Correlation between defect and magnetism of low energy 800 keV Ar\(^{4+}\) irradiated ZnO thin films

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Abstract. Present work demonstrates ion beam irradiation induced modification in physical properties of ZnO thin films prepared by sol-gel spin coating technique. Different fluence viz: \(5 \times 10^{14}, 10^{15}, 5 \times 10^{15}\) and \(10^{16}\) ions/cm\(^2\) were chosen for irradiation. Measurements of structural, optical and magnetic properties of these films have been performed. XRD patterns of the films exhibit wurtzite structure ZnO. Optical transmittances of these films were recorded in the wavelength range of 250-1000 nm, and band gap of the respective films have been estimated. Irradiated films did not show significant degradation in the crystalline structure however a noticeable shift of band edge with fluence has been observed and explained. Pristine ZnO film exhibits diamagnetic behaviour at room temperature. However prominent hysteresis has been observed for lowest fluence \((5 \times 10^{14}\) ions/cm\(^2\)) irradiated films. The correlation between defects and ferromagnetism has been established in this work.

1. Introduction.

The II-VI semiconductor ZnO has direct band gap \((E_g \sim 3.3\) eV at 300 K\) [1] and large exciton binding energy (~60 meV) [2]. Because of wide band gap and large exciton binding energy ZnO became an important materials for potential application in optoelectronics and spintronics [2, 3]. In the last decade ZnO has attracted much attention following the prediction of room temperature ferromagnetism in Mn doped ZnO by Dietl et. al. [3], commonly called diluted magnetic semiconductor. Extensive efforts were directed towards achieving of room temperature ferromagnetism in transition metal (example: Mn, Co, Fe...etc.) doped ZnO (TM:ZnO) [4, 5]. However experimental results are different for different samples and did not converge to a definite conclusion. This controversy was highlighted further when ferromagnetism has been observed in undoped ZnO [6], ZnO nanocrystals and ZnO nanorods [6, 7], low energy Ar\(^{+}\) implanted ZnO single crystal [8]. The ferromagnetism observed in un-doped oxides is called \(d^0\) ferromagnetism [9].

Defects in ZnO and their role on structural, optical, electronic, and magnetic properties have been widely investigated in recent days [10, 11]. Perhaps the most successful and accepted model for describing ferromagnetism in ZnO is carrier (and nowadays defect) induced bound magnetic polaron (BMP) model [12, 13]. However in absence of any transition metal doping which kind of point defects such as; zinc interstitials (Zn\(_i\)), oxygen vacancy (V\(_O\)) and zinc vacancy (V\(_Zn\)) can act as agents for developing BMP in ZnO is still to be understood properly. Incorporation of defects in ZnO can be made by ion beam irradiation. Present work demonstrate how purposeful defects engineering through ion irradiation (800 keV Ar\(^{4+}\) beam) promotes ferromagnetism in un-doped ZnO films. Here we choose non-magnetic ions Ar ions for irradiation so that chances of chemical or magnetic effects in the target could be minimized [14, 15]. The correlation between defects and ferromagnetism has been established in this work.
2. Experimental Details

Synthesis of ZnO thin films has been carried out by using spin coating unit. Appropriate amount of zinc-acetate \([\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}]\) was taken and mixed with a solution containing 2-propanol and diethanolamine (DEA). Details of synthesis procedure were presented in our earlier work [1, 2]. Finally the films were annealed at 500°C for 30 minutes in order to achieve good crystalline quality. Thickness of these films was 500 nm [1]. Different fluence (like; \(5\times10^{14}, 10^{15}, 5\times10^{15}\) and \(10^{16}\) ions/cm\(^2\)) were chosen for irradiation. The estimation of irradiation fluence ‘F’ (ions/cm\(^2\)) has been done by using the following relation:

\[
F = \frac{(I_p \times t)}{e \times n \times A} \text{ions/cm}^2 \quad \text{.................(1)}
\]

Here \(I_p\) represents the ion current, \(t\) is the total time for a particular sample to be irradiated, \(e\) is the electronic charge (1.6\times10^{-19}\) C), \(n\) is the charge state of the Ar beam (here it is \(= 4\)) and \(A\) represents area of the beam [15]. During irradiation the samples were kept under high vacuum chamber at room temperature. Post annealing treatment just after irradiation has not been performed to recover of the irradiation induced damages. Surface morphology of these films was investigated through SEM (Scanning Electron Microscope). The irradiation experiment was performed at Inter University Accelerator Center (IUAC), New Delhi. In this work we mainly focus on structural optical and magnetic properties of un-irradiated and irradiated films. Details of experiments and discussions on experimental results are presented in the following section.

