Effect of 50 MeV Li$^{3+}$ irradiation on structural and electrical properties of Mn-doped ZnO

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Abstract
The present work aims to study the effect of ion irradiation on structural and electrical properties and their correlation with the defects in the Zn$_{1-x}$Mn$_x$O-type system. Zn$_{1-x}$Mn$_x$O ($x = 0.02$, 0.04) samples have been synthesized by the solid-state reaction method and have been irradiated with 50 MeV Li$^{3+}$ ions. The concomitant changes have been probed by x-ray diffraction (XRD), temperature-dependent electrical resistivity and positron annihilation lifetime (PAL) spectroscopy. The XRD result shows a single-phase wurtzite structure for Zn$_{0.98}$Mn$_{0.02}$O, whereas for the Zn$_{0.96}$Mn$_{0.04}$O sample an impurity phase has been found, apart from the usual peaks of ZnO. Ion irradiation removes this impurity peak. The grain size of the samples is found to be uniform. For Zn$_{0.98}$Mn$_{0.02}$O, the observed sharp decrease in room temperature resistivity ($\rho_{RT}$) with irradiation is consistent with the lowering of the full width at half maximum of the XRD peaks. However, for Zn$_{0.96}$Mn$_{0.04}$O, $\rho_{RT}$ decreases for the initial fluence but increases for a further increase in fluence. All the irradiated Zn$_{0.98}$Mn$_{0.02}$O samples show a metal–semiconductor transition in temperature-dependent resistivity measurements at low temperature. But all the irradiated Zn$_{0.96}$Mn$_{0.04}$O samples show a semiconducting nature in the whole range of temperatures. Results of room temperature resistivity, XRD and PAL measurements are consistent with each other.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Dilute magnetic semiconductors (DMS) have attracted much research interest because of their potential applications in the field of spintronics [1, 2]. Ferromagnetism (FM) has been achieved both in II–VI and III–V semiconductors by the addition of 3d transition metal (TM) elements [3, 4]. The euphoria started following the prediction of room temperature ferromagnetism (RTFM) in Mn-doped ZnO by Dietl et al [5]. Thereafter, very often researchers reported intrinsic FM in TM-doped ZnO [6–10]. However, the results are quite contradictory regarding the origin of FM in the host semiconductor [1, 10–13]. It is also conjectured that defects play a crucial role in controlling the magnetic properties of such systems [7, 8, 14–16]. Apart from the magnetic properties, structural, optical and electrical properties of TM-doped ZnO are also attracting a lot of research interest [15, 17–19].
Energetic ion beam irradiation is an efficient tool for introducing defect states in solid materials. Consequently, it is an important technique for controlled modifications of structural, optical and magnetic properties of semiconductors [20, 21]. There are reports of irradiation studies on ZnO, both with light [22–24] and heavy [25, 26] ions. But there are only limited reports of ion irradiation effects on TM-doped ZnO. Kumar et al reported RTFM and a metal–semiconductor transition in 200 MeV Ag$^{15+}$ ion-irradiated ZnO thin films implanted with Fe and observed that oxygen vacancies and/or Zn interstitials are introduced into the system due to irradiation [27]. Fukuoka et al [28] and Sugai et al [29] investigated the effect of high energy Xe and Ni ion irradiation on the electrical, optical and structural properties of Al-doped ZnO films. They observed an increase in conductivity of the Al-doped films with ion irradiation and suggested that the irradiation-induced bandgap modification has a close relation with the conductivity increase. Formation of single-phase Co-implanted ZnO thin films using swift heavy ion (SHI) irradiation has been reported by Angadi et al [21] and Kumar et al [30]. They found a decrease in the electrical resistivity of the irradiated samples and observed close interplay between electrical and magnetic properties. Also, very recently Kumar et al reported SHI-induced modifications in Co-doped ZnO thin films and concluded that SHI irradiation can be used to improve the quality of the thin films by intrinsically modifying the structural and optical properties [20]. To the best of our knowledge, there is no such report on irradiation-induced modification of electrical transport in Mn-doped ZnO systems and so a systematic investigation has been carried out.

