Effect of Metal Ions Irradiation on Different Properties of ZnO Thin Films for Optoelectronic Devices

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IN THE NAME OF ALLAH, THE MOST MERCIFUL, THE MOST KIND
Dedicated To
My Father (late), Mother (late)
&
Family
Acknowledgement

All praises and thanks are for almighty ALLAH Who is the Most Gracious and Merciful. He is the most compassionate and beneficent, who consecrated mankind with the knowledge and ability to think into his secrets. He bestows me the sense of knowledge and enables me to accomplish this task. All respects to Holy Prophet Muhammad (PBUH), who directed the humanity and mankind from the world of darkness to an era of peace and enlightened the hearts with Almighty Allah’s message.

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ABSTRACT

ZnO is well known material due to its versatile properties for a number of applications. The properties of ZnO can be modified by using numbers of techniques. Among these techniques, the ions irradiation is found to be plausible technique to modify the properties of ZnO thin films in broader range. The endeavor of the present project is to irradiate the ZnO thin films with different ions and fluence to modify its various properties. The project can be divided into two steps. First step consists of fabrication of ZnO thin films by using pulsed laser deposition and rf magnetron sputtering. In second step, the ZnO thin films are irradiated with ion beams of Ni$^{+2}$, Au$^{+1}$, Co$^{+1}$, Fe$^{+1}$ and Mn$^{+1}$ with different energies and fluence. In first set ZnO thin films prepared from PLD technique are irradiated with 700 keV Ni$^{+2}$ ions at the ion fluence of $1 \times 10^{13}$, $1 \times 10^{14}$, $2 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$. XRD results show improved crystallinity at low fluence, while deterioration is observed at the highest ion fluence. Scanning electron micrographs show the formation of small grains at ion fluence $1 \times 10^{13}$ ions/cm$^2$, micro-rods at fluence $1 \times 10^{14}$ and $2 \times 10^{14}$ ions/cm$^2$ and ultimate fracturing of thin film surface at ion fluence $5 \times 10^{14}$ ions/cm$^2$. Faraday rotation measurements are also performed and show the variation in Verdet constant with ion fluence. The optical band gap energy ($E_g$) of the thin films is determined using spectroscopic ellipsometry, which shows an increase in $E_g$ from 3.04 eV to 3.19 eV when the fluence increases to $2 \times 10^{14}$ ions/cm$^2$ and decrease to 3 eV at highest fluence. The electrical resistivity varies from $3.84 \times 10^1$ to $2.35 \times 10^6$ $\Omega$cm. These modifications in properties are well explained on the basis of annealing effect and oxygen vacancies induced by irradiation. The Density Functional Theory (DFT) calculations support the experimental results of resistivity trend. In the same Ni$^{+2}$ irradiated ZnO thin films annealed at the temperature of 500 °C, the crystallite size varies from 21.02 to 28.31 nm. SEM micrographs show the nanospheres on the surface of films. The $E_g$ varies in the range of 2.97 to 3.08 eV. The results, after annealing treatment of Ni$^{+2}$ irradiated ZnO thin films, show that structural damages are healed and the stresses among the grains of crystal are decreased. In next set, ZnO thin films are prepared from rf magnetron sputtering technique. These films are irradiated with 700 keV Au$^{+1}$ ions at the ion fluence of $1 \times 10^{13}$, $1 \times 10^{14}$, $2 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$. XRD results show that the crystallite size crystallite size varies from 6.97 to 9.63 nm due to which the crystallinity of thin films improves. SEM micrograph shows acicular structures on the surface of ZnO thin film at high fluence $5 \times 10^{14}$ ions/cm$^2$. FTIR spectroscopy shows absorption band splitting due to the formation of nanostructures of ZnO. The optical study reveals that the $E_g$ of ZnO thin films changes form
3.08 eV (pristine) to 2.94 eV at high fluence (5 × 10^{14} ions/cm^2). The electrical resistivity decreases from pristine value with increase in ions fluence. All the results can be explained by localized heating effect produced by ion irradiation of thin films. In next set, ZnO thin films are prepared from rf magnetron sputtering technique. These films are irradiated with 80 keV Co^{+1} ions at the ion fluence of 1 × 10^{13}, 1 × 10^{14}, 5 × 10^{14}, 1 × 10^{15}, and 1 × 10^{16} ions/cm^2. XRD results show that the crystallite size increases with increase in ions fluence up to 1 × 10^{15} ions/cm^2 and the crystallite size decrease due to the formation of CoO phase with further increase in the ion fluence. SEM micrograph shows the spherical nano-grains on the film surface which agglomerate with increasing the ions fluence. High fluence is causing fracturing of larger sized grain into smaller sized particles. The E_g varies in the range of 2.80 to 3.02 eV and electrical resistivity varies in the range of 1.01 × 10^{-2} to 6.12 × 10^{-5} Ωcm. In next set, ZnO thin films are prepared from rf magnetron sputtering technique. These films are irradiated with 80 keV Fe^{+1} ions at the ion fluence of 1 × 10^{13}, 1 × 10^{14}, 5 × 10^{14} and 1 × 10^{15} ions/cm^2. XRD results show that the crystallite size decreases with increase in ions fluence. SEM micrographs show that formation of micro sized leaf structure on the surface of thin films. AFM study shows that the rms roughness is increased from pristine value to the ions fluence of 1 × 10^{14} ions/cm^2. There is slight decrease in rms roughness at the highest fluence of 1 × 10^{15} ions/cm^2. The E_g varies in the range of 2.63 to 3.10 eV, electrical resistivity varies in the range of 2.18 × 10^{-2} to 2.35 × 10^{-6} Ωcm, in the fluence range 1× 10^{13} to 1 × 10^{15} ions/cm^2. In last set, ZnO thin films are prepared from rf magnetron sputtering technique. These films are irradiated with 80 keV Mn^{+1} ions at the ion fluence of 1 × 10^{13}, 1 × 10^{14}, 5 × 10^{14} and 1 × 10^{15} ions/cm^2. XRD results show that the crystallite size decreases from pristine value at fluence of 1 × 10^{14} ions/cm^2. The crystallite size again increases with increases in ions fluence (i.e. 5 × 10^{14} and 1 × 10^{15} ions/cm^2). SEM micrographs show that formation of micro rods at the ions fluence of 1 × 10^{14} ions/cm^2 and micro crystal with different sizes appears on the surface at the high ions fluence i.e. 5 × 10^{14} and 1 × 10^{15} ions/cm^2. AFM study shows that there is small variation in rms roughness after ions irradiation. The E_g varies in the range of 2.06 to 3.13 eV. The results show that the properties of ZnO thin films have been modified in broader range. The values of E_g and electrical resistivity suggest that these ions irradiated thin films can be utilized for the fabrication of optoelectronic devices such as blue or UV LED’s and transparent conducting oxides etc.
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CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 ZnO Overview

ZnO is one of the most promising materials, which belongs to II-VI group semiconductor. ZnO shows high potential for wide range of application due to its matchless properties. Although the material system has been studied since about 1940, there is now considerable renewed interest to complete understanding of the properties of ZnO bulk material as well as thin films like the structural, electrical, optical and magnetic properties. ZnO is an ideal candidate for optoelectronic devices such as laser diodes, blue and UV light emitting diodes due to its wide band gap semiconducting nature. ZnO thin films have also stimulated much interest for other applications such as in the field of piezoelectricity, solar cell, transparent conductive electrodes, displays and sensors. Its high transparency in visible region provides the opportunity to make transparent electronics [1-7]. The fabrication of hetero structures is another motivating research on ZnO. The ZnO band gap can be tuned by divalent substitution on the cation site e.g. Cd substitution decreases the optical band gap, while Mg significantly increases the band gap without altering the structure of ZnO [8]. The ZnO based electronic devices are proved to be highly resistant in radiation environments [9–11]. Moreover, the manipulation of spin in semiconductors (spintronic devices) offers the opportunity to create a new class of electronic devices by controlling the injection, transfer and detection of the particle spin rather than the flow of charge as in conventional electronic devices. The some important applications for spintronic devices are spin transistor, spin valve, fast permanent semiconductor memories, ultrahigh data storage systems and quantum computing [12]. So there is an ample room to study ZnO material to explore its different properties for range of applications.

The crystal structures of ZnO exist in three kinds: The first is the zinc blende type structure, the second is the rock salt NaCl type structure and the third is the wurtzite type structure which is hexagonal. The most thermodynamically stable structure of ZnO is hexagonal wurtzite which exists under ambient conditions. The zinc blende and rock salt structures are formed under particular conditions. For example, the zinc blende type structure shows stability if its growth takes place on cubical type substrates while the NaCl type ZnO
structure is formed only under high pressures. There are some other semiconductors which also have the same hexagonal crystal structures such as the structure of GaN, ZnSe and ZnTe, etc.

**Figure 1.1:** Wurtzite crystal structure of ZnO. Zinc and oxygen atoms are shown in white and yellow colors respectively.

The wurtzite structure of ZnO is hexagonal close packed ‘hcp’ bravais lattice, which is composed of two interpenetrating hexagonal close packed (hcp) sublattices of Zn and O atoms as shown in Fig.1.1. The ZnO preferentially oriented along the plane (0001) because the less surface energy is required along this direction. The hexagonal wurtzite structure is formed due to the alternate stacking of Zn and O along the plane direction. The alternate planes of Zn$^{+2}$ and O$^{-2}$ ions indicate the direction of bonds. The electronic configuration of Zinc is (1s)$^2$(2s)$^2$(2p)$^6$(3s)$^2$(3p)$^6$ and the electronic configuration of Oxygen is (1s)$^2$(2s)$^2$(2p)$^4$. The binding in ZnO crystal lattice involves the sp$^3$ hybridization geometry. In ZnO crystal, the sp$^3$ bonding states constitute the valence band whereas the conduction band originates from its anti bonding counterpart [13].
Some of the important properties of ZnO are given in Table 1.1 [14].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (a) at 300 K</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>Lattice parameters (c) at 300 K</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>Ratio a/c</td>
<td>1.602</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Stable phase</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>1-1.2 mho</td>
</tr>
<tr>
<td>Linear expansion coefficient (/K)</td>
<td>(a: 6.5 \times 10^6) K(^{-1})</td>
</tr>
<tr>
<td></td>
<td>(c: 3.0 \times 10^6) K(^{-1})</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008 - 2.029</td>
</tr>
<tr>
<td>Energy band gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>Exciton binding Energy</td>
<td>60 meV</td>
</tr>
</tbody>
</table>

### 1.2 Thin Films

The fabrication of thin films and its utilization in different applications is one of the prominent research fields. In general, a layer of material on substrate with the thickness less than 1000 nm is known as thin film. This type of technology has been used for more than fifty years in making, optical coatings, microelectronics, instrument hard coatings, storage devices and decorative parts. The cost of thin film is nominal as compared to the bulk material. Thin films properties are different and better than bulk material due to the facts which are mentioned below:

i. Thin films are not completely dense
ii. Thin films are quasi 2D structure
iii. Thin films are under stress
iv. Thin films have different defect structure than the bulk
v. There is strong influence between surface and interface

Due to these facts, the thin films show remarkably different properties than their bulk material as given below:

i. Optical properties: absorption coefficient, optical energy band gap and non-linear optical properties etc.
ii. Mechanical properties: elastic modulus, plastic deformation, stress, strain and dislocation density etc.

iii. Electrical properties: dielectric constant, conductivity, resistivity, carrier mobility and current density etc.

iv. Thermal properties: thermal expansion coefficient, thermal conductivity, specific heat etc.

There are many parameters of thin films that are kept under control during the active growth of thin films. These parameters can be optimized by translating such conditions during deposition according to the requirements [15].

Thin film technology also has applications other than semiconductor technology as given in table 1.2.

<table>
<thead>
<tr>
<th>Application areas</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optics</td>
<td>• Antireflection coating on lenses or solar cells.&lt;br&gt;• Reflection coatings for mirrors.&lt;br&gt;• Coatings to produce decorations (colour, lustre). Interference filters.&lt;br&gt;• Photosensitive coating of &quot;analog&quot; film for old camera.</td>
</tr>
<tr>
<td>Chemistry</td>
<td>• Diffusion barrier protection against corrosion / oxidation.&lt;br&gt;• Sensors for liquid / gaseous chemicals.</td>
</tr>
<tr>
<td>Mechanics</td>
<td>• &quot;Hard&quot; layers (e.g. on drill bits).&lt;br&gt;• Adhesion providers.&lt;br&gt;• Friction reduction.</td>
</tr>
<tr>
<td>Magnetics</td>
<td>• Hard discs (Video / Audio tape).</td>
</tr>
<tr>
<td>Electricity</td>
<td>• Insulating /conducting films; e.g. for resistors, capacitors.&lt;br&gt;• Piezoelectric devices.</td>
</tr>
<tr>
<td>Thermal</td>
<td>• Barrier layers.&lt;br&gt;• Heat sinks.</td>
</tr>
</tbody>
</table>

1.3 Deposition Techniques

Different techniques are employed to deposit high quality ZnO thin films such as chemical vapor deposition, spin coating, sputtering, rf magnetron sputtering, sol gel method, physical vapor deposition, molecular beam epitaxy, electro-deposition and pulsed laser deposition etc.[16]. In present work, pulsed laser deposition technique (PLD) and rf-magnetron sputtering techniques are used for deposition of good quality oxide thin film.
1.3.1 Pulsed Laser Deposition (PLD)

This deposition method is important for the growth of homogenous and high quality thin films with controlled manner. Vacuum system, laser and chamber are main components of PLD system. The PLD of mechanism undertakes the ablation of target material. It depends on the laser properties and the thermo chemical properties of the target material. When incident laser energy received, the target material gets absorbed this energy. This electromagnetic energy changes into the energy of electronic excitation, then into the thermal energy and finally converts into mechanical energy. Due to this incident energy, the ablation, sputtering and evaporation of material results the formation of plasma. Plasma plume is consisted of a combination of the energetic groups like molecules, atoms, ions, clusters and micron sized particulates. The key advantage of such a method is its versatility and usefulness. By the use of pulsed laser deposition, semiconductor, metals, oxide and polymer can be grown. Laser energy density is quite high and it can eject material smoothly from surface of target [17]. The schematic diagram of the PLD apparatus is shown in the Fig.1.2.

![PLD Diagram](image)

**Figure 1.2:** The schematic diagram of the PLD apparatus.

1.3.2 Sputtering

Sputtering is also one of the best and simple deposition techniques of ZnO thin films as compared to chemical methods. In this method, films are produced with higher purity and there is easy control over composition, homogeneity and film thickness. Sputtering process involves the formation of gas plasma by applying high voltage between cathode (target holder) and anode (substrate holder). The ions and particles are ejected from the surface of
the target and diffuse away from the target and are deposited on the substrate. But for non-conducting and insulating samples, a high frequency generator is used between the electrodes called rf sputtering. Magnet is also used in this arrangement (rf magnetron sputtering) when high deposition rate at low substrate temperature is needed. Non-stoichiometric ZnO thin films are prepared if metallic zinc target in the presence of oxygen and argon gas atmosphere are sputtered [18, 19]. But the other method, in which a pellet of Zinc Oxide target (99.999% purity) is used, is suitable to achieve right stoichiometry. The schematic diagram of rf Magnetron sputtering is shown in Fig.1.3.

![Schematic diagram of rf Magnetron sputtering](image)

**Figure 1.3:** The schematic diagram of rf Magnetron sputtering.

### 1.4 Defects, Impurities and Ion Implantation

Defects produced in thin films can have important and visible impact on optical, structural, magnetic and electronic properties. The defects modify the properties of semiconductors where the defect density is often smaller than one defect atom per million host atoms. By introduction of the defects after or during growth, the extra energies states are introduced within the energy band. Usually the defects can be categorized as

- Point defects
- Line defects
- Defect complexes
The Point defects and the defect complexes do play the dominant role. They change the material characteristics. The line defects have only small impact on the optical behavior of semiconductors. The impurity atoms in the lattice site of the material can produce different kind of point defects. These types of defects are termed as interstitial defects, substitutional defects, vacancy defects and Frenkel defects.

In interstitials atom A as impurity occupies a place in between typical lattice sites. Interstitials are represented by A\textsubscript{i} (i.e. Zn\textsubscript{i}, O\textsubscript{i}). In vacancies, atom A is missing in the lattice results in a vacancy. It deprives of one electron in the crystal. [20].

