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Effect of swift heavy ion on structural and optical properties of undoped and doped nanocrystalline zinc oxide films

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ABSTRACT

Swift heavy ion (SHI) induced modification in structural and optical properties of undoped and doped nanocrystalline (nc) ZnO films deposited by sol-gel method are investigated. These nanocrystalline films were irradiated by MeV ions of Au, Ag and Ni at various ion fluences. The structural properties were studied using X-ray diffraction and it shows that the average crystallite size of ZnO films is observed to increase by the irradiation. The atomic force microscopy (AFM) study of films shows that the roughness of the films varies with increase in the fluence. A maximum transmittance is observed to be 85% in the visible region for doped films. It is also shown that the bandgap of undoped and doped ZnO films is varied using SHI irradiation. The modifications of structural and optical properties are explained in terms of thermal spikes induced by SHIs. Copyright © 2013 VBRI press.

Keywords: nc-ZnO; swift heavy ion; sol-gel; band gap narrowing and widening; ZnO:B

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Introduction

Zinc Oxide (ZnO) is II–VI compound semiconductor with hexagonal wurtzite structure. ZnO has a direct band gap of about 3.37 eV [**1**] and large exciton binding energy of 60 meV at room temperature [**2**]. Annealing [**3**], doping [**4**] and irradiation [**5-8**] can tune the properties of ZnO film. ZnO have attracted much attention and research activities in view of their potential application such as light emitting diode [**9**], spintronic device [**10**], transparent conductive electrodes [**4, 11**], laser [**12**] and solar cells [**13, 14**]. Effect of boron doping on the properties of the transition is explained by the defects induced disorder and strain in ZnO crystallites created by high density of electronic excitations. ZnO film is reported by different preparation techniques [**15-17**]. Recently, Xu *et. al* have reported that boron doped ZnO are very useful material for a magnetic application [**18**].

The defects in ZnO can be altered by various treatments like thermal annealing in controlled environment or by ion beam irradiations. It is known that the thin films of ZnO cannot be amorphized by ion irradiations [**19**]. SHI irradiation is a unique technique to modify structural, optical, opto-electronic and transport properties of materials [**20, 21**]. When SHI penetrate a solid, it slows down via two processes of direct transfer of energy to target atoms through elastic collisions i.e. nuclear energy loss (S_n), or electronic excitation and ionization of target atoms by inelastic collision i.e. electronic energy loss (S_e). The second process is predominant in case of SHI irradiation. It supplies huge excitations (S_e) as compared to that produced by elastic collisions (S_n), if the thickness of target is much smaller as compared to the range (~9 μm) of the projectile ions. SHI modifies the properties by two processes of: (i) controlling the type and density of defects [**22**], and (ii) by creating the stress and strain in the structure [**23**]. This technique presents the advantage of permitting to control the amount of energy to the system through the ion mass, energy, and fluence, and it is much localized in narrow cylinder along the ion path known as ion tracks. Therefore, the process of heavy ion irradiation can be used to understand and control the evolution kinetics of phonon structures in the nanocrystalline materials. Many groups have reported effect of irradiation on ZnO films [**6-9, 19-23**], but to the best of our knowledge there is no work is on the SHI irradiation of boron doped ZnO film. Therefore, present work reports the SHI irradiation induced modification in the structural and optical properties of the sol-gel grown undoped and boron doped ZnO thin films.

Experimental

Undoped and boron doped ZnO (ZnO and ZnO:B) films were successfully grown on corning (1737) glass substrate by sol-gel method using spin coating technique. Zinc acetate dihydrate (Merck) was used as starting material. Methanol (AR, Merck) and Monoethanolamine (Merck) were used as the solvent and stabilizer, respectively. The zinc precursor solution was prepared by dissolving zinc acetate dehydrate in methanol so as prepare concentration of 0.2 mol/l. The molar ratio MEA/Zn was fixed to 1 for all samples. Trimethyl borate is dissolved in the solution and concentration of boron is fixed 0.6 at.%. The doping concentration of boron in ZnO:B film was optimizing in our previous work [**4**]. The mixture solution was stirred by using a magnetic stirrer at 25°C for 2 h. The clear transparent and homogenous solution thus obtained was left to age for 72 h. Substrate was cleaned ultrasonically, first in acetone and then subsequently in methanol for ten minutes each. They were further cleaned with deionized water for 20 min. One drop of solution was drop onto substrate, which were rotated at 2500 rpm for 30 sec by a spin coating unit. After deposition, films were dried in air at 230° C for 10 min over hot plate to evaporate the solvent and remove organic residuals. The process from coating to drying has been repeated for fifteen times to obtain the desired thickness of the films. The film thickness is observed into be approximately 280 nm. The films were inserted to a microprocessor controlled furnace and annealed in air at 450°C temperature for 1 h heating rate of furnace is fixed 5°/min.