2. Experiments

The Zn$_{1-x}$Mn$_x$O ($x = 0.02, 0.04$) samples were synthesized by the conventional solid-state reaction method [6, 16, 31]. A stoichiometric amount of ZnO and MnO$_2$ powders (each of purity 99.99%; Sigma-Aldrich, Germany) have been weighed, mixed and ground together. The samples were initially milled for 32 h followed by annealing at 400°C for 8 h. The resulting powder was again milled for another 64 h. All the milling was performed in a 'Fritsch planetary mono mill' machine (model no. Pulverisette 6) using an agate ball and container. In order to avoid large grain size reduction (and hence to avoid the grain-size-related effects), the samples have been milled at a ball-to-mass ratio of 1:1. The powder thus obtained was then pressed into pellets, followed by final sintering at 500°C for 12 h. The reasons for choosing 500°C as the final sintering temperature has been discussed earlier [31]. The synthesized Zn$_{0.98}$Mn$_{0.02}$O and Zn$_{0.96}$Mn$_{0.04}$O samples have been irradiated with a 50 MeV Li$^{3+}$ ion beam. The samples have been irradiated at four different fluences of $1 \times 10^{12}$, $1 \times 10^{13}$, $5 \times 10^{13}$ and $1 \times 10^{14}$ ions cm$^{-2}$. The irradiation experiment was carried out using a focused beam, carefully scanned over an area of 1 cm × 1 cm, after mounting the samples on the ladder in a high vacuum irradiation chamber. In order to avoid the possibility of Li-implantation-related effects, the irradiation experiments were performed on samples of thickness of around 200 μm, less than the penetration depth (220 μm) of a 50 MeV Li$^{3+}$ ion beam in Mn-doped ZnO.

The phase characterization of the Zn$_{1-x}$Mn$_x$O ($x = 0.02, 0.04$) samples before and after irradiation has been carried out using a powder x-ray diffractometer (Phillips, model PW1830) with Cu Kα radiation. All x-ray diffraction (XRD) measurements were carried out in the range of 2θ $\leq 80°$ in θ–2θ geometry. The electrical resistivity as a function of temperature of all the samples was measured using the conventional two-probe technique. A Keithley electrometer (model 6514) was employed to measure the resistance. Positron annihilation lifetime (PAL) measurements at RT were performed on the Zn$_{0.98}$Mn$_{0.02}$O sample with $0, 1 \times 10^{12}$, $5 \times 10^{13}$ ions cm$^{-2}$ irradiation fluence. For the PAL study, a 10-μCi $^{22}$Na positron source (enclosed in 2 μm thin Mylar foil) was sandwiched between two identical plane-faced pellets of the samples. The PAL spectra were measured with a fast–slow coincidence assembly having 182 ± 1 ps time resolution [14]. Measured spectra were analyzed by the computer program PATFIT-88 [32] to obtain the possible lifetime components $\tau_i$ and their corresponding intensities $I_i$.

3. Results and discussion

Figure 1 reveals that the synthesized Zn$_{1-x}$Mn$_x$O sample with $x = 0.02$ is in single phase and no traces of any impurity peak has been detected. No detectable amorphization has been observed up to the highest fluence ($1 \times 10^{14}$ ions cm$^{-2}$), reflecting the high radiation hardness of ZnO-based systems. For a 4 at.% Mn doped un-irradiated sample (figure 2), apart from the peaks corresponding to those of the ZnO hexagonal wurtzite structure, a weak (112) peak of ZnMn$_2$O$_4$ has been observed at 2θ $= 29.11°$ [31]. Interestingly, this impurity peak disappeared just after irradiation with the lowest fluence ($1 \times 10^{12}$ ions cm$^{-2}$), as shown in the inset of figure 2. This indicates that the impurity phase has been dissolved and the sample has become single-phased, at least within the detection limit of XRD. Irradiation-induced dissolution of the impurity phase had also been observed earlier for Ag-ion-irradiated...
Figure 2. XRD of an un-irradiated and irradiated 4 at% Mn-doped ZnO sample. Inset: enlarged view of XRD in the range 28°–30°.

