

# 220 keV Nitrogen ion beam induced Modification of ZnO thin films

Vikesh Chaudhary<sup>a,b</sup>, Amena Salim<sup>a</sup>, Ritu Vishnoi<sup>a</sup>, Jyotsna Bhardwaj<sup>a</sup>, P. Kumar<sup>c</sup>, Umesh Kumar Dwivedi<sup>b</sup>, Pushpendra Kumar<sup>d</sup>, Ganesh D. Sharma<sup>e</sup>, Rahul Singhal<sup>a</sup>

<sup>a</sup>Malaviya National Institute of Technology Jaipur, JLN Marg, Malviya Nagar, Jaipur- 302017, India

<sup>b</sup>Amity University Rajasthan, Jaipur-303002, India

<sup>c</sup>Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110067, India

<sup>d</sup>Manipal University Jaipur, Jaipur-303007, Rajasthan, India

<sup>e</sup>The LMN Institute of Information Technology, Jamdoli, Jaipur, India

**Abstract :** Zinc oxide (ZnO) is a promising material, due to its effective surface area, high reliability, high pore volume, and low toxicity. Here, ZnO thin films are fabricated on a quartz substrate using an RF magnetron sputtering setup. By irradiating samples at different doses with a 220 keV ion beam of Nitrogen, the effect of irradiation on ZnO films is observed and analyzed using a variety of techniques, including RBS (Rutherford Backscattering Spectrometry), ultraviolet (UV) - visible spectroscopy, Raman spectroscopy, FESEM (Field Emission Scanning Electron Microscope), and XRD (X-ray Diffraction). The UV-visible spectra confirm that there is a minimal effect of 220 keV N beam irradiation on ZnO absorption modes. A slight shifting of absorption peaks is rather seen. The effect of the beam on the surface morphology of ZnO is studied at different fluences. The growth of crystalline ZnO with wurtzite structure was revealed by X-ray diffraction and Raman spectra in both pristine and irradiated thin films.

**Keywords :** RF sputtering; Thin film; Low energy ion irradiation; Structural properties; Optical properties

## Introduction

Metal oxide thin films and nanostructures have attracted a lot of attention in the past few decades due to their unique physical and chemical properties and a vast range of applications in various fields of nanotechnology. ZnO has been a promising material for a range of applications in recent years. The ability of ZnO to emit light in the blue region of the electromagnetic spectrum, as well as the high light-matter coupling strength and stability of its excitons at room temperature, make it ideal for the development of next-generation optoelectronic devices like polariton lasers at room temperature. Because of its high abundance, cost-efficient fabrication process, chemical/thermal stability, nontoxicity, excellent radiation hardness, low electrical resistivity, a wide bandgap ( $E_g$ ) of 3.36 eV, high exciton binding energy, as well as high transparency at room temperature, ZnO nanostructure has emerged as a key player. Due to its simplicity of synthesis, remarkable features, and variety of applications, such as artificial photosynthesis, photocatalysis [1], photodetectors [2,3],

FET [4], solar cells [5], and LEDs [6] ZnO thin films are intensively explored. Biosensing [7-9], Gas sensing [10-13], and UV detection [14] are just a few of the fields where ZnO thin films have been widely used. The corporal properties of thin films are mainly determined according to the method of preparation and process parameters.

In the past, spray pyrolysis, e-beam deposition, hydrothermal, thermal evaporation, and RF sputtering technologies have all been established for the fabrication of high-quality ZnO thin films [15-17]. RF sputtering of ZnO is a well-known approach between these technologies. Different parameters such as pressure, deposition time, gas flow rate, and RF power can be used to improve the properties of thin films grown by RF sputtering. RF sputtering is a good choice for growing ZnO thin films because it provides convenient control of crystallographic orientation, good interfacial adhesion with the substrate, and a high packing density of the thin film grown [18-19].

Many researchers compared the irradiation studies of ZnO with different energy and beams.

\*Corresponding author: (E-mail: rsinghal.phy@mnit.ac.in)

However, an exhaustive study is still lacking. In the present work with irradiation using a 220 keV N ion beam at changing doses, structural and optical alterations in ZnO thin films were observed and analyzed. The structural and optical quality of the 220 keV N ion beam irradiation ZnO thin film was enhanced compared to the pristine ZnO thin film.