Ion implantation of ZnO thin films is plausible technique for impurity doping. The defects production due to ion implantation also alters the different properties of the materials such as electrical, optical and structural properties of the ZnO thin films. This method is used in metal finishing, device fabrication and many applications in material research. The incident ions change the elemental and fundamental composition of the target material. If the composition of incident ions is different from the target material, then the ions stop in the target. They transfer their energy and momentum to electrons and atomic nuclei of the target material. They affect chemical and physical changes [21, 22]. These can cause change in crystal structure and damage of target or even devastated. Incident ions lose energy at the rate of dE/dx. It depends upon mass, energy of the ion and material of substrate. The penetrating depth of ions determined and given in equation 1.1:

$$R = \int_{E_0}^{0} \frac{1}{dE/dx}$$  \hspace{1cm} (1.1)

Where R is the range and E\textsubscript{0} is the energy of incident ion. If sign of dE/dx is negative then it indicates loss of energy per increment of path. Otherwise the values are taken positive. When incident ions penetrate into the solid undergoing collisions with the atoms and electrons of the target material, the distance travel and energy loss per collision are random. That’s why the energy of same kind of ions has not the similar range, so there is wide range in distribution of ion energy inside the material. This range distribution is mentioned as range straggling [23]. The interaction of incident ions with a solid is a non-equilibrium process. When incident ion penetrates into solids, ions lose its energy by two ways: (i) One of the mechanisms in which the incident ions loss their energies to the atoms of the target by the electronic excitation and ionization through inelastic collisions. This type of energy losses are
called electronic energy losses and is denoted by \((dE/dx)_e\), (ii) The second mechanism, in which the incident ion transfer their energies to the target atom through elastic scattering is called nuclear energy loss and it is denoted by \((dE/dx)_n\) [24]. Beside two mechanisms, another event takes which is known as charge exchange process between the incident ion and the atoms of the solid target material. The equation consisting of the three processes can be represented as:

\[
\frac{dE}{dx}_{\text{loss}} = \frac{dE}{dx}_{\text{Elect}} + \frac{dE}{dx}_{\text{Nucl}} + \frac{dE}{dx}_{\text{charge exchange}}
\]

(1.2)

Where \(\frac{dE}{dx}_{\text{Elect}}\) is the loss due to electrons, \(\frac{dE}{dx}_{\text{Nucl}}\) is loss due to nuclei and \(\frac{dE}{dx}_{\text{charge exchange}}\) is loss due to charge exchange. As charge exchange loss indicates a small part of total energy loss therefore it is neglected [23]. The nuclear and the electronic energy losses by the incident ion into the target material are schematically shown in the Fig.1.4.

Figure 1.4: The behavior of nuclear and electronic stopping loss versus projectile ion energy.

1.5 Literature Survey

The brief literature survey of ion irradiation of ZnO thin films is given below:

ZnO is important material due to its multi-functional characteristics (like semiconducting, optical, magnetic, piezoelectric etc.) for the optoelectronics based devices. The important requirement for several applications is the adding of various elements in ZnO for improving and modifying different properties. ZnO is n-type semiconductor material and its conductivity is precisely controlled by adding the impurities from 3rd group of elements like Al, Ga or In or growing in oxygen deficient environment [25]. In addition the transition metal doped ZnO thin films show the prospective operation of dynamic spintronic devices at room
temperature. These transition metal doped ZnO offers the prospective for realizing room temperature operation of active spintronic devices but also rich attractive for basic and primary physics. The existence of transition metal ion in ZnO lattice enhances the phonon scattering thus reduces thermal conductivity, which increase the thermoelectric efficiency. The atomic structure of transition metals has unfilled electrons in d-shell. Some of the elements are Ti, V, Mn, Cr, Fe, Co, and Ni having unpaired electrons. The change in the optical band gap is the interaction of band electrons of ZnO with d-electrons of transition metals due to the exchange interaction of sp-d [26, 27]. Ion implantation technique is one of the most imperative methods to introduce metal ions into ZnO (bulk or thin films) matrix to change different properties of ZnO material. Different research groups work to tailor the properties of ZnO by ions irradiation.

Agarwall et al [28] reported in his work that when ZnO thin films were irradiated with 100 MeV Au\(^{+8}\) ions, the alteration in the surface, structural, and optical properties were observed. At low fluence, the crystallinity of ZnO thin films improved but the transmittance was decreased, while at high fluence the transmittance was increased. At highest fluence the agglomeration of grain was observed. The photoluminescence property has also been modified by ion irradiation.

Sing et al, studied swift heavy ions induced structural changes on ZnO, when 120 MeV Ag\(^{+9}\) ions were irradiated at different fluence. XRD results revealed that the intensity of (002) reflection was decreased and shifted to higher diffraction angle with increasing the ion fluence. At the highest fluence, the grains observed on the surface are more irregular in shape and size. The swift ion irradiation produced the oxygen vacancies and shifting of the peak to higher wavelength was due to the presence of stresses in thin films [29].

Zhang et al showed that the optical absorption and transmittance spectra of ZnO thin film irradiated with 80 keV Au ions has been shifted to high energy range. The optical band gap has increased due to thermal expansion and induced lattice mismatch between film and substrate. The PL spectra show that ultra violet band edge and blue emission was observed due to the formation of oxygen vacancies. With implantation of Au ions and then annealing at high temperature, the green emission has also been observed [30].

When Cr\(^{+}\) ions were implanted on ZnO thin films having energy 150 keV, the structural damages were observed in thin film. It was observed that thermal annealing effect at 80 °C
relaxed the ion implanted stress in the thin films which improve the crystallinity of thin films. These ions implanted films also showed ferromagnetic behavior at room temperature reported by Li et al [31].

It was observed by Agarwal [32] with 100 MeV Ag ions irradiation the quality of ZnO thin films was improved while optical band gap was decreased up to the bulk value due to the formation of larger grains on the surface of thin films. The AFM study revealed that the surface roughness remained constant after heavy ion irradiation. They conclude heavy ion irradiation improve the nanocrystalline quality of thin film which was used in device fabrication.

The modification in different properties of singly charged nickel ions having energy 80 MeV irradiated ZnO thin films were studied by Ratheesh et al [33]. The irradiation effect modified the electrical and optical properties but absorption edge and grain size remained unchanged. For pristine films, the activation energy observed was 0.6 eV. Three activation energies were observed i.e., 0.36, 0.56, and 0.75 eV, when thin films were irradiated with nickel ions. Due to oxygen vacancies, one type of structural defect was found prominent which played a crucial role in alteration of the properties of ZnO thin films.

An important work done by Guner [34] is that when ZnO thin films were implanted with Co$^{+1}$ ions having energy 40 keV at high fluence i.e. $0.25 \times 10^{17}$ ion/cm$^2$ to $2 \times 10^{17}$ ion/cm$^2$. The crystallinity of ZnO thin film was reduced with incorporation of Co$^{+1}$ into the matrix of ZnO while the electrical conductivity was increased with increasing the concentration of Co$^{+1}$ ions. Moreover, the Co-ZnO thin film showed ferromagnetic behavior at room temperature.

The work of Kumar et al [35] showed that tuning of optical band gap and ferromagnetism in carbon irradiated ZnO films. The film was deposited on Si substrate by using the rf sputtering technique then irradiated with 100 keV carbon ions. It was observed that the optical band gap was changed with increase in carbon ion fluence due to non-uniform distribution of ‘C’, which occupies the interstitial positions along with substitutional site of ZnO lattice. The study also revealed that lower concentration of carbon ions occupies the substitutional sites while at high concentration it occupies the interstitial sites.

Okay et al studied 40 keV Ni ion implanted ZnO thin films annealed at 1000°C for the duration of half an hour. It was observed that there was formation of a second phase of NiO
at the high fluence of Ni ions. The optical band edge was shifted to UV range as compared to the optical band edge of pristine due to the formation of NiO phase. The NiO phase was appeared due to reduction and oxidation in ZnO thin films. The room temperature ferromagnetism behavior was also observed in pristine and implanted annealed thin film as the source of ferromagnetism was due to the formation of Ni nanoparticles. On the other hand, the growth of new magnetic phase was observed in implanted annealed samples [36].

Pan et al [37] investigated the donor-acceptor pair produced emission at 385 nm when N\textsuperscript{+} ions were implanted on ZnO. The same damages were observed when ZnO was implanted with P\textsuperscript{+} and Ar\textsuperscript{+} ions. The donor acceptor pair (DAP) luminescence was seen to be dependent on dopant concentration i.e. the energy shifting was downward with increasing nitrogen concentration.

In a very interesting report, 300 keV Fe\textsuperscript{+10} ions implantation lead to p-type ZnO. After irradiation, the PL peak was shifted to higher wavelength. Hall measurement result showed that the ZnO shows p-type conductivity at the temperature <200 K. When temperature was increased from this value, the material showed n-type conductivity. Fe\textsuperscript{+10} ions produced residual defect (native point defect) which created p-type conductivity in ZnO [38].

Parbuk et al showed that ion implantation induced impurity and the structural defects considerably modified and altered the surface, optical, magnetic and electrical properties of ZnO. In this work, ZnO thin film was irradiated with 100 MeV O\textsuperscript{+7} ions at room temperature and liquid nitrogen temperature. It was observed that transmission and PL intensity was decreased at liquid nitrogen temperature as compared to pristine and room temperature. It was described that at liquid nitrogen temperature ion irradiation induced the lattice damages and created the energy defects below the conduction level that reduced the optical band gap. The surface roughness and grain size were decreased at liquid nitrogen temperature and room temperature in contrast with pristine as the strain relaxation occurred among the grains. The crystallinity and the structure of surface powerfully manipulate the optical characteristics [39].

Zang et al [40] reported that when Xe ions having energy 308 MeV were irradiated on ZnO thin films with different fluence, the grain size and lattice constant of films were changed. With increasing the Xe ion fluence the cracks were produced in thin films and as a result, the compressive stress was increased. In addition the increasing ion fluence of Xe produced
donor shallow acceptor levels in thin films that took part vital role in PL process and optical properties.

An important work done by the Ham et al, showed that with incorporation of the hydrogen ions having energy 200 keV and fluence $10^{13}$ ions/cm$^2$ on ZnO thin films increased the refractive index and energy band gap. The increase in the optical band gap energy due to proton implantation introduced the hydrogen shallow donors or point defects rather than the damages [41].

Mal et al showed that when Ag$^{+9}$ ions having energy 300 MeV were irradiated on ZnO thin films, different properties were modified without changing the crystal structure. The swift heavy ion irradiation produced only the point defects. These induced defects helped the generation of some degree of 3-D ferromagnetism in the irradiated films [42].

Thomas et al demonstrated that p-type ZnO formed when using irradiation from group V-elements having different ion fluence and energy on ZnO Li doped crystal. The carrier concentration was found by Hall measurement as the function of annealing temperature [43].

Kohiki et al worked to enhance the conductivity of ZnO thin films with implantation of hydrogen ion. In this work they used 100 keV H$^{+1}$ ions at 373 K with different ion fluence. It was observed that the conductivity was increased from $10^{-7}$ ($\Omega$-cm)$^{-1}$ to $10^{2}$ ($\Omega$-cm)$^{-1}$, when the samples were annealed at 473 K in the presence of N$_2$. They concluded from their work that implantation of hydrogen formed OH$^{-}$ ions, which created the donor level resulting in the increase in conductivity [44].

1.6 Objective of Work

From literature review, it can be seen that ion irradiation is a suitable technique to modify different properties of ZnO thin films. The ZnO thin films with irradiation with several types of ions having some other energies and fluence need to be explore for wide range of applications related to optical and optoelectronics. The present thesis involves such experiments, their results and possible applications. In this project, the experiment comprises of two steps. In first step fabrication of ZnO thin films and in second step the films were irradiated with different ions and fluence to modify the different properties of ZnO thin film. The ZnO thin films were prepared by pulsed laser deposition (PLD) and rf magnetron
sputtering techniques. The films of ZnO were implanted with ions beams of Ni, Au, Co, Fe and Mn with different parameters. The modification in structural, surface, electrical, magneto-optical and optical properties of these ions irradiated ZnO thin films are observed, which can be utilized in the fabrication of different optoelectronic devices.
CHAPTER 2

EXPERIMENTAL WORK

Experimental work is comprised of two main steps. First step is the deposition of ZnO thin films on glass substrates. Second step is the ion irradiation on ZnO thin films. These two steps are discussed in the following sections.

2.1 ZnO Thin Films Preparation

In present work two deposition techniques have been employed for the growth of ZnO thin films: the first is pulsed laser deposition (PLD) and second is the radio frequency (rf) magnetron sputtering techniques. A concise description of the growth of ZnO thin films by these two techniques is given below.

2.1.1 Pulsed Laser Deposition (PLD)

First the PLD method is used for the growth of zinc oxide thin films. PLD is a sophisticated versatile technique for thin film growth based on physical vapor deposition. For PLD, the pure ZnO bulk target prepared by solid-state reaction method. The required amount of pure ZnO (99.99%) was measured using micro-electrical balance. It was heated in electric furnace in the presence of air at the temperature of 850 °C for 12 hours. The powder was cold pressed at 5 tons load by using hydraulic press to form ZnO pellets. The pellets were sintered in presence of oxygen at the temperature of 900 °C for duration 12 hours.

![Figure 2.1](image1.png)

**Figure 2.1:** A Schematic diagram of pulsed laser deposition (PLD) chamber.
The density of the pellets was 82% of the original density of ZnO unit cell. The schematic diagram of PLD technique is shown in Fig. 2.1. In experiment, high energy ultraviolet KrF Excimer laser \((\lambda = 248 \text{ nm}, \phi = 2.5 \text{ J/cm}^2, N_i = 7500, \nu = 10 \text{ Hz}, \tau = 20 \text{ ns})\) was focused on target at an incident angle of 45° with target normal. The laser beam was focused with the help of UV lens of focal length 20 cm. The ultrasonically cleaned glass substrates \((10 \text{mm} \times 10 \text{mm} \times 1 \text{mm})\) located at 5 cm from target. The PLD chamber was evacuated down to base pressure of \(~10^{-5} \text{ mbar}\) by rotary and turbo molecular pumps. The target was rotated and translated to avoid the wastage of target material and uniform surface ablation. This uniform surface ablation leads to smooth surface of ZnO thin films. The substrate temperature was 300 °C and the pressure of oxygen was \(10^2 \text{ mbar}\) inside the chamber. The thickness of the films was found to be \(250 \pm 10 \text{ nm}\) by ellipsometric method.

### 2.1.2 rf Magnetron Sputtering

ZnO thin films were fabricated on glass substrate \((10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm})\) by rf magnetron sputtering (Model PFG 600 RF). A commercially sintered pure ZnO target \((99.99\%)\) with diameter 3 inch and thickness 3 mm was used for the sputtering process.

![rf Magnetron sputtering machine.](image)

Before deposition, glass substrates were cleaned by mild soap solution then washed thoroughly in deionized water and boiling water. Finally substrates were cleaned by ethanol using ultrasonic bath for 15 minutes. During the deposition the pressure was maintained at \(1.33 \times 10^{-5} \text{ mbar}\) and Argon gas was flown into the chamber at pressure \(1.6 \times 10^{-5} \text{ mbar}\).
The rate of Argon flow was maintained at 50 sccm. The substrate was placed 10 cm from the target and was adjusted at the DC-biasing of 945 V. The forward direct power (FWDP) was 100 W and reference power (REFP) was adjusted at zero watt for all depositions. The radio frequency (rf) of source was 13.56 MHz. The deposition time for one set (05 samples) was one hour at the temperature of 25 °C. The deposition time for other three set (15 samples) were 30 minutes at the temperature of 25 °C. The chamber of rf magnetron sputtering is shown in Fig. 2.2. The thickness values of ZnO thin films were found to be ~ 80 nm and ~ 200 nm for the deposition time of 30 minutes and one hour respectively using spectroscopic ellipsometry.

### 2.2 Ion Irradiation

In second step of experiment prepared ZnO thin films were irradiated by different ions having different energy and fluence. The metal ions (Ni$^{+2}$, Au$^{+1}$, Co$^{+1}$, Fe$^{+1}$ and Mn$^{+1}$) were formed by feeding a reactive chlorine gas in the ion source. When chlorine ions chemically reacted with metal walls of the ion source, the metal chlorides were formed. Electrons emitted from filament were accelerated through a potential for the ionization of metal chloride to form plasma of metal and chlorine ions. For separation of chlorine ions from the required metal ions, magnet analyzer was used. The schematic diagram of ion implanter is shown in the Fig. 2.3.