Figure 3. Variation of FWHM and intensity of the (101) peak with irradiation fluence for a 4 at% Mn-doped ZnO sample.

Figure 4. Variation of FWHM and intensity of the (101) peak with irradiation fluence for a 4 at% Mn-doped ZnO sample.
peak of the ZnMn$_2$O$_4$ phase, which dissolves with the lowest fluence dose. Thus upon irradiating with $1 \times 10^{12}$ ions cm$^{-2}$ fluence dose the sample becomes single phase in nature. But we found that, with increasing dose of irradiation ($1 \times 10^{13}$ ions cm$^{-2}$), the FWHM of the (101) peak decreases and the peak intensity increases and no appreciable change for higher doses of irradiation ($5 \times 10^{13}$–$1 \times 10^{14}$ ions cm$^{-2}$) is seen. This observation suggests that the crystalline quality of the 4 at.% Mn-doped ZnO samples becomes better with higher doses of irradiation. In the present sample the doping concentration of Mn is higher than Zn$_{0.98}$Mn$_{0.02}$O and hence the resultant defective state after irradiation can be very different. So, a different trend in XRD features is not unexpected.

Close inspection of figure 1 indicates a higher angle shift of the (101) peak in the case of the Zn$_{0.98}$Mn$_{0.02}$O sample just after irradiation with a fluence of $1 \times 10^{12}$ ions cm$^{-2}$. But with increasing irradiation fluence, there is no further shift of the (101) peak. This might be due to release of residual strain in the system with irradiation [39]. But in the case of the Zn$_{0.96}$Mn$_{0.04}$O (figure 2) sample XRD peaks shift towards lower angles after irradiation. It indicates simply enhancement of the lattice parameter. The un-irradiated Zn$_{0.96}$Mn$_{0.04}$O sample contains an impurity peak of ZnMn$_2$O$_4$, which dissolves just with an initial fluence of irradiation ($10^{12}$ ions cm$^{-2}$). So incorporation of Mn ions in the host ZnO matrix increases with dissolution of the impurity phase.

Thus the observed shift of the (101) peak towards lower angles (enhancement of the lattice parameter) seems to be quite justified as the ionic radii of Mn$^{2+}$ (0.67 Å) is higher than that of Zn$^{2+}$ (0.60 Å) [40]. There must be some higher angle shifting of the (101) peak due to release of residual strain in the system with irradiation in the case of Zn$_{0.96}$Mn$_{0.04}$O samples also. But lower angle shifting of the (101) peak due to more Mn incorporation with irradiation predominates over the earlier strain release effect.

Figure 5 represents the scanning electron microscopy (SEM) images of Zn$_{0.98}$Mn$_{0.02}$O samples, both un-irradiated and irradiated with a fluence of $1 \times 10^{14}$ Li$^{3+}$ ions cm$^{-2}$. 

Figure 6. SEM micrographs of Zn$_{0.96}$Mn$_{0.04}$O samples: (a) un-irradiated and (b) irradiated with fluence of $1 \times 10^{14}$ Li$^{3+}$ ions cm$^{-2}$.
boundaries. If the retarding force generated is higher than the driving force for grain growth due to Zn, the movement of the grain boundary is impeded [41]. This in turn gradually decreases grain size with increasing irradiation. All the SEM micrographs show closely packed grains with no significant amount of agglomeration. Further distribution of grain size throughout the samples is uniform and homogeneous.

Temperature-dependent resistivity measurements have been carried out for Zn$_{0.98}$Mn$_{0.02}$O and Zn$_{0.96}$Mn$_{0.04}$O samples as shown in figures 7 and 8, respectively. For Zn$_{0.98}$Mn$_{0.02}$O, a monotonic decrease in $\rho_{RT}$ with increasing irradiation fluence has been observed (inset of figure 7(a)) with two orders of magnitude reduction due to the highest fluence ($1 \times 10^{14}$ ions cm$^{-2}$). In a recent work, lowering of $\rho_{RT}$ by four orders of magnitude has been found in 1.2 MeV Ar-irradiated ZnO [34]. Huge resistance loss due to irradiation by light/heavy energetic ions has also been observed by other groups [42]. The reason for the change in resistivity due to irradiation, particularly in doped ZnO systems, is a matter of investigation till now [17]. The decrease of resistivity is due to increase of donors or deactivation of compensating acceptors or both. In polycrystalline samples, most of the vacancy clusters reside near the GB region as mentioned earlier. The region is devoid of carriers (depletion region) and acts as a potential barrier during the transport of carriers between the grains. Increased donor density can reduce the height of the potential barrier in n-type ZnO. On the other hand, recovery of a fraction of GB defects can also lower the

Figure 7. (a) Thermal variation resistivity of the un-irradiated Zn$_{0.98}$Mn$_{0.02}$O sample. Inset: variation of $\rho_{RT}$ of Zn$_{0.98}$Mn$_{0.02}$O with irradiation fluence. (b) Thermal variation resistivity of all irradiated Zn$_{0.98}$Mn$_{0.02}$O samples.

Figure 8. Thermal variation resistivity of all irradiated Zn$_{0.96}$Mn$_{0.04}$O samples. Inset: variation of $\rho_{RT}$ of Zn$_{0.96}$Mn$_{0.04}$O with irradiation fluence.

carrier scattering at the GB. At the same time, Dong et al [17] proposed that the presence of large vacancy clusters and huge oxygen vacancies are the source of reduced resistance in ion-irradiated ZnO. It should be mentioned here that electronic energy deposition can excite (and also ionize) the atoms and, after de-excitation within a few ps, a reorganization of local defect structure is possible. This process is more effective near the highly defective regions, i.e. at the GB. We feel that the resultant stable defect structure creates large oxygen vacancies (OV) as dominant defects in ZnO-based systems. Indeed, our PAL results (discussed later) reflect the existence of a vacancy cluster in the pristine Zn$_{0.98}$Mn$_{0.02}$O sample. However, XRD or PAL studies do not support further clustering of vacancies due to Li ion irradiation. Hence, it can be summarized that the recovery of a fraction of GB defects as well as the presence of OVs due to irradiation contribute to the reduction of resistivity in these polycrystalline samples. The thermal variation of resistivity measurement of the irradiated Zn$_{0.98}$Mn$_{0.02}$O sample shows an interesting behavior. Though the un-irradiated Zn$_{0.98}$Mn$_{0.02}$O sample is semiconducting in nature throughout the temperature range of measurement, after irradiation it shows a metal to semiconductor transition. Most interestingly, no such transition is observed in the case of the Zn$_{0.96}$Mn$_{0.04}$O sample (all samples, irradiated and un-irradiated, showing semiconducting behavior in the measured temperature range). Recently, different groups reported a metal–semiconductor transition in both doped and undoped ZnO systems [21, 27, 43]. It is noteworthy to mention that our observation is slightly different. We observed that the sample is metallic in the low temperature regime and semiconducting at higher temperature. Also the sample irradiated with the lowest fluence shows multiple transitions but for the samples irradiated with higher fluences ($1 \times 10^{13}$–$1 \times 10^{14}$ ions cm$^{-2}$), only one transition has been observed. Angadi et al [21] and Nistor et al [43] have shown that the presence of oxygen vacancies possibly gives rise to a metal–semiconductor transition in ZnO thin film. Further we observe that the transition temperature shifts towards lower temperature with increasing doses of irradiation
irradiation fluences. Where orthopositronium formation is favorable [14]. As the
in polycrystalline samples, there always exist microvoids atoms. Decay of orthopositr onium into parapositronium first lifetime component \( \tau_1 \) is close to the positron lifetime at zinc vacancies in ZnO. Indeed, Wang et al [44] have attributed the origin of \( \tau_1 \) from the diffused zinc vacancies at

