

**ION BEAM MODIFICATION OF TRANSPARENT
CONDUCTING OXIDE (TCO) THIN FILMS BY keV IONS**

by

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31 November 2019

Candidate's Declaration

I declare that ION BEAM MODIFICATION OF TRANSPARENT CONDUCTING OXIDE (TCO) THIN FILMS BY keV IONS is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

I further declare that I submitted the thesis to originality checking software and that it falls within the accepted requirements for originality.

I further declare that I have not previously submitted this work, or part of it, for examination at Unisa for another qualification or at any other higher education institution.

Olakunle Oluwaleye

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Abstract

In this work, ion beam induced modification in ITO and ZnO thin films of thickness 100 and 120 nm, respectively, used in spin based magnetoelectronic and optoelectronic nanodevices have been studied. These films were implanted by Co^+ and V^+ ions at different energies. The implanted films have been characterized by different material characterization techniques, and the effects of transition metal ion implantation on their properties have been investigated.

Lattice parameters showed interesting changes while the transmittance of thin film implanted at 1×10^{16} ions/cm² increased to 82.34 %. An increase in bandgap was observed with increase in ion fluence from 0 to 1×10^{16} ions/cm². The thin film implanted to 5×10^{16} ions/cm² showed decreased in roughness with root mean square (Rq) roughness of approximately 17.4 nm, and the grain size decreases to 4.59 nm. It was found that low thermal factor affects the stability of implanted films by 15.70 %.

In Co^+ ion implanted RF - magnetron sputter deposited zinc oxide thin films, the lattice strain was observed to decrease by 10.92 %, while grain size increased by 34.82 % at high ion fluence. Hence, ion implantation enhanced the mechanical strength of ZnO. The optical band gaps of implanted samples showed interesting improvement.

The crystalline quality of ITO thin films was observed to be enhanced upon implantation. It was found that the Co^+ ion implanted ITO thin films have good ability to retain a certain amount of residual magnetic field at zero magnetizing force, as ion fluence increases. The Co^+ ion implanted ITO thin films were found to exhibit clear room temperature ferromagnetism. The shift in hysteresis loops along applied magnetic field axes provides information about the exchange bias on as-grown and Co^+ ion implanted ITO thin

films in relation with grain size. At low ion fluence, a sharp increase in conductance was recorded. Therefore, the modification of ZnO and ITO thin films eventually leads to enhanced properties. Co^+ and V^+ ion implanted ZnO and ITO thin films have potential applicability in optoelectronics, spin based magnetoelectronic and energy nanodevices.

Keywords:

ZnO and ITO thin films, polyethylene terephthalate (PET) substrates, transparent conducting oxides, structural, optical, electrical and magnetic properties, Ion implantation, exchange bias, thermal stability, Dilute magnetic semiconductors

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List of Acronyms

- TCO: Transparent Conducting Oxides
- SnO₂: Tin oxide
- In₂O₃: Indium oxide
- ITO: Indium Tin Oxide
- ZnO: Zinc Oxide
- FE-SEM : Field Emission - Scanning Electron Microscopy
- AFM: Atomic Force Microscopy
- XRD: X-Ray Diffraction
- UV-Vis: Ultraviolet-Visible Spectroscopy
- VSM: Vibrating Sample Magnetometry
- PPMS: Physical Properties Measurement System
- I - V: Current - Voltage
- TFTs: thin film transistors
- TTFTs: Transparent thin film transistors
- W-H: Williamson-Hall
- FTIR: Fourier Transform Infrared Spectroscopy
- SRIM: Stopping and Range of Ions in Matter
- TRIM: Transport and Range of Ions in Matter

- H_{ex} : Exchange bias
- FM: Ferromagnetic
- AntiFM: Antiferromagnetic
- M_s : Magnetic moment
- H_c : Coercivity

Chapter 1

Introduction

1.1 Background

Transparent conducting oxide (TCO) thin films of tin oxide (SnO_2), indium oxide (In_2O_3), zinc oxide (ZnO) and their mixtures are a special group of materials identified with electronic conductivity and transparency. These materials have been extensively used in optoelectronic applications such as solar cells, flat-panel displays, and light emitting diodes (LEDs) [3]. Ion implantation makes it possible to substitute some fraction of TCO thin film atoms by group IB - IIIB transition metals. TCO thin films have been found to be potential candidates for applications in spin based magnetoelectronics and nanodevices [5, 6, 7].

TCOs are transparent due to their large band-gaps. They can also accommodate very high electronic doping concentrations to produce high conductivities. These thin films are traditional oxides and are structurally defined as tetrahedrally-coordinated cation and n-type carriers [5]. Furthermore, the

fundamental sources responsible for charge transport in these thin films are: oxygen vacancies, interstitial metal ion impurities, and doping ions [5]. The oxygen vacancies and the interstitial metal ion impurities are inherent and always act as electron donors [5, 1].

TCOs based on SnO_2 are of great significance in the field of nanodevices as a wide band-gap semiconductor [5]. The conduction electron-carrier generation results from the presence of oxygen vacancies in SnO_2 . This is also the case in both ZnO and In_2O_3 . SnO_2 thin films have found wide range of applications in corrosive environments as a result of their stability [7]. In addition, SnO_2 thin films are scratch resistant, can withstand high temperatures and are chemically inert [8]. For example, when doped with fluorine the electrical conduction of the thin films was improved [8, 9, 10, 11].

Indium oxide (In_2O_3) thin films are highly degenerate wide band-gap semiconductors [12]. Indium Tin Oxide (ITO) produces the highest available transmittance for visible light and the lowest electrical resistivity [12]. Its high conductivity is due to its high free carrier density [12]. Consequently, the ITO has been a material of choice on one of the electrodes in flat panel displays. It is generally believed that both substitutional tin atoms and oxygen vacancies are responsible for electron conduction in ITO [13].

Zinc oxide (ZnO) is a direct band-gap semiconductor with large exciton binding energy at room temperature [14]. This makes ZnO colourless and transparent. It is an essential material, which is widely used in voltage-dependent resistors (VDR) or varistors. A varistor has a non-ohmic current-voltage characteristic that is comparable to that of a diode [5]. Furthermore, piezoelectric properties of ZnO are used in surface-acoustic waves (SAW), optical wave-guides and laser diodes [14].

It is important to study how ion beams affect these notable roles of TCO thin

films in magnetoelectronics, optoelectronics and nanodevices. Ion beams are useful tools for the modification of materials [15, 16]. Such modifications take place at atomic and grain level, leading to alteration in the materials properties [5]. Hence, ion beams can help to control and tailor the properties of materials as per requirements [5]. As a result new materials with desirable properties, for specific applications, can be developed [5].

Moreover, the high interest in TCO thin films due to their numerous applications in nanotechnology have led to intense research in order to improve the properties of these materials. Furthermore, emerging physics from production and application of these thin films is of huge interest [5]. However, it is highly desirable to produce TCO materials with controlled and tailored properties. This will eventually lead to improved properties, and more uses for TCO materials. Amongst features motivating the exploration of new, modified and improved TCO nanodevices are high transparency, high conductivity, high work function, and low cost. Furthermore, best mechanical durability, high mobility, least toxicity, best chemical durability, increasing emphasis on improved processibility and environmental properties are additional driving factors. All these factors provide the driving force for the improvement of TCO materials both technologically and economically across a broad spectrum of applications.

Studies have shown that among the TM dopants ionic radius difference between tin (0.69 Å) and cobalt (0.75 Å) is small enough to permit cobalt to occupy tin sites in the tin oxide lattice structure [17, 18, 19]. As a result, cobalt characterized by electronic structure $[\text{Ar}] 3d^7 4s^2$, is found to be a suitable candidate which may be incorporated well in the indium tin oxide matrix and, possibly, resulting in interesting ITO properties. Furthermore, among the 3d TM dopants, from ^{21}Sc to ^{29}Cu , ionic radius difference between

Zn (0.74), cobalt (0.75) and vanadium (0.79) is small enough to allow cobalt and vanadium to fit Zn sites in the zinc oxide lattice structure [20]. In addition, vanadium dopants are interesting because V^{2+} can substitute for Zn^{2+} . This substitution is important, because it makes vanadium characterized by electron configuration $[Ar] 3d^3 4s^2$ to be a suitable candidate which may be **incorporated** well in the zinc oxide lattice structure and, possibly, resulting in ZnO thin films with completely different properties.

In addition, the incorporation of TM in ITO and ZnO thin films by ion implantation will result in the splitting of degenerated 3d states of free TM ions [21, 22, 23, 24]. The crystal structures of ITO (tetrahedral symmetry in cubic crystal) and ZnO (trigonal symmetry in hexagonal wurtzite) are usually influenced by the TM electron configuration [21, 25]. Besides, the TM electron configuration is further split due to vibrational contributions and spin-orbit interaction [24]. Consequently, the split of TM electron configuration results in partly allow transitions between these intra-3d states [21, 22, 23, 24]. In addition to spin based magnetoelectronic applications, these intra-3d states transitions could be used in optoelectronics and nanodevices [26].