![Figure 2.3: Schematic diagram of low energy ion accelerator.](image)

After ion formation, the ions were magnetically deflected into accelerating column, gaining energy and hit the thin film samples. In present work, ions irradiation was carried out using facility from National Center for Physics (NCP) Islamabad, Pakistan and Accelerator
laboratory, University of Helsinki, Finland. The ZnO thin films were irradiated with Ni$^{+2}$, Au$^{+1}$, Co$^{+1}$, Fe$^{+1}$ and Mn$^{+1}$ ions with different parameters given below:

**Set 1:**

Five identical ZnO thin films were prepared by using Pulsed Laser Deposition (PLD) technique. The films thickness was 250 ± 10 nm measured by spectroscopic ellipsometry. SRIM simulation software was used to find the best energy range of Ni ions for implantation in ZnO thin films. Four ZnO thin films were irradiated with Ni$^{+2}$ ions having energy 700 keV at four different ion fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $2 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$ under vacuum ~10$^{-5}$ mbar. One sample is kept unexposed for reference. The beam current was 22 nAcm$^{-2}$ on the target for all samples. During irradiation the sample were tilted to 5° to avoid channeling effect. All the samples were electrically grounded with silver paste.

**Set 2:**

The set 1 was annealed at temperature of 500 °C in vacuum for the duration of one hour.

**Set 3:**

In this set, five identical ZnO thin films were prepared by using rf- magnetron sputtering technique. The films thickness was 200 ± 10 nm measured by spectroscopic ellipsometry. SRIM simulation software was used to find the best energy range of Au ions for implantation in ZnO thin films. Four ZnO thin films were irradiated with Au$^{+1}$ ions having energy 700 keV at different ion fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $2 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$ under vacuum ~10$^{-5}$ mbar. One sample is kept unexposed for reference. The beam current was 20 nAcm$^{-2}$ on the target for all samples. All the samples were tilted through 5° to avoid channeling effect and electrically grounded during irradiation.

**Set 4:**

In this set, five identical ZnO thin films were prepared by using rf- magnetron sputtering technique. The films thickness was 80 ± 10 nm measured by spectroscopic ellipsometry. SRIM simulation software was used to find the best energy range of Co ions for implantation in ZnO thin films. Four ZnO thin films were irradiated with Co$^{+1}$ ions having energy 80 keV at different ion fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions/cm$^2$ under vacuum ~10$^{-5}$ mbar. One sample is kept unexposed for reference. The beam current for the fluence of $1 \times 10^{13}$ ions/cm$^2$ was kept 0.2 μAcm$^{-2}$ and the beam current was 0.5 μAcm$^{-2}$ for all remaining fluence. All the samples were tilted through 5° to avoid channeling effect and electrically grounded during irradiation.
EXPERIMENTAL WORK

Set 5:
In this set, five identical ZnO thin films were prepared by using rf- magnetron sputtering technique. The films thickness was 80 ± 10 nm measured by spectroscopic ellipsometry. SRIM simulation software was used to find the best energy range of Fe ions for implantation in ZnO thin films. Four ZnO thin films were irradiated with Fe$^{+1}$ ions having energy 80 keV at four different ion fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$ under vacuum ~10$^{-5}$ mbar. One sample is kept unexposed for reference. The beam current were kept 15, 40, 40, and 50 nA/cm$^2$ for the fluence of $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$ respectively. All the samples were properly electrically grounded and tilted through small angle of 5° during ion irradiation to avoid channeling effect.

Set 6:
In this set, five identical ZnO thin films were prepared by using rf- magnetron sputtering technique. The films thickness was 80 ± 10 nm measured by spectroscopic ellipsometry. SRIM simulation software was used to find the best energy range of Mn ions for implantation in ZnO thin films. Four ZnO thin films were irradiated with Mn$^{+1}$ ions having energy 80 keV at four different ion fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$ under vacuum ~10$^{-5}$ mbar. One sample is kept unexposed for reference. The beam current for the fluence of $1 \times 10^{13}$ ions/cm$^2$ is kept 0.2 μA/cm$^2$ and the beam current was 0.25 μA/cm$^2$ for all remaining fluence. All the samples were tilted through 5° to avoid channeling effect and proper electrically grounded. The details of experimental work are tabulated in the following table 2.1.

**Table 2.1:** Details of thin films irradiation with different ions energy and fluence.

<table>
<thead>
<tr>
<th>ZnO Thin films</th>
<th>Deposition Technique</th>
<th>Film Thickness (nm)</th>
<th>Ions Type</th>
<th>Energy (keV)</th>
<th>Ion Fluence (ions/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1 [5 films]</td>
<td>PLD</td>
<td>250 ± 10</td>
<td>Ni$^{+2}$</td>
<td>700</td>
<td>$1 \times 10^{13}$, $1 \times 10^{14}$ and $5 \times 10^{14}$</td>
</tr>
<tr>
<td>Set 2 [5 films]</td>
<td>Same samples of set 1 after annealing at 500°C for one hour.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set 3 [5 films]</td>
<td>Sputtering</td>
<td>200 ± 10</td>
<td>Au$^{+1}$</td>
<td>700</td>
<td>$1 \times 10^{13}$, $1 \times 10^{14}$ and $5 \times 10^{14}$</td>
</tr>
<tr>
<td>Set 4 [6 films]</td>
<td>Sputtering</td>
<td>80 ± 10</td>
<td>Co$^{+1}$</td>
<td>80</td>
<td>$1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$</td>
</tr>
<tr>
<td>Set 5 [5 films]</td>
<td>Sputtering</td>
<td>80 ± 10</td>
<td>Fe$^{+1}$</td>
<td>80</td>
<td>$1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$</td>
</tr>
<tr>
<td>Set 6 [5 films]</td>
<td>Sputtering</td>
<td>80 ± 10</td>
<td>Mn$^{+1}$</td>
<td>80</td>
<td>$1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$</td>
</tr>
</tbody>
</table>
The low energy accelerator is used to irradiate ZnO thin films with 80 keV Co\textsuperscript{+1}, Fe\textsuperscript{+1} and Mn\textsuperscript{+1} ions and its target assembling chamber are shown in Fig. 2.4(a-b).

![Figure 2.4: (a) Low energy ion accelerator, (b) Target assembling chamber.](image)

### 2.3 Characterizations Techniques

The characterization of pristine and ions irradiated films has been done by using different techniques like X-ray diffractometer, Scanning Electron Microscope, Atomic Force Microscope, Faraday rotation, Four Point Probe, Spectroscopic Ellipsometry and Fourier Transform Infrared Spectroscopy. A brief discussion for these techniques is explained in the following.

#### 2.3.1 X-ray Diffraction Technique (XRD)

X-ray diffraction is an important and versatile technique to determine the crystal structure of different material (metals, ionic compounds, polymers and metallic alloys). XRD gives the information about the phase, lattice planes, lattice strain and dislocation density of the
material. The XRD graph comprises a number of reflections in the form of intensity peaks taken along Y-axis while diffraction angle (2θ) is taken along X-axis. In X-ray diffraction, the peaks represent the set of planes align in particular direction and the peak positions show the crystal structure of material. The material is probed with x-ray having wavelength close to the lattice spacing. The condition for diffraction is given by Bragg’s law in equation 2.1 [45].

\[
\lambda = 2d \sin \theta
\]  

(2.1)

Here \( \lambda \) represents the wavelength of incident x-ray, \( d \) is inter atomic spacing and \( \theta \) is the angle of incident x-ray and surface normal of crystal.

The crystallography parameters such as crystallite size (D), lattice parameter (c) are calculated by using equations 2.2–2.4 [46–48].

\[
D = \frac{k \lambda}{\beta \cos \Theta}
\]\n
(2.2)

\[
c = \frac{\lambda}{\sin \Theta}
\]\n
(2.3)

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + h^2 + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]\n
(2.4)

‘k’ is constant and its value is approximately \( \approx 1 \), ‘\( \beta \)’ is the full width at half maximum (FWHM) that is measured in radian. ‘\( a \)’ and ‘\( c \)’ are crystallite lattice parameters, ‘\( d \)’ is lattice spacing and ‘\( \lambda \)’ is x-ray wavelength \( \approx 1.5418 \) Å. In the present work, XRD measurements were taken to analyze the structural modifications of unexposed and ions exposed ZnO thin films.

2.3.2 Field Emission Scanning Electron Microscope (FESEM)

A high resolution field emission scanning electron microscope (FESEM) is used to investigate the surface morphology. It is most practical and multitalented instrument for surface analysis, nano-structural texture for thin films and also for bulk materials. The principle involves that the electron beam is emitted from tungsten cathode and is attracted towards anode, which is focused on the specimen using objective lens. The electron beam is energized with the use of scan coil. The magnetic field produced due to varying voltage
which deflects the electron beam back and forth on the sample in controlled way. When electron beam falls on sample, it generates wide range of useful signals i.e. backscattering electrons, the secondary electrons, the auger electrons, photons and X-rays. In FESEM, most important signal is of backscattered electrons signal, the secondary electrons signal and X-rays signal. But the signal of secondary electrons provides the detail about the morphology of surface. While the backscattered electrons signal gives the detail of atomic number of entities which are scattered [49, 50]. The information of material composition percentage is provided by the X-ray signal. In present project model VEGA3 TESCAN and S4800 of field emission Scanning electron Microscope were used to study the surface morphology of pristine and ions irradiated ZnO thin films.

2.3.3 Atomic Force Microscopy (AFM)

The atomic force microscopy is powerful tool which is being used to study the different types of samples down to nanoscale level. The atomic force microscopy is used not only used for three dimensional topography but it provides a lot of information about surface measurement of material which help for scientific and engineering technology. It is the novelty of AFM technique to scan the surface of sample with atomic resolution to Angstrom scale resolution. In the operation of AFM, a cantilever (a sharp tip) scans over the surface of sample. When the tip of cantilever approaches close to the surface of sample, the attractive force between surface of sample and the tip come into play. The detection for the deflection of cantilever towards the surface or away from surface is down by using a laser beam. The deflection of the cantilever tip gives the information about the raised and lowered features of the sample surface by measuring the deflection of laser beam. The information on the surface topography is monitored with position-sensitive photo diode (PSPD) array. The information collected from the surface of the sample is given to a computer, which generates graph of topography and other different properties of surface [51-53]. In our work the AFM of model XE7 Park Systems is used in tapping mode to study the surface topography of pristine and ions irradiated ZnO thin films.

2.3.4 Faraday Magneto-Optic Rotation

Verdet constant was calculated from Faraday rotation measurements. The apparatus was comprised of a sodium vapor lamp for light source, monochromator, an electromagnet,
polarizers and detectors. Beam of helium-neon laser with wavelength 633 nm was polarized. The schematic diagram of magneto-optic effect is shown in Fig. 2.5.

![Schematic diagram of Faraday Effect](image)

**Figure 2.5:** The schematic diagram of Faraday Effect.

This polarized light was passed normally through ZnO thin films. The analyzer was placed at 45° with respect to the incident polarization. The modulated light intensity was detected by a Silicon photo detector. The strength of magnetic field about 100 G was produced by Helmholtz coils with resonant LC circuit. The samples were placed inside the Helmholtz coils and the detected signal was fed into a lockin amplifier, which was locked at the frequency of the applied ac field. For the measurement of magnetic field Guass meter was used and Faraday rotation was determined by \( \frac{i_{ac}}{2i_{dc}} \), where \( i_{ac} \) was the measured signal form lockin amplifier and \( i_{dc} \) photocurrent measured in the absence of applied magnetic field. When incident plane polarized light was passed through a medium of thickness (path length, \( l \)) which is placed in a magnetic field (\( B \)), it rotates through a certain angle called Faraday rotation angle (\( \theta_F \)) and this is known as magneto-optic effect. The ratio of \( \theta_F \) to the product \( Bl \) is known as Verdet Constant (\( V \)) and is shown by in equation 2.5[54].

\[
V = \frac{\theta_F}{Bl} \quad (2.5)
\]

### 2.3.5 Four point probe apparatus

The electrical resistivity of thin film or bulk samples is measured using standard four point probe method. The four probes are equally spaced over the sample surface. The current is passed through outer probes and the voltages are measured between two inner probes. Four point probes eliminate measurement error because the electrical contacts for the current and
voltage leads are separate. Fig. 2.6 shows the schematic of four point probe setup. This technique primarily applies in the study of semiconductor materials, research and industrialized fields.

Figure 2.6: Schematic diagram of four point probe technique.

Electrical resistivity of thin films was calculated by substituting the observed data in equation 2.6[55].

\[ \rho = \left( \frac{\pi}{\ln 2} \right) \left( \frac{V}{I} \right) t \]  

(2.6)

Where the term in first parentheses is the correction factor, I is the current applied between two outer probes, V is the voltage drop across inner probes, and t is the thickness of thin film.

The electrical conductivity of thin films can be obtained by using the relation.

\[ \sigma = \frac{1}{\rho} \]  

(2.7)

By using the following equation sheet resistance of films can be calculated;

\[ R_s = \frac{\rho}{t} \]  

(2.8)
2.3.6 Spectroscopic Ellipsometry (SE)

One of the accurate techniques to measure the optical properties of bulk and thin films is a Spectroscopic ellipsometry. It is a sensitive and nondestructive method to determine refractive index, absorption, extinction coefficient, transmission and optical energy band gap of material. Accurate thickness of thin film can also be measured with the help of this technique. Typical ellipsometry configuration is shown in Fig. 2.7. When linearly incident polarized light is reflected from film surface the measured change in polarization to determine the response of the sample. The light reflected from the sample is in elliptical shape. So the shape, size and the orientation of the ellipse depend on the properties of the sample upon which the light is reflected. Using quarter-wave plate and analyzer, the polarization of the reflected wave can be determined. The orientation of quarterwave plate and the analyzer are changed until the reflected wave cannot passes through the analyzer [56]. The equation 2.9 is used to calculate the change in polarization.

\[
P = \frac{R_p}{R_s} = [\tan(\Psi)][e^{i\Delta}] \quad (2.9)
\]

Where

\(P = \text{change in the polarization}\)

\(R_p = \text{component oscillating parallel in plane of incidence}\)

\(R_s = \text{component oscillating perpendicular to the plane of incidence}\)

\(\tan\Psi = \text{ratio of reflection amplitude}\)

\(\Delta = \text{the phase shift}\)

The flow chart of this technique is shown in Fig. 2.8.
2.3.7 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the material. In this technique, the infra red light incident on the material sample interacts the atomic bonds of the specimen at a particular wavelength. When the incident photon of the IR light interacts the bond of the material, it stretches and vibrates due to the absorption of incident photon energy.
The vibration in frequency determines the shape of molecules and the nature of the atoms which are bounded. The absorption spectrum of light shows that the kind of material being examined, because different type of materials interact with IR light in different ways. The absorbance of the light in the material is proportional to its concentration [57]. Thermo-Nicolet 6700 P FTIR Spectrometer (USA) was used in this project for pristine and ions irradiated ZnO thin films.
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Nickel (Ni$^{+2}$) Ions Irradiation of ZnO Thin Films

Two steps comprises the experimental part: in first part deposition of thin films and in the second part the thin films were irradiated with different ions and fluence. Pulsed laser deposition method is used for the deposition of ZnO film on glass substrate. Four ZnO thin films irradiated with Ni$^{+2}$ ions having energy 700 keV and fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $2 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$ using Pelletron tandem accelerator at National Center of Physics (NCP) Islamabad, Pakistan. One of ZnO thin film kept unexposed as a reference.

3.1.1 SRIM Simulation of Nickel (Ni$^{+2}$) Ions Irradiation of ZnO Thin Films

The SRIM Monto Carlo simulation code is used to calculate different parameters related to the ion beam interaction with material and ion beam processing [58, 59]. This computer simulation gives the information about the energetic ions in materials. It is also used in studies of ion implantation, radiation damage, sputtering and transmission of ions. This code has distinct advantages; it allows more precise treatment of elastic scattering, easy determination of energy and angular distribution [60]. When ion penetrates a solid it slows down via two processes i.e. electronic energy loss ($S_e$) and nuclear energy losses ($S_n$). In first process electronic excitation or ionization of target atoms by inelastic collision and in second process direct energy transfer to target atom through elastic collision take place. When an energetic ion enters in a solid, it interacts with the electrons of the materials and the electron experiences strong impulse due to the Coulomb attractive force. If this impulse is sufficient enough, it causes the excitation or ionization. These excitation or ionizations are the outcome of the inelastic collisions. The velocity of incident ion decreases due to ion encounter with the electrons in the material. In second phenomena, the incident ion comes to rest after making several collisions with lattice atoms. This individual elastic collision between the incident ion and lattice is termed as nuclear energy losses ($S_n$) [61, 62].

Implantation profile of Ni$^{+2}$ ions in ZnO thin film is simulated with the help of SRIM-2008 program [63, 64]. Fig. 3.1(a) shows the result of Monte Carlo simulation where as Fig. 3.1(b)
shows the implantation profile of 700keV Ni$^{+2}$ ions irradiated on ZnO thin films having thickness of 250 nm.