3. Results & Discussion

3.1 Ion Irradiation

After entering into target (here ZnO films), Ar beam loses its energy either by collision with electrons of the target atoms and ionized them or by elastic collisions with the target atoms nuclei. Using SRIM (stopping power and ranges of ion in matter) simulation we can estimate the energy loss of 800 keV Ar\(^{4+}\) beam inside the target material, depicted in Figure 1. The electronic energy loss (\(S_e\)) and nuclear energy loss (\(S_n\)) as a function penetration depth of the ion beam has been presented in Figure 1. For SRIM calculation we have taken density of ZnO as 4gm/cm\(^3\) and displacement threshold energy as 18.5 eV and 41.4 eV for Zn and O atom in the ZnO lattice respectively [10]. The SRIM calculation helps us to visualize that energy loss due to \(S_e\) largely predominates over nuclear energy loss \(S_n\) in the entire trajectory of the ion beam. Inside the target material a trail of defects like; point defects, defect clusters, structural phase formation may be formed along the trajectory of the ion beam [10]. However most of these defects annihilate immediately (dynamic recovery of defects) after their generation, makes ZnO the most radiation hard material [1, 14].

3.2 Structural Analysis

Figure 2 (a) displays the XRD patterns of ZnO and irradiated films. All these films exhibit a similar structure of hexagonal wurzite ZnO. For XRD measurements we have used the Synchrotron Radiation facility of Photon Factory KEK Japan and wave length used for X-ray diffraction was 1Å. For un-irradiated film, the calculated values of lattice constants are \(a = 3.246\) Å and \(c = 5.203\) Å, comparable with reported values of the lattice constants [1]. Upper panel of figure 2 (b) shows the SEM micrographs of pure and irradiated (F: \(10^{16}\) ions/cm\(^2\)) samples. The images exhibit more or less homogeneous size distribution of the nanoparticles in each film. Lower panel of figure 2 (b) exhibits
the enlarged view of XRD pattern of selected films. After irradiation no appreciable shift in peak positions has been observed. In addition crystalline quality of these films is also more or less maintained (lower panel of figure 2 (b)) even for highest fluence \(10^{16} \text{ ions/cm}^2\) irradiated films, which further support radiation hardness of the material ZnO. A close inspection of figure 2 (b) reveals that almost insignificant enhancement in FWHM of the XRD peaks, implies low energy (800 keV) Ar irradiation is less sensitive to make changes in crystalline quality of the films [10]. However optical and magnetic properties of these films get substantially modified after irradiation.

3.3 Optical study

Optical properties of these films were characterized by UV-Visible spectroscopy. The UV-Visible spectra were recorded in the wavelength range 200 nm to 1100 nm. While recording data an identical glass substrate has been taken as reference for base line correction. All of them exhibit visible transmittance better that 90% and sharp absorption edge near 385 nm. In the right panel of figure 3 (b) exhibits variation optical absorption coefficient: \(\alpha(\lambda)\) against wave length (\(\lambda\)) for different films. Absorption coefficient ‘\(\alpha(\lambda)\)’ for optically transparent thin films was calculated by using the following relation

\[
I = I_o \exp(-\alpha d)
\]  

Here \(I\) represent the intensity of transmitted light, \(I_o\) the intensity of incident light and \(d\) is the thickness. And transmittance ‘\(T\)’ is defined as \(I/I_o\). A close inspection of figure 3 (b) shows that absorption edge gets shifted towards higher energy and an enhancement in absorption just below the band edge (between 2.8 eV to 3.2 eV) has been observed. Pronounced sub band gap absorption arises from transitions between defect induced intra-gap levels also called band tailing effect [2, 5]. ZnO is a direct band gap semiconductor; band gap \(E_g\) for all the films has been estimated by using the equation:

\[
\alpha = \frac{A(h\nu - E_g)}{h\nu}
\]