The synthesis of ZnO thin films on quartz substrate utilizing an RF magnetron sputtering method and a high-quality ZnO target for a systematic study of the effect of low energy ion irradiation on structural and optical aspects of ZnO thin films is described in this paper. ZnO is a semiconducting semiconductor with n-type characteristics. ZnO is well-known for its photoconductive characteristics. The deposited ZnO thin film's microstructural and optical characteristics concerning beam have been investigated and reported here.

## Experimental Plan

### ZnO thin film preparation

RF magnetron sputtering was used to deposit the nanocrystalline ZnO thin layer on the quartz substrate. The thickness of the film was ~200 nanometres. Both the Si wafer and the quartz substrate were thoroughly cleaned before deposition. Silicon wafers were cleaned using standard procedures, and the quartz substrate was cleaned with acetone and isopropanol, then rinsed in deionized water before being mounted to the substrate holder. A ZnO thin film was deposited over quartz and silicon substrates using a ZnO target (2-inch dia target) consisting of 99.9% pure ZnO powder from MERK Chemical Limited in Mumbai, India. ZnO thin film was deposited by RF & DC magnetron sputtering machine at Material Research Center (MRC), MNIT Jaipur. An  $8.32 \times 10^{-5}$  mbar,  $9.73 \times 10^{-3}$  mbar, and 30 minutes were chosen as the base pressure, deposition pressure, and deposition time, respectively. During the deposition, the rate of deposition was tried to keep fixed, while the argon flow rate was kept constant at 5.0 sccm.

### Irradiation of ZnO thin film

Following deposition, these ZnO thin films were irradiated with a 220 keV N Ion beam at various fluences of  $1 \times 10^{13}$  to  $1 \times 10^{16}$  ions/cm<sup>2</sup> using a low energy ion accelerator at the Inter-University Accelerator Centre (IUAC) in New Delhi, India.

## Results and Discussion

### Rutherford backscattering spectroscopy

RBS is an effective technique for estimating material thickness and compositional parameters. This

was accomplished using a 3.0 MeV He<sup>++</sup> beam. Figure 1 shows the RBS spectrum of a pure ZnO thin film on a silicon (Si) substrate. The spectrum was simulated using the Rutherford Universal Manipulation Program (RUMP) to determine the thin film thickness [20]. The simulated fit is also depicted in figure 1. The film thickness was calculated to be ~200 nm with RUMP software.

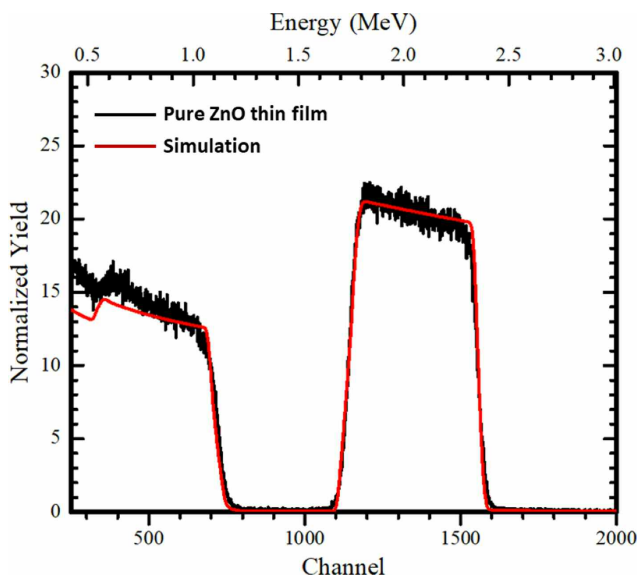


Figure 1: Rutherford backscattering spectrum of ZnO thin film with 220 keV N ion beam irradiation along with its fit.

### UV-visible spectroscopy

The optical properties of ZnO are studied via UV-visible absorption spectroscopy. The ZnO thin film was deposited on a quartz substrate and irradiated with an N ion beam at different doses for absorption spectroscopy measurement, including  $1 \times 10^{13}$ ,  $1 \times 10^{14}$ , and  $1 \times 10^{16}$  ions/cm<sup>2</sup>. The optical absorption of a spectrum of irradiated and pristine thin films was studied in the region of 400 nm to 1000 nm as shown in figure 2. The graph shows that there is no substantial change in band edge after irradiation, while absorption in the visible area increases. This means that the fundamental crystal structure remains unchanged. The lack of irradiation effect on the vibration mode indicates that the atomic order at a long distance is not affected significantly. The lattice is not amorphized since this structural transition reduces the gap in semiconductors. Changes between intra-gap levels connected to defects such as oxygen vacancies, zinc interstitial, and so on are attributed to absorption at low ion energy irradiation. As there is no shift in peak position, this is in good agreement with the XRD data.