It should be noted that focus will only be on transition metal ion implanted ITO and ZnO thin films at low energy (keV). However, various studies have been reported on ion beam irradiated TCO thin films at higher energy (MeV ions), and this is discussed briefly in Chapter 2 in order to provide an overview on modification of TCO thin films by MeV ions. Besides, it is important to investigate the effects of transition metals on the properties of ITO and ZnO thin films for development of better dilute magnetic semiconductors (DMSs), optoelectronics and nanodevices.

It has been shown that the most desirable properties and applications of ITO and synthesized ZnO thin films are highly band gap sensitive [20], which may

affect the behavior of nanodevices. In addition, magnetic moment, transmittance, average strain and stress, surface morphology and absorbance are strongly dependent on the level of modification [20]. Therefore, using either doping during growth or doping by ion implantation affects the properties of the doped thin films [27, 28, 29].

Ion implantation is popularly used for film modification after growth. It offers numerous advantages, such as incorporation of defects at a predetermined depth, controlled and precise fluence. There are numerous studies on transition metal (Sc, Fe, Cr etc.) doped ITO and ZnO thin films during growth in order to modify their physical properties[30, 31, 32]. For example, Chanda et al. [33] and Babu et al. [30] recently reported investigations of cobalt doped ZnO and synthesized ITO during growth. Thus, various doping during growth techniques, such as RF/DC magnetron sputtering [34, 35, 36], ion beam-assisted deposition[37], electron beam evaporation [38] as well as pulsed laser ablation [39] have been applied for modification of ITO and ZnO thin films. TM doped TCO dilute magnetic semiconductors (DMSs) are proving to be the most attractive classes of magnetic materials developed in recent years [40]. These materials exhibit ferromagnetism at or above room temperature applicable in spintronics-based multifunctional nanodevices [32, 40].

1.2 Problem statement

Wang et al. [41] have studied magnetic and structural properties of Fe^+ ion implanted ZnO single crystals, and did not find any correlation between Fe nanoparticles and ferromagnetism. However, they reported improvement in the crystal quality of the ZnO crystals. On the other hand, Ip et al.[42] have reported Mn^+ or Co^+ ion implanted ZnO. Although, there was no significant

change observed in the structural properties of Mn^+ or Co^+ ion implanted ZnO they, however, exhibited ferromagnetism. These studies indicate TM ion implantation in thin films is yet to be fully explored. To our understanding, modification of ITO thin films grown on flexible polymer substrates and ZnO thin films on borosilicate glass using transition metal ion implantation has rarely been reported in literature. Thus, the unique characteristics of partially filled 3d-shells and the charge states of TM ions will contribute to a better understanding on modification of TCO thin film properties. In particular, the characteristics of TM ions help to understand magnetic behavior within the DMSs [32, 40].

1.2.1 Aims and objectives

Implanting nanostructures with ion beams is a new emerging technology to modify nanomaterials. Ion implantation provides an active research field for the low-temperature processing especially in semiconductor technology. The ultimate aim of this study is to investigate the effects of transition metals, such as Co^+ and V^+ ions, on properties of ITO on flexible polyethylene terephthalate (PET) $(\text{C}_{10}\text{H}_8\text{O}_4)_n$ substrates and ZnO thin films on borosilicate glass for applications in spin based magnetoelectronic and optoelectronic, nanodevices and other applications, such as energy devices. The thin films will be characterized prior to and after implantation to investigate physical property changes following ion implantation. Properties of interest are as follows:

- Structural properties: crystallite size, strain, d -value, lattice constant, dislocation density, thermal and chemical stability, morphology properties and chemical bond analysis;

- Electrical properties: resistivity and conductivity;
- Optical properties: transmittance, absorption and band gap; and
- Magnetic properties: exchange bias, magnetic moment, coercivity and retentivity;

This study will provide fundamental information on transition metal ion implantation effects on TCO thin films, which may enhance their properties for applications in spin based magnetoelectronic and optoelectronic nanodevices.

1.3 Justification and significance of the research project

This study will provide crucial information and insight into the transition metal ion implantation effects on TCO thin films, establishing the physical mechanism underlying modification of TCO thin film properties. It is envisaged that this could lead to the enhancement of TCO nanodevices. This research will, therefore, contribute to a better understanding on using ion beam technology to analyze or modify nanomaterials. Furthermore, information on the effects of Co^+ and V^+ ion beam implantations on the properties of ITO and ZnO thin films will be documented and published in international peer review [journals](#) [17, 43].

1.4 Layout of the thesis

The layout of this thesis is as follows:

- Chapter 2 contains the review of transition metals, transparent conducting oxides, types of TCO materials, a discussion on the physics of

ion beam interactions with TCOs and modes of energy loss. A brief critical review of previous investigations and related problems of the TCO thin films modifications by ion beams, and ion beam analysis and microanalytical microscopy techniques are discussed in this chapter.

- The adopted methodology is discussed in Chapters 3 and 4. The methodology has three parts: First part is a simulation using Transport and Range of Ions in Matter (TRIM-2013) [44] to determine ion beam implantation parameters (energy, ion range, fluences), and it is presented in Chapter 3. Chapter 4 presents the second part of the methodology which is on (1) synthesis of ZnO thin films on boron silicate glass substrates using Radio Frequency (RF) Magnetron Sputtering and (2) implantation of the ITO and ZnO thin films using calculated ion beam parameters. Ion beam analysis and microanalytical microscopy techniques used to characterize Co^+ ion implanted ITO thin films, Co^+ ion implanted ZnO thin films and V^+ ion implanted ZnO thin films are discussed in the last part of Chapter 4.
- Chapters 5 and 6 present the discussion of the results.
- Chapter 7 will be the summary and concluding remarks on major findings.

Chapter 2

Theoretical Overview of Ion Beam Modification of Transparent Conducting Oxide (TCO) Thin Films

2.1 Introduction

The basic physical principles governing the behaviour of materials are well understood through materials physics [5]. However, the question of how certain nanomaterials behave under the influence of ion implantation requires more investigation. To investigate this problem, it requires a detailed understanding of the physics in this domain and ion-matter interaction in the nano-scale range of the particle size. Ion-matter interaction produces various types of non-equilibrium and non-linear states which can provide possibilities to develop new materials [5].

Implanting thin film with energetic ions results in the creation of a wide va-

riety of defect states in the thin film. As a result, the structural, electrical, optical, magnetic properties together with the thermal and chemical stability of the thin film change. The changes depend on mass of the incident ions, implantation energy and fluence [28].

El-Sayed (2004) [45] has shown that the ionization or excitation and possibly displacement of atoms from their sites in the lattice of TCO thin films occur after ion implantation. Furthermore, structural and microstructural phase transformation of high energy heavy ion irradiated TCO thin films have been reported [46, 29, 47].

Based on literature, it is well established that there are appreciable demands for TCO nanodevices as well as the need for new TCO nanodevices. In the field of optoelectronic devices, indium tin oxide (ITO) is recently in high demand [48]. ITO material comprises of In_2O_3 doped with some amount of atomic percent of Sn. Tin substitutes for In in the crystal lattice. The high demand of ITO films for flat panel displays and solar cells may not only make the price of ITO continue to rise, but it can also make indium not to be available in the near future. To enable simpler and cheaper device designs in flat panel displays, in particular to reduce signal loss and delay, it is of interest to further improve the properties of ITO. Moreover, present dominant markets for TCOs are in architectural window applications and fast growing photovoltaics industry [5]. Besides, demand is growing for materials having lower sheet resistance while retaining good optical properties [48]. The possible importance and application of ZnO devices are extensively discussed in [14], and it is reported that ZnO nanostructures may lead to a new generation of devices.

In this Chapter, an overview of the physical properties of transition metals in TCO and the characterization techniques used in this investigation are

discussed.

2.2 Transparent conducting oxide (TCO) materials

TCOs are combinations of a metal (A) and nonmetal (B), usually an oxygen, to form semiconductors, A_xB_y (where x and y are the relative molar fractions of the compound materials), characterized by different optical and electrical properties. Examples of TCOs are Nickel(II)oxide (NiO), Zinc oxide (ZnO), Chromium(III) oxide (Cr_2O_3), and Tin dioxide (SnO_2). Popular TCOs include Indium oxide (In_2O_3), Cadmium oxide (CdO), Gallium (II) peroxide (GaO_2), Titanium (II) oxide (TiO), Indium-Zinc-Oxide (In-Zn-O) etc.

By doping these TCO thin films, their properties such as optical, electrical and magnetic. can be modified. Basically, doping of TCOs can be done in three different ways, viz. doping during growth, ion implantation or diffusion. In diffusion process, higher controllability or more precise control, shallow implant, reproducibility of defects and impurity doping cannot be achieved [49]. As a result, diffusion is not very appropriate method to be used for TCO thin films modification. In addition, diffusion method requires high temperature.

Doping during growth has been extensively studied and realized in a successful way for TCO thin films, probably from 1907 up to date [50, 51, 52, 53, 54], and [55]. Some of the examples of doped TCOs during growth are CdO grown by thermally oxidation [56], Al doped ZnO thin films grown by chemical vapor deposition [57], [58] and [59], nitrogen doped SnO_2 grown by magnetron sputtering [60] and [61], $In_2O_3:Sn$ grown by Spray pyrolysis [62] and $In_2O_3:Sn$ grown by sputtering [63]. Further examples of doped TCOs during

growth include SnO_2 prepared by spin coating annealing [45], $\text{Mg}_{12}\text{Al}_{14}\text{O}_{33}$ [64], InGaZnO_4 prepared by sintering [65] and a-InGaZnO grown by PLD [66].