The annealed films were irradiated with 120 MeV Ag^{+9}, 50 MeV Ni and 120 MeV Au+9 ions using the 15UD Pelletron Accelerator facility at Inter University Accelerator Centre (IUAC), New Delhi. Electronic energy loss (S_e) of Ag, Ni and Au ions in the ZnO is 21.67 KeV/nm, 12.65 KeV/nm and 24.63 KeV/nm, while nuclear energy loss (S_n) is 0.105, 0.049 KeV/nm and 0.044 KeV/nm as estimated from SRIM simulations [**24**]. The focused ion beam was scanned over an area of 1 cm^2 with the fluences of $1x10^{11}$ to $3x10^{13}$ ions/cm^2 and the beam current was kept constant 1 pnA (particles nanoampere). The modifications of the properties are expected mainly due to the electronic excitation induced by SHI, as the range of the ions is much larger than the film thickness. Crystalline nature of the ZnO films was confirmed by PAN alytical X'pert PRO diffractometer using the CuK_α radiation having a wavelength of 1.5140°A. The film thickness was measured by surface profiler ambious XP-1. The band gap of ZnO films were measured by optical transmittance using a Shimadzu Solid Spec 3700 double beam spectrophotometer.

Results and discussion

Structural analysis of ZnO and ZnO:B films

Fig. 1 shows X-ray diffraction (XRD) pattern of ZnO and ZnO:B films annealed at 450°C temperatures with different fluence. A strong diffraction peak (002) of ZnO with hexagonal wurtzite crystal structure (JCPDS card No. 79-0206) is observed in pristine and irradiated films. It indicates that most of the grains in ZnO and ZnO:B have a strong orientation along *c*-axis (002) plane as reported in JCPDS card No. 79-0206. The peak intensity of ZnO and ZnO:B is changed after irradiation. The transfer of energy from the ion to the target is mainly due to electronic energy loss. According to thermal spike model [**25**] this transfer of very large amount of energy to the target is responsible for the formation of very high temperature zones along the ion paths formed by SHI during irradiation. This results in the melting of ZnO and other impurity phases if present, to form a homogeneous mixture followed by rapid thermal quenching in the range of 10^{12}-10^{14}K/s. The formations of removal of defects, structural strain and order/disordering thus produced in this process is responsible for the modifications in structural and other properties in various materials. Crystallite size of the ZnO and ZnO:B has been calculated using XRD data [**26**]

$$d = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where, k is correction factor (0.94), λ is X-ray wavelength (1.5406°A), β is the full width half maximum and θ is Bragg diffraction angle. The crystallite size of ZnO is observed 25±0.6 and 32±1.0 nm for pristine and irradiated films. The crystallite size is increased from 17±0.5 to 52±1.0 nm with increase fluences in ZnO:B films.

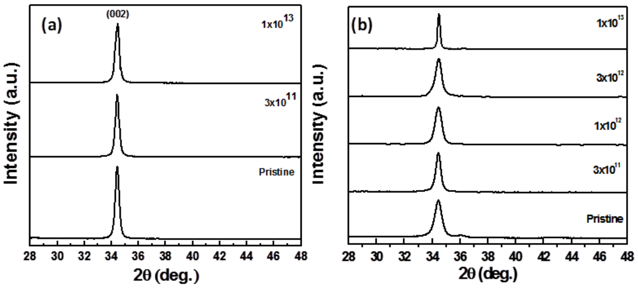

Fig. 1. (a) X-ray diffraction pattern of pristine and irradiated ZnO films at different ion fluencies and **(b)** X-ray diffraction pattern of pristine and irradiated ZnO:B films at different ion fluencies.

Effect of different S_e on as-deposited pure ZnO films

The effect of energy loss on the growth of ZnO crystallites is studied by performing irradiation experiments using 50 MeV Ni and 120 MeV Au ions on undoped as-deposited ZnO films. The ion and their energy are chosen such that Au is having S_e almost by a factor of 2 larger in ZnO crystallites as compared to Ni. XRD patterns of the as-deposited, Ni irradiated and Au irradiated ZnO films at $1x10^{13}$ ion /cm^2 fluences are shown in **Fig. 2**. The diffraction peaks appear at 31.8, 34.4 and 36.3^o, which correspond to (100), (002) and (101) planes respectively of hexagonal wurtzite ZnO. The crystallite size is calculated by Debye-Scherer formula [**26**] and it is obtained to be 5.4±0.4, 6.3±0.5 and 10.6±0.5 nm for as-deposited, Ni irradiated and Au irradiated films respectively. The increase in the crystallite size for Ni irradiated film is about 16%; while it is about 96% for Au irradiated film. This variation in the growth of the crystallites for Ni and Au irradiation could be ascribed to the difference in the electronic stopping power. However, from the present experiment it is clear that the rate of the growth of crystallites strongly depends on the electronic stopping power, but the exact dependence of the growth of the crystallites on electronic stopping power and the role of the nuclear stopping power in this domain could not be determined from the presented preliminary data. The lattice constant '*c*' of ZnO film is also calculated from the diffraction pattern and obtained to be 5.22, 5.23 and 5.19 °A for as-deposited, Ni irradiated and Au irradiated film; respectively. The variation in the lattice constant of the Ni irradiated film is almost same, while there is a significant decrease for Au irradiated ZnO film. Such kind of decrease in the lattice constant is reported by *Singh et al* [6, 8] and is attributed to the stress in the crystallites induced by high density of defects created by huge electronic stopping power of Au.