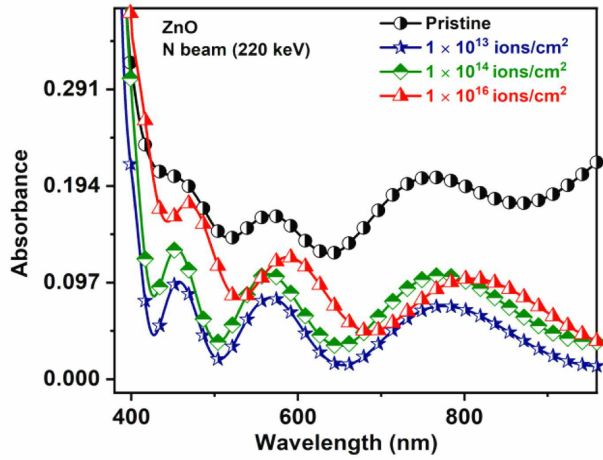


Figure 2: UV-visible spectra of as-deposited and irradiated ZnO thin film with 220 keV N ion beam.

### Surface morphology

The surface topography and morphology of ZnO thin films are studied using FESEM images of pristine and irradiated thin films of ZnO. Figure 3 depicts the pristine thin film's precise and quite well surface topography as the ion fluence of the 220 keV N ion beam increases. The pure ZnO thin film has a smooth and uniform surface with small ZnO grains, as shown in FESEM micrographs of the thin films (Figure 3). When a 220 keV N ion passes through a thin layer, it loses most of its energy due to nuclear collisions. The arriving ion transfers its energy to the target material and produces surface as well as volume changes in the thin film in this way. The planer defects are produced by the Cascade collision, which also starts the structural transition in the thin film. Irradiation with a 220 keV N ion beam produces an uneven wrinkle network structure, which seems to be clearer and denser in thin films of ZnO.

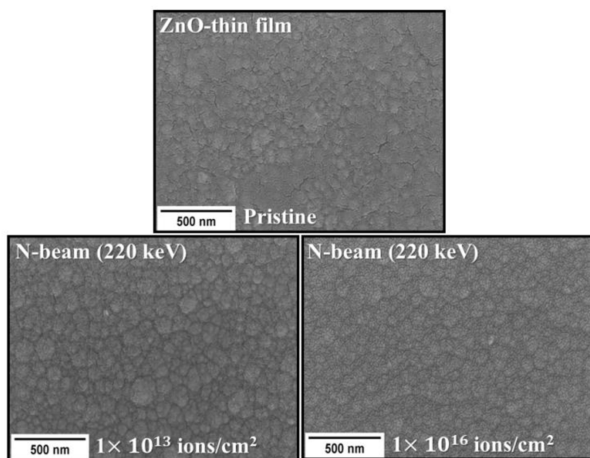


Figure 3: The FESEM images of as-deposited and irradiated ZnO thin film with 220 keV N ion beam.

### Raman spectroscopy

Figure 4 shows the obtained Raman spectra of as-deposited and 220 keV N ion beam irradiated thin films. The group theory predicted the Raman active phonon modes for the wurtzite structure of ZnO [21]. For pure and 220 keV N ion beam irradiated thin films, typical spectra exhibit two bands at 580  $\text{cm}^{-1}$  and 438  $\text{cm}^{-1}$ . A<sub>1</sub> (LO) mode is given to the crisp and highly intense band at 580  $\text{cm}^{-1}$ , which is in good agreement with theoretical predictions. The characteristic mode of the ZnO wurtzite phase is observed at roughly 438  $\text{cm}^{-1}$ , which is related to the E<sub>2</sub> (high) mode, which also exhibits a significant peak at 33.92° in the XRD spectrum. The presence of the E<sub>2</sub> (high) mode in the spectra of pure ZnO thin films indicated the wurtzite structure's creation. With 220 keV N ion beam irradiation, there is an increase in the intensity of the A<sub>1</sub> (LO) mode, while the E<sub>2</sub> (high) mode decreases in intensity, which is responsible for reduced crystallinity and defect formation in the ZnO matrix.