In the last two decades, there has been a rapid and constant growth in the number of TCO materials. Thus, there is continuation of development of TCO materials with progressive discovery of newer novel materials leading to diversity of TCOs. In addition to the traditional metal oxide based TCOs (SnO_2 , In_2O_3 , InSnO and ZnO), TCO materials now comprise graphenes, selenides, thin metal films, nitrides, conducting transparent polymers, sulphides, nanotubes and composites [50]. The technological advances in TCOs are driven by, amongst others, growing concern for climate change which then promotes the use of solar energy. TCOs are crucial components in solar cells and photovoltaics for solar energy applications. Furthermore, technological advances in TCOs can be attributed to studies of appropriate novel TCO materials and material-combinations (e.g delafossite materials, see Subsection 2.3.3). The emerging applications, such as sensor and transparent thin film transistors (TTFTs), can widen the use of TCOs and require completely different TCO properties, in special cases. Transparent spin based magneto-electronic is another application that contributes to technological advances in TCOs. TM doped TCO dilute magnetic semiconductors (DMSs) are some of the most attractive classes of magnetic materials developed in recent year[40]. TCO thin films are important components in any devices whose functions are based on both optical transparency and electrical conductivity.

2.3 Classification of TCO thin Films

TCO thin films can be discussed under two classes namely n-type and p-type, according to the defects and type of conduction [48]. These defects form split off acceptor levels above the valence band maximum in the case of p-type conduction, and donor levels below the conduction band minimum in the case of n-type conduction. It should be noted that the focus of this study is on n-type TCOs of ZnO and ITO thin films.

TCO thin films are naturally n-type degenerate semiconductors [48]. However, ZnO and ITO thin films are desirable in a wide range of technological applications. If binary TCO thin films are ion-implanted to increase the density of conducting electrons, the thin films can be classified as n-type. ITO is a typical example, which is formed from tin doped indium oxide. A more closely TCO to ITO in characteristics is Al doped ZnO (AZO). Similarly, TCO compounds can be formed when TCOs are combined to form material such as ZnIn_2O_3 and ZnSnO_3 [48].

2.3.1 n-Type Indium Tin Oxide (ITO) thin films

ITO is a ternary TCO grown by doping binary In_2O_3 with Sn metal. It is popularly grown by physical vapor deposition (PVD), such as magnetron sputtering and pulsed laser deposition (PLD) [48]. Its elemental composition typically comprises of 90% In_2O_3 and 10% Sn by weight. Sn doped In_2O_3 has cubic crystal structure, space group Ia-3 (Figure 2.1). In addition, indium oxide exhibit high transmission of visible light and high free carrier density. These characteristics enable ITO thin films to play crucial roles in TM doped TCO dilute magnetic semiconductors (DMSs), optoelectronics and nanodevices applications. Commercial ITO is popular due to its low re-

sistivity [12]. By avoiding extremely high carrier density, both conductivity and transparency with appreciable low resistivity can be achieved in ITO thin films.

The parabolic band structure of both indium oxide (Figure 2.2 (a)) and ITO

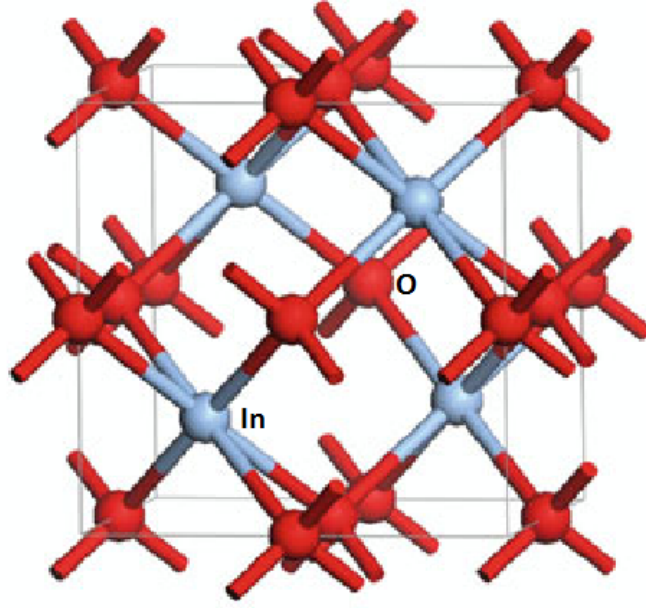


Figure 2.1: In_2O_3 crystal structure

(Figure 2.2 (b)) is illustrated in Figure 2.2. It is characterized by band gaps (E_g), valence band maxima and conduction band minima where Fermi wave number (K_F) and dispersion relations are presented. The occupied states are indicated by the shaded areas. The valence and conduction bands are shifted upward in Sn doped In_2O_3 (Figure 2.2 (b)). As a result, widening of the band gap by a Burstein-Moss shift (W) [1] is observed. This can be attributed to the lowest states in the conduction band being filled up [1].

In Figure 2.2 (b), m_c and m_v represent effective masses of the conduction band and the valence band, respectively. Furthermore, the direct band gap

(E_{go}) is equal to 3.75 eV. By optimizing Sn during the growth of ITO, the mobility, carrier concentration and the band gap (E_g) are increased. Consequently, it increases the carriers for conduction without changing the ITO transparency.

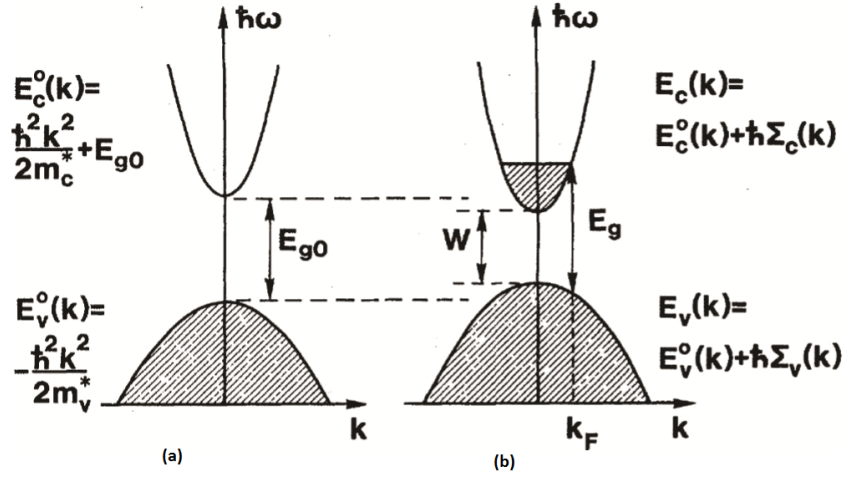


Figure 2.2: The proposed parabolic band structure of (a) In_2O_3 and (b) ITO [1]

2.3.2 n-Type ZnO thin films

ZnO is an n-type TCO thin film characterized by the hexagonal wurzite crystal structure as depicted in Figure 2.3 and direct band gap of 3.35 eV. The crystal structure has each O or Zn atom attached to four neighbors of the other atom. It has lattice constants of $a = 3.24 \text{ \AA}$ and $c = 5.19 \text{ \AA}$. ZnO is desirable particularly for solar energy applications (photovoltaic or solar cell). Apart from being a TCO, ZnO is a good candidate for a wider range of applications due to its wide band gap, and is a prototype direct band gap. It is found to be an alternative material for gallium nitride [67].

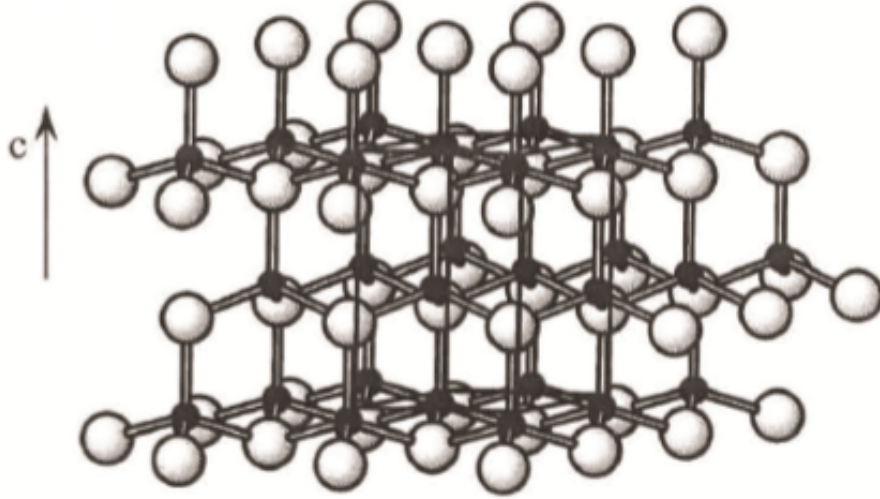


Figure 2.3: ZnO hexagonal wurzite crystalline structure popularly adopted

2.3.3 p-Type TCO materials

To develop p-type TCOs has proved to be harder. As discussed earlier, most of the wide band gap binary oxides have valence bands dominated by O 2p states. As a result, on acceptor formation, the acceptor states are localized on oxygen ions, leading to low conductivity. Therefore, developing p-type TCOs with good conductivity has remained a major problem [48]. After p-type NiO was identified in 1997, p-type CuAlO_2 was reported as a good candidate, due to its improved conductivity [68], [69]. Generally, the p-type TCOs reported up to now have lower conductivity than the conductivity reported for n-type TCOs.