It is found from simulated results that about 80% of Ni$^{+2}$ ions are transmitted through the film, and 0.1% of ions are back scattered from ZnO thin films. The mean projected Ni$^{+2}$ ions range in ZnO film was 310 nm and straggling was 100 nm. It shows that the energy of incident ions was larger enough in this thickness of ZnO thin films, so majority of ions were stopped in glass substrate rather than the implantation in ZnO thin films. Fig. 3.2 shows the stopping power of Ni$^{+2}$ ion irradiated ZnO thin film. It is evident from the figure that nuclear stopping is negligible except at the lower energy. Nuclear stopping increases when the mass of the ion increases. The nuclear stopping is larger than electronic stopping at lower energy and the nuclear stopping is decreased gradually with increase energy. At stopping power of 78eV/Å both nuclear and electronic stopping powers are equal. With further increase in energy, the electronic stopping increases linearly while nuclear stopping decreases and become constant. It depicts that the electronic excitation process is dominant for ions having energy in MeV.

**Figure 3.1:** SRIM simulation results. (a) Scattering cascade of target atom in 250 nm ZnO thin films after irradiation with 700 keV Ni$^{+2}$ ions and (b) Ion range profile.
3.1.2 XRD Analysis

The XRD patterns of pristine and Ni$^{+2}$ ions irradiated ZnO thin films are shown in Fig. 3.3a. It is evident that unexposed ZnO thin film shows a strong c-axis texture with the (0 0 2) plane reflection occurring at 34.24° showing preferred direction along c-axis. The prominent ZnO (0 0 2) and lower intensity NiO (2 2 0) planes appeared when ZnO thin films were irradiated with 700 keV Ni$^{+2}$ ions indicating that ZnO primarily stayed crystalline after irradiation and nickel ions form the NiO phase. This is attributed to strong annealing processes going on during ion irradiation. In addition to the NiO phase formation, Ni$^{+2}$ ions are also incorporated at the Zn sites, which is corroborated by a variation in 2$\Theta$ position of ZnO (0 0 2) plane. The Ni$^{+2}$ ions are certainly producing damage in ZnO thin film as well. Most probably the cumulative effect of ion damage and Ni-Zn replacement results in the shift of 2$\Theta$ values. The crystallography parameters such as crystallite size, lattice parameter are calculated by using equations 2.2-3.4 [46-48]. Table 3.1 shows different parameters obtained from the XRD spectra of the ZnO films. Table shows that all irradiated ZnO thin films show shifts towards higher 2$\Theta$ values and a reduced lattice constant ‘c’ as compared to pristine ZnO thin films indicating the presence of compressive stresses. The crystallite sizes for all samples calculated by using the Scherrer’s formula are plotted as function of fluence in Fig. 3.3b. The crystallite size for pristine ZnO thin film was 9.4 nm, which increased to 14.3 nm when the ion fluence was increased to the $2 \times 10^{14}$ ions/cm$^2$.
The crystallite size is again decreased to 13.6 nm with further increasing the fluence to $5 \times 10^{14}$ ions/cm$^2$. The increase in crystallite size with increasing ion fluence indicates improved crystallinity (reduced damages) of ZnO thin films, which is attributable to the total energy deposited by the high energy and high fluence ions in electronic excitations or ionizations in ZnO thin films. The deposited energy of incident ions in films releases the strains among different grains causing their reorientation in the same direction by reducing...
the interfacial energy resulting in improved crystallinity of ZnO thin films. But the reduced crystallite size at the highest fluence of \(5 \times 10^{14}\) ions/cm\(^2\) is due to high energy deposition causing crystalline damages instead of the desired ion annealing processes as observed in other reference [65].

**Table 3.1:** XRD peak position, d-spacing, lattice parameter, FWHM, and crystallite size for pristine and Ni\(^{+2}\) ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ions fluences (ions/cm(^2))</th>
<th>(2\Theta) (degree)</th>
<th>d-spacing (Å)</th>
<th>Lattice parameter (c) Å</th>
<th>FWHM (degree)</th>
<th>Crystallite Size D(nm) = (\frac{k\lambda}{\beta \cos \theta})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>34.24</td>
<td>2.5709</td>
<td>5.228</td>
<td>0.88</td>
<td>09.4</td>
</tr>
<tr>
<td>(1 \times 10^{13})</td>
<td>34.28</td>
<td>2.5980</td>
<td>5.220</td>
<td>0.74</td>
<td>11.2</td>
</tr>
<tr>
<td>(1 \times 10^{14})</td>
<td>34.76</td>
<td>2.6021</td>
<td>5.179</td>
<td>0.69</td>
<td>12.0</td>
</tr>
<tr>
<td>(2 \times 10^{14})</td>
<td>34.40</td>
<td>2.6054</td>
<td>5.220</td>
<td>0.58</td>
<td>14.3</td>
</tr>
<tr>
<td>(5 \times 10^{14})</td>
<td>34.38</td>
<td>2.6137</td>
<td>5.211</td>
<td>0.61</td>
<td>13.6</td>
</tr>
</tbody>
</table>

### 3.1.3 Surface Morphology

Fig. 3.4(a-e) shows scanning electron micrographs of pristine and Ni\(^{+2}\) ions irradiated ZnO thin films with different ion fluence. It is evident that pristine ZnO thin film exhibits smooth surface morphology having just few particulates over the surface (Fig. 3.4a).

**Figure 3.4:** Scanning electron micrographs of pristine and Ni\(^{+2}\) ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) \(1 \times 10^{13}\) ions /cm\(^2\), (c) \(1 \times 10^{14}\) ions /cm\(^2\), (d) \(2 \times 10^{14}\) ions /cm\(^2\) and (e) \(5 \times 10^{14}\) ions /cm\(^2\).
When ZnO thin film is irradiated with the fluence of $1 \times 10^{13}$ ions/cm$^2$ (Fig. 3.4b), the small regular square and rectangular shaped crystals of size $\sim$ 72 nm to 3 μm appear on the surface of films. There is also the evidence of agglomeration of these square and rectangular shaped crystals form longer chains (clearly seen on the lower left corner of the micrograph). The appearance of these crystals also point to an improvement in crystallinity of thin films as indicated by XRD results. Upon further irradiation with using the higher fluence of $1 \times 10^{14}$ ions/cm$^2$, the crystals most probably agglomerate and appear in the form of micro rods(Fig. 3.4c). The diameter and the length of these microrods varied in the range of 0.8-1.25 μm and 3.3-20 μm respectively. These microrods increased in size and number density when thin films were irradiated with $2 \times 10^{14}$ ions/cm$^2$ (Fig. 3.4d). At this dose, the diameter and length of microrods varied in the range of 1-2 μm and 6.6-26 μm respectively. This thin film showed the highest degree of crystallinity among all the films. Further the ion fluence was increased to $5 \times 10^{14}$ ions/cm$^2$ where the dose became so high causing fracturing and forming ruptured (and perhaps sputtered) flakes on the film surface instead of forming crystals or microrods (Fig. 3.4e). Therefore the crystallinity of this thin film also decreased, as confirmed by the XRD results. The SEM results were hence found to be in good agreement with XRD results.

### 3.1.4 AFM Analysis

Surface topography studies of pristine and Ni$^{+2}$ ions irradiated ZnO thin films were performed by using atomic force microscope (AFM) in tapping mode. Fig. 3.5 (a-e), shows the 2-D surface profile (scan area 2 μm × 2 μm) of pristine and Ni$^{+2}$ ions exposed ZnO thin films. The surface roughness obtained from software by taking full area of pristine film is about 5.25 nm due to the inhomogeneous division of grains on the surface. The roughness was decreased after ion irradiations to value 4.96 nm, 4.96 nm and 4.07 nm at the fluence of $1 \times 10^{13}$, $1 \times 10^{14}$ and $2 \times 10^{14}$ ions/cm$^2$ respectively. The decrease in roughness of ion irradiated ZnO thin films shows the development of smaller sized nano-crystallites, grain growth and the best filling of pores upon radiation due to local annealing effect. The appearance of the nano-crystallites structures also signifies the improvement in crystallinity of thin films. At the high fluence $5 \times 10^{14}$ ions/cm$^2$the roughness is increased to 13.02 nm due to fracturing on the film surface instead of forming crystals or micro structure. Therefore the crystallinity of this thin film also decreased as indicated by XRD results.
RESULTS AND DISCUSSION

Figure 3.5: 2-D atomic force microscopic profile of pristine and Ni$^{+2}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions /cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $2 \times 10^{14}$ ions /cm$^2$ and (e) $5 \times 10^{14}$ ions /cm$^2$.

3.1.5 Faraday Magneto-Optic Rotation

When plane polarized light is passed through a medium of a thickness (path length) ‘l’ which is placed in a magnetic field ‘B’, it rotates through a certain angle called Faraday rotation angle ($\theta_F$) and this is known as magneto-optic effect. The ratio of $\theta_F$ to the product ‘Bl’ is known as the Verdet Constant ‘V’ \[66\]

The Faraday rotation angle ($\theta_F$) as a function of magnetic field (B) for pristine and Ni$^{+2}$ ions irradiated ZnO thin films using different ion fluence are shown in Fig. 3.6a. It is evident that $\theta_F$ varies linearly with the applied ac magnetic field amplitude. The slope of these lines divided by the sample length through which the laser beam penetrates is the Verdet constant. The Verdet constants (V) of all films are plotted as a function of ion fluence in Fig. 3.6b. All the values of V are positive suggesting that these films exhibit diamagnetic behavior \[67\]. The value of V was 53 rad/ (T-m) for pristine ZnO thin film, and decreased significantly to 31 rad/ (T-m) when irradiated with the fluence $1 \times 10^{13}$ ions /cm$^2$. The error bars of ±2 rad/ (T-m) at the 95% confidence level are also shown in Fig. 3.6b. The negative contribution from the implanted Ni$^{+2}$ ions indicates paramagnetic nature of the transition
metal ions which are embedded inside a diamagnetic host matrix of ZnO. Studies on paramagnetic rare-earth ions doped into glasses and ceramic crystals are well known [68-70].

**Figure 3.6:** (a) The Faraday rotation (θ_F) versus magnetic field and (b) Verdet constant as a function of ion fluence of pristine and Ni^{2+} ion irradiated ZnO thin films.
In most of these cases, the large paramagnetic contribution to the Faraday rotation overwhelms the diamagnetic effect, leading to large negative Verdet constants. This is particularly true for temperatures lower than room temperature where the magnetization (and the magnetic moment per ion) is enhanced, in compliance with the Curie’s law. The essential decrease in Verdet constant in the Ni\textsuperscript{2+} implanted samples is in complete agreement with similar investigations \[71, 72\] wherein temperature dependent magnetization studies are performed on transition-metal implanted ZnO. In both of these reports, magnetometry measurements point towards paramagnetic or superparamagnetic behavior. For example, in the reference \[71\], room temperature hysteresis loops acquired by SQUID vibrating sample magnetometry (VSM) are clearly pointing towards paramagnetism. In our case, as the fluence of ion was increased to the value of 2 \times 10^{14} ions /cm\textsuperscript{2}, so the estimated value of V increased to 45 rad/ (T-m). Subsequently the V again decreased to 36 rad/ (T-m) at the fluence 5 \times 10^{14} ions /cm\textsuperscript{2}. However, in all cases, the Verdet constant for the irradiated films was significantly smaller than in the pristine film. This is due to negative contribution to the Faraday rotation imparted by paramagnetic Ni\textsuperscript{2+} ions. The magneto-optic measurements however are unable to conclusively reflect the irradiated flux of ions. The reason is that Faraday rotation measurements work differently than several other techniques for magnetization measurement such as VSM. While the latter is a global technique in the sense that it delivers a signal averaged over the entire volume of the sample, magneto-optic signals originate only from the local region within the sample that is exposed to the laser’s beam width. Since the spatial distribution of the magneto-optic scatterers, i.e. the paramagnetic Ni\textsuperscript{2+} ions is unknown from sample to sample and must be determined by other methods, we do not expect to see a linear relationship between the Verdet constant and the ion fluence. Nevertheless, in all cases the Verdet constants are smaller than the pristine film.
3.1.6 Optical Analysis

The transmission spectra are obtained from spectroscopic ellipsometry in the transmission mode and are shown in Fig. 3.7.

![Optical transmission curves as a function of wavelength of pristine and Ni^{+2} ions irradiated ZnO thin films.](image)

**Figure 3.7:** Optical transmission curves as a function of wavelength of pristine and Ni^{+2} ions irradiated ZnO thin films.

It is evident from the figure that optical transmission of all irradiated films was higher than pristine ZnO thin film, and it also increased with the increase in ion fluence. The sharp increase of transmission in ultraviolet region signifies the direct band gap transitions. The optical band gap energies are estimated by using following Tauc’s relation 3.1 [73].

\[
(\alpha \nu) = A (\nu - E_g)^n
\]

Where \(\alpha\) is absorption coefficient, \(\nu\) is incident photon energy, \(E_g\) is optical band gap energy. The exponent ‘n’ indicates the type of transitions. If \(n = 0.5, 2, 1.5\) and 3 related to allowed direct transition, indirect transition, forbidden direct transition and forbidden indirect transition respectively. Considering allowed direct transitions (\(n = 0.5\)), \((\alpha \nu)^2\) versus \(\nu\) curves of pristine and Ni^{+2} ions irradiated ZnO thin films are shown in Fig. 3.8 a-e. It can be observed that the curve of pristine ZnO thin film has almost steadily increasing behavior but the all the irradiated ZnO thin films show two humps in the curve. \(E_g\) is approximated by extrapolation of Tauc’s curves to energy axis. The intersection of extrapolation to horizontal axis gives the \(E_g\) value. \(E_g\) of unexposed and ion irradiated ZnO thin films as a function of ion...
fluence is shown in Fig. 3.8. $E_g$ of pristine ZnO thin film is 3.04 eV, which is lower than the reported value of 3.37 eV. The low $E_g$ is attributed to the presence of some inherent defects and oxygen vacancies in ZnO thin film. It is evident from the figure that $E_g$ increases from 3.04 eV (pristine film) to 3.19 eV with the increase in ion fluence to $2 \times 10^{14}$ ions/cm$^2$.

![Figure 3.8: $(\alpha h\nu)^2$ versus $h\nu$ curves of ZnO thin films. (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $2 \times 10^{14}$ ions/cm$^2$ and (e) $5 \times 10^{14}$ ions/cm$^2$, (f) Optical band gap energy as a function of ion fluence.](image-url)
But when the ion fluence increases to \(5 \times 10^{14} \text{ ions/cm}^2\), \(E_g\) decreases to 3 eV. The variation in \(E_g\) as a function of fluence can be well correlated with the crystalline structure of thin films. As the dose increases, the Ni\(^{+2}\) ions substitute in ZnO matrix along with improved crystallinity showing substantial modification in band gap energy. The crystalline structure improves and \(E_g\) increases. The decrease in \(E_g\) at fluence \(5 \times 10^{14} \text{ ions/cm}^2\) is attributed to two reasons: Firstly the reduced crystallinity due to Ni defects which produced donor levels just below the conduction band [74, 75] and secondly the exchange interaction of sp and d due to band electrons of ZnO and localized d-electrons of Ni\(^{+2}\) ions respectively [76, 77].

3.1.7 Electrical Resistivity

Electrical resistivity measurements were carried out for pristine and Ni\(^{+2}\) ions irradiated ZnO thin films using four point probe method. The electrical resistivity of thin films was calculated by substituting the observed data in equation 3.2 [78].

\[
\rho = \left( \frac{\pi}{\ln 2} \right) \left( \frac{V}{I} \right) t
\]

(3.2)

Here term in first parentheses is the correction factor. The ‘V’ potential difference drops across the inner probe whereas the current ‘I’ is applied across the two outer probes. The thickness of thin film is ‘t’. Thus the Fig. 3.9 shows the variation of electrical resistivity with increasing ion fluence.

\[\text{Figure 3.9: Variation of electrical resistivity of pristine and Ni}^{+2}\text{ ions irradiated ZnO thin films.}\]
The electrical resistivity of ZnO thin films decrease from $3.84 \times 10^{-1} \, \Omega\cdot\text{cm}$ (pristine) to $4.47 \times 10^{-4} \, \Omega\cdot\text{cm}$ at the fluence of $1 \times 10^{13}$ ions /cm$^2$. The possible reason for decrease in electrical resistivity is that the incoming ions produce some structural defects, creation of oxygen vacancies and zinc interstitial in thin film as explained in [79]. By further increase in ions fluence to $2 \times 10^{14}$ ions /cm$^2$ the electrical resistivity increases to $4.42 \times 10^{-1} \, \Omega\cdot\text{cm}$. The appropriate reason is that the incident ions energy produced localized annealing effect at high fluence along with the Ni$^{+2}$ ions substitution in the ZnO matrix. Due to ion annealing effect the oxygen vacancies reduced and structural defect healed as a result in improved crystallinity of thin films and hence the electrical resistivity of ZnO thin film has been increased as observed in reference [80]. Upon further increase in fluence to $5 \times 10^{14}$ ions /cm$^2$, the electrical resistivity again decreased to $7.11 \times 10^{-2} \, \Omega\cdot\text{cm}$. At high fluence causing fracturing and forming ruptured and perhaps sputtered flakes on the film surface instead of forming crystals. Therefore, the crystallinity of thin film was reduced and hence the electrical resistivity decreased.

