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Impact of swift heavy ion (120 MeV, Ag^{9+}) on doped ZnO:Al thin film

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Version October 5, 2019 submitted to Materials

Featured Application: In the present study the effect of swift heavy ion (SHI) irradiation on ZnO:Al thin film have been studied at different fluence. XRD and atomic force micrographs confirms fragmentation of particles in the irradiated films and increase in surface roughness which helps in increasing the efficency of adsorption rate in the gas sensor and hence these fragmentation of particles and increase in surface roughness due to SHI irradiation can increase the performance of a gas sensor which can be used in hostile environment.

Abstract: In the present work, doped ZnO (ZnO:Al) thin film has been grown on Silicon (Si) substrate by DC sputtering. The obtained thickness of the film is 230 ± 5 nm. The films were subjected to swift heavy ion (SHI) irradiation 120 MeV, Ag^{9+} with different fluences ranging from 3×10^{11} to 3×10^{13} ions/cm^2. To study the impact of SHI, both pristine and irradiated samples were characterized to obtain the structural, surface morphological and electrical properties using X-ray diffractometry (XRD), atomic force microscopy (AFM) and hall effect measurement system respectively. From XRD results it is observed that there is change in crystallinity of the film with increase in irradiation fluence. The surface morphological studies through AFM shows the increase in surface roughness with increase in fluence. A significant change is also observed in electrical parameters viz conductivity, mobility and carrier concentration. Conductivity, mobility and carrier concentration decreases with increasing fluence.

Keywords: ZnO:Al; Swift heavy ion; XRD; AFM; Hall measurement

1. Introduction

Zinc oxide (ZnO) belongs to the family of semiconductor with direct wide band gap of energy (3.37 eV), high exciton binding energy and display high chemical stability[1]. This property paves great application in opto-electronics devices which is observed in both the visible and UV regions, gas sensors, field-emission devices[2]. Instability exists in pure ZnO due to the environment being corrosive or due to thermal edging in contact with the open atmosphere. Point defects and oxygen vacancies makes it resistive. Al(Aluminum) a group III element is added as dopant to enhance the stability[3]. Adding trivalent impurities such as Al to the ZnO thin film makes it more structural stable with improved optical properties. A stable ZnO displays a hexagonal wurtzite crystal structure. Enough research is available on the synthesis of Zinc oxide based compounds but study on manipulation of grown films is less. Swift Heavy ion irradiation has emerged to be a simple and versatile tool in the thin film industry for surface nanostructuring without damaging the sample. SHI bombardment instigate a high density of excitations of electrons in the material which remodify structural, electrical and optical properties [4] and generate defects. In this paper, DC magnetron sputtering technique was used to synthesize Zinc Oxide (ZnO) doped with Aluminum (Al) the samples were irradiated with SHI of having different fluence of 3×10^{11}, 3×10^{12} and 3×10^{13} respectively. The modification in structural and electrical properties due to SHI are studied and discussed.

2. Experimental Details

Alumunium doped Zinc oxide (Al-ZnO) films of thickness 230 ± 5 nm were grown on Silicon substrates by the process of DC magnetron sputtering. Removing of unwanted oxides from the surface of Si is performed by etching using acid solution (HF:DI::3:1). After cleaning, the substrate were put in a sputtering chamber. For the deposition, the chamber pressure were set at 5×10^{-6} and 3×10^{-3} mbar was maintained as working pressure. For getting a uniform growth, the substrates were rotated at 20 rpm and the distance between the substrate target and sample was kept at 15 cm. Argon gas of 30 standard cubic centimetre per minute (SCCM) was passed into the sputtering chamber where $ZnO:Al_2O_3$ (2%wt) target with a diameter 3" with purity(99.99%) were used to deposit Aluminum doped ZnO thin film. Post deposition, the thin films were ion irradiated with 120 MeV Ag^{9+} beam at fluence 3×10^{11}, 3×10^{12} and 3×10^{13} ions/cm^2 respectively at Inter University Accelerator Centre, New Delhi. The Ag^{9+} ions from the plasma were extracted by plasma chamber which are highly polarized gaining energy accelerating at high speed to impact and impart a kinetic energy of 120 MeV. Before bombardment of high energy stream of ions to the Al:ZnO target and to ensure purity, dipole magnet was used for a thorough examination of the mass and energy of the high energy ion beam. Maintaining uniform ion flux during ion irradiation on the surface of the thin film was achieved by scanning the high energy beam using a magnetic scanner over a area of 2.0×2.0 cm^2. A beam current of 9 nA was constantly provided during the entire ion irradiation process.
The study of microstructure was done by X-ray diffractometry (XRD)technique using (XRD-6100) of Shimadzu Inc in the range of $20^o - 80^o$, the target used for XRD is Cu (Cu-Kα1 line,$\lambda = 1.54056 A^o$). The surface morphology was studied by AFM (Atomic force microscope)technique. Electrical properties were investigated by Hall measurement system (HMS-3000,Ecopia) at room temperature. The thickness of the deposited film was measured using EDXRF (EDX-7000).

3. Results and Discussion

3.1. Structural Analysis

XRD data of as-deposited Al:ZnO and 120 MeVAg^{9+} ion irradiated samples at different fluence 3×10^{11}, 3×10^{12} and 3×10^{13} ion/cm^2 confirm that Al:ZnO thin films display a polycrystalline hexagonal wurtzite structure.The patterns of diffraction matches with standard JCPDS card number 75-0576. Structural changes are observed after swift heavy ion irradiation from the diffraction pattern (figure 1) the silicon (Si) peaks appear within a range of 52^o to 60^o bragg's diffraction angle. Due to increase in the concentration of dopants, in the present case Aluminum (Al) in the ZnO thin film where Zn^{2+} successfully gets substituted by Al^{3+} along the interstitial sites of the ZnO lattice structure. As the substitution occurs successfully hence secondary peak of Al is not found in the XRD pattern[5]. The change observed in the relative peak intensity diffracted with the increasing ion fluence depict a modification in the orientation of the plane of ZnO thin films upon SHI irradiation. Pristine and SHI irradiate thin films are having similar peaks as fluence increases with minor shift which signifies release of residual stress and presence of strain which creates distortion in the crystal lattice[6]. From the diffraction pattern we observe a substantial decrease of relative peak intensity for the plane (002)2θ (34.0^o), with increase of ion fluence suggest that amorphization process occurs and

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crystallinity decrease at that plane as high temperature zones are generated due to ion irradiation. Using Debye-Scherrer in (equation 1) at (002) plane crystallinity was calculated which is seen table 1.

$$D = \frac{K\lambda_k}{\beta_{hkl}Cos\theta} \tag{1}$$

where β_{hkl} defined as full width at half maximum (FWHM), K which is constant (0.90),λ_k is the wavelength of the incident X-ray ($\lambda_k = 0.1540$nm),D gives the crystallite size with θ representing bragg's angle. The lattice constant along (100) plane is calculated by

$$a = \frac{\lambda_k}{\sqrt{3}Sin\theta} \tag{2}$$

corresponding (002) plane, the lattice constant c is calculated by

$$c = \frac{\lambda_k}{Sin\theta} \tag{3}$$

The lattice constant a=3.29A^0 and c=5.27A^0, c/a=1.60 which is the ratio for the lattice parameter of a ideal hexagonal structure[6].

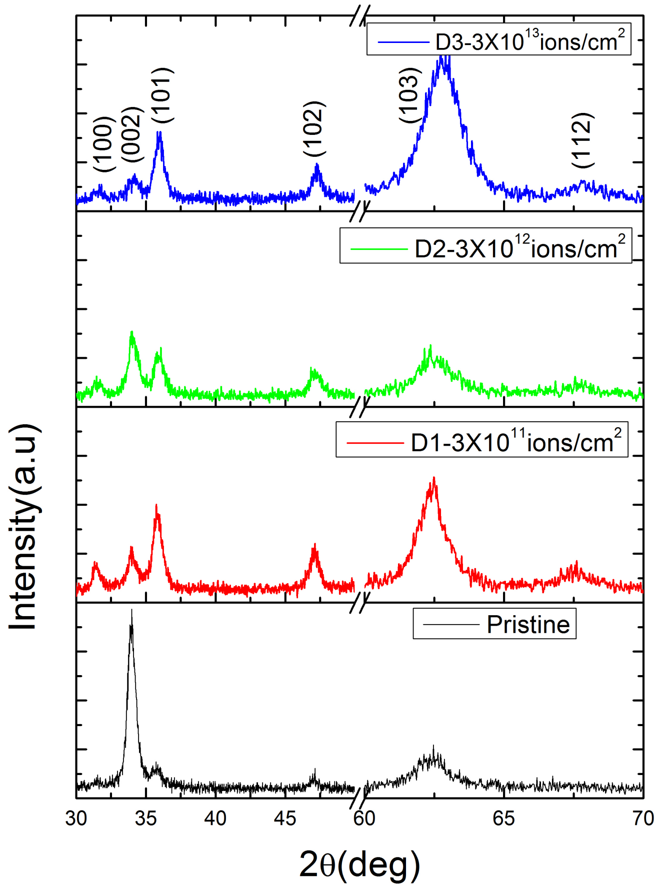

Figure 1. X-ray diffraction of the pristine and 120 MeV Ag^{9+} ion-irradiated with various fluence of Al:ZnO films.

Table 1. Analysis of X-ray diffraction at (002) plane of pristine and 120 MeV Ag^{9+} ion irradiated Al:ZnO films.

SL.No.	Sample name	FWHM	Crystallite size(nm)	strain	Dislocation density(10^{-5})
1	Pristine	0.71	11.6	0.16	7.31
2	D1-3 $\times 10^{11}$	0.48	17.2	0.11	3.34
3	D2-3 $\times 10^{12}$	0.77	10.7	0.18	8.59
4	D3-3 $\times 10^{13}$	0.47	17.67	0.11	3.19

From table 1 its observed that crystallite size increase up to 3×10^{11} ions/cm^2 but decrease for 3×10^{12} and increase again for 3×10^{13} which stipulate the observed increase in the ZnO:Al crystallite size as increment of 1D defects (point defects) create nucleation center and density of such centre increase with fluence. The decrease in the crystallite size can be ascribed to inelastic collision between the beam's incident atom moving at high velocity towards the target material which leads to fragmentation[7]. The dislocation density(δ_k) was calculated by the following formula.

$$\delta_k = \frac{1}{D^2} \tag{4}$$

The dislocation density decrease up to the fluence 3×10^{11} and increase for the fluence 3×10^{12} and again decrease up to fluence 3×10^{13}. The released strain (s) in the Zinc oxide thin film during irradiation along the plane (002) was calculated by

$$s = \frac{\beta_{hkl}}{4 \tan \theta} \tag{5}$$

The change in dislocation density and strain is due to point defects which are created in cascaded manner along the path of swift heavy ion which leads to material modification. This process can be explained by thermal-spike model where there is rapid change in energy which is thermal in nature from electronic subsystem to an atomic subsystem within a time frame of 10^{-14} to 10^{-12} s. It is so instantaneous which result imperfection in the crystal and distorting the crystal lattice structure[8]. With increasing fluence, it results a reorientation of plane and with increase in distortion induced by SHI irradiation. Hence strain in the thin film increase[3].

3.2. Surface morphology

Analysis of surface morphology was conducted by Atomic Force Microscopy and software WS×M 3.1 was used to investigate RMS surface roughness and to generate the particle size distribution curves for analysis (figure 3).

The change in RMS roughness is calculated and tabulated in table 2.

Table 2. RMS roughness vs fluence.

Sl.No.	Sample	RMS roughness(nm)
1	pristine	7.13
2	3×10^{11}	16.91
3	3×10^{12}	29.71
4	3×10^{13}	23.18

With increase ion fluence the RMS roughness increase (figure 2). This increase of roughness can be attributed to creation of nanoparticle at surface of the thin film with island formation which occur simultaniously. Fragmentations of particles are observed in the irradiated films, such a change is attributed to generation of high density electronic excitation due to swift heavy ion irradiation under multiple ion impacts near the surface[9]. The change in RMS roughness at the surface of the thin

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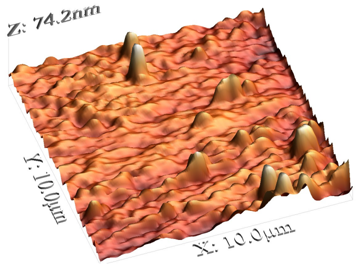
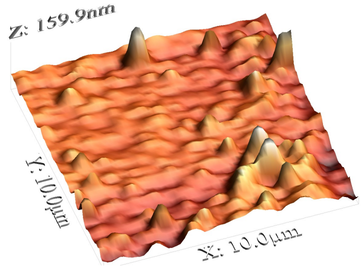
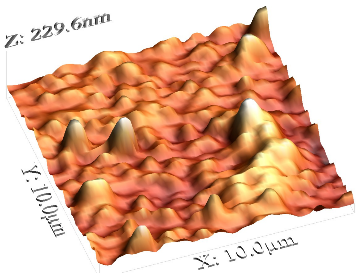


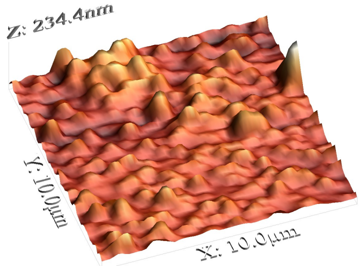
(a) Pristine



(b) 3×10^{11}fluence

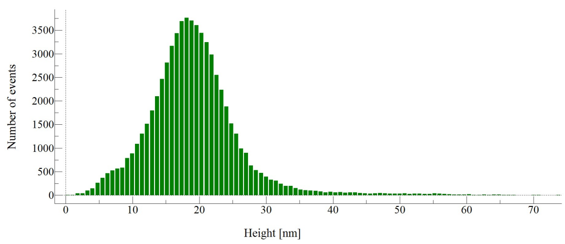


(c) 3×10^{12}fluence

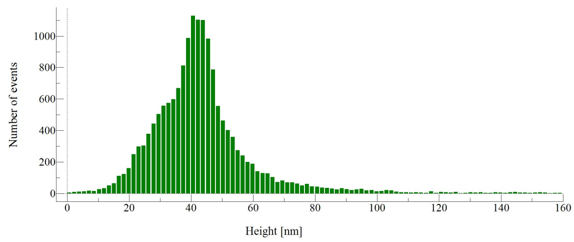


(d) 3×10^{13}fluence

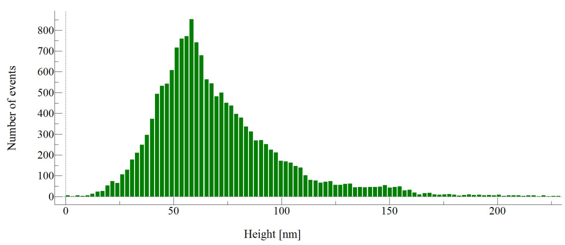
Figure 2. Surface roughness with increasing fluence.



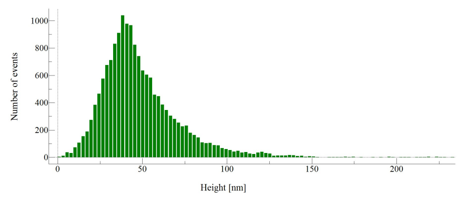
(a) Pristine



(b) 3×10^{11}fluence



(c) 3×10^{12}fluence



(d) 3×10^{13}fluence

Figure 3. Particle size distrubition.

film can be seen from particle size distribution curves. A slight dip in roughness at 3×10^{13} can be attributed to agglomeration of grains under disorder which is induced by SHI[7].

3.3. Electrical properties

Hall Effect measurement was used to analyze electrical properties of ZnO:Al and tabulated in table 3.

Table 3. Hall measurement of ZnO:Al pristine and 120 MeV Ag^{9+}.

Sl.No	Sample	carrier concentration (cm^{-3})	mobility (cm^2/Vs)	Conductivity (siemens)
1	Pristine	1.36×10^{22}	18.2	3.97×10^{4}
2	3×10^{11}	3.34×10^{21}	11.7	6.31×10^{3}
3	3×10^{12}	1.73×10^{21}	10.2	2.83×10^{3}
4	3×10^{13}	1.06×10^{21}	6.6	1.13×10^{3}

During the entire process of irradiation, the observed carrier concentration of ZnO:Al film decrease while there is a increase in resistivity. The entire phenomenon observed can be attributed to SHI induced defects which are present at the deep level inside the band gap of the material which act as trapping mechanism for mobile carriers[8]. It is seen that grain boundary can change the electrical properties of the given sample. The decrease in crystallinity of ZnO:Al suggest increase in grain boundary which in turn increases the electrical resistivity. Scattering effect caused by increase of impurity in the concentration of donor atom can sometime cause a decrease in mobility[10].

4. Conclusions

The ZnO:Al thin film were deposited on Si substrate and film were subjected to swift heavy ion irradiation with varying fluences. The change observed in morphological, structural and electrical properties of thin film ZnO:Al irradiated by swift heavy ion suggest that SHI can help in modifying surface morphology/roughness of a thin film which can be suitable for gas sensor application.

Author Contributions: L.M., V.K., and U.P.S. conceived and designed the experiments; V.K. and U.P.S. contributed to the sample preparation and microstructure characterization; L.M., V.K., and U.P.S. contributed to the data analysis; L.M. wrote the paper.

Funding: This research received no external funding

Acknowledgments: The author would like to thank Dr Fouran Singh, IUAC for his support during experiment and discussion and Mr. Ram Kumar, NIT Rouerkela for AFM characterization. One of the author (L.M.) like to thank KIIT (Deemed to be University) for providing financial assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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