Here \(h\) is the plank constant, \(\nu\) is the frequency of the incident photon and \(A\) is constant [2]. Figure 4 (a) represents the variation of \((\alpha h\nu)^2\) against energy of ZnO and irradiated films. The estimation of band gap \(E_g\) of respective films have been made by linear extrapolation of straight line to \((\alpha h\nu)^2 = 0\) (to the energy axis) [2]. Inset of figure 4 (a) shows gradual variation of \(E_g\) against fluence. The \(E_g\) gradually increases from 3.268 eV (ZnO film) to 3.290 eV for irradiated film (F: \(10^{16}\) ions/cm²).
Figure 4 (b) shows the room temperature Photoluminescence (RT-PL) spectra of ZnO and irradiated films. A prominent UV emission band (~380 nm) and broad visible emission (450-550 nm) has been observed for ZnO film. Irradiation causes a large reduction in UV emission intensity, consistent with the previous reports [10, 15]. Irradiation produces same defects states that may induce some non-radiative recombination processes hence UV emission quenches [15] for irradiated films as shown in the upper panel of figure 4 (b). Broad visible emission originates due to defects, mostly either vacancy types (V_{O}, V_{Zn}) or interstitial types (O_{I}, Zn_{I}) or impurities in ZnO [1, 10]. Broad visible emission (green emission) has been observed in all irradiated films except for highest fluence we see that visible emission intensity quenches appreciably.

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Figure 4. (a) Variation of $(a\nu)^2$ against $E$ of ZnO and irradiated films. (b) RT-PL spectra of ZnO and irradiated films (F: $10^{16}$ ions/cm$^2$) Lower panel of 4 (b) shows the broad visible emission of irradiated films.
In case of intermediate fluence (F: 10^{15} and 5 \times 10^{15} ions/cm^2), it has been observed that the intensity of visible emission becomes comparable but better than that of irradiated film (F: 5 \times 10^{14} ions/cm^2). The broad visible emission (480 nm to 560 nm) in PL study is originated from defects states. The observed Green emission is mostly attributed to the recombination of electrons trapped in singly ionized oxygen vacancies (Vo\(^+\)) with photo generated holes [14, 15]. Intensity of green emission is a measure of concentration of defects present in samples. Hence for irradiated film (F: 10^{16} ions/cm^2), concentration of Vo\(^+\) is supposed to be minimum.

Broad visible emission indicates that solely Vo\(^+\) type’s defects is not responsible for emission. We believe that, major contribution of such defect level emission at room temperature comes from Zn\(_n\), V\(_O\), O\(_Zn\) related defects [10]. Look et al. [16] have shown that most stable defects in ZnO after irradiation are Zn vacancy (V\(_Zn\)), Zn antisite (Zn\(_O\)), Oxygen vacancy (V\(_O\)) and anti-site Oxygen (O\(_Zn\)). There is another kind, interstitial Zn (Zn\(_I\)), however Zn\(_I\) recombines immediately with nearby V\(_Zn\) [10]. This ultimately lowers the no of vacancies and interstitial defects at the Zn site. Most important thing that we observed a non-monotonous variation in intensity of visible emission, indicating a complex competition between generation and recovery of defects with fluence of irradiation, controls this visible emission.

### 3.4 Magnetic Measurements

Magnetization measurements of all these films against temperature: M(T) and field: M(H) were performed. But we present the most significant observation here. Actual values of moments could be determined after subtracting the diamagnetic background from glass substrate from the experimental data, as described in [17]. M(T) variation was recorded in zero field cooled (ZFC) and field cooled (FC) mode at a constant field strength of (H = 150 Oe) in the temperature range 300 K to 5 K, presented in Figure 5 (a) and (b). Magnetic moment increases slowly with decrease of temperature and a sharp rise below 100 K has been noticed. Figure 5 (c) and (d) (right panel) represents the M(H) variation of irradiated (F: 5 \times 10^{14} and 10^{16} ions/cm^2) films at 300 K. M(H) for pure ZnO film has been given here as reference. At the lowest fluence we observe a clear hysteresis and at the highest fluence (10^{16} ions/cm^2) only a slight irreversibility near origin (H = Oe) has been observed, indicating some cooperative interaction build up in diamagnetic ZnO in the low fluence irradiated films. Absence of hysteresis in ZnO and presence hysteresis in low energy Ar\(^{4+}\) irradiated ZnO (F: 5 \times 10^{14} ions/cm^2) is really a noteworthy phenomenon highlighted in this present work and strongly connected with intrinsic defects structure of this sample [18-20].

![Figure 5](image-url). The left panel (a) and (b) represents the M(T) variation of irradiated films. Right panel represents the M(H) variation of irradiated films (F: 5 \times 10^{14} and 10^{16} ions/cm^2). Inset of figure 5 (d) represents the M(H) variation of diamagnetic ZnO.
MT variation of irradiated films indicates that some defects present in irradiated films gives paramagnetic contribution to the magnetization. We have used low energy Ar$^{4+}$ beam for irradiation. As Ar is nonmagnetic, hence the unusual magnetic behaviour of these films must have some strong correlations with these defects, generated as a consequence of irradiation. An intense debate is going on regarding defect induced visible emission in ZnO films. After dynamic recovery some of the irradiation induced defects like; (V$_{Zn}$-ZnI), isolated Vo will stabilize [10]. In PL spectra, we see that with increasing fluence visible emission quenches due to creation of some non-radiative defect centres and we strongly believe that V$_{Zn}$ related complexes act as such recombination centres [15]. The reduced strength in magnetic signal at the intermediate fluence (F: $10^{15}$ and $5 \times 10^{15}$ ions/cm$^2$), not shown in figure 5 and also at highest fluence (F: $10^{16}$ ions/cm$^2$) possibly due to restructuring of defects acting against the BMP formation needed for ferromagnetism in oxides.

4. Conclusion.

The study on structural, optical, magnetic and micro-structural properties of low energy (800 keV) Ar$^{4+}$ irradiated ZnO films exhibit some interesting observations. Low energy ion irradiation induces large concentration of defects in these films, identified from optical characterization. Irradiated (F: $5 \times 10^{14}$ ions/cm$^2$ and F: $10^{16}$ ions/cm$^2$) films exhibits a non-monotonous degree/strength of magnetic (ferromagnetic) behaviour at 300 K, indicating a close interplay between defects and magnetism in these films. Defect induced formation of bound magnetic polarons (BMP) actually controls the magnetic property of the films. High transmittance of these films makes them suitable for transparent spin electronic device applications.

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6. Reference.

[1] S K, Neogi Md A, Ahmed A, Banerjee and S, Bandyopadhyay 2019 Appl. Sur. Sci. 481 443-453
[2] R, Karmaker S K, Neogi A, Banerjee and S, Bandyopadhyay 2012 Appl. Sur. Sci. 263 671-677
[3] T, Dietl H, Ohno F, Matsukura J, Cibert and D, Ferrand 2000 Science 287 1019
[4] S K, Neogi R, Ghosh G K, Paul S K, Bera S, Bandyopadhyay 2009 J. Alloy. Compd. 487 671-677
[5] S, Chattopadhyay S K, Neogi A, Sarkar M D, Mukadam S M, Yusuf A, Banerjee and S. Bandyopadhyay 2011 J. Magn. Mag. Mats. 323 363
[6] Y, Zhang and E, Xie 2010 Appl. Phys. A 99 955-960
[7] S, Banerjee M, Mandal N, Gayathri and M. Sardar 2007 Appl. Phys. Lett. 91 182501-3
[8] R P, Borges R. C, Silva S, Magalhaes M. M, Cruz and M, Godinho 2007 J. Phys.: Condens. Matter 19 476207
[9] J M D, Coey 2005 Solid State Sci. 7 660-667
[10] S, Chattopadhyay S, Dutta D, Jana, S, Chattopadhyay A, Sarkar, P, Kumar D, Kanjilal, D K, Mishra and S K, Ray 2010 J. Appl. Phys. 107 113516
[11] S, Chattopadhyay S K, Neogi P, Pandit S, Dutta T, Rakshit D, Jana S, Chattopadhyay A. Sarkar and S.K. Ray 2012 J. Luminiscence 132 6-11
[12] J M. D, Coey M, Venkatesan and C.B. Fitzgerald 2005 Nat. Mater. 4 173
[13] K R, Kittilstved and D R, Gamelin 2005 J. Am. Chem. Soc. 127 5292
[14] S K, Neogi N, Midya P, Pramanik A, Banerjee A, Bhattacharya G. S, Taki J B M, Krishna and S, Bandyopadhyay 2016 J. Magn. Mag. Mats 408 217

[15] N, Midya S. K, Neogi, Md. A, Ahmed A, Banerjee P, Kumar D, Kanjilal and S, Bandyopadhyay 2017 RSC Advances 7 771

[16] D C, Look J W, Hemskey and J R, Sizelove 1999 Phys. Rev. Lett. 82 2552

[17] S, Yang Y, Zhang 2013 J. Magn. Mag. Mats 334 52-58

[18] W, Liu W, Li, Z, Hu, Z, Tang, and X, Tang 2011 J. Appl. Phys. 110 013901

[19] N. H, Hong J, Sakai N. T, Huong N, Poirot, and A, Ruyter, 2005 Phys. Rev B. 72 045336

[20] E Z, Liu Y. He and J Z, Jiang 2008 Appl. Phys. Lett. 93 132506