### 3.1.8 Simulations

DFT simulations for pristine ZnO, ZnO with Oxygen vacancy and ZnO doped with Ni were performed to probe the physics behind the variation observed in the experiments. Fig. 3.10 shows the structures of the super cell used for above mentioned three cases. The band structures and density of states were calculated using DFT for wurtzite ZnO with ideal structure, with oxygen vacancy and with Zn substitute by Ni.

![Figure 3.10: Supercell used for the DFT calculations. (a) Pure ZnOwurtzite structure, (b) ZnOwurtzite structure with Oxygen vacancy, (c) ZnOwurtzite structure with Zn atom substituted by Ni atoms.](image-url)
The Ni ion bombardment can easily knock out the Zn ions from the host ZnO. Due to very similar atomic radii Ni is a substitute atom to substitute the host Zn. Generalized Gradient Approximation (GGA+U) was used for all the simulations with 4 k points in each direction as shown in the Fig. 3.10(a-c). An onsite Hubbard potential was fixed at 10 eV for 3d electrons of Zn atoms to achieve band gaps similar to those of the experimental values. The value of 10 eV gives the band gap of 3.4 eV for ZnO which is consistent with the experimentally found values of band gap for ZnO. The sudden decrease in the resistivity shown in the Fig. 3.9 could be explained by the Ni ion substitution of Zn. As it can be clearly seen that two new energy levels are introduced due to Ni ion just below conduction band minima at 1.6 eV and 0.9 eV above Fermi level as shown in the Fig. 3.11(e). Peaks corresponding to these two levels can be seen in the density of states shown in Fig. 3.11(f).

**Figure 3.11:** Band structure (left panels) (a, c, e) and density of states (right panels) (b, d, f) of ZnO thin films. (a, b) pure ZnO, (c, d) ZnO with oxygen vacancy and (e, f) ZnO with Ni$^{2+}$ irradiation.

These states provide transmission channels for the electron conductance causing significant reduction of resistivity consistent with four probe results shown in the Fig. 3.9. However due
to further increase in the fluence of Ni ions an increase in resistivity. The ZnO thin film does contain a lot of oxygen vacancies inherently due to the mobile nature of oxygen ions. These oxygen vacancies provide a band with significant density of state just around the Fermi level see Fig. 3.11(d). Due to the high fluence, Ni ions impart more and more energy to the film initiating annealing like process due to increase in the temperature. Due to this, the crystallite size of the film increases as shown in the table 3.1, causing decrease in defects and oxygen vacancies. Thus the resistivity of film increase the increase in resistivity for the fluence $1 \times 10^{14}$ ion/cm$^2$ and higher the increase in crystallinity is much more important compared to its competing effect of Ni substituting which tries to decrease resistivity. This is because of the fact that film acts as transparent to the bombarded ions due to their high energy and they pass through only imparting their energy to the film with almost no implantation. At high fluence $5 \times 10^{14}$ ions/cm$^2$, the dose became so high causing fracturing and defects in ZnO thin films. The decrease in resistivity due to impurity Ni ions is much greater compared to the increase due to the competing factor of annealing due to thermal energy transfer and hence the overall trend is monotonic and decreasing.

3.2 Nickel (Ni$^{+2}$) Ions Irradiation of ZnO Thin Films Annealed at 500 °C

3.2.1 XRD Analysis

The XRD pattern of pristine and Ni$^{+2}$ ions irradiated ZnO thin films annealed at 500 °C in vacuum for the duration of one hour is shown in the Fig. 3.12a. The XRD graph shows one peak of ZnO (002) plane at 34.47°, which depicts that the wurtzite phase oriented along c-axis is formed in the film. The prominent ZnO (0 0 2) planes appeared when ZnO thin films were irradiated with 700 keV Ni$^{+2}$ ions (section 3.1) indicating that ZnO primarily stayed crystalline after irradiation. After irradiation nickel ions form the NiO phase which disappears due to annealing under high vacuum. The Ni$^{+2}$ ions are certainly producing damage in ZnO thin film and also well substituted in the ZnO lattice site [81]. Most probably the cumulative effect of ion damage and Ni-Zn replacement results in the shift of 2Θ values. The annealing effect recovers the damages resulting in improvement of the crystallinity of ZnO thin films. Table 3.2 shows different parameters obtained from the XRD spectra of the ZnO thin films [46-48]. It is evident from the Table that all irradiated ZnO thin films show shifts in 2Θ values and variation in lattice constant ‘c’ as compared to pristine ZnO thin films. The decrease in d-spacing at higher fluence is still indicating the existence of
compressive stresses. The micro strain and dislocation density decrease from the pristine value at the fluence of $2 \times 10^{14}$ ions/cm$^2$ but this value again increases at the high fluence $5 \times 10^{14}$ ions/cm$^2$.

![XRD patterns and crystallite size](image)

**Figure 3.12:** (a) XRD patterns of annealed (500°C) pristine and Ni$^{+2}$ ions irradiated ZnO thin films and (b) Crystallite size as a function of ion fluence.

This is attributed to the fact the damages recover and the stresses are released among different grains causing their reorientation in the same direction by reducing the interfacial energy resulting in improved crystallinity of ZnO thin films after annealing at low fluence.
But at high fluence, the incident energy and ion fluence are high that produced more damages which result in deterioration of the crystalline structure. The crystallite size measured from Scherer’s formula is plotted as function of dose as shown in Fig. 3.12b. The crystallite size for pristine ZnO thin film was 22.02 nm. When fluence is increased to $2 \times 10^{14}$ ions/cm$^2$, the crystallite size increased to 28.31 nm whereas it is again decreased to 21.02 nm upon increasing the fluence to $5 \times 10^{14}$ ions/cm$^2$. The increase in crystallite size with increasing ion fluence indicates improved crystallinity (reduced damages) of ZnO thin films when annealed at 500 °C. But the reduced crystallite size at the highest fluence of $5 \times 10^{14}$ ions/cm$^2$ is due to high energy deposition causing crystalline damages and annealing process not completely healed the ion damages in film.

Table 3.2: XRD peak position, d-spacing, lattice parameters, crystallite size, dislocation density and micro strain for pristine and Ni$^{+2}$ ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ions fluences (ions/cm$^2$)</th>
<th>2θ (degree)</th>
<th>d-spacing (Å)</th>
<th>Lattice Parameters c (Å)</th>
<th>Crystallite Size D(nm) = $k \lambda / \beta \cos \theta$</th>
<th>Dislocation Density 1/D$^2$</th>
<th>Micro Strain $\epsilon = \beta \cos \theta / 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>34.47</td>
<td>2.6179</td>
<td>5.2053</td>
<td>22.02</td>
<td>2.06 x 10$^{-3}$</td>
<td>1.57 x 10$^{-3}$</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>34.54</td>
<td>2.6074</td>
<td>5.1929</td>
<td>22.74</td>
<td>1.09 x 10$^{-3}$</td>
<td>1.53 x 10$^{-3}$</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>34.39</td>
<td>2.6037</td>
<td>5.2176</td>
<td>23.92</td>
<td>1.75 x 10$^{-3}$</td>
<td>1.48 x 10$^{-3}$</td>
</tr>
<tr>
<td>$2 \times 10^{14}$</td>
<td>34.39</td>
<td>2.5979</td>
<td>5.2176</td>
<td>28.31</td>
<td>1.25 x 10$^{-3}$</td>
<td>1.24 x 10$^{-3}$</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>34.47</td>
<td>2.6077</td>
<td>5.2053</td>
<td>21.02</td>
<td>2.26 x 10$^{-3}$</td>
<td>1.65 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

Fig.3.13 shows that the comparison of crystallite size versus ion fluence for annealed and unannealed ZnO thin film.

Figure 3.13: Comparison of crystallite size as a function of ions fluence for annealed and unannealed ZnO thin film.
It is clear from the figure that the crystallite size of annealed ZnO thin films increases due to recovery of damages and reduction of oxygen vacancies as compared to the unannealed samples.

### 3.2.2 Surface Morphology

The scanning electron micrographs of pristine and Ni$^{+2}$ ions irradiated ZnO thin films at different ion fluence and annealed at 500 °C is shown in Fig. 3.14. It is evident that pristine ZnO thin film exhibits smooth surface morphology having just few particulates over the surface (Fig. 3.14a).

![Figure 3.14: Scanning electron micrographs of pristine and Ni$^{+2}$ ions irradiated ZnO thin films at different ion fluence annealed at 500°C. (a) Pristine, (b) $1 \times 10^{13}$ ions /cm$^2$, (c) $1 \times 10^{14}$ ions /cm$^2$, (d) $2 \times 10^{14}$ ions /cm$^2$ and (e) $5 \times 10^{14}$ ions /cm$^2$.](image)

When ZnO thin film is exposed with ion fluence of $1 \times 10^{13}$ ions /cm$^2$ (Fig. 3.14b), the small regular square and rectangular shaped crystals of different size appear at the surface of thin films. The appearance of these crystals also point to an improvement in crystallinity of thin films as indicated by XRD results. Upon further irradiation at the higher dose of $1 \times 10^{14}$ ions /cm$^2$, the crystals most probably agglomerate and appear in the form of circular shapes nano
spheres on the surface of film (Fig. 3.14c). These nano spheres increased in size but number density decreased when thin film were irradiated with $2 \times 10^{14}$ ions /cm$^2$ (Fig. 3.14d). This thin film showed the highest degree of crystallinity among all the films which is confirmed by the XRD results. Upon further increasing the fluence to $5 \times 10^{14}$ ions /cm$^2$ due to agglomeration and annealing effect nanorods appear on the surface of thin film. Some rectangular shape nanocrystals are clearly seen which stack on one another. The diameter and the length of these nanorods varied in the range of 5-15 nm and 20-70 nm respectively. Therefore the crystallinity of this thin film also decreased, as confirmed by the XRD results. The SEM results are good in agreement with the XRD results. If the SEM micrographs of unannealed (Fig. 3.4a-e) and annealed (Fig. 3.14a-e) are compared, then it can be seen that micro rods in unannealed ZnO thin films are transformed into smaller nanospheres which are homogeneous distributed over the entire surface in annealed ZnO thin films. The size of nanospheres of ZnO thin films irradiated by $2 \times 10^{14}$ ions /cm$^2$ is also increased after annealing. So the combined effect of higher fluence and annealing at 500°C is responsible for increase in the size of nanospheres.

### 3.2.3 Optical Analysis

The optical analysis and optical band gap of unexposed and Ni$^{+2}$ ions irradiated annealed ZnO thin films calculated by using Tauc’s relation in equation 3.1 [73]. It can be observed that the curve of pristine ZnO thin film has almost steadily increasing behavior. Optical band gap is approximated by extrapolation of Tauc’s curves to energy axis. The intersection of extrapolation to horizontal axis gives the $E_g$ value shown in the Fig. 3.15(a-e). Optical band gap energy of pure and ion exposed ZnO thin films as a function of ion fluence is shown in Fig. 3.15f. Optical band gap of pristine ZnO thin film is 3.00 eV, which is lower than the reported value of 3.37 eV. The low optical band gap is attributed to the presence of some inherent defects and oxygen vacancies in ZnO thin film. It is evident from the figure that optical band gap increases from 3.00 eV (pristine film) to 3.08 eV with the increase in ion fluence to $2 \times 10^{14}$ ions/cm$^2$. But when the ion fluence increases to $5 \times 10^{14}$ ions/cm$^2$, optical band gap decreases to 2.97eV. The variation in optical band gap as a function of fluence can be well correlated with the crystalline structure of thin films. As the dose increases, the Ni$^{+2}$ ions substitute in ZnO matrix along with improved crystallinity showing substantial modification in band gap energy. The crystalline structure improves and optical band gap increases. The decrease in optical band gap at fluence $5 \times 10^{14}$ ions/cm$^2$ is attributed to two
reasons: Firstly the reduced crystallinity due to Ni defects which produced donor levels just below the conduction band and secondly the exchange interaction of sp and d due to band electrons of ZnO and localized d-electrons of Ni$^{2+}$ ions respectively.

Figure 3.15: $(\alpha h\nu)^2$ versus $h\nu$ curves of ZnO thin films annealed at 500°C, (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $2 \times 10^{14}$ ions/cm$^2$, (e) $5 \times 10^{14}$ ions/cm$^2$ and (f) Optical band gap energy as a function of ion fluence.
3.3 Gold (Au\(^{+1}\)) Ions Irradiation of ZnO Thin Films

3.3.1 SRIM Simulation of Gold (Au\(^{+1}\)) Ions Irradiation of ZnO Thin Films

Implantation profile of Au\(^{+1}\) ions in ZnO thin film is simulated with the help of SRIM-2008 program [63, 64]. Fig. 3.16 shows the results of Monte Carlo simulation. Fig. 3.16(a) shows the scattering cascade of target atoms where as fig. 3.16(b) shows the ion range profile of 700 keV Au\(^{+1}\) ions irradiated ZnO thin films having thickness of 200 nm.

![Figure 3.16: SRIM simulation results. (a) Scattering cascade of target atom in 200 nm ZnO thin films after irradiation with 700 keV Au\(^{+1}\)ions and (b) Ion range profile.](image)

It is found from simulated results that most of the Au\(^{+1}\) ions are implanted, almost zero percent of ions are back scattered and transmitted through the ZnO thin films. The range of Au\(^{+1}\) ions in ZnO film is 101 nm and straggling was 29 nm. It shows that the energy of incident ions is sufficient to stop in this thickness of ZnO thin films, so that majority of ions are substituted in ZnO thin film. The stopping power of 700 keV Au\(^{+1}\) ion irradiated ZnO thin film at different energies is shown in the Fig. 3.17. It is evident from the figure that nuclear stopping power is larger than electronic stopping power at \(E \leq 6\) MeV and electronic stopping power becomes larger at \(E \geq 6\) MeV. At \(E = 6\) MeV, both the stopping powers become equal which is 321 eV/Å. The nuclear stopping is found to be \(6.02 \times 10^2\) eV/Å while the electronic stopping power \(1.436 \times 10^5\) eV/Å at 700 keV. Thus main modifications are expected due to nuclear stopping power as compared to electronic stopping power.
3.3.2 XRD Analysis

The XRD spectra of unexposed and Au\textsuperscript{+1} irradiated ZnO thin films are shown in Fig. 3.18a. The pristine ZnO thin film shows a strong stacking along c-axis with (002) plane at 34.18°. When ZnO thin films were exposed using 700 keV Au\textsuperscript{+1} ion with fluence of $1 \times 10^{13}$ ions/cm\textsuperscript{2}, $1 \times 10^{14}$ ions/cm\textsuperscript{2}, $2 \times 10^{14}$ ions/cm\textsuperscript{2} and $5 \times 10^{14}$ ions/cm\textsuperscript{2}, the ZnO remained crystalline in nature. No other peaks corresponding to any impurity phases were observed after irradiation, which indicates that the grains in ZnO have a strong orientation along c-axis (002) plane only. The XRD parameters such as crystallite size and lattice parameter are calculated by using equations 2.2-2.4 and given in table 3.3 [46-48]. The crystallite size measured from Scherer’s relation is plotted as function of dose as shown in Fig. 3.18b, indicating that the crystallite size of pristine film was 9.63 nm which reduced to 6.97 nm at the fluence of $1 \times 10^{13}$ ions/cm\textsuperscript{2}. The decrease in crystallite size at this fluence is attributed to the generation of defects in ZnO thin films as observed in reference [82]. At high fluence (i.e. $1 \times 10^{14}$ to $5 \times 10^{14}$ ions/cm\textsuperscript{2}), the crystallite size is gradually increased from 7.26 nm to 9.01 nm. At high fluence, incident ions transfer enough energy to the lattice causing local increase in temperature along the path of ions. This temperature produced localized annealing effect, resulting reduction in compressive stresses among the grains, and agglomeration of the...
grain occurs which increased the crystallinity of the ZnO thin films as explained in reference [83].

