into motion. It is well established that this irradiation induced atomic mobility results in a number of macroscopic effects, such as, the ion-beam induced plastic deformation (IBID), which may be attributed to the electronic energy loss $S_e$ of the incident ions in the target material [1-7]. However, the issue of conversion of electronically deposited energy to the motion of target atoms is still under discussion and several mechanisms have been proposed by various groups without any general agreement so far.

SHI irradiation is a well-proven technique for the enhancement of critical current density ($J_c$) in the case of high temperature superconducting cuprates (HTSC) [8]. Therefore, when superconductivity at 39 K was
discovered in magnesium diboride (MgB$_2$) [9], the material was tested for irradiation induced effects by a number of groups in the light of possible exploitation of its unusually high $J_c$. So far, MgB$_2$ has been irradiated with neutrons [10], protons [11,12], uranium and lead [13] beams by various groups. However, initially promising in terms of $J_c$ enhancement [11,12], the results turned out to indicate that MgB$_2$ might be a radiation hard material [13]. Thus, the way SHI beams interact with MgB$_2$ material and modify its physical properties is a topic that deserves attention.

2 Problem Formulation

In this paper, which is essentially an extension of our previous work on MgB$_2$, we try to explore the issue with a different viewpoint. Thin films deposited by different methods under different conditions 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 [14]. In order to show it arises from different microstructural changes after irradiation, we examined the same thin films as used in Ref. [14] by scanning electron microscopy (SEM). The SEM results, show for the first time, the evidence of SHI irradiation induced flow patterns on the PLD film surface and absence of the same in the EBE film. The observed flow patterns on the surface of PLD film point to a significant mass transfer induced by irradiation, which may be correlated with the observed changes in its superconducting properties. In this paper, we discuss the possible reasons for the occurrence of the flow patterns on one of the film surface, 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 dependent on its pristine micro-structure.

2.1 Samples

Two thin films of MgB$_2$, deposited by PLD and EBE, used for the present studies are the same as in Ref.[14]. Preparation and characterization details of these films are reported elsewhere [15,16]. 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 $\times$ 4-6 mm $\times$ 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 pristine sample.

2.2 Experimental

Irradiation of the films was carried out using the pelletron accelerator facility at Nuclear Science Centre (NSC), New Delhi, India, by 200 MeV $^{107}$Ag ion beam. Irradiation temperature was maintained 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 irradiated, as well as the pristine samples using Leo 440 (Oxford Microscopy, England) instrument. Moreover, the magnetic measurements on these films were carried out using vibrating sample magnetometer (VSM) set-up.

3 Results and discussion

Fig.1 shows a typical SEM picture 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 most of the film. On the other hand, the SEM pictures of pristine EBE film show a ‘tiled’ structure with the size of ‘tiles’ ranging between 3 to 4 $\mu$m, and the gap between tiles extending up to about 200-300 nm [Fig.2]. The tiled structure seems to be agglomerate of small flat grains of size around 500 nm.
The SEM pictures of the irradiated samples show interesting results. In the irradiated PLD film, a definite flow pattern is observed [Fig.3, shown at lower magnification to reveal the patterns clearly] on the surface, marking significant mass movement. Measured by the method used in reference [3,4], the flow length is found to be about 1-2 µm. This observed flow pattern in irradiated PLD film is similar to the ion beam induced shear flow observed in amorphous metallic alloys subjected to SHI irradiation [3-7]. 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, that the flow patterns are indeed due to the mass movement, we test our observations within the framework of the viscoelastic model of Trinkaus [17,18] originally developed to explain the structural modifications of amorphous solids subjected to SHI beams. Based on this model, the expression for shear shift of near surface atoms [17,18] is given by,

\[
\Delta x = 6 \frac{R_p \phi}{\beta S_e} \frac{1.16(1+\nu)\beta S_e}{3\epsilon(5-4\nu)\rho C} \sin \theta \cos \theta \tag{1}
\]

where, \(R_p\), \(\nu\), \(\beta\), \(S_e\), \(\rho\), 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. \(\theta\) is the tilt angle of the incident beam with respect to the target-surface [3,6], and \(\phi\) is the ion fluence (number of ions incident on the surface per unit area, i.e., product of ion flux and irradiation time). We have, \(S_e = 1.66 \text{ keV/Å} \) [19], \(\phi = 10^{11} \text{ ions/cm}^2\), \(\beta = 5.0 \times 10^{-7} \text{ K}^{-1}\) at 100 K [20], and \(\rho = 2.7 \text{ g/cm}^3\) [21]. At room temperature, \(C\) is approximately given by \(3k_B N_A/M\), where \(k_B\) is the Boltzmann constant, \(N_A\) is the Avogadro number and \(M\) is the molar weight of the material. This gives \(C = 543.09 \text{ J/(kgK)}\). Also, \(\nu = 1/3\) for most of the solids. Putting these values and using thickness \((t = 0.55 \mu m)\) of the film instead of projected range \(R_p\) in equation 1 (since the ions pass only this distance through the material), we get, \(\Delta x = 0.53 \mu m\), for
average value of $\sin \theta \cos \theta = 0.5$. Although, this calculated value of shear shift is lower than that obtained from the SEM pictures (1-2 $\mu$m) 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/(kgK) (at 100 K, value obtained by extrapolating data in ref. [22] using an exponential fit), we get $\Delta x = 1.52$ $\mu$m. This calculated value is in excellent agreement with that experimentally measured. Therefore, we conclude that the observed flow patterns do indicate towards the ion beam induced mass movement. On the other hand, however, no flow pattern was observed (even at higher magnifications, as shown in Fig.4) on the irradiated surface of EBE film.

Magnetic measurements carried out with these films using the VSM technique indicate to a possible correlation between the superconducting properties and the ion beam induced mass movement. For example, the critical temperature $T_c$, determined by the onset of zero field cooled (ZFC) diamagnetic signals (Fig.5), is found to be severely degraded in the PLD film after irradiation from 29 K to 25.5 K.

Fig.5: Normalized magnetization as a function of temperature for both unirradiated (Unirr) and 200 MeV $^{107}$Ag ions irradiated (irr) PLD and EBE films of MgB$_2$. The onset of signals is also shown by arrows.

Whereas, it has increased only slightly for the EBE film from 31 K to 32 K. Similarly, the critical current density as a function of applied field $J_c(B)$ (Fig.6), and irreversibility line $B^*(T)$ also degrade severely after irradiation in PLD film, but nearly no change in these properties is observed in the EBE film [14]. For instance, after irradiation, in case of PLD film the $J_c(4.2$ K, 1 T) changes from $3.7 \times 10^5$ A.cm$^{-2}$ to $2.2 \times 10^4$ A.cm$^{-2}$ and $B^*(4.2$ K) changes from 8.3 T to 3.8 T. Whereas, the same in case of EBE film are $1.2 \times 10^5$ A.cm$^{-2}$ to $1.1 \times 10^6$ A.cm$^{-2}$ and 3.6 T to 3.5 T, respectively.

Fig.6: Critical current density as a function of applied magnetic field at different temperatures for both PLD and EBE films. The open and filled symbols represent data taken before and after 200 MeV $^{107}$Ag ions irradiation, respectively.

A significant modification of superconducting properties of PLD film and the radiation hardness of the EBE film may be attributed to the observed mass transfer in the former and the absence of the same in the latter. Looking for an explanation for this difference in observations, we may point out the following three reasons based mainly on the microstructures of the films:

(i) Pristine crystallinity: It is known that the symmetry of 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 [1]. Therefore, it could be assumed that under irradiation, the PLD film behaved like an ‘amorphous’ target,
whereas, the EBE film as a ‘crystalline’ one. This assumption is further supported by the facts that the PLD film has higher normal state resistivity (at room temperature, one order of magnitude higher than that of the EBE film) [15,16]. Moreover, the relatively lower post-annealing temperature of 700 °C for the PLD film should have resulted in a more amorphous film [15], which is also evident in the SEM picture (Fig.1). Further, the XRD measurements (θ-2θ scan) [15], done on the PLD film show 16.4° (001) and 33.2° (002) MgB2 peaks. The other observed peaks at 24.5° and 28.33° may be due to the non-stoichiometric and/or secondary phases of the compound. The small peak at 27.2°, which may be a position that could be due to the (101) reflection of the MgB2 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 [16] the occurrence of bulk crystallization with the pronounced peaks for (001), (101) and (002). These observations also indicate to the amorphous nature of PLD and more crystalline nature of EBE films. Due to their amorphous behaviour under irradiation, the mass transfer (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 a large-scale atomic rearrangements, possibly resulting in its chemical degradation.

(iii) Starting surface topography: The SEM pictures show nearly spherical agglomerates in PLD film as compared to nearly flat tile-like in the EBE film. This makes the film more damage prone by offering more variations in the effective tilt-angle $\theta$ 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 [3,5,6].

(iii) Grain size within the agglomerates: The SEM pictures clearly show that the agglomerates in the PLD film consist of much smaller grains as compared to that 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 [14].

It has been reported earlier [23] that 200 MeV $^{107}$Ag ions create latent tracks of diameters ranging from 5.0 nm to 8.0 nm in MgB2. Tracks of this size are known to produce flow patterns on the surfaces of amorphous targets [3,5], although crystalline materials have not been reported to show such patterns. This is because in crystalline materials, due to their highly symmetric structure, any possibility of occurrence of visible IBID is negligible [1]. It is IBID, which manifests itself as flow patterns in amorphous solids subjected to SHI irradiation [3-6]. Therefore, it could be argued that when subjected to irradiation, the PLD film behaved like an ‘amorphous’ target, whereas, the EBE film, like a crystalline one. Moreover, the same argument can also be used to state that the more number of atoms per displaced atom in the displacement cascade, contributed to the observed flow patterns in PLD film as compared to the EBE film. This statement, in turn, means that the mass movement in the EBE film was lesser, and this is why the irradiation induced modifications, and hence the observed effects were not significant.

4 Conclusion
The difference in the effects of SHI irradiation on $T_c$, $J_c(B)$, and irreversibility line of superconducting MgB2 films prepared by PLD and EBE can be correlated with their different microstructures. The PLD film shows significant mass movement on the surface as evidenced by the observed mass-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. Thus, when subjected to irradiation,
the PLD film has behaved like an ‘amorphous’ target, leading to the observed changes in its microstructure as well as superconducting properties. On the other hand, the absence of shear flow in the irradiated EBE film, and hence its radiation hardness, may be attributed to its crystalline behaviour under irradiation. It may therefore be concluded that microstructures play a significant role in the irradiation-induced changes in superconducting properties of MgB2.

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