\[ \tau_1 \approx 1400 \text{ ps with intensity } 3.5\% \] originates due to the annihilation of positrons from positronium atoms. Decay of positronium into parapositronium through pickoff annihilation gives rise to such a large lifetime. In polycrystalline samples, there always exist microvoids where orthopositronium formation is favorable [14]. As the first lifetime component \( \tau_1 \) and the intermediate one \( \tau_2 \) have changed significantly with irradiation fluence, we feel that both have a defect-related origin. \( \tau_2 \) and \( \tau_1 \) provide a qualitative indication about the spatial extension of the defects (i.e. defect size). The corresponding intensities \( I_1 \) and \( I_2 \) respectively reflect the relative abundance of such defect sites. For the un-irradiated sample the value of \( \tau_1 \) is close to the positron lifetime at zinc vacancies in ZnO. Indeed, Wang et al [44] have attributed the origin of \( \tau_1 \) from the diffused zinc vacancies at

\[ (\tau_1, 1400 \text{ ps with intensity } 3.5\%) \] originates due to the annihilation of positrons from positronium atoms. Decay of orthopositronium into parapositronium through pickoff annihilation gives rise to such a large lifetime. In polycrystalline samples, there always exist microvoids where orthopositronium formation is favorable [14]. As the first lifetime component \( \tau_1 \) and the intermediate one \( \tau_2 \) have changed significantly with irradiation fluence, we feel that both have a defect-related origin. \( \tau_2 \) and \( \tau_1 \) provide a qualitative indication about the spatial extension of the defects (i.e. defect size). The corresponding intensities \( I_1 \) and \( I_2 \) respectively reflect the relative abundance of such defect sites. For the un-irradiated sample the value of \( \tau_1 \) is close to the positron lifetime at zinc vacancies in ZnO. Indeed, Wang et al [44] have attributed the origin of \( \tau_1 \) from the diffused zinc vacancies at

\[\begin{array}{cccccc}
\text{Irradiation fluence (ions cm}^{-2}\text{)} & \tau_1 \text{(ps)} & I_1 \text{(\%)} & \tau_2 \text{(ps)} & I_2 \text{(\%)} & I_3 \text{(\%)} & \tau_{av} \text{(ps)} \\
0 & 222 \pm 1 & 59.3 \pm 0.01 & 401 \pm 2 & 37.5 \pm 0.01 & 1406 \pm 40 & 3.2 \pm 0.01 & 291 \pm 3 \\
1 \times 10^{12} & 167 \pm 1 & 37.3 \pm 0.01 & 335 \pm 2 & 57.8 \pm 0.01 & 1530 \pm 44 & 4.9 \pm 0.01 & 269 \pm 3 \\
5 \times 10^{13} & 188 \pm 1 & 48.1 \pm 0.01 & 350 \pm 2 & 48.4 \pm 0.01 & 1772 \pm 52 & 3.5 \pm 0.01 & 269 \pm 3 \\
\end{array}\]

Table 1. The fitting parameters found from positron annihilation lifetime measurements on \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \) samples irradiated with different irradiation fluences.

Homogenization of defects with higher fluence may be responsible for the vanishing of multiple transitions leading towards semiconducting behavior with increasing doses of irradiation.