Following this, focus has since been shifted to delafossites material-combination [70], [71]. The delafossites chemical formula can be written as BDO_2 , where B is a monovalent cation and D is a trivalent cation. It has layered crystal

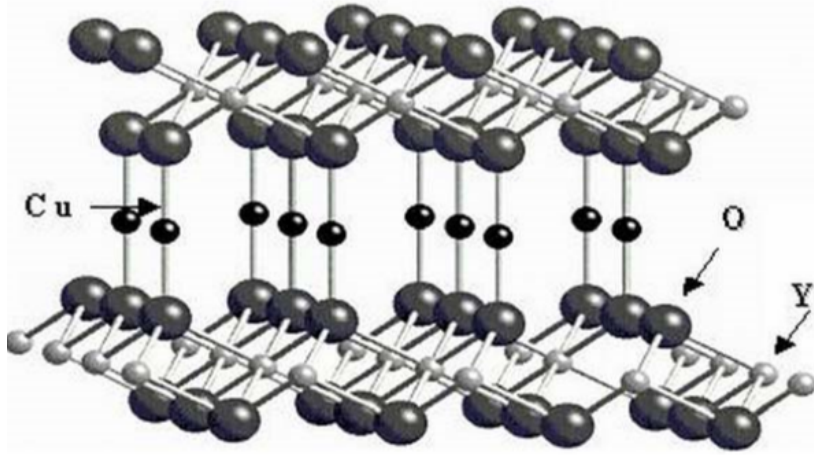


Figure 2.4: The delafossite crystal structure

structure. The layers of DO_2 and a cation are stacked. They are perpendicular to the c -axis, and it is a hexagonal. Figure 2.4 shows two alternating layers that have somewhat distorted edge-shared DO_6 octahedral and closepacked B-cation planes in two-dimensional creating linear $\text{O} - \text{B}^+ - \text{O}$ as observed in popular p-type material Cu_2O [70], [71]. In addition, the oxygen atoms are coordinated by one B^+ cation and three D^{3+} cations [72]. Cu based defossalites, CuDO_2 , is now a class of p-type materials. Thus, many Cu(1) based delafossites TCOs have been formed such as CuGaO_2 , CuInO_2 , CuCrO_2 and SrCu_2O_2 . These p-type TCOs are characterized with transparency and conductivity. Moreover, p-type Mg doped CuCrO_2 is still the delafossite known with highest conductivity.

In the last eight years, significant progress has been made in identifying a good p-type TCO material with higher conductivity and transparency. P-type ZnO has been recognized as a promising candidate with a potential of higher conductivity and transparency, when doped with shallow acceptors like nitrogen [48]. It is reported that when ZnO is doped with As, P, Sb and

F species it gives higher conductivity and transparency [48].

However, realization of good TCOs could significantly impact a new generation of transparent electrical contacts for p-type semiconductors and organic optoelectronic materials and, in conjunction with n-type TCOs, could lead to a next generation of transparent electronics.

2.4 TCO thin film properties of interest

2.4.1 Magnetic properties

Transition metals (TMs) are often used as dopants in non-magnetic TCO thin films in order to impart magnetic behavior [73, 74]. The physical properties of ITO and ZnO thin films, which makes them scientifically important and technologically desirable TCO thin films, have already been discussed in subsections 2.3.1 and 2.3.2, respectively. Just as the incorporation of dopants by using ion implantation to modify optical, electrical and structural properties is an important area of scientific research, imparting magnetic properties to a host of thin film such as ITO or ZnO using ion implantation is another highly relevant field of study. TM implanted dilute magnetic semiconductors (DMSs) are a special class of materials in which magnetic ions have been implanted into non-magnetic TCOs [40, 32]. DMSs exhibit semiconductor properties together with ferromagnetism at or above room temperature useful in spintronics-based multifunctional nanodevices [32, 40].

Basically, the origin of ferromagnetism in DMSs can be attributed to the TM 3d electronic structure, together with its host lattice structure interaction, which results in a spin-spin exchange mechanism between the magnetic ions [40]. Furthermore, the mechanisms commonly used to describe spin-coupling are bound magnetic polaron [75, 76, 77], double exchange [78, 79, 80], and

carrier exchange[40]. For carrier exchange interaction, a high number of free carriers for the spin coupling between 3d states is necessary [40]. This makes ITO a potential candidate in transparent spintronic applications due to its high carrier concentrations, according to the Zener model [40]. However, ZnO exhibits double positive exchange spin coupling mechanism with Co, V, and with all transition metal ions characterized by two charge state (2+), as shown in Table 2.2 [78, 81, 82].

As discussed in Chapter 1, TM ions, such as Co, are found to be incorporated well in ITO due to the comparable ionic radii of tin (0.69 Å) and cobalt (0.75 Å). Likewise, ionic radius differences between Zn (0.74 Å), cobalt (0.75 Å) and vanadium (0.79 Å) are small enough to allow cobalt and vanadium to occupy Zn sites in the zinc oxide lattice structure [20]. Moreover, the incorporation of TM ions into ITO and ZnO thin films by ion implantation results in the splitting of degenerated 3d states of free TM ions [4]. The partially filled 3d-orbital characteristics and the charge states (Tables 2.2 and 2.1) of TM ions contribute to better understanding of the magnetic behavior within the DMSs.

From Table 2.1, Cr has half-filled 4s-orbital while Co, V and the rest of TM have fully filled 4s-orbitals. Moreover, Table 2.2 shows charge states with corresponding electronic configuration of the 3d-orbital together with spin S of the 3d-orbital [4]. The d-orbital of TMs has ten available states to be fully-filled with electrons, however the 3d band of Co^+ and V^+ are partially-filled with 8 and 4 electrons associated with 1 and 2 spin, respectively. It can be clearly observed from Table 2.2 that Co^+ and V^+ ions can perfectly fit ITO and ZnO crystal sites due to partially-filled 3d-orbital and ionic radius difference, particularly with indication that all TM atoms fit a zinc crystal lattice [83, 84].

Table 2.1: The electronic configuration of TM ions [4]

TM	Electron configuration
Sc	$3d^1 4s^2$
Cr	$3d^5 4s^1$
Ti	$3d^2 4s^2$
V	$3d^3 4s^2$
Fe	$3d^6 4s^2$
Mn	$3d^5 4s^2$
Ni	$3d^8 4s^2$
Co	$3d^7 4s^2$

Table 2.2: Charge states, electronic configuration of the 3d-orbital together with spin of TM [4]

TM $3d^n$ -orbital electron	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$
Spin ($S = n/2$)	0	1/2	1	3/2	2	5/2	2	3/2	1
TM charge states	Sc ³⁺ V ⁵⁺ Mn ⁷⁺ Cr ⁶⁺ Ti ⁴⁺	Sc ²⁺ V ⁴⁺ Mn ⁶⁺ Cr ⁵⁺ Ti ³⁺	Sc ⁺ V ³⁺ Mn ⁵⁺ Cr ⁴⁺ Ti ²⁺	Sc ⁰ V ²⁺ Mn ⁴⁺ Cr ³⁺ Ti ⁺	V ⁺ Mn ³⁺ Cr ²⁺ Ti ⁰	Fe ³⁺ V ⁰ Mn ²⁺ Cr ⁺	Fe ²⁺ Mn ⁺ Ni ⁴⁺ Cr ⁰	Fe ⁺ Mn ⁰ Ni ³⁺	Fe ⁰ Mn ⁻ Ni ²⁺ Co ³⁺ Co ²⁺ Co ⁺

Thus, numerous studies have been reported on V or Co doped ZnO during growth and V or Co doped ZnO by implantation magnetic properties and modification of its other properties, amongst others, as briefly discussed below:

Yüksel et al. [85] synthesized Co doped ZnO DMS by using autocombustion method and determined its magnetic behavior, structural, compositional and morphological properties and found that Co doped ZnO exhibited clear ferromagnetism at 300K, a large coercivity of 560 Oe and good crystallinity.

By using ion implantation, Ip et al.[42] have doped ZnO with Mn^+ or Co^+ , after using catalyst-driven molecular beam epitaxy method to grow the ZnO on Ag-coated Si substrates. The implantation doses were ranging from 1 to 5×10^{16} ions/ cm^{-2} , and the Mn^+ or Co^+ implanted ZnO was annealed at 700°C for 300 sec. They reported that there was no significant change observed in the structural properties of the Mn^+ or Co^+ ion implanted ZnO, however, it exhibited ferromagnetism above 300 K with coercive fields greater than 100 Oe. Their results were similar to those reported for ion implantation of Mn^+ or Co^+ ions into bulk single-crystal ZnO.

The magnetization–coercivity (M–H) measurements of un-doped ZnO and Co doped ZnO were carried out by Chanda et al. [33] and observed that un-doped ZnO exhibited diamagnetism at 2 and 300 K. However, the induced coexistence of ferromagnetism and superparamagnetism at 300K and at 2k were observed in Co-doped ZnO.