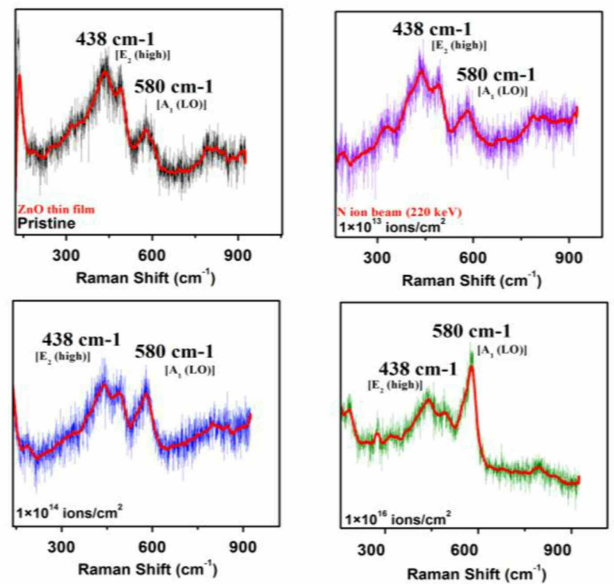


Figure 4: Raman spectra of as-deposited and irradiated ZnO thin film with 220 keV N ion beam.

### X-ray diffraction analysis

The X-ray diffraction (XRD) technique was used to analyze the structural properties of as-deposited and 220 keV ion beam of N irradiation thin films of ZnO. Figure 5 illustrates the XRD pattern for pure ZnO and 220 keV N ion beam irradiated thin films at different doses of  $1 \times 10^{13}$ ,  $1 \times 10^{14}$ , and  $1 \times 10^{16}$  ions/cm<sup>2</sup> with (002), (101), and (110) reflection planes. Pure ZnO thin film reveals its crystalline nature and demonstrates the hexagonal wurtzite structure [22]. As seen in Figure, the clean sample has substantial texturing along the C-

axis, with the (002) peak at  $33.92^\circ$ , which is the preferred orientation of ZnO along the C-axis. Irradiation does not affect peak position or intensity. This demonstrates that irradiation has minimum impact on the ZnO bonding.

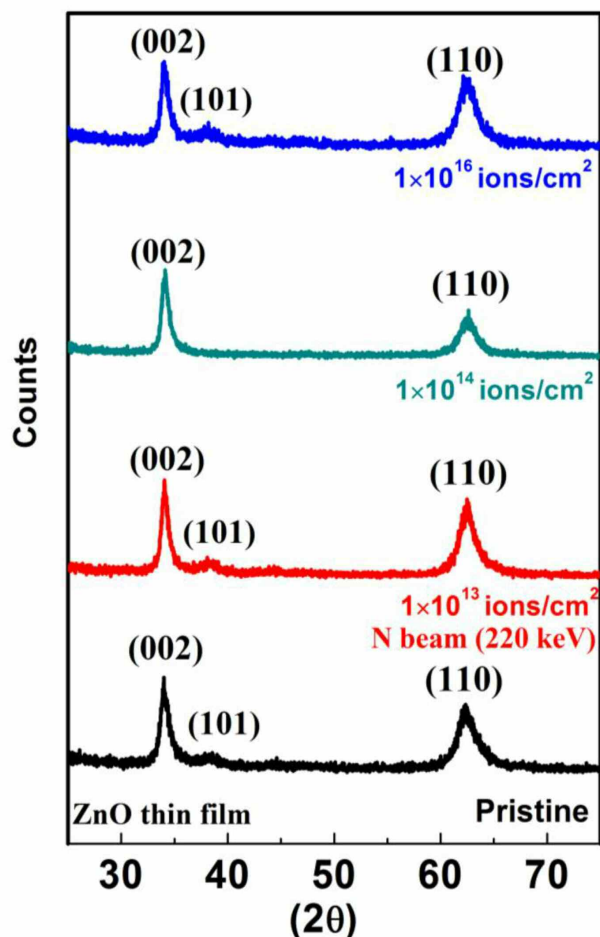


Figure 5: XRD spectra for as-deposited and irradiated ZnO thin film with 220 keV N ion beam.

## Conclusions

In the present study, with 220 keV N ion beam irradiation at varying doses, structural and optical alterations in ZnO thin films were considered. RF magnetron sputtering at room temperature to create pure ZnO thin films on Si and quartz substrates. RBS modeling revealed that the thickness of ZnO thin films is around 200 nm. The structural and optical quality of the 220 keV N ion beam irradiation ZnO thin film was improved when compared to the as-grown ZnO thin film, as evidenced by XRD, FESEM, UV-visible, and Raman studies. The formation of hexagonal wurtzite structure with good crystalline character is revealed by X-ray diffraction spectra and Raman spectra. FESEM was used to examine the surface features of the films, which revealed considerable changes in the thin film.

## Acknowledgment

We are thankful to the Materials Research Centre, MNIT, Jaipur, for providing characterization facilities. Dr.RituVishnoi(One of the authors) acknowledges the financial support by DST New Delhi in terms of the Woman Scientist Project (SR/WOS-A/PM- 47/2019). The student fellowship is also highly acknowledged. The financial support by UGC-DAE-CSR (Indore Centre-Ref No. CRS-294) is also gratefully acknowledged.

## References

- [1] H.Zeng, W.Cai, P. Liu, X.Xu, H. Zhou, C. Klingshirn, H. Kalt, ACS nano, 2(8)(2008), 1661-1670.
- [2] D.Y.Guo, C.X.Shan, S.N. Qu, D.Z.Shen, Scientific Reports, 4(1) (2014), 1-6.
- [3] S. Dhara, P.K. Giri, Journal of Applied Physics, 111(4) (2012)044320.
- [4] F.Fleischhaker, V. Wloka, I.Hennig, Journal of Materials Chemistry, 20(32), (2010) 6622-6625.
- [5] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P. Yang, Nature materials, 4(6), (2005) 455-459.
- [6] Hwang, D.K., Kang, S.H., Lim, J.H., Yang, E.J., Oh, J.Y., J.H. Yang, S.J. Park, Applied Physics Letters, 86(22), (2005)222101.
- [7] K. Jindal, M. Tomar, V. Gupta, Analyst, 138(15) (2013) 4353-4362.
- [8] S.K. Arya, S.Saha, J.E. Ramirez-Vick, V. Gupta, S. Bhansali, S.P. Singh,Analyticachimicaacta,737 (2012) 1-21.
- [9] K. Muthukrishnan, M. Vanaraja, S. Boomadevi, R.K. Karn, V. Singh, P.K. Singh, K. Pandiyan,Journal of Alloys and Compounds,673 (2016) 138-143.
- [10] V.L. Patil, S.A. Vanalakar, P.S. Patil, J.H. Kim,Sensors and Actuators B: Chemical,239 (2017) 1185-1193.
- [11] N.H. Al-Hardan, M.J. Abdullah, A.A. Aziz,International journal of hydrogen energy,35(9) (2010) 4428-4434.
- [12] N. Srinatha, Y.S. No, V.B. Kamble, S. Chakravarty, N. Suriyamurthy, B. Angadi, A.M.Umarji, W.K. Choi,RSC advances,6(12) (2016) 9779-9788.
- [13] P.P. Sahay, R.K. Nath, Sensors and Actuators B: Chemical,133(1) (2008) 222-227.

- [14] N. Akin, U. CerenBaskose, B. Kinaci, M. Cakmak, S. Ozcelik, *Applied Physics A*, 119(3) (2015) 965–970.
- [15] A. El Manouni, F.J. Manjón, M. Mollar, B. Marí, R. Gómez, M.C. López, J.R. Ramos-Barrado, *Superlattices and Microstructures*, 39(1–4) (2006) 185–192.
- [16] S.H. Jeong, J.W. Lee, S.B. Lee, J.H. Boo, *Thin solid films*, 435(1–2) (2003) 78–82.
- [17] Y.J. Wu, Y.S. Wei, C.Y. Hsieh, P.M. Lee, C.H. Liao, Y.S. Liu, C.Y. Liu, *Journal of Sol–Gel Science and Technology*, 73(3) (2015) 647–654.
- [18] S.K. Singh, R. Singhal, *Thin Solid Films*, 653 (2018) 377–383.
- [19] S. Sharma, S. Vyas, C. Periasamy, P. Chakrabarti, *Superlattices and Microstructures*, 75 (2014) 378–389.
- [20] A. Climent-Font, U. Wätjen, H. Bax, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 71(1) (1992) 81–86.
- [21] D.C. Agarwal, R.S. Chauhan, A. Kumar, D. Kabiraj, F. Singh, S.A. Khan, D.K. Avasthi, J.C. Pivin, M. Kumar, J. Ghatak, P.V. Satyam, *Journal of Applied Physics*, 99(12) (2006) 123105.
- [22] D.C. Agarwal, A. Kumar, S.A. Khan, D. Kabiraj, F. Singh, A. Tripathi, J.C. Pivin, R.S. Chauhan, D.K. Avasthi, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 244(1) (2006) 136–140.