We have also investigated the resistivity of the 4 at% Mn-doped sample, \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \). We found that \( \rho_{RT} \) of the un-irradiated \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) sample is higher than that of the 2 at% Mn-doped sample. Interestingly, we observed a two orders of magnitude reduction in the \( \rho_{RT} \) value for the \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) sample with initial irradiation fluence \( (1 \times 10^{12} \text{ ions cm}^{-2}) \). Such a reduction of \( \rho_{RT} \) with irradiation was also observed for \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \). But unlike \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O}, \rho_{RT} \) of the \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) shows a small but steady increase as the irradiation fluence is further increased from \( 1 \times 10^{12} - 1 \times 10^{14} \text{ ions cm}^{-2} \) (figure 7(b)). Since the \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) sample contains a higher percentage of Mn, the equilibrium defective state (after irradiation) of the sample is different from that of \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \). As the \( \rho_{RT} \) value is very high, we have not attempted to measure the low temperature resistivity of the un-irradiated \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) sample. However, we have measured the thermal variation of resistivity of all the irradiated \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) samples (figure 8). It is noteworthy to mention that we have been able to measure the resistivity for these samples only down to 170 K, below which resistivity tends to be beyond the limit of the instrument. All the irradiated \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) samples remain semiconducting down to the lowest temperature measured.

PAL measurements on un-irradiated and little-irradiated \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \) samples show interesting features. The possible impurity phase-related problem may complicate the PAL data for 4 at% Mn-doped samples and so the measurement for this sample is avoided. The results of PAL spectrum analysis are shown in table 1. All the PAL spectra are found to be best fitted with three lifetime components. The longest lifetime component \( \tau_3 \), 1400 ps with intensity 3–5% originates due to the annihilation of positrons from positronium atoms. Decay of orthopositronium into parapositronium through pickoff annihilation gives rise to such a large lifetime. In polycrystalline samples, there always exist microvoids where orthopositronium formation is favorable [14]. As the first lifetime component \( \tau_1 \) and the intermediate one \( \tau_2 \) have changed significantly with irradiation fluence, we feel that both have a defect-related origin. \( \tau_2 \) and \( \tau_1 \) provide a qualitative indication about the spatial extension of the defects (i.e. defect size). The corresponding intensities \( I_1 \) and \( I_2 \) respectively reflect the relative abundance of such defect sites. For the un-irradiated sample the value of \( \tau_1 \) is close to the positron lifetime at zinc vacancies in ZnO. Indeed, Wang et al [44] have attributed the origin of \( \tau_1 \) from the diffused zinc vacancies at

4. Conclusion

The un-irradiated and 50 MeV \( \text{Li}^{3+} \)-ion-irradiated \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) \((x = 0.02, 0.04) \) samples were characterized by XRD, temperature-dependent resistivity and room temperature PAL spectroscopy.

The XRD result indicates a wurtzite-type structure for \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \) but the impurity (112) peak of \( \text{ZnMn}_2\text{O}_4 \) was observed apart from the usual peaks of \( \text{ZnO} \) for \( \text{Zn}_{0.96}\text{Mn}_{0.04}\text{O} \). Ion irradiation removes the impurity phase. SEM micrographs indicate homogeneity of the samples with uniform particle size. Room temperature resistivity values decrease abruptly with irradiation. Generation of oxygen vacancy, \( \text{Zn} \) interstitial and recovery of a part of the defects at the GB due to irradiation may be the reason for resistivity reduction. The temperature-dependent electrical resistivity results for irradiated \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \) samples show shifting of the metal–semiconductor transition temperature towards the lower side with increasing fluence of irradiation. The \( \rho_{RT} \) values of the \( \text{Zn}_{0.98}\text{Mn}_{0.04}\text{O} \) are higher compared to that of \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \) samples. No metal–semiconductor transition
is observed in any irradiated Zn$_{0.96}$Mn$_{0.04}$O samples from the temperature-dependent resistivity measurement, at least down to 170 K. PAL spectroscopy data analysis indicates that an increasing fluence of irradiation causes lowering of defects in Zn$_{0.96}$Mn$_{0.04}$O. This fact is also supported by XRD and electrical resistivity measurements.

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