Co implantation imparted magnetic behavior in ZnO was studied by Notorn et al. [86] and induced ferromagnetic properties were observed together with changes in structural properties. It was further observed that at 5 K coercive fields were less than 300 Oe, but at room temperature no hysteresis loop was observed.

Hong et al. [87] have investigated V doped ZnO thin films by using laser ablated method. They reported that V atoms substituted for Zn atoms in ZnO lattices. As a result, ferromagnetism at 300 K was observed showing a spin-glass-like behavior at temperatures less than 300 K. However, Zhou et al. [88] did not observe traces of ferromagnetism in V ion implanted ZnO, with the V ion implanted ZnO remaining in a crystalline state after implantation.

So given the above discussions and additional references [89, 90, 91, 92] on magnetic behavior of Co and V doped ZnO during growth and Co and V doped ZnO by implantation, changes in other properties of ZnO have not been fully explained. Therefore, we report on changes in other properties of ZnO on the same ion dopants in Chapter 5.

2.4.2 Electrical and optical properties

The electrical and optical properties of TCO are dominated by free electrons in the range of wavelengths that is relevant to optoelectronics and nanodevices. As a result, one can use Drude's theory [93] formulated for free electrons in metals to explain electrical and optical properties of TCO in the visible and the near-infrared regions. The theory assumes that when an electromagnetic field interacts with free electrons, it will cause the electrons to oscillate. This means the field may be polarized within the material [94, 95, 96, 97]. The popular one dimension Lorentz differential equation of motion of the oscillating electrons is given as[50]

$$m^* \ddot{\vec{x}} + \frac{m^*}{\tau} \dot{\vec{x}} + Kx = e \vec{E}(t). \quad (2.1)$$

Where:

- m^* equal to the effective mass;

- τ represents relaxation time of the electrons;
- $\ddot{\vec{x}}$ is the position of electrons;
- x is the displacement;
- e equal to the charge of the electron;
- $\dot{\vec{x}} = \vec{v}$ is the velocity of electrons;
- K represents the restoring force per unit displacement between the electrons and their host ion cores; and
- $\vec{E}$ is the electric field strength.

From Equation 2.1, the current density is given as [50]

$$\vec{J} = \frac{-\omega n e^2 \vec{E} / m^*}{[(\sqrt{K/m^*})^2 + \omega^2]}, \quad (2.2)$$

where n equal to carrier concentration, e equal to the charge of the electron and ω is the angular frequency. By considering the free electrons in a TCO, $\sqrt{K/m^*}$ can be equal to zero, because it is assume that restoring force K to the ion core equals zero [50]. Therefore, by dividing Equation 2.2 by $\vec{E}$, optical conductivity can be written as [50]

$$\sigma(\omega, \tau) = \frac{\omega n e^2}{m^*} \left\{ \frac{i\omega^2 + \omega/\tau}{\omega^4 + \omega^2/\tau^2} \right\} = \frac{n e^2}{m^*} \left\{ \frac{i\omega\tau^2 + \tau}{1 + \omega^2\tau^2} \right\} = \left\{ \frac{\sigma_0}{1 + \omega^2\tau^2} \right\} + \left\{ \frac{\sigma_0 i\omega\tau}{1 + \omega^2\tau^2} \right\}, \quad (2.3)$$

where τ represents relaxation time. Equation 2.3 consists of real and imaginary parts of the conductivity as a function of frequency. It controls the free-carrier absorbance in a TCO, where $\sigma_0 = \text{d.c. conductivity}$ given as $\frac{n e^2 \tau}{m^*}$ (Equation 2.5).

In a medium with negative dielectric permittivity, the wave vector is usually

imaginary resulting in the exponential decay of light. This means electromagnetic light can not travel through such a medium. Thus, there will be a total reflection of the electromagnetic light, incident on the medium. Furthermore, the plasma wavelength or frequency is given as [50]

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0\varepsilon_\infty m^*}}, \quad (2.4)$$

where m^* equal to the effective mass, n equal to carrier concentration, e equal to the charge of the electron and ε equal to permittivity. From Equation 2.4, the plasma wavelength ω_p depends on the carrier concentration n . Therefore, there is transparency from TCO thin films to the electromagnetic light whose wavelength is higher than the plasma wavelength. This means that TCO thin films will exhibit transparent characteristics at wavelengths greater than plasma wavelengths, because the varying electric field of the incoming light will no longer have any effect on the electrons. However, TCO thin films will reflect the incoming light at wavelengths lower than plasma wavelengths. Moreover, TCO thin films will absorb the incoming light at wavelengths greater than the band gap of the material. In nearly all the TCOs, the plasma wavelength is near the infrared, while the visible region can be found in the higher transparent wavelength range (400 nm to 700 nm). The plasma wavelength is directly proportional to the square root of the carrier concentration (Equation 2.4). Therefore, the resistivity, the plasma wavelength and the carrier concentration of TCOs usually increase in the same proportion [98].

Mobility and carrier density

ITO and ZnO thin films are characterized by relatively high carrier concentrations due to induced defects in the thin films and the impurity concentration

around the conduction band minimum. A high carrier concentration will result in absorption of electromagnetic light. Consequently, there is a compromise between optical transmission and electrical conductivity properties in ITO and ZnO thin films. If there is an increase in either the mobility or the carrier concentration of ITO and ZnO thin films, it will result in reduction in their electrical resistivities. A typical semiconductor has a mobility that is determined to be around $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [50]. By increasing the number of carriers, it will result in increased of visible light absorption. However, the increase in carrier mobility does not have negative influences on the figure of merit (FOM) of ITO and ZnO thin films [50]. Thus, the aim should basically be to increase carrier mobility in ITO and ZnO thin films, and hence FOM of the thin films, since this would eventually increase the electrical conductivity and optical transmission. Therefore, conductivity σ is directly proportional to the carrier density as shown in equation 2.5.

$$\sigma = \frac{ne^2t}{m}, \quad (2.5)$$

where t is the film thickness, n is the carrier density, e represents electronic charge and m represents the mass of charge carriers.

The absorption coefficient and the photon energy

To this point, the concept of band structure and direct band gap energies have been discussed. However, TCO optical properties have been probed using UV-Vis spectrometry. As a result, the focus here will be on the optical band gap energies of ITO and ZnO thin films.

Therefore, the results of optical transmittance (T) and optical absorption obtained from UV-Vis are analysed using the Tauc model [99] to estimate the optical band gap energies of the thin films. The model best defined the

relation between the absorption coefficient and the incoming photon energy as

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (2.6)$$

where A is a constant, E_g is the optical band gap and α is given as

$$\alpha = \left(\frac{1}{d}\right) \ln \left(\frac{1}{T}\right), \quad (2.7)$$

where d is the thickness of the films.

2.4.3 Structural properties

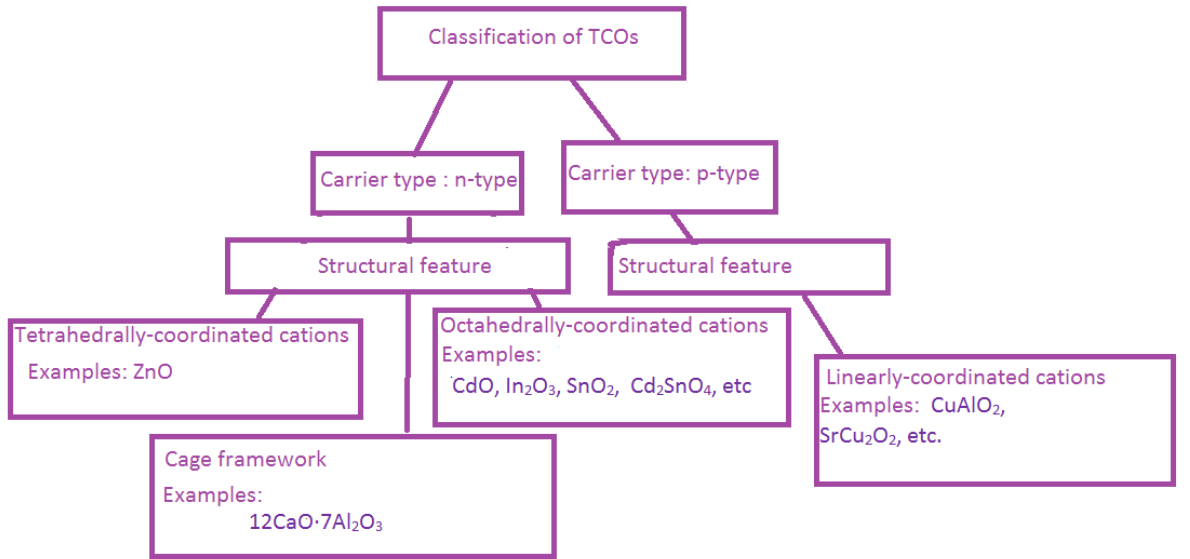


Figure 2.5: Structural classification of TCOs into four major classes

Figure 2.5 shows structural classification of TCOs into four major classes [50]. The first class, characterized by n-type, is tetrahedrally coordinated by

oxygen cations. The renowned TCO oxide in this class is Zinc oxide. The biggest group of TCOs belong to the second class of octahedrally-coordinated cations, which is also characterized by n-type. Examples of TCOs in this class include Cd_2SnO_4 , In_2O_3 , CdO and CdIn_2O_4 . These TCO materials are n-type multifaceted oxide materials with good performance [50]. The third class, characterized by p-type carrier, has oxygen with cations in linear coordination. In addition, the third class includes delafossites materials (discussed in Subsection 2.3.3). The cage-structure oxide, $12\text{CaO}7\text{Al}_2\text{O}_3$, is the last class also characterized with n-type [50].

2.4.4 Thermal and chemical stability

A temperature, which is somewhat greater than the deposition temperature, will not in any form affect TCOs. The resistivity of TCOs usually increases when they are heated to high temperatures for lengthy period. Furthermore, the chemical stability of TCOs depends on their ability to stand against corrosive chemical environments. Material chemical stability is inversely proportional to the ease with which the material can be scratch. As discussed earlier (Chapter 1), SnO_2 thin films are popularly applicable in corrosive environments due to their scratch resistance and high thermal and chemical stabilities. However, ZnO is not chemically inert, and cannot withstand acidic attack.

With EXPO2014 software [100], one can perform Isotropic (Iso) refinements using the average factors calculated from the simulated crystal structures to determine thermal parameters. The B-factors, indicating the relative vibrational motion of different parts of the crystal structure due to thermal effect, is the Debye -Waller factors. For a given atom in a stationary position, its

atomic scattering factors, f , change to f_T as follows [101]:

$$f_T = f \exp(-B \sin^2 \theta / \lambda^2), \quad (2.8)$$

where, T represents temperature, B is mathematically defined as $B = 8\pi^2 \langle u^2 \rangle$, $\langle u^2 \rangle = U$ = mean square vibrational amplitude. This theoretical calculation is employed in this work to estimate the thermal and chemical stabilities of TCO. Chapters 5 and 6 discuss the detailed results obtained from EXPO2014 software to estimate the thermal and chemical stability of ITO and ZnO thin films.

2.5 Ion beam implanted TCO thin films

Ion implantation is a doping technique with numerous advantages, as discussed earlier (Section 1.1). When a dopant is ionized, and accelerated into a thin film, it will travel through the material until all its energy is lost and comes to rest, then the ion is said to be implanted into the thin film. However, acceleration energy, ion beam type and substrate material determine the average penetration depth in thin films. As a result, from each ion implanted, atoms of TCO thin films will be displaced from their original positions. This would result in modification of individual TCO thin film properties. However, when the projected range of an ion beam is longer than the film thickness, the ion species will travel all the way into the substrate. Therefore, ion beam will induce damage in both the thin film and the substrate. The concentration of the dopant introduced into the thin film is directly proportional to the ion fluence.

2.5.1 Ion beam interactions with TCO thin films

Remarkable developments in ion beam technology are making it possible to modify materials with desirable properties for specific applications. In order to analyze changes induced in TCO thin films by ion implantation, it is important to discuss how ions lose energy when they interact with materials. There are two ways in which energy is lost when ion travels through a solid material. First, the nuclear energy loss as a result of elastic collisions with the nuclei of materials at low energies. At these energies, the incident ion loses its energy to the nuclei of materials. Secondly, energy loss occurs at higher energies, where ions experience inelastic collisions, and it leads to excitation of electrons. This is called the electronic energy loss.

Stopping power

When an ion travels through a material, as it penetrates deep into the material, it will interact with atoms in its path and lose energy (E) per unit path length of the ion (x), and it will stop at some point. The interaction involves two independent processes namely nuclear stopping and electronic stopping as discussed earlier (Subsection 2.5.1). Figure 2.6 shows the contribution of both the nuclear and the electronic stopping to the total stopping power. Lower energy phase (phase 1) in Figure 2.6 is characterized by nuclear stopping. This is indicated for its maximum height in the left corner of the phase 1 while the electronic stopping is evident for its maximum at the center of intermediate energies phase 2. Therefore, the total stopping power S can be mathematically defined as [2]

$$S = \left(\frac{dE}{dx} \right)_n + \left(\frac{dE}{dx} \right)_e, \quad (2.9)$$

where subscripts n and e represent nuclear and electronic stopping powers, respectively. Equation 2.9 measures the relative distribution of ion and how deep the ion travels into the materials. If S is divided by target density, ρ , the stopping cross section, Ω , can be determined as follows [2]:

$$\Omega = -\frac{dE}{\rho dx}, \quad (2.10)$$

and the travel length L of ions having initial incident energy of E_i is defined as [2]

$$L = -\frac{1}{\rho} \int_0^{E_i} \frac{dE}{dx}. \quad (2.11)$$

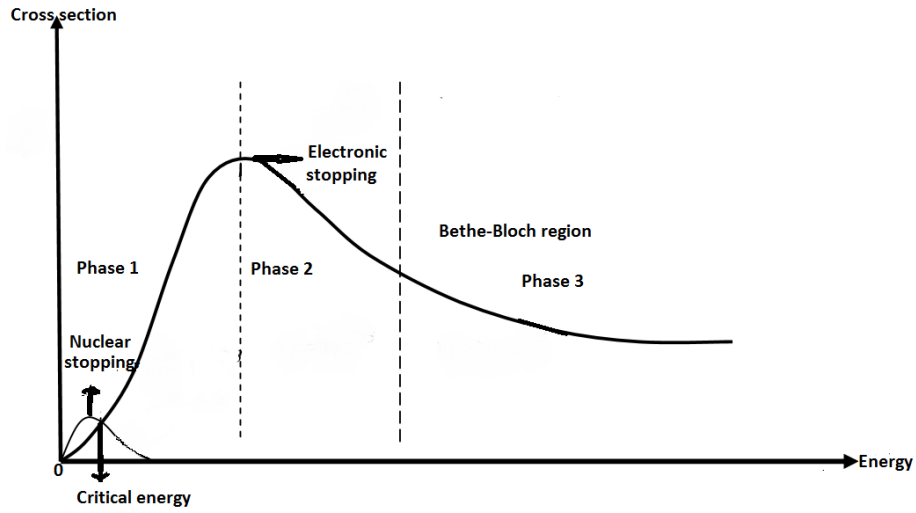


Figure 2.6: Illustration of both nuclear and electronic stopping contributions to the total stopping power process as a function of energy [2]

Nuclear stopping

From classical kinematics, equation 2.12 describes nuclear stopping as the coulombic c interatomic potential between two positive charges of ion and

target atoms during a collision. Equation 2.12 can be used for the approximation of nuclear scattering when the ion energies are greater than the nuclear critical energy given as $0.01Z_1Z_2(Z_1^{0.23} + Z_2^{0.23})(m_1 + m_2)/m_2$ keV, m equal to atomic mass [102]

$$V_c(r) = \frac{q^2 z_1 z_2}{4\pi\epsilon_0 r}, \quad (2.12)$$

where, Z_1 and Z_2 = atomic numbers, $V_c(r)$ = coulombic (c) interatomic potential, r = interatomic distance, q = electron charge and ϵ_0 = permittivity of free space. Nuclear stopping can also be described as collision events between an energetic ion and nucleus of atom, which results in scattering and transferring of all its energy to the atom in the material lattice.

Equation 2.12 accounts only for Coulombic potential. It does not consider screening function $\Phi(r)$ that needs to be considered if the ion energies are less or approximately equal to $0.01Z_1Z_2(Z_1^{0.23} + Z_2^{0.23})(m_1 + m_2)/m_2$ keV, there is usually spinning of electrons around the atomic nucleus. By considering screening effects, there are numerous methods for the calculation of interatomic potentials that have been reported, one of which is the Hartree-Fock charge distributions method [2, 103].

Nuclear stopping, which is a nuclear ion-atom interaction as discussed earlier, is a classical two-body problem. By factoring in screening function, the nuclear interaction is determined by the ion-atom Coulomb interaction potential screened by the electron. Therefore, the screened ion-atom interaction potential $V(r)$ is mathematically defined as [102]

$$V(r) = V_{elastat}(r) + V_k(r) + V_{ex}(r) \equiv \frac{\epsilon^2 z_1 z_2}{r} \Phi(r), \quad (2.13)$$

where $V_{elastat}(r)$, $V_k(r)$ and $V_{ex}(r)$ are electrostatic potential, kinetic potential and exchange potential, respectively, $\Phi(r)$ is equal to the screening function and

$$\epsilon^2 = \frac{q^2 z_1 z_2}{4\pi\epsilon_0}. \quad (2.14)$$

Moreover, the screening function has been simplified and presented as a universal function for an atom [102]. Consequently, the universal screening function is given by Thomas and Fermi [102]

$$\Phi(r) = \Phi_{Uni} \left(\frac{r}{a_{Uni}(Z)} \right), \quad (2.15)$$

where $\Phi_{Uni}(x)$ represents numerical screening function and $a_{Uni}(Z)$ is equal to screening length as a function of atomic number Z .

In addition, equation 2.13 will become universal ion-atom interaction potential $V(r)$ when it is combined with equation 2.15.

Furthermore, Figure 2.7 illustrates collision and scattering events of ion M_1

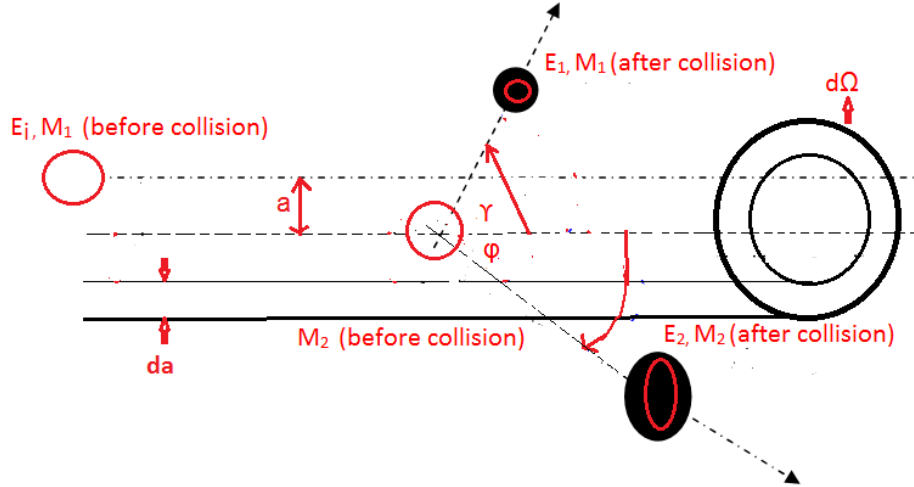


Figure 2.7: Scattering geometry of the implanted ion with initial incident energy

with initial incident energy E_i . The events are in relation to a differential scattering cross section $d\Omega$ and a projection of the projectile path onto the

target material atom M_2 axis, which is referred to as the impact parameter (a). As can be seen from the geometry of collision and scattering events (Figure 2.7), M_1 and M_2 were scattered into different directions as a result of M_1 colliding with M_2 , at scattered angles γ and φ , respectively. Thus, there is nuclear contribution $T(a)$ from M_1 to M_2 during the collision event. By applying the principle of conservation of energy and momentum, the nuclear contribution $T(a)$ is determined by working either in the center of mass frame (Equation 2.16) or in the laboratory system (Equation 2.17) [104],

$$T(a) = E_i \frac{4M_1M_2}{(M_1 + M_2)^2} \sin^2 \left[\frac{\varphi(a)}{2} \right]. \quad (2.16)$$

Equation 2.16 is given as a function of nuclear contribution to the target atom $T(a)$, scattered angle φ , impact parameter (a), atomic mass of implanted ion M_1 , initial incident energy E_i and atomic mass M_2 of target atom, where differential scattering cross section $d\Omega$ is equal to $2\pi a da$. Furthermore, the nuclear contribution calculated in the laboratory system is given as,

$$T(a) = E_i \frac{4M_1M_2}{(M_1 + M_2)^2} \cos^2[\varphi]. \quad (2.17)$$

By integrating over nuclear contribution to transferred energy T for all possible impact parameters, the nuclear stopping S_n can be determined as

$$S_n = N \int_0^{T_{max}} T d\Omega. \quad (2.18)$$

From Equation 2.18, N represents target atom per unit volume and T_{max} equal to maximum energy transfer.

Electronic stopping

During the electronic stopping process, the energy loss of incoming ion during interaction changes the arrangement of both the electrons of ion and atom.

There are different processes responsible for the energy loss in the electronic stopping process, which depend on the ion energy below and above the electronic critical energy. This means that the way the incoming ion interacts with electron is described in different models. Moreover, above and below the electronic critical energy, given as $22 (m_1/u) Z_1 Z_2^{0.4}$ keV, where u is equal to atomic mass unit, there are crucial states of electronic ion-atom interaction [102].

There are two main processes triggered by incoming ions with energies above the critical energy, namely, ionization and excitation of the atom (Figure 2.6 phase 2, where $v_1 \approx Z^{2/3}$). During these ionization and excitation processes, the incoming ion does not change, meaning that the ion is not strip of its electrons. By assuming absolute ionization of the ion, the solution of classical two-body collision problem of ion with free electron at rest is given as [102]

$$\hat{T}_e(a_e) = E \frac{4m_e}{m_1} \frac{1}{1 + (2a_e/b_e)^2}, \quad (2.19)$$

where $\hat{T}_e(a_e)$ is the classical estimation of the energy transferred to a single electron of the target atom, a_e represents impact parameter of the ion with respect to the electron, m_e is equal to the mass of the electron, which is less than the mass of the ion m_1 , E is equal to energy and b_e equal to collision diameter defined as [102]

$$b_e = \frac{\epsilon^2 z_1 m_1}{m_e E}, \quad (2.20)$$

where Z_1 represents atomic number, ϵ is equal to permittivity of free space and E is equal to energy. The energy transferred $T_e(a)$ to all electrons of the target atom is calculated by

$$T_e(a) \approx Z_2 \hat{T}_e(a), \quad (2.21)$$

In Figure 2.6 phase 3, the ion velocity v_1 is far greater than $v_o Z^{2/3}$ (first Born approximation). In this high energies phase, the ion is completely stripped

of all its electrons. The phase is popularly known as the Bethe-Bloch region [105, 106, 107, 108]. As can be seen in Figure 2.6, the electronic stopping cross section $\hat{S}_e(E)$ in this phase is described by the Bethe-Bloch non-relativistic expression defined as [105, 106, 107, 108].

$$\hat{S}_e(E) = \frac{4\pi Z_1^2 Z_2 \epsilon^4}{m_e V^2} L, \quad (2.22)$$

where L is defined as $L = In \left(\frac{2m_e V^2}{I} \right)$ and the average ionization energy I is mathematically defined as [102]

$$In(I) = \sum_n f_n In(E_n - E_0). \quad (2.23)$$

E_n and E_0 are energy transitions, and f_n the corresponding dipole oscillator strengths for target atoms. The average ionization energy I is approximated within the statistical model of the atoms, and it is approximated to be $10 \text{ eV } Z_2$.

On the other hand, there are some corrections to Equations 2.22 and 2.23 given as additional ΔL to L detailed by Ziegler [109]. These corrections are the shell correction C/Z_2 , the density effect correction $\delta/2$, Bloch correction $L_2 Z_1^2$, Barkas correction $L_1 Z_1$ and relativistic correction as given in Equation 2.24,

$$\Delta L = -In \left[1 - \left(\frac{v}{c} \right)^2 \right] - \left(\frac{v}{c} \right)^2 - \frac{C}{Z_2} - \frac{\delta}{2} + L_1 Z_1 + L_2 Z_1^2, \quad (2.24)$$

where v is the velocity, c represents speed of light, $C = \sum_{i=1}^{Z_2} e^{iqr_j}$, q represents wave vector and r is equal to the distance. However, there is a change of the ion and the target atom momentum including the transfer of energy from the ion to the target below the critical energy state, due to swap of the electrons of the projectile ion and the target atom, because, below the critical energy state, there is an increasing ion-atom interaction time that permits

the electrons of the atom and the ion to swap. Therefore, Firsov original model [102] determined the analytical transferred energy $T_e(a)$ below critical energy of 22 (m₁/u) $Z_1 Z_2^{0.4}$ keV as

$$T_e(a) = \frac{0.35(Z_1 + Z_2)^{5/3} \epsilon^2 / a_0}{[1 + 0.16](Z_1 + Z_2)^{1/3} a / a_0]^5} \frac{v}{v_0}, \quad (2.25)$$

where $v_0 = \epsilon^2 / \hbar$, v is the velocity, $a_0 = \hbar^2 / (m_e \epsilon^2)$ is the Bohr radius and $\hbar = h / (2\pi)$

Due to the swap of electron, the derivation of new model suggested by Firsov [110, 111] for the transferred energy from the projectile ion to a target is detailed in [102]. Bhalla et al. [112], Winterbon [113], Cheshire et al. [114], Land and Brennan [115] further reported modification of the original Firsov model.

Energy loss in compound targets

The concept of energy transfer discussed to this point was about a target consisting of single element. The energy transfer in target compounds consisting of two or more elements is yet to be discussed. Moreover, compound targets are the most popular systems and are very crucial in this study since the materials of interest are compound TCOs of ZnO and ITO thin films (Subsection 1.2.1).

Ions and compound targets interaction processes are well described by Bragg's rule [102], where it is assumed that the interaction processes between ions and compound targets $C_a D_b$ of different elements C and D (where a and b are the relative molar fractions of the compound materials) are statistically independent of the incoming target atoms and without the influence of their binding. Then, the total stopping power S of incoming ion penetrating the

compound target and the expression for multiple scattering ψ are given in Equations 2.26 and 2.27, respectively [102]

$$S = -\frac{dE}{dz} = \sum_i \left[N_i (\hat{S}_{n,i} + \hat{S}_{e,i}) \right] \quad (2.26)$$

$$\psi^2 = \Delta z \sum_i \left[N_i (Q_{n,i} + S Q_{e,i}) \right], \quad (2.27)$$

for a target atom of type i $Q_{n,i}$ and $Q_{e,i}$ are the nuclear and electronic additions to the multiple scattering cross section, N is the atomic density and i equal to the different types of compound target elements (C, D..)

Therefore, the condition under which a material will be modified due to the nuclear energy loss will depend on the probability to annihilate the material, the beam's ability to induce stable or metastable phase transitions, the diffusion properties of the implanted species and on the defects formed [5]. On the other hand, materials will be modified through electronic energy loss due to the efficiency and the rate of energy transfer from the target electrons to the target lattice [5]. Moreover, depending on the materials properties, modification of materials can be achieved when the energy transferred to electrons is higher and above the threshold value for electronic energy loss [5]. Therefore, tailored new materials with unique properties can be produced, as ion beams induce non-equilibrium states in materials.

2.6 Ion beam analysis techniques

Ion beam analysis or material characterization using ion beams provide a non-destructive way to investigate the elemental composition or properties of a material. When ion beams hit the surface of a material, it results in numerous processes such as scattering, photon emission or reaction simultaneously [5]. As a result of this interaction, secondary radiation and particles are emitted.

Through these processes various analytical techniques have been developed. These techniques are classified based on the process and the method of detection of the products resulting from the interaction. Furthermore, each technique gives unique information. There are different techniques available for the characterization of materials such as Vibrating Sample Magnetometry (VSM), Current –Voltage (I-V) Characterization, Ultraviolet-Visible Spectroscopy (UV-Vis), X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) . In this work, these techniques were used to analyse the properties of Co^+ ion implanted ITO thin films on PET substrates, Co^+ ion beam implanted ZnO on borosilicate glass substrates and V^+ ion implanted ZnO on borosilicate glass substrates. The techniques are discussed in more detail in Chapter 4.

2.7 Ion beam modification of TCO thin films by keV ions

In recent years, reports have shown the possibilities of materials modification by keV to MeV ion beams [5, 116, 8]. There has been increasing evidence that the properties of materials can be modified in a controlled way to make them useful for specific applications when irradiated with ion beams [5]. The materials were modified by keV ion beams at different fluences and under different physical conditions such as temperature and pressure [5].

In the literature, there is very little information on ion beam modification by keV ions, most of the information available is modification by MeV ions. Therefore, previous studies reported on modification of properties of the TCO thin films by MeV ion beams are briefly discussed below.

CdO thin films irradiated with 120 MeV Ag⁹⁺ ions

The changes induced in electrical, optical and structural properties after CdO thin films were irradiated with 120 MeV Ag⁹⁺ ions were reported in 2011 by Kumaravel et al. [116]. It was demonstrated that Swift Heavy Ion (SHI) irradiation decreases surface roughness and charge carrier concentration. An increase in the resistivity of CdO thin films due to radiation induced defects was observed [116]. In contrary, optical transmittance decreased when the fluences of Ag⁹⁺ ions were increased.

SnO₂ thin films irradiated with 120 MeV Ag⁹⁺ ions and 100 MeV Au⁸⁺ ions

Irradiating SnO₂ thin films with 120 MeV Ag⁹⁺ ions revealed that their crystallite size increased with increase in fluence up to 1×10^{12} ions cm⁻² [8]. Thereafter, their crystallite size started to decrease when the films were irradiated at fluences from 1×10^{11} ions cm⁻² to 1×10^{13} ions cm⁻² [8]. The surface morphological modification of SnO₂ thin films was achieved, and the band-gap of irradiated thin films was found to be in the range of 3.56 - 3.95 eV compared to 2.1-3.1 eV for un-irradiated SnO₂ thin films. With regards to the electrical properties of the thin film, it was observed that resistivity decreased when the ion fluence was gradually increased up to 5×10^{12} ions cm⁻² [8]. The resistivity was thereafter found to increase with further increase in ion fluence.

In another study, SnO₂ thin films were irradiated with 100 MeV Au⁸⁺ ions by Manoj et al. [7]. The changes in structural and optical properties of irradiated SnO₂ were attributed to thermal annealing due to ion beam induced nanocrystallinity. It has further been reported [7] that the decrease in optical

band gap observed in irradiated SnO_2 can be attributed to the variation in grain size due to structural modification.

Indium based oxides

Direct-current magnetron sputtering deposited ITO thin films were implanted with either 50 keV O^+ or 120 keV Ar^+ ions to a fluence varying between 3×10^{13} and 1×10^{16} ion/ cm^2 for the O^+ implantation, and a fluence of 1×10^{16} ion/ cm^2 for the Ar^+ implantation and effect of O^+ ion implantation was studied by Vink et al. [117]. They observed that ion implantation of ITO thin films results in the deactivation of carriers as a function of the O^+ implantation fluence.

In_2O_3 thin films were irradiated with 100 MeV O^{7+} ions at different fluences [12]. Their surfaces were modified with surface roughness significantly reduced, and their resistivities were observed to have decreased by about one order of magnitude at high fluences [12]. Furthermore, the average optical properties and charge mobility of irradiated thin films were observed to have decreased. Moreover, the preferred orientation (222), was changed to (400) after irradiation. In as-deposited films, their obtained irregularly shaped grains were changed to "radish-like" shaped grains when irradiated at a fluence of 5×10^{11} ions cm^{-2} [12].

On the other hand, studies of structural properties of Molybdenum doped In_2O_3 thin films with 100 MeV O^{7+} ions showed that the X-ray diffraction intensity of the prominent (222) peak decreased when ion fluence was increased [12]. The total destruction of (211) peak was observed at a fluence of 1×10^{13} ions cm^{-2} . Also revealed to have decreased at this fluence were charge mobility, average transmittance, grain size and root mean square values of

irradiated Molybdenum doped In_2O_3 thin films [12].

In 2010, structural modification in sub-stoichiometric indium oxide (In_xO_y) by 120 MeV Ag^{9+} ions were studied by Tripathi et al. [118]. Indium clusters with small amounts of In_2O_3 phases were observed as a separated phase after irradiation [118]. The loss of oxygen led to a phase separation of In_xO_y into In and In_2O_3 [118]. Improvement in the crystallinity of indium cluster was further observed, also as a result of the preferential loss of oxygen that occurred during amorphous indium oxide irradiation [118]. The stoichiometric In_2O_3 was found to be radiation resistant and an increase in its electrical conductivity was observed after irradiation [118].

In addition, ion beam modification of transparent conducting ITO thin films has been studied by Heynes et al. [119]. In the study, the effects of ion implantation of different chemical species such as N^+ , O^+ , F^+ , Ne^+ and In^+ on the electrical and optical properties of ITO were examined under a variety of conditions such as low to moderate to higher fluence. At low to moderate fluences, damage effects and reduction of conductivity at fluences of approximately $10^{14}/\text{cm}^2$ were observed. When the implanted concentration becomes equal to the free-carrier concentration at higher doses, In^+ was found to improve conductivity slightly while species such as O^+ reduced the conductivity by several orders of magnitude [119].

ZnO thin films

Khoiki et al. [120] doped H^+ ions, accelerated to an energy of 100 keV, into the rf magnetron sputtering deposited ZnO by ion implantation and determined its conductivity and found that the conductivity increases by magni-

tude of $10^2 \Omega^{-1} \text{ cm}^{-1}$ after implantation. Structural and photoluminescence behaviors of Gd, N and Na implanted and annealed ZnO single crystal were studied by Kennedy et al. [121] and Gd ions were implanted at 40 keV while N and Na were implanted using 23 keV ion energy. They observed the presence of structural disorders in Gd implanted and oxygen annealed ZnO. It has further been observed that low temperature photoluminescence spectra from as-deposited and Gd implanted ZnO showed transitions from neutral bound exciton and two electron satellites. In N and Na implanted and annealed ZnO, a slight change was observed.

Moreover, ion beam modification of ZnO thin film properties, such as structural, electrical and magnetic properties, by keV to MeV ions has been reported by Angadi et al. [122]. The ZnO thin films were implanted with 80 keV Co^+ ions at fluences from 1×10^{16} to 5×10^{16} ions/ cm^2 . Angadi et al. [122] observed Co clusters upon implantation, however the Co clusters disappeared after irradiation resulted in decreased resistivity. In addition, ZnO co-implanted with Ag^{+15} and Co^+ ions and Ag^{+15} ions were implanted at 200 MeV exhibit room temperature ferromagnetism together with increased coercive field.

Chapter 3

Simulation of ion beam implantation parameters

3.1 Introduction

This study is divided into three parts, which are: (i) simulation of ion beam implantation parameters (energy, ion range, fluences etc. using SRIM and Transport and Range of Ions in Matter (TRIM-2013) [44], (ii) and (iii) which have been discussed in Chapter 4. It was crucial to start with simulations in order to determine Co^+ and V^+ ion beam implantation parameters and to estimate expected experimental results. Therefore, this chapter discusses theoretical calculations prior to ion implantation using SRIM-2013 software. SRIM is a popular software for simulating penetration and scattering of ions in a material. Moreover, SRIM can be used to simulate the energy and angular distributions of backscattered ions, together with transmitted ions in amorphous materials [2]. Furthermore, SRIM software is widely used to produce 3-D plots, determine ion distribution and ion projected range. SRIM is based on some approximations amongst others, there is a possibility

for a target atom with enough momentum and energy to be sputtered. In addition, the recombination of interstitial atoms with vacancies and influence of neighboring atoms are neglected (binary collision). By considering the approximations, SRIM shows excellent simulation efficiency. The software displays a reasonable degree of accuracy with error approximated between 5 % and 10 % [109].

3.2 SRIM and TRIM-2013 simulation

Table 3.1 presents SRIM and TRIM-2013 calculated ion beam implantation parameters such as projected ranges, R_p , implantation energies, film thