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# 120 keVAr ion beam irradiation of magnetron sputtered ZnO thin films

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**Abstract** : The effect of low energy ion irradiation of Ar beam ($Ar^{+1}$) having 120 keV energy has been investigated on transparent ZnO thin films to study the modifications in structural properties along with optical properties of ZnO.Here the synthesis of ZnO thin films has been done on quartz substrate by sputtering the target of pure ZnO using the RF magnetron technique.Surface morphological properties have been observed by FESEM (Field Emission Scanning Electron Microscope) techniques andreveal the variation in the growth of surface grains. To observe the impact of ion irradiation on different characteristics of ZnO thin film various characterizations such as RBS(Rutherford Backscattering Spectrometry), UV-visible spectroscopy, Raman Spectroscopy,XRD(X-Ray Diffraction) have also been performed.The XRD data shows that the as-deposited and irradiated samples exhibit hexagonal wurtzite structure with marked intensities at (002) and (103) orientations.The absorption spectra obtained by UV-visible Spectrophotometer reveal that with the increase in ion doses of Argon beam a slight shifting of peaks is observed.Overall, there is a minimal effect of Ar ion irradiation on ZnO thin films.

**Keywords** : ZnO; Optical properties; Low energy; Ion irradiation; RF sputtering ; Thin films

## Introduction

ZnO is very interesting due to its abundance and non-toxicity.It is recognized as an III-VI compound semiconductor having a hexagonal wurtzite structure.ZnO is well known for its great applications in the various fields of devices including ultraviolet LEDs,solar cells, transparent conductive electrodes,varistors, etc[1-4]. It has a wide bandgap of ~ 3.37eV and is also preferred due to its useful properties i.e,piezoelectricity, biocompatibility,chemical stability, nonlinearity, high optical transparency, etc[5-6]. ZnO is chosen to be the best optoelectronic material[7-8]. Fabrication of ZnO thin films can be done using many techniques suchaschemical vapordeposition[9],RF magnetron sputtering[10], thermalvapordeposition[11], Solgel[12], Pulse laser deposition[13], Molecular beam epitaxy[14]. Magnetron Sputtering technique is widely used, as it performs with a high rate of deposition as well as toxic gas-free emissions.

Ion beam irradiation is a widely accepted technique for modifying the properties of different materials.In the present study, using RF-magnetron sputtering technique, the transparent conductive thin films of ZnO are synthesized and their properties such as structural and optical are investigated before

and after the treatment of ion irradiation.For 220 keVAr beam,here nuclear loss is dominating over the electronic loss and therefore, effects are mainly produced by collision cascades.ZnO is chosen because it has unique and novel properties i.e. piezoelectric, optical for fabricating devices, and to enhance the performance of electrochemical devices.

## Experiment

By RF magnetron sputtering technique, transparent and conductive ZnO thin films were

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prepared using a sputtering target of ZnO with 2 inches diameter (prepared by using 99.99% pureZnO powder by Alfa Aesar). For the deposition of thin films, quartz and silicon substrates of size 1 ′ 1 cm2 were cleaned by using acetone,propanol, and trichloroethylene with an ultrasonication process.Using the Sputtering unit, at the rate of 5.0 sccm,the flow of Ar gaswas maintained in the chamber to create plasma. The pressures measured on the chamber by penning gaugebefore and after deposition were 8.32 ′ $10^{-5}$ mbar and 9.73 ′ $10^{-3}$ mbar respectively. The deposition was performed for 3 hours at 100 watts power to synthesize ZnO thin films of about 200 nm.The thin films of ZnO were irradiated with 120 keVAr beam with doses ranging from $1\times10^{13}$ to $1\times10^{16}$ ions/$cm^2$in Low Energy Ion Beam facility (LEIBF) centre at IUAC (New Delhi). During irradiation, a stable current of 1μA was maintained and a beam with a spot size of diameter~3.0 mm was focused over the area of 1x1 $cm^2$ to cover the whole sample. The value of both losses (electronic as well as nuclear) was found to be 32.01 eV/Å and 60.6eV/Årespectively.During the ion irradiation process, throughout the experiment, the pressure of ~ $2\times10^{-6}$ mbar was maintained in the chamber of LEIBF.

For the study of induced modifications using ion beam, various characterization techniques were used forsynthesized ZnO thin films.The estimation of the thickness of the filmwas obtained by the Rutherford Backscattering spectroscopy. RBS-AMS System (PARAS) facility at IUAC, New Delhi,India has been used.The optical properties of the films were observed using a UV-visible spectrometer with a model of dual U-3300 Hitachi spectrometer.By Scanning Electron Microscopy (Nova Nano FE-SEM 450 (FEI)),the surface micrographs of thin films were recorded.The structural properties were detected by Raman Spectroscopy (532 nm laser) and X-ray Diffractometer (Panalytical X Pert Pro).

**Result and Discussion**

**Rutherford Backscattering Spectroscopy**

For the thickness determination of thin film,the most promising technique is Rutherford Backscattering spectroscopy.With using 2 MeV He+ ion beam, the simulation of the RBS spectrum of pristine sample (ZnO thin film) was done with the help ofRutherford Universal Manipulation Simulation Program (RUMP)software[15],as shown in figure 1.Using RBS analysis, the estimated thickness of ZnO film is found to be200 nm.

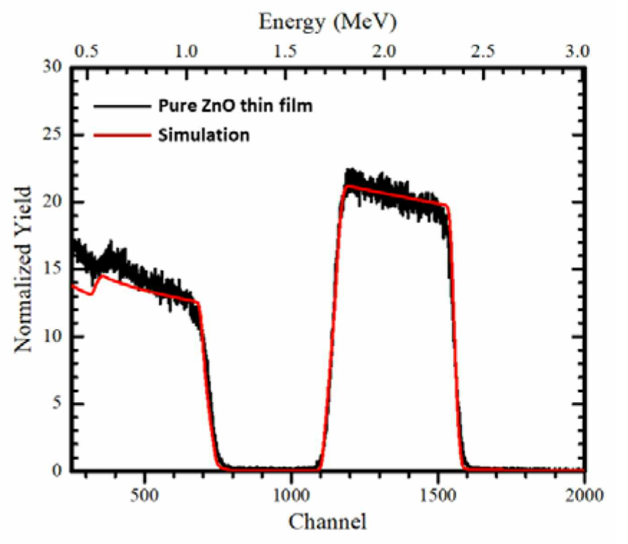


*Figure 1 RBS spectra for as-deposited thin film of ZnO .*

**X-Ray Diffraction Analysis(XRD)**

XRD reveals the structure properties and crystallinity of as-deposited sample and 120 keVAr irradiated samples at different fluencesranging from ($1\times10^{13}$ions/$cm^2$to$1\times10^{16}$ions/$cm^2$). Figure 2 shows the XRD patterns for as-deposited as well as irradiated samples.It shows the two major planes i.e (002) and (103) with quite significant intensities and is visible at particular 34.23° and 62.50°respectively which confirms the hexagonal wurtzite structure of ZnO having crystallinity[16]. After irradiation,no significant shifting in peak position is found which reveals that no structural transformation occurred in films with irradiation by Ar beam. The average grain sizes of as-deposited as well as irradiated films are calculated by using Debye Scherrer's formula which is given as[17]

$$Crystallite\ size\ (D) = \frac{0.9\lambda}{\beta\ Cos\theta}\ (1)$$

Where λ denotes wavelength of incident CuKα radiation

β is Full-width half maximum (FWHM)

θ is Bragg's angle

The average crystallite size of grains varies from 5.7 nm to 9.9 nm with increasing doses.

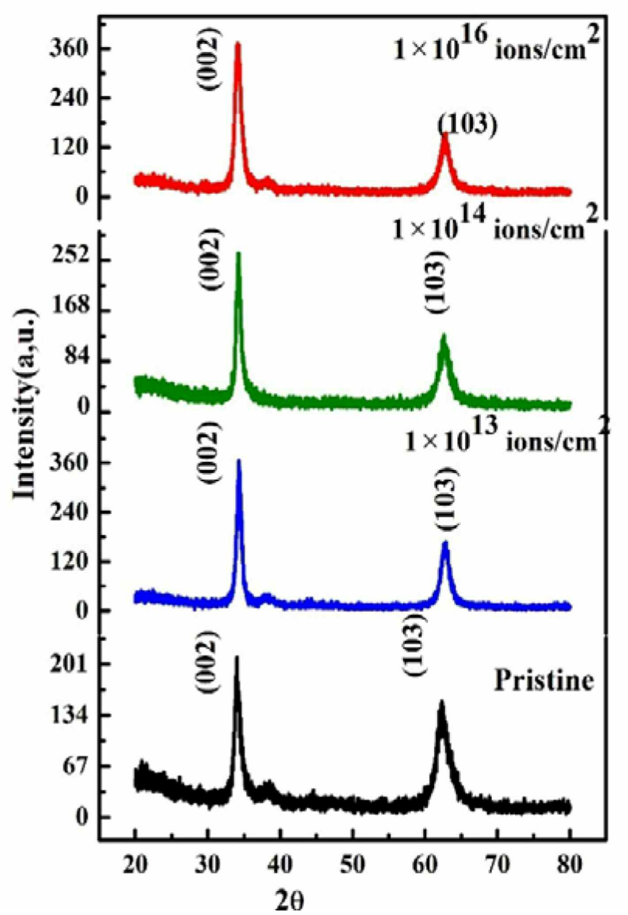


*Figure 2 XRD pattern for pristine as well as irradiated ZnO samples.*

### UV-visible Spectroscopy

The absorption spectra of pristine and irradiated ZnO samples with 120 keVAr ion beam are shown in Figure 3. The recorded absorption spectra are in the wavelength ranges from200 nm-1100 nm. The pristine film is almost transparent absorption modes are seen in spectra.With an increase in ion doses, there is a slight shiftingof absorption peaks.It is also shown from the figure the band edge remains unchanged after irradiation but optical absorption gets increases in the visible region due to the creation of defects such as anti-site oxygen and oxygen vacancies in the film.It is found that the atomic order of the ZnO lattice structure remains unaffected at a larger distance due to theless effect of ion irradiation on modes of vibration and electronic gap.There is a reduction in the semiconductor gap as the lattice structure is not amorphized.

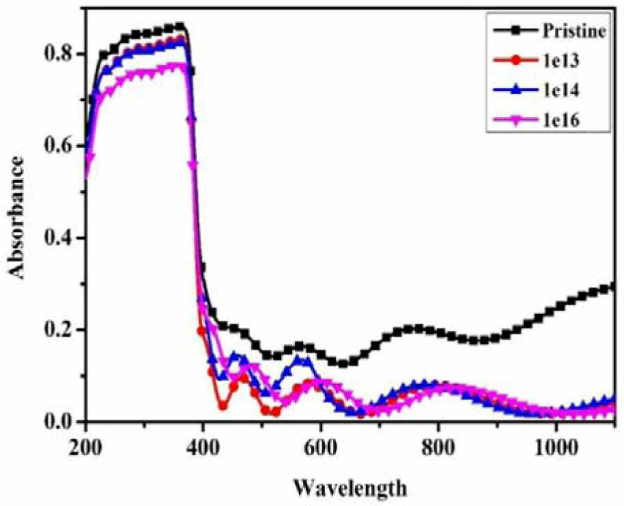


*Figure 3. UV-visible absorption spectra of as-deposited ZnO thin film and Ar irradiated thin films*

### Surface morphological investigations

The surface micrographs of pristine and irradiated samples were recorded by using Scanning Electron Microscopy (SEM).Figure4 shows surface images that reveal the agglomeration in particles of ZnO with the increase in doses. With the treatment of ion irradiation growth of smaller grains on the surface of films is observed and with further increase in doses, smoothness isobserved[18].

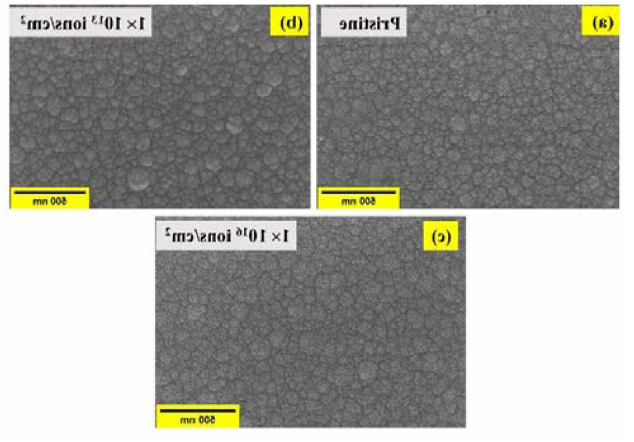

*Figure 4. SEM images of pristine as well as irradiated ZnO thin films.*

### Raman Spectroscopy

To understand the disorders and defects in a lattice, the Raman spectroscopy of thin films was used. The space group of ZnO having a hexagonal wurtzite structure is associated with  symmetry. Based on the group theory, ZnO consists of eight sets of normal phonon modes as  with  are represented as acoustic modes, and the remaining other six modes  are denoted as optical phonon modes at Brillouin Zone (the point at

).Figure 5 shows the Raman spectra of pure ZnO andArirradiated ZnO thin films reported in the wave number ranges from 200-800 $cm^{-1}$. From the typical Raman spectra, the two bands are observed at 437 cm-1 and 578 $cm^{-1}$. At 578 $cm^{-1}$, the sharp and intense band observed which is assigned to particular mode A1 (LO) mode which is matched with theoretical results.The other band particularly at position of 437 $cm^{-1}$ associated with the E2 (high)mode which confirms the formation of wurtzite structure[19]. The A1 (LO) mode at 578 $cm^{-1}$ is increasing in intensity with ion irradiation. Its intensity is maximum for a sample irradiated at the dose of $1x10^{16}$ ions/$cm^2$.

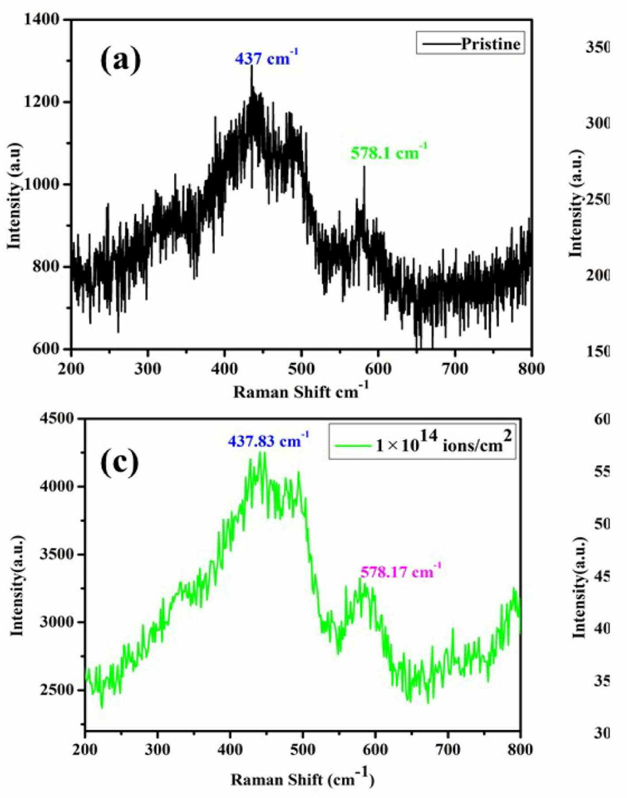


Figure 5. Raman spectra of as-deposited and 120 keVAr irradiated samples.

## Conclusion

We have studied the modifications in structural and optical properties of pure ZnO thin film prepared by using sputtering technique (RF-magnetron) and irradiated thin films by 120 keVAr ion beam at fluences ranges from low fluence 1´1013ions/cm2 up to highest fluence 1´1016ions/cm2. It is concluded from these techniques observed structure of pure ZnO is hexagonal wurtzite and it is still maintained after irradiation treatment of the Ar ion beam. With RBS simulation, the estimated thickness of ZnO is found to be ~ 200 nm.Surfacemorphological investigations revealed the smoothness and homogeneity after irradiation. Raman spectra revealed the modification in crystallinity of thin films with irradiation treatment.


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