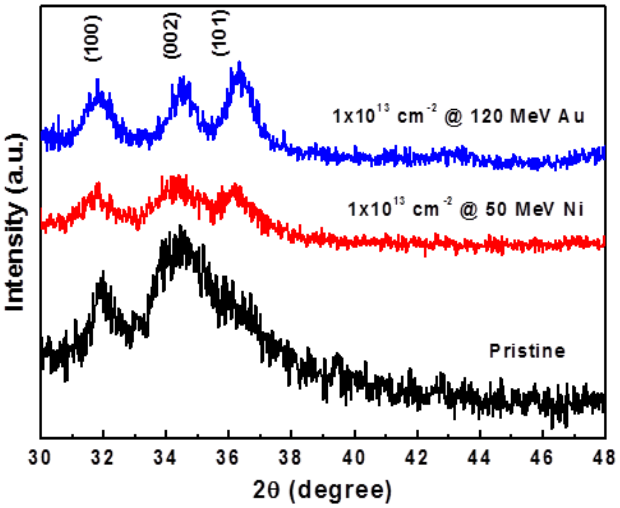

Fig. 2. X-ray diffraction pattern of As-deposited and Ni or Au irradiated ZnO film.

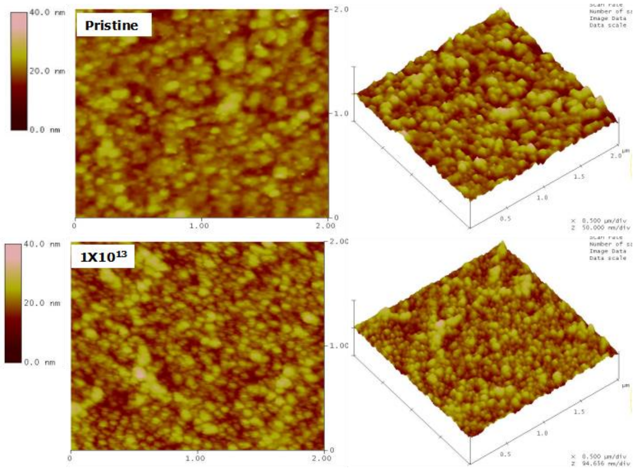

Fig. 3. AFM micrographs of pristine and irradiated ZnO films.

Surface morphology of ZnO and ZnO:B films

The surface topography of the pristine and irradiated ZnO and ZnO:B films were studied using Atomic Force Microscopy (AFM) in the tapping mode. **Fig. 3** shows the two and three dimensional micrograph in 2×2 μm^2 of ZnO films. The root mean square (rms) roughness of ZnO films was decreased from 3.97 to 3.22 nm after irradiation. The grain size of ZnO film is decreased from 86 to 39 nm after irradiation. The energetic heavy ions provide sufficient energy for promoting the sputtering from the surface of the grains that leads to reduction in the grain size of ZnO films. **Fig. 4** shows the two and three dimensional micrograph in 2×2 μm^2 of ZnO:B films. In ZnO:B films roughness is increased from 2.17 to 10.38 nm after irradiation. The grain size of ZnO:B film is increased from 47 to 82 nm after irradiation. Such drastic change in the size and shape of the grains at higher fluence is attributed to the high density of electronic excitations induced by SHI irradiation under multiple ion impacts in the near surface region [**27**]. *Kumaravel et.al* [**28**] has also reported increased in grain size with increase in roughness of films due to the increase of density and size of metal particles on the surfaces of the films.

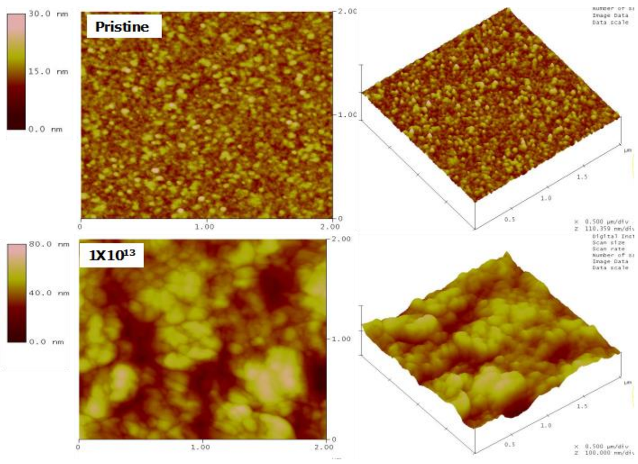

Fig. 4. AFM micrographs of pristine and irradiated ZnO:B films

Optical properties of ZnO and ZnO:B films

Fig. 5 shows the influence of irradiation on the transmission of ZnO and ZnO:B films. The average transmittance is increased with increase in fluences in ZnO film but it is decreased in ZnO:B film due to the change in roughness of films. Pristine sample of ZnO had 65% transmittance in visible region and it is increased to 85%. The increase in the transmittance of ZnO films after irradiation may be due to decrease optical scattering caused by decrease in the roughness of film (3.97 to 3.22 nm) as demonstrated by the AFM images (**Fig. 3**). *Singh et. al* [**29**] have reported that the transmittance of indium tin oxide films is increased from 75 to 84 % in visible region and the increase in transmittance is increased for electrode in Dye Sensitized Solar cell. However, pristine sample of ZnO:B have obtained 91% transmittance in visible region and it is reduced to 85%. The reduction in optical transmittance due to irradiation may be resulting from the increase in metal to oxygen ratio (Zn/O) in irradiated films, causing increase in carrier density. *Kumar et. al* [**7**] have also reported that the transmittance of ZnO films is decreased with fluence. In a direct band gap semiconductor, the absorption coefficient α is correlated to the optical band gap by this equation [**30**]-

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \tag{2}$$

where, hυ is photon energy, A is constant and E_g is the optical band gap. The band gap E_g is determined by extrapolating of the linear part of the α^2 curve towards the hυ axis. The band gap of ZnO and ZnO:B is shown in **Fig. 6**. The bandgap of ZnO is varied from 3.24 to 3.26 eV with change in fluence. No much more change is observed in the band gap of ZnO after irradiation. Bandgap of ZnO:B films is decreased at low influence but it is increase at higher influence. The band gap of ZnO:B films is changed from 3.27 to 3.37 eV with change in fluences. It has been established that in lower fluencies ZnO:B film inclusion of band gap narrowing due to many body effects is necessary to account for the net shift in the band gap. Band gap of ZnO:B is increased at higher fluence can be explained in term of Burstein-Moss (B-M) shift. *Jain et al* [**31**] reported the modification of band gap of ZnO due to the doping of Al, Y and Sc and analyzed in terms of band gap narrowing and band gap widening phenomena. ZnO:B is showing narrowing and widening in bandgap with vary in the fluences.

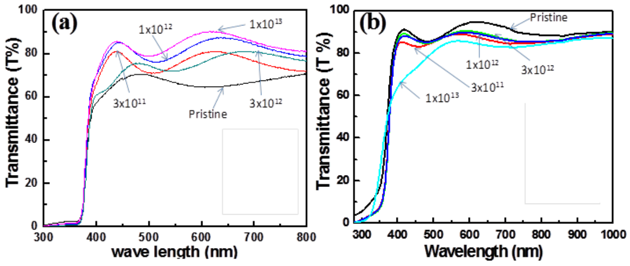

Fig. 5. Optical Transmittance spectra of pristine and irradiated ZnO and ZnO:B films at different ion fluencies.

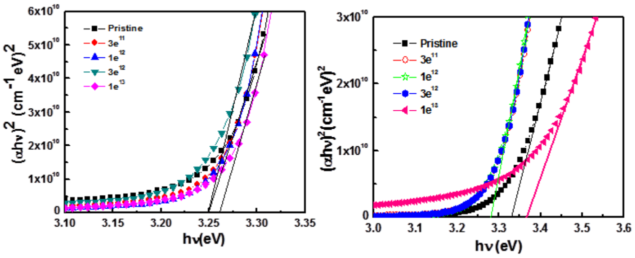

Fig. 6. Band gap variation of doped ZnO and ZnO:B films with annealing temperature, calculated by Tauc's plot method.

Conclusion

We have investigated modifications of structural and optical properties of ZnO and ZnO:B films with 120 MeV Ag ion irradiation. We have observed the modifications of the intensity of XRD, surface morphology and Bandgap by ion irradiation. The transparency of ZnO and ZnO:B is change after irradiation. Band gap narrowing and widening is observed in ZnO:B with changed in ion flunce from 1×10^{11} to 3×10^{13} ion /cm^2. The observed modification in structural and optical properties was understood in the term of thermal spike model.

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