**Figure 3.18:** (a) XRD patterns of pristine and Au$^{+1}$ ions irradiated ZnO thin films (b) Crystallite size as a function of ion fluence.
Table 3.3: XRD ZnO (002) peak position, lattice parameter, FWHM and crystallite size for pristine and Au$^{+1}$ ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ions fluences (ions/cm$^2$)</th>
<th>$2\Theta$ (degree)</th>
<th>Lattice parameter (c) Å</th>
<th>FWHM (degree)</th>
<th>Crystallite Size D(nm) = $\frac{k\lambda}{\beta \cos \theta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>34.18</td>
<td>5.247</td>
<td>0.87</td>
<td>9.63</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>34.12</td>
<td>5.256</td>
<td>1.20</td>
<td>6.97</td>
</tr>
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<td>$1 \times 10^{14}$</td>
<td>34.52</td>
<td>5.196</td>
<td>1.15</td>
<td>7.26</td>
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<tr>
<td>$2 \times 10^{14}$</td>
<td>34.48</td>
<td>5.203</td>
<td>0.98</td>
<td>8.56</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>34.48</td>
<td>5.203</td>
<td>0.93</td>
<td>9.01</td>
</tr>
</tbody>
</table>

3.3.3 Surface Morphology

The scanning electron micrographs of pristine and ion exposed ZnO films are shown in figure 3.19 (a-f). It shows that pristine ZnO thin film (Fig. 3.19a) has smooth surface without any voids and cracks. A few small nano- and submicron sized particulates are distributed over the film surface.

Figure 3.19: Scanning electron micrographs of pristine and Au$^{+1}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions /cm$^2$, (c) $1 \times 10^{14}$ ions /cm$^2$, (d) $2 \times 10^{14}$ ions /cm$^2$, (e) $5 \times 10^{14}$ ions /cm$^2$ and (f) another portion of film at $5 \times 10^{14}$ ions /cm$^2$. 
When ZnO thin film is Au$^{+1}$ irradiated with fluence $1 \times 10^{13}$ ions/cm$^2$ (Fig. 3.19b), formation of micro cracks, mixture of flakes and sputtering of material are observed on surface, which reduced the crystallinity of thin film confirming XRD results. Further irradiation with fluence $1 \times 10^{14}$ ions/cm$^2$ and $2 \times 10^{14}$ ions /cm$^2$ small spherical micron size particulates agglomerate to form larger crystallites at the surface which is due to localized annealing effect (Fig. 3.19c-d). Upon further increasing fluence to $5 \times 10^{14}$ ions /cm$^2$, the micron sized spherical particulates and micro-grains are transformed into ganglia rods, micro sized crystals and acicular nanostructure as in [84] which are distributed over the surface of thin film (Fig. 3.19 e-f). This phenomenon increases the crystallinity of ZnO thin film. The SEM results are in good agreement with XRD results.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of pristine, ions irradiated ZnO thin films and of glass substrate for reference are shown in Fig. 3.20. The inset is showing the FTIR spectra in the range of 350 to 600 cm$^{-1}$. The FTIR spectra of bare glass substrate indicate no vibration peak of ZnO. Absorption band at 432 cm$^{-1}$ is due to Zn-O stretching vibration visible in all samples. It can be seen that a second absorption band at 395 cm$^{-1}$ starts appearing in the samples irradiated with different Au$^{+1}$ ions fluence.

![FTIR Spectrum of Au$^{+1}$ ions irradiated ZnO thin films at different ion fluence.](image)

**Figure 3.20:** FTIR Spectrum of Au$^{+1}$ ions irradiated ZnO thin films at different ion fluence.

The band at 395 cm$^{-1}$ becomes stronger with the increase in the fluence. The appearance of new absorption band at 395 cm$^{-1}$ is an indication of the formation of ZnO acicular...
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nanostructures in the film as observed in reference [84]. Such acicular structures are clearly visible in the Fig. 3.19f. Absorption bands at 2361 cm\(^{-1}\) is due to the O=\(\text{C}=\text{O}\) adsorbed from the atmosphere. It can be seen that sample with highest fluence \(5\times10^{14}\) ions/cm\(^2\) shows biggest peak at 2361 cm\(^{-1}\), which is clear indication of adsorption of atmospheric CO\(_2\) [85-87]. A broad peak at 2920 cm\(^{-1}\) in all the samples is due to presence of hydrocarbons [88]. This feature is also present in the FTIR of the substrate as well and could be a reminiscent of the chemical cleaning process of the substrate. It is also interesting to note the interference fringes are appeared which is an indication of good quality film of ZnO.

3.3.5 Optical Analysis

Spectroscopic ellipsometry measurements were carried out in the wavelength range 300 to 800 nm. Fig. 3.21(a-b) shows that the refractive index (n) and extinction coefficient (k) for pristine and Au\(^{+1}\) ion irradiated ZnO thin films at the fluence i.e. \(1 \times 10^{13}\) ions/cm\(^2\), \(1\times10^{14}\) ions/cm\(^2\), \(2\times10^{14}\) ions/cm\(^2\) and \(5\times10^{14}\) ions/cm\(^2\). The refractive index (n) is maximum (2.36) at the wavelength of 382 nm for pristine ZnO thin film while it decreases gradually with increasing wavelength (Fig. 3.21a). By increasing fluence, the curves of refractive index show almost similar trend but the curves are shifted to lower values up to \(2\times10^{14}\) ions/cm\(^2\). The curve of refractive index ‘n’ at \(5\times10^{14}\) ions/cm\(^2\) is again shifted upward and is highest among irradiated films which may be due to the presence of acicular nanostructures. The extinction coefficient (k) versus wavelength of pristine and ion irradiated ZnO thin films is shown in Fig. 3.21b. All the curves show gradually decreasing trend as the wavelength increases. The extinction coefficient curves are shifted to lower values by increasing the ions fluence to \(2\times10^{14}\) ions/cm\(^2\) while extinction coefficient curves for to \(5\times10^{14}\) ions/cm\(^2\) fluence are shifted to higher values. The value of extinction coefficient is almost same ~ 0.238 for all films at wavelength i.e. \(\lambda = 382\) nm which may also be due to the formation of acicular nanostructures on ZnO thin films at this fluence.

The optical band gap energies of unexposed and Au\(^{+1}\) ions irradiated ZnO thin films calculated by using following Tauc’s relation in equation 3.1 [73].
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Figure 3.2: Spectroscopic Ellipsometry of pristine and Au\textsuperscript{+1} ions irradiated ZnO thin films. (a) Refractive index and (b) Extinction coefficient.

The optical band gap for allowed direct transition was obtained by the intercept of the linear region of $(\varepsilon h \nu)^2$ versus $h \nu$ and plots are shown in Fig. 3.22(a-e) for all films. The optical band gap energy obtained from Tauc curves versus ion fluence in figure 3.22f. The band gap of pristine ZnO thin film is 3.08 eV which is gradually reduced to 2.82 eV when the ions fluence increases from $1 \times 10^{13}$ ions/cm\textsuperscript{2} to $2 \times 10^{14}$ ions/cm\textsuperscript{2}. The red shift in the optical
band gap is because of the incorporation of Au$^{+1}$ metal dopants in a semiconductor, which lead to the widening of the valence band causing the reduction of optical band gap energy.

Figure 3.22: $(ahv)^2$ versus $hv$ curves of ZnO thin films. (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $2 \times 10^{14}$ ions/cm$^2$, (e) $5 \times 10^{14}$ ions/cm$^2$ and (f) Optical band gap energy as a function of ion fluence.
Another reason for reduction in optical energy band gap may be due to the quantum confinement and the formation of larger grains due to the structural changes [82, 89]. The $E_g$ increases to 2.94 eV, when the influence is further increased to $5 \times 10^{14}$ ions/cm$^2$. This increase in the $E_g$ is caused by the increase in the concentration of Au incorporation, which is resulted in the reduction of the tail of valance and conduction band [90].

### 3.3.6 Electrical Resistivity

Electrical resistivity of pristine and Au$^+1$ ions irradiated ZnO thin films is measured using four point probe method. Fig. 3.23 shows the change in resistivity with ion fluence. It is found that the electrical resistivity of ZnO thin films decreases with increase in ions fluence. By the increase in ion fluence, electrical resistivity decreases from 6.25 $\times 10^{-2}$ $\Omega$-cm (pristine) to 6.15 $\times 10^{-6}$ $\Omega$-cm (at fluence $5 \times 10^{14}$ ions/cm$^2$). When Au$^+1$ ions irradiation on ZnO thin films with different fluence creates oxygen vacancies and Zinc interstitial that decrease the electrical resistivity and consequently improved the electrical conductivity of thin films as shown in reference [91].

![Figure 3.23: Variation of electrical resistivity of pristine and Au$^+1$ ions irradiated ZnO thin films.](image_url)
3.4 Cobalt (Co\textsuperscript{+1}) Ions Irradiation of ZnO Thin Films

3.4.1 SRIM Simulation

The implantation profile of Co\textsuperscript{+1} ions in ZnO thin film is simulated with the help of SRIM-2008 program [63, 64]. Fig. 3.24 shows the results of Monte Carlo simulation. Fig. 3.24(a) shows the scattering cascade of target atoms where as fig. 3.24(b) shows the ion range profile of 80 keV Co\textsuperscript{+1} ions irradiated ZnO thin films having thickness of 80 nm.

![Figure 3.24: SRIM simulation results. (a) Scattering cascade of target atom in 80 nm ZnO thin films after irradiation with 80 keV Co\textsuperscript{+1} ions and (b) Ion range profile.](image)

It is found from simulated results that about 0.2% of Co\textsuperscript{+1} ions are transmitted through the film, and 0.2% of ions are back scattered from ZnO thin films. The mean projected range of Co\textsuperscript{+1} ions in ZnO film is 36.9 nm and longitudinal straggling is 16 nm. It shows that the energy of incident ions is enough for implantation in 80 nm ZnO thin films instead of transmission. The majority of ions is stopped in films and substitute with Zn\textsuperscript{+2} ions in ZnO matrix. Fig. 3.25 shows the stopping power of Co\textsuperscript{+1} ions irradiated ZnO thin films. It shows that the nuclear stopping power is larger than electronic stopping power at E \leq 1\text{MeV} and the nuclear stopping power is decreased gradually. With increases ion energy at \sim 1\text{MeV} both nuclear and electronic stopping power are equal i.e. 80 eV/Å. With further increase in energy, the electronic stopping increases linearly while nuclear stopping decreases and become negligibly constant. It depicts that the electronic excitation process is dominant for Co\textsuperscript{+1} ions having higher energy.
### RESULTS AND DISCUSSION

**Figure 3.25:** Nuclear and electronic stopping power of Co⁺¹ ion irradiated on ZnO thin films.

#### 3.4.2 XRD Analysis

Figure 3.26(a) shows the x-ray diffraction (XRD) spectra for pristine and Co⁺¹ ions irradiated ZnO thin films. The ions are irradiated at energy 80 keV with different ion fluence i.e. $1 \times 10^{13}, 1 \times 10^{14}, 5\times10^{14}, 1\times10^{15}$ and $1\times10^{16}$ ions/cm². It can be seen that a prominent peak is observed at $2\theta \sim 34.34°$ in all films showing preferential c-axis orientation along (002) plane having wurtzite structure. A reflection peak of CoO is observed at $2\theta \sim 42.46°$ beside ZnO (002) at high fluence of i.e. $1\times10^{16}$ ions/cm². The crystallographic parameters such as d-spacing, crystallite size, dislocation density and micro strain [46-48] are calculated and given in table 3.4. Fig. 3.26(b) shows the crystallite size as a function of ion fluence. It can be observed that the crystallite size of Co⁺¹ ions irradiated ZnO thin films increases from~ 7 nm (pristine ZnO) to 22.75 nm when the fluence is increased to $1\times10^{15}$ ions/cm². It indicates that the ion beam promotes the grain growth in ZnO thin films at specific irradiation dose range [92, 93]. Moreover at this fluence the lattice strain has also been decreased. The decrease in lattice strain shows that ZnO thin films have been relaxed after ion irradiation at the specific fluence range (i.e. $1 \times 10^{13}, 1 \times 10^{14}, 5\times10^{14}$ and $1\times10^{15}$ ions/cm²).
At high ion fluence of $1 \times 10^{16}$ ions/cm$^2$, the crystallite size is decreased to 12.50 nm which indicates more damage of ZnO lattice at this fluence. The cobalt also makes a new phase of CoO, which also deteriorates the ZnO lattice.
Table 3.4: XRD peak position, lattice parameter, FWHM, crystallite size, dislocation density and microstrains for pristine and Co$^{+1}$ ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ions fluence (ions/cm²)</th>
<th>2θ (Degree)</th>
<th>Lattice Parameters (Å)</th>
<th>FWHM $\beta$=(θ₂−θ₁) (Radian)</th>
<th>Crystallite Size D(nm)= $\frac{k\lambda}{\beta \cos \theta}$</th>
<th>Dislocation Density (nm)$^2$ $\frac{1}{D^2}$</th>
<th>Micro Strain $e = \frac{\beta \cos \theta}{4}$</th>
</tr>
</thead>
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<td>Pristine</td>
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<td>0.0205</td>
<td>7.08</td>
<td>19.95×10$^{-3}$</td>
<td>0.0049</td>
</tr>
<tr>
<td>1×10$^{13}$</td>
<td>34.49</td>
<td>5.202</td>
<td>0.0155</td>
<td>9.37</td>
<td>11.39×10$^{-3}$</td>
<td>0.0037</td>
</tr>
<tr>
<td>1×10$^{14}$</td>
<td>34.57</td>
<td>5.191</td>
<td>0.0151</td>
<td>9.63</td>
<td>10.78×10$^{-3}$</td>
<td>0.0036</td>
</tr>
<tr>
<td>5×10$^{14}$</td>
<td>34.64</td>
<td>5.179</td>
<td>0.0148</td>
<td>9.84</td>
<td>10.33×10$^{-3}$</td>
<td>0.0035</td>
</tr>
<tr>
<td>1×10$^{15}$</td>
<td>34.90</td>
<td>5.141</td>
<td>0.0064</td>
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<td>01.93×10$^{-3}$</td>
<td>0.0015</td>
</tr>
<tr>
<td>1×10$^{16}$</td>
<td>34.70</td>
<td>5.170</td>
<td>0.0116</td>
<td>12.50</td>
<td>06.4×10$^{-3}$</td>
<td>0.0028</td>
</tr>
</tbody>
</table>

3.4.3 Surface Morphology

Figure 3.27(a-f) shows the SEM micrographs of pristine and Co$^{+1}$ ions irradiated ZnO thin films with energy 80 keV, at fluence 1×10$^{13}$, 1×10$^{14}$, 5×10$^{14}$, 1×10$^{15}$ and 1×10$^{16}$ ions/cm². These micrographs show that all the films are of good quality and significant change in morphology is observed after Co$^{+1}$ ion irradiation with different fluence. Fig. 3.27(a) shows that the pristine ZnO thin film exhibits smooth surface with no fracture or cracks. The nano sized (< 25 nm) spherical particle are uniformly distributed on the surface of film. When ZnO thin films are irradiated with fluence (1×10$^{13}$ and 1×10$^{14}$ ions/cm²), the small spherical shaped nano sized grains morphology with uneven distributed pores are observed (Fig.3.27b-c). Upon further irradiation at the fluence of 5×10$^{14}$ ions /cm² the spherical nano-grains start agglomeration and increase in the size to ~ 40 nm (Fig.3.27d). At the fluence of 1×10$^{15}$ ions/cm², the larger sizes of crystals are observed on the surface of thin films due to agglomeration of the small nano sized particle. This thin film showed the highest degree of crystallinity amongst all the films as confirmed by XRD results (Fig.3.27e). Upon further increasing the fluence to 1×10$^{16}$ ions /cm², the dose become so high causing fracturing of larger sized grain into smaller sized particles(Fig.3.27f). The crystallinity of ZnO thin film is also reduced due to the formation of new phase of CoO confirmed by the XRD results. The SEM results were hence found to be consistent with the XRD results.
**3.4.4 Optical Analysis**

The variation of refractive index and extinction coefficient with increasing wavelength from 383 to 900 nm is shown in Fig. 3.28(a-b). Fig. 3.28(a) shows that there is gradual decrease in the refractive index for pristine and Co$^{+1}$ ions irradiated ZnO thin films at different fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions/cm$^2$ from 383 – 900 nm.
Figure 3.28: Variation of refractive index (a) and extinction coefficient (b) with wavelength for pristine and Co$^{+1}$ ions irradiated ZnO thin films.
The maximum value of refractive index is found in the range 2.2–2.35 in all thin films at wavelength $\lambda \approx 383$nm. With increase in wavelength, the refractive indices of films are decreased to 2–2.07 at wavelength i.e. $\lambda \approx 900$ nm. The refractive index curves are not shifting regular pattern when the Co$^{+1}$ ion fluence is increased from pristine film to highest fluence used i.e. $1 \times 10^{16}$ ions/cm$^2$. Figure 3.28b represents the change in the extinction coefficient with wavelength. It is evident from the figure that the extinction coefficient ‘k’ decreases when wavelength increases from 383 nm to almost 600 nm for all ZnO thin films. The extinction coefficient again little bit increases in the wavelength range ~ 600 - 900 nm. There is a sharp band edge at wavelength i.e. $\lambda = 475$ nm. There is not regular shifting of extinction coefficient ‘k’ curves with increasing the Co$^{+1}$ ion fluence. The films are showing higher absorption in short wavelength region and are transparent in the visible and IR region of the spectrum. The optical band gap energies are estimated by using Tauc’s relation equation 3.1 [73]. Figure 3.29 a-f shows the graph of $(\alpha h\nu)^2$ versus $h\nu$ of pristine and Co$^{+1}$ ions irradiated ZnO thin films. The band gap energy ($E_g$) of pristine and irradiated ZnO thin films obtained from Tauc’s curves with the variation of ion fluence is shown in figure 3.30. $E_g$ of pristine ZnO thin film is 3.10 eV, which is lower than reported value of 3.37 eV. The low $E_g$ is ascribed to the presence of some inherent defects and Oxygen vacancies in ZnO thin film. It is evident from the figure that $E_g$ decreases from 3.10 eV (pristine film) to 2.80 eV with the increase in ion fluence to $5 \times 10^{14}$ ions/cm$^2$. When the ion fluence increases to $1 \times 10^{15}$ ions/cm$^2$, the $E_g$ increase to 2.88 eV, and the value of $E_g$ increases to 3.02 eV by further increase in fluence to $1 \times 10^{16}$ ions/cm$^2$. The variation in $E_g$ as a function of fluence can be well correlated to the crystalline structure of thin films. At the lowest fluence, the Co$^{+1}$ ions are well substituted in ZnO matrix along with improved crystallinity showing substantial modification in band gap energy. The decrease in $E_g$ at fluence of $1 \times 10^{13}$, $1 \times 10^{14}$ and $5 \times 10^{14}$ ions/cm$^2$ is mainly due to the sp-d exchange interaction between the localized d-electron of Co ion and band electrons of ZnO [94, 95]. The ionic radii of Cobalt ions is 0.745 Å and Zinc ions is 0.74 Å which are close, so majority of Co ions are substituted in the ZnO lattice [96]. The increase in $E_g$ at the fluence $1 \times 10^{16}$ ions/cm$^2$ is attributed to the closeness of ionic radii of Co and Zn. The band gap is broadened due to the increase in the transition tail width and shift effect. This variation in band gap with high fluence of Co$^{+1}$ ion may be explained in term of Moss-Burstein effect [97-98].
Figure 3.29: $(a \nu)^2$ versus $h \nu$ curves of ZnO thin films. (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $5 \times 10^{14}$ ions/cm$^2$, (e) $1 \times 10^{15}$ ions/cm$^2$ and (f) $1 \times 10^{16}$ ions/cm$^2$. 
3.4.5 Electrical Resistivity

The variation of electrical resistivity of pristine and Co$^{+1}$ ions irradiated ZnO thin films is shown in the Fig. 3.31.

![Image of resistivity variation](image-url)

**Figure 3.31:** Variation of electrical resistivity of pristine and Co$^{+1}$ ion irradiated ZnO thin films at different ions fluence.
It can be seen that electrical resistivity decreases from $5.39 \times 10^{-2} \ \Omega \text{cm}$ (pristine thin film) to minimum value $6.12 \times 10^{-5} \ \Omega \text{cm}$ at fluence of $1 \times 10^{15} \ \text{ions/cm}^2$. But further increase in ion fluence to $1 \times 10^{16} \ \text{ions/cm}^2$, electrical resistivity increase to $1.01 \times 10^{-2} \ \Omega \text{cm}$. The decrease in electrical resistivity can be explained by the increase in carrier concentration and displacement of the electrons, which are coming from the Co$^{+1}$ donors in the substitutional sites of Zn$^{+2}$ in the films [99, 100]. The formation of new phase of CoO, at highest ion fluence is also responsible for increase in the electrical resistivity of thin film.
3.5  Iron (Fe\(^{+1}\)) Ions Irradiation of ZnO Thin Films

3.5.1  SRIM Simulation

The implantation profile of Fe\(^{+1}\) ions in ZnO thin is film simulated with the help of SRIM-2008 program [63, 64]. Fig. 3.32 shows the results of Monte Carlo simulation. Fig. 3.32(a) shows the scattering cascade of target atoms where as fig. 3.32(b) shows the ion range profile of 80 keV Fe\(^{+1}\) ions irradiated ZnO thin films having thickness of 80 nm.

![Figure 3.32: SRIM simulation results. (a) Scattering cascade of target atom in 80 nm ZnO thin films after irradiation with 80 keV Fe\(^{+1}\) ions and (b) Ion range profile.](image)

It is found from simulated results that about 0.3% of Fe\(^{+1}\) ions are transmitted through the film, and 0.7% of ions are back scattered from ZnO thin films. The range of Fe\(^{+1}\) ion in ZnO film was 37.6 nm and straggling was 16.3 nm. It shows that the energy of incident ions is enough for implantation in 80 nm thickness of ZnO thin films instead of transmission. The majority of ions is stopped in films and substitute with Zn\(^{+2}\) ions in ZnO matrix. Fig. 3.33 shows the stopping powers of Fe\(^{+1}\) ion irradiated on ZnO thin films. It shows that the nuclear stopping power is larger than electronic stopping power at \(E \leq 1\) MeV and the nuclear stopping power is decreased gradually. With increases in ion energy at \(\sim 1\) MeV, both nuclear and electronic stopping powers are equal i.e. 82 eV/Å. The nuclear stopping power is calculated to be \(1.535 \times 10^2\) eV/Å, while the electronic stopping power is \(1.988 \times 10^1\) eV/Å. With further increase in energy, the electronic stopping increases linearly while nuclear
stopping decreases and become negligibly constant. It depicts that the electronic excitation process is dominant for Fe$^{+1}$ ions having higher energy.

![Graph showing electronic and nuclear losses](image_url)

**Figure 3.33**: Nuclear and electronic stopping power of Fe$^{+1}$ ion irradiated on ZnO thin films.

### 3.5.2 XRD Analysis

Figure 3.34a shows the x-ray diffraction (XRD) spectra for pristine and Fe$^{+1}$ ions irradiated ZnO thin films. The ions having energy 80 keV, with different fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$. It can be seen that a prominent peak is observed at $2\theta \sim 34.34^\circ$ in all thin films corresponding to ZnO (002) plane. No other peaks corresponding to impurity phases are observed after irradiation. The results indicate that the grains in ZnO have a strong orientation along c-axis (002) plane only. All ZnO thin films are nano crystalline with hexagonal wurtzite structure have preferential (002) growth. The crystallographic parameter such as d-spacing, crystal lattice, crystallite size, dislocation density and micro strain are calculated using equation in 2.2-2.4 [46-48] and given in table 3.5. Fig. 3.34b shows the crystallite size as a function of ion fluence. It can be seen that the crystallite size of Fe$^{+1}$ ion irradiated ZnO thin films has been decreased when the fluence increases to maximum value. It depicts that the ion beam deteriorates the grain growth in ZnO thin films. This is attributed to the fact that energy of incident ions was enough for implantation in the 80 nm thickness of thin films, so most of Fe$^{+1}$ ions are well substituted in
Zn sites and no diffraction peak is attributed to Fe related secondary phases as observed in [101].

Figure 3.34: (a) XRD patterns of pristine and Fe$^{+1}$ ions irradiated ZnO thin films (b) Crystallite size as a function of ions fluence.
Moreover at this fluence, the dislocation densities as well as lattice strain are increased. The increase in dislocation density due to increase in number of grain boundaries, which results in decrease of the crystallite size [102]. The increase in lattice strain shows that ZnO thin films deteriorate after ion irradiation at the fluence (i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$). This is due to stress arising from the difference in ionic radii between of the host material Zn (0.74 Å) and the dopant Fe (0.62 Å).

**Table 3.5:** XRD peak position, lattice parameter, crystallite size, dislocation density and micro strains for pristine and Fe$^{+1}$ ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ions fluence (ions /cm$^2$)</th>
<th>$2\theta$ (Degree)</th>
<th>d-spacing (Å)</th>
<th>Lattice Parameters (Å)</th>
<th>Crystallite Size $D$(nm)=$\frac{k\lambda}{\beta \cos \theta}$</th>
<th>Dislocation Density (nm)$^{-2}$</th>
<th>$\frac{1}{D^2}$</th>
<th>Micro Strain $\epsilon = \frac{\beta \cos \theta}{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>34.36</td>
<td>2.6099</td>
<td>5.210</td>
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<tr>
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<td>6.93</td>
<td>20.82 $\times 10^{-3}$</td>
<td>5.00 $\times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

### 3.5.3 Surface Morphology

Figure 3.35(a-e) shows the SEM micrographs of pristine and Fe$^{+1}$ ions irradiated ZnO thin films with energy 80 keV, at fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$. These micrographs show that all the films are of good quality and significant change in morphology after Fe$^{+1}$ ion irradiation is observed with different fluence. Fig. 3.35(a) shows that the pristine ZnO thin film exhibits smooth surface with no fracture or cracks. When ZnO thin film is irradiated with fluence $1 \times 10^{13}$ ions/cm$^2$, the small spherical shaped nano sized particulates agglomerates to form micro size leaf type structures on the surface of ZnO thin films (Fig. 3.35b). The micro leaves are circular and pyramids in shape with different sizes are observed on the surface of thin film. With further increase in fluence to $1 \times 10^{14}$ and $5 \times 10^{14}$ ions /cm$^2$, circular and pyramids micro sized leaf structures start to agglomerates and form longer leaf structures (Fig. 3.35c-d).
RESULTS AND DISCUSSION

Figure 3.35: Scanning electron micrographs of pristine and Fe$^{4+}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions /cm$^2$, (c) $1 \times 10^{14}$ ions /cm$^2$, (d) $5 \times 10^{14}$ ions /cm$^2$ and (e) $1 \times 10^{15}$ ions /cm$^2$.

Upon further increasing the fluence to $1 \times 10^{15}$ ions /cm$^2$, the size and dimensions of the micro-sized leaf are increased on the surface of ZnO thin film (Fig. 3.35e). As the fluence increases, the fracted shape structures with more filigree arms are appeared. This is attributed to the impurity effect of Fe ion on the film structures. The incorporation of more Fe ions in ZnO leads to the higher nucleation density. The surface morphology of irradiated thin films shows qualitatively that the surface roughness has increased from pristine film.

3.5.4 AFM Analysis

Surface profile of pristine and Fe$^{4+}$ ions irradiated ZnO thin films are studied by atomic force microscope (AFM) in tapping mode. Fig. 3.36 (a-e) shows the 2-D and inset 3-D profiles of pristine and Fe$^{4+}$ ions irradiated ZnO thin films with scan area $2\mu\text{m} \times 2\mu\text{m}$. The root mean square (rms) roughness of pristine film is about 1.16 nm. The particle size observed on the surface of thin film varies from 30 to 70 nm. At low fluence $1\times10^{13}$ ions/cm$^2$, the rms roughness is increased to 2.06 nm and the particle size increased and varies from 50 to 300 nm. The size of the particulate increases due to the formation of nanocluster.
Figure 3.36: Atomic force microscopy graphs (2-D and 3-D) of pristine and Fe$^{+1}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $5 \times 10^{14}$ ions/cm$^2$ and $1 \times 10^{15}$ ions/cm$^2$.

With further increase in ion fluence to $1 \times 10^{14}$ ions/cm$^2$, the rms roughness further increases to 2.39 nm and the distribution of the particles on the surface lies between 40-150 nm. At this fluence, there is formation of smaller sized nano-crystallites and grain growth is observed. Upon further increase in fluence to $5 \times 10^{14}$ ions/cm$^2$, the size of the particle lies in the range of 50-180 nm and the roughness slightly decreases to 2.32 nm. It indicates that at this fluence the average particle size and roughness are decreased due to reduction in size of nanostructures by the energy deposition during the ion bombardment. At highest fluence used $1 \times 10^{15}$ ions/cm$^2$, the roughness again increases to 3.65 nm and the size of the particle on the surface lies between 40-200 nm which implies that at this fluence the nanostructures are transformed to big submicron sized.
3.5.5 Optical Analysis

The measurements in variation of optical constants such as refractive index (n) and extinction coefficient (k) in wavelength range from 383 to 900 nm are shown in Fig. 3.37 (a-b).

**Figure 3.37:** Variation of refractive index (a) and extinction coefficient (b) with wavelength for pristine and Fe$^{+1}$ ion irradiated ZnO thin films.
RESULTS AND DISCUSSION

Fig. 3.37 (a) shows that there is gradual decrease in the refractive index in pristine and Fe$^{+1}$ ion irradiated ZnO thin films at different fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5\times10^{14}$ and $1\times10^{15}$ ions/cm$^2$ as wavelength increases from 383 to 900 nm. The maximum value of refractive index is found in the range of 2.28-2.38 in all thin films at wavelength $\lambda \approx 383$nm, and refractive index decrease to 2.02 to 2.06 at wavelength $\lambda \approx 900$ nm. All the ion irradiated thin films have lower refractive index as compared to pristine film in whole wavelength range. The refractive index curve shift is random with the increase in ion fluence. The pristine and Fe$^{+1}$ ion irradiated ZnO thin films show transparency (Fig. 3.37b). The extinction coefficient has maximum value in the range of 0.21 to 0.35 for pristine and Fe$^{+1}$ ion irradiated ZnO thin films at $\lambda \approx 383$ nm with different fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5\times10^{14}$ and $1\times10^{15}$ ions/cm$^2$. Extinction coefficient reduces gradually with increase in wavelength. There is a band edge at $\lambda \approx 600$ nm and the extinction coefficient becomes stagnant with further increase in wavelength from visible to IR indicating that all pristine and ion irradiated ZnO thin films are transparent in the wavelength range from $\lambda \approx 600$ to 900 nm. The extinction coefficient curves shift irregularly with increasing ion fluence.

The optical band gap energies are estimated by using Tauc’s relation 3.1 [73]. Fig. 3.38 (a-e) shows the plot of $(\alpha h\nu)^{2}$ versus $h\nu$ of pristine and Fe$^{+1}$ ions irradiated ZnO thin films. The band gap energy ($E_g$) estimated from Tauc’s curves of pristine and irradiated ZnO thin films as a function of ion fluence is shown in Fig. 3.38f. $E_g$ of pristine ZnO thin film is 3.10 eV, which is slightly lower than that reported value of 3.37 eV. It can be attributed to more native defects or Oxygen vacancies in ZnO thin film. It is evident from the figure that $E_g$ decreases from 3.10 eV (pristine film) to 2.63 eV with the increase in ion fluence to $1 \times 10^{15}$ ions/cm$^2$. The variation in $E_g$ as a function of fluence can be well correlated to the crystalline structure of thin films. There are two main reasons for the reduction of band gap energy. One of the possible reasons is that the incorporation of Fe ions produced defect levels just below the conduction band. The other possible reason is the interaction of band electrons of ZnO with d-electrons of Fe atom due to the exchange interaction of sp-d [103, 104].
RESULTS AND DISCUSSION

Figure 3.38: $(\alpha h\nu)^2$ versus $h\nu$ curves of ZnO thin films. (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $5 \times 10^{14}$ ions/cm$^2$ and (e) $1 \times 10^{14}$ ions/cm$^2$ and (f) Optical band gap energy as a function of ionfluence.
3.5.6 Electrical Resistivity

Fig. 3.39 shows the variation of electrical resistivity of pristine and Fe$^{+1}$ ion irradiated ZnO thin films. It can be seen that the electrical resistivity gradually decreases from $6.52 \times 10^{-2}$ Ω·cm (pristine film) to minimum value $2.35 \times 10^{-6}$ Ω·cm at highest fluence of $1\times10^{15}$ ions/cm$^2$. The decrease in electrical resistivity can be explained by the increase in carrier concentration and displacement of the electrons, which are coming from the ions Fe$^{+1}$ donors in the substitutional sites of Zn$^{+2}$ in the films. Another possible reason for decrease in electrical resistivity is that the incoming ions produced some structural defects and oxygen vacancies in thin film.

Figure 3.39: Variation of electrical resistivity of pristine and Fe$^{+1}$ ions irradiated ZnO thin films at different ions fluence.
3.6 Manganese (Mn$^{+1}$) Ions Irradiation of ZnO Thin Films

3.6.1 SRIM Simulation

The implantation profile of Mn$^{+1}$ ions in ZnO thin film is simulated with the help of SRIM-2008 program [63, 64]. Fig. 3.40 shows the results of Monte Carlo simulation. Fig. 3.40(a) shows the scattering cascade of target atoms whereas fig. 3.40(b) shows the ion range profile of 80 keV Mn$^{+1}$ ions irradiated ZnO thin films having thickness of 80 nm.

![SRIM simulation results](image)

**Figure 3.40:** SRIM simulation results. (a) Scattering cascade of target atom in 80 nm ZnO thin films after irradiation with 80 keV Mn$^{+1}$ ions and (b) Ion range profile.

It is found from simulated results that about 1.7% of Mn$^{+1}$ ions are transmitted through the film, and 0.5% of ions are back scattered from ZnO thin films. The range of Mn$^{+1}$ ion in ZnO film was 38.9 nm and straggling was 17.3 nm. It shows that the energy of incident ions is enough for implantation in 80 nm thickness of ZnO thin films instead of transmission. The majority of ions is stopped in films and substitute with Zn$^{+2}$ ions in ZnO matrix. Fig. 3.41 shows the stopping power of Mn$^{+1}$ ion irradiated on ZnO thin films. It shows that the nuclear stopping power is larger than electronic stopping power at $E \leq 1$ MeV and the nuclear stopping power is decreased gradually. With increases ion energy at $\sim 1$ MeV both nuclear and electronic stopping power are equal i.e. $75$ eV/Å. The nuclear stopping power is calculated to be $1.464 \times 10^2$ eV/Å, while the electronic stopping power is $1.871 \times 10^1$ eV/Å. With further increase in energy, the electronic stopping increases linearly while nuclear stopping decreases and become negligibly constant. It depicts that the electronic excitation process is dominant for Mn$^{+1}$ ions having higher energy.
The XRD spectra of unexposed and Mn$^{+1}$ ions implanted ZnO thin films are shown in Fig. 3.42(a). The ions are irradiated with energy 80 keV with different fluence i.e. $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$. The figure indicates that the grains in ZnO have strong orientation along c-axis (002) plane. It depicts that the ZnO remained crystalline in nature after irradiation. No other phase is observed which indicates that after implantation the Mn$^{+1}$ ions are well substituted at the Zn site of ZnO matrix. The crystallographic parameters such as d-spacing, crystallite size, micro strain and the dislocation density are measured from XRD peaks and tabulated in table 3.6. It is evident from the table that all irradiated ZnO thin films show shifts towards higher 2$\Theta$ values and a reduced lattice constant ‘c’ as compared to pristine ZnO thin films indicating the presence of compressive stresses. Intrinsic stresses involve due to impurities and crystal defects in irradiated ZnO films. While extrinsic stresses arise due to the lattice mismatch among the ZnO film and glass substrate. Fig.3.42b shows the crystallite size with variation of ion dose. It is clear that the crystallite size of Mn$^{+1}$ ions irradiated ZnO thin films has been decreased from pristine value at the fluence of $1 \times 10^{13}$ and $1 \times 10^{14}$ ions/cm$^2$ and the intensity of ZnO (002) plane is reduced. It is the indication that due to incorporation of Mn$^{+1}$ ion the crystallinity of film deteriorates.
The dislocation density as well as micro strain has been increased at the low fluence of incident ions. This is most likely due to replacement of the larger ionic radii Mn (0.080 nm) ions to the smaller radii Zn (0.074 nm) [105, 106]. With further increasing the fluence

Figure 3.42: (a) XRD patterns of pristine and Mn$^{+1}$ ions irradiated ZnO thin films. (b) Crystallite size as a function of ions fluence.
RESULTS AND DISCUSSION

(i.e. $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$), crystallite size is increased. This fact is attributed that the energy of incident ions were comparable to thickness of thin films, so most of Mn$^{+1}$ ions are well substituted in Zn lattice sites that promoted the grain growth in ZnO thin films. Moreover at this fluence the dislocation density as well as lattice strain has been decreased. The dislocation density decreases due to agglomeration. The number of grain boundaries decreases, which results the increase in the crystallite size. The decrease in lattice strain shows that ZnO thin films are relaxed after ion irradiation at the high fluence.

Table 3.6: XRD peak position, lattice parameter, crystallite size, dislocation density and micro strain for pristine and Mn$^{+1}$ ions irradiated ZnO thin films.

<table>
<thead>
<tr>
<th>Ion fluence (Ions/cm$^2$)</th>
<th>$2\theta$ (Degree)</th>
<th>d-spacing ($\AA$)</th>
<th>Lattice Parameters ($\phi$, $\psi$) ($\AA$)</th>
<th>Crystallite Size (D(nm)) = $\frac{k\phi}{\beta \cos \phi}$</th>
<th>Dislocation Density (nm)$^{-2}$</th>
<th>Micro Strain $e = \frac{\beta \cos \phi}{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>34.41</td>
<td>2.6061</td>
<td>5.212</td>
<td>8.51</td>
<td>$13.81 \times 10^{-3}$</td>
<td>4.07 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>34.57</td>
<td>2.5947</td>
<td>5.189</td>
<td>7.79</td>
<td>$16.49 \times 10^{-3}$</td>
<td>4.45 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>34.89</td>
<td>2.5714</td>
<td>5.143</td>
<td>6.19</td>
<td>$26.10 \times 10^{-3}$</td>
<td>5.60 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>34.96</td>
<td>2.5662</td>
<td>5.133</td>
<td>9.50</td>
<td>$11.08 \times 10^{-3}$</td>
<td>3.70 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>34.96</td>
<td>2.5662</td>
<td>5.133</td>
<td>11.66</td>
<td>$7.36 \times 10^{-3}$</td>
<td>2.97 $\times 10^{-3}$</td>
</tr>
</tbody>
</table>

3.6.3 Surface Morphology

Figure 3.43(a-e) shows the SEM micrographs of pristine and Mn$^{+1}$ ions irradiated ZnO thin films with energy 80 keV, at fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$. These micrographs show that all the films are of good quality. The modification in surface morphology after Mn$^{+1}$ ion irradiation with different fluence is observed. Fig. 3.43(a) shows that the pristine ZnO thin film exhibits smooth surface. When ZnO thin film are exposed with ion at the fluence $1 \times 10^{13}$ ions/cm$^2$ the size of spherical crystals decreases due to irradiation and some nanostructures are observed on the surface of thin film having different shape and size (Fig.3.43b). When ZnO thin film is implanted with fluence $1 \times 10^{14}$ ions/cm$^2$, formation of cracks, mounds of spherical particles and sputtering of material along with formation of nano rod of diameter 50 nm and length 400 nm are clearly seen on film surface (Fig. 3.43c). When fluence increases to $5 \times 10^{14}$ ions /cm$^2$, small spherical size particulates agglomerate to form larger crystallites on film surface. The shapes of particulates are spherical and rectangular and the size of these crystals varies from 20 nm to 150 nm (Fig. 3.46d). Upon further increasing fluence to $1 \times 10^{15}$ ions /cm$^2$, the small nano sized crystal agglomerates. The size and density of spherical and rectangular particulates is increased and maximum size
of rectangular shape crystal is 350 nm observed on the surface of thin film (Fig. 3.43e). This thin film showed the highest degree of crystallinity among all the films as confirmed by XRD results.

![Figure 3.43](image)

Figure 3.43: Scanning electron micrographs of pristine and Mn$^{+1}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $5 \times 10^{14}$ ions/cm$^2$ and (e) $1 \times 10^{15}$ ions/cm$^2$.

3.6.4 AFM Analysis

Surface topography of pristine and Mn$^{+1}$ ions irradiated ZnO thin films are studied by atomic force microscope (AFM) in tapping mode. Fig. 3.44 (a-e), shows the 2-D and inset 3-D micrograph of pristine and Mn$^{+1}$ ions irradiated ZnO thin films with scan area 2μm × 2μm. The rms roughness of unexposed film is about 2.89 nm due to the uniformly distribution of grains on film surface. The particles size observed on the surface of thin film varies from 50 - 225 nm. At low fluence $1\times10^{13}$ ions/cm$^2$, the rms roughness is decreased to 1.06 nm. The particle size is also decreased and varies from 40 - 80 nm. The rms roughness increased to 2.07 nm at fluence of $1\times10^{14}$ ions/cm$^2$ and the size distribution of the particles varies from 50 - 100 nm. The increase in the size of particles indicates that the agglomeration is started on the surface of thin film. With further increase in fluence to $5\times10^{14}$ ions/cm$^2$, the rms roughness further increases to 3.13 nm and the distribution of the particles on the surface lies between 55 - 200 nm. Thus due to agglomeration, the smallest grains form rod like
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A structure of diameter 200nm and length is 500nm. At highest fluence $1 \times 10^{15}$ ions/cm$^2$, the roughness is increased to the maximum value 3.65 nm and the size of the particle on the surface lies in the range of 50 - 200 nm. All the films have rms roughness values in the range of 1.06 to 3.6 nm indicating overall smooth surfaces of thin films.

![Atomic force micrographs](image)

**Figure 3.44:** Atomic force micro graphs (2-D and 3-D) of pristine and Mn$^{+1}$ ions irradiated ZnO thin films at different ion fluence. (a) Pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $5 \times 10^{14}$ ions/cm$^2$ and (e) $1 \times 10^{15}$ ions/cm$^2$.

### 3.6.5 Optical Analysis

The measurements in variation of optical constants such as refractive index (n) and extinction coefficient (k) in wavelength range from 383 to 900 nm are shown in Fig. 3.45 (a-b). Fig. 3.45a shows that there is gradual decrease in the refractive index in pristine and Mn$^{+1}$ ion irradiated ZnO thin films at different fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$ as wavelength increase from 383 to 900 nm. The maximum value of refractive index is found in the range of 2.19-2.74 in all thin films at wavelength $\lambda \approx 383$nm, and refractive index decreases to 2.09-1.95 at wavelength $\lambda \approx 900$ nm. All the ion irradiated thin films have lower refractive index as compared to pristine film in whole wavelength range.
The refractive index curve shift is random with the increase in ion fluence. The variation of refractive index (a) and extinction coefficient (b) with wavelength for pristine and Mn$^{+1}$ ion irradiated ZnO thin films.

**Figure 3.45:** Variation of refractive index (a) and extinction coefficient (b) with wavelength for pristine and Mn$^{+1}$ ion irradiated ZnO thin films.
The refractive index curve shift is random with the increase in ion fluence. The figure indicates that refractive index is decreasing with wavelength from 400-700nm and with further increase in wavelength (700 to 900nm) the refractive index remains constant. So the pristine and Mn$^{+1}$ ion irradiated ZnO thin films show transparency in visible and IR wavelength. Figure 3.45b shows the variation of the extinction coefficient with wavelength. The extinction coefficient has maximum value in the range of 0.23 to 0.76 for pristine and Fe$^{+1}$ ion irradiated ZnO thin films at $\lambda \approx 383$ nm with different fluence $1 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$. At this wavelength, pristine film has maximum value of extinction coefficient while the ion irradiated films have same trend of curves. Extinction coefficient reduces gradually with increase in wavelength. There is a band edge at $\lambda \approx 465$ nm and the extinction coefficient becomes stagnant with further increase in wavelength from visible to IR indicating that all pristine and ion irradiated ZnO thin films are transparent in the wavelength range from $\lambda \approx 600$ to 900 nm.

The optical band gap energies are estimated by using Tauc’s relation [73]. Fig. 3.46(a-e) shows the plot of (αhv)$^2$ versus hv of pristine and Mn$^{+1}$ ions irradiated ZnO thin films. The bandgap energy ($E_g$) of pristine and irradiated ZnO thin films as a function of ion fluence is shown in Fig. 3.46f. $E_g$ of pristine ZnO thin film is 3.10 eV, which is slightly less than that of exact value of 3.37 eV due to more inhabitant defects or vacancies of Oxygen in ZnO thin film. It is evident from the figure that $E_g$ decreases from 3.10 eV (pristine film) to 2.06 eV with the increase in ion fluence from $1 \times 10^{13}$ to $1 \times 10^{14}$ ions/cm$^2$. The decrease in the band gap is the interaction of band electrons of ZnO with d-electrons of Mn atom due to the exchange interaction of sp-d. [107]. At the fluence of $5 \times 10^{14}$ to $1 \times 10^{15}$ ions/cm$^2$ the $E_g$ increases to 2.64eV. The variation in $E_g$ as a function of fluence can be well correlated with the crystalline structure of thin films. As the dose increases, the Mn$^{+1}$ ions substitute in ZnO matrix along with improved crystallinity showing substantial modification in band gap energy.
Figure 3.46: $(αhν)^2$ versus $hν$ curves of ZnO thin films. (a) pristine, (b) $1 \times 10^{13}$ ions/cm$^2$, (c) $1 \times 10^{14}$ ions/cm$^2$, (d) $2 \times 10^{14}$ ions/cm$^2$, (e) $5 \times 10^{14}$ ions/cm$^2$ and (f) Optical band gap energy as a function of ion fluence.
CHAPTER 4
SUMMARY AND CONCLUSIONS

In present project, the ZnO thin films are irradiated with Ni$^{+2}$, Au$^{+1}$, Co$^{+1}$, Fe$^{+1}$ and Mn$^{+1}$ with different energies and fluence. All the thin films are characterized using different techniques. In 700 keV Ni$^{+2}$ irradiated ZnO thin films, the XRD crystallite size varies from 9.4 to 14.3 nm, the optical band gap varies in the range of 3.00 to 3.19 eV, electrical resistivity varies in the range of 3.84 $\times$ 10$^1$ Ohm-cm to 2.35 $\times$ 10$^6$ Ohm-cm whereas Verdet constant varies from 31 rad/T.m to 53 rad/T.m, in the fluence range 1$\times$ 10$^{13}$ to 5 $\times$ 10$^{14}$ ions/cm$^2$. In the same Ni$^{+2}$ irradiated ZnO thin films annealed at the temperature of 500 °C, the optical band gap varies in the range of 2.97 to 3.08 eV and the crystallite size varies from 21.02 to 28.31 nm. The results after annealing treatment of Ni$^{+2}$ irradiated ZnO thin films show that the structural damages are healed and the stresses among grains of crystal are reduced. So the crystallinity of all ZnO thin films is improved and optical band gap is reduced after annealing. In 700 keV Au$^{+1}$ irradiated ZnO thin films, the XRD crystallite size varies from 6.97 to 9.63 nm, the optical band gap varies in the range of 2.82 to 3.08 eV and electrical resistivity varies in the range of 3.18 $\times$ 10$^{-2}$ Ohm-cm to 6.15 $\times$ 10$^{-6}$ Ohm-cm, in the fluence range 1$\times$ 10$^{13}$ to 5 $\times$ 10$^{14}$ ions/cm$^2$. In 80 keV Co$^{+1}$ irradiated ZnO thin films, the XRD crystallite size varies from 7.08 to 22.75 nm, the optical band gap varies in the range of 2.80 to 3.02 eV and electrical resistivity varies in the range of 1.01 $\times$ 10$^{-2}$ Ohm-cm to 6.12 $\times$ 10$^{-5}$ Ohm-cm, in the fluence range 1$\times$ 10$^{13}$ to 1 $\times$ 10$^{16}$ ions/cm$^2$. In 80 keV Fe$^{+1}$ irradiated ZnO thin films, the XRD crystallite size varies from 6.93 to 10.75 nm, the optical band gap varies in the range of 2.63 to 3.10 eV, electrical resistivity varies in the range of 2.18 $\times$ 10$^{-2}$ Ohm-cm to 2.35 $\times$ 10$^{-6}$ Ohm-cm, in the fluence range 1$\times$ 10$^{13}$ to 1 $\times$ 10$^{15}$ ions/cm$^2$. In 80 keV Mn$^{+1}$ irradiated ZnO thin films, the XRD crystallite size varies from 6.19 to 11.66 nm, in the fluence range 1$\times$ 10$^{13}$ to 1 $\times$ 10$^{15}$ ions/cm$^2$.

If all the ions irradiated ZnO thin films are considered, it can be seen that the optical band gap of ZnO thin films can be well tuned in a wide range of 2.06 to 3.19 eV. The variation in optical band gap is due to the formation of extra sub levels between and within the valence and conduction bands. Another possible reason of change in the optical band gap is the interaction of band electrons of ZnO with d-electrons of transition metals due to the exchange interaction of sp-d. The variation in optical properties can be well correlated with the microstructure of ZnO thin films. The electrical resistivity of ions irradiated ZnO thin films is
found in semiconducting range after ion irradiation. If the optical band gap and electrical conductivity of the ions irradiated ZnO thin films are considered, it can be construed that such thin films can be used in the fabrication of optoelectronic devices such as blue, violet or UV LEDs and transparent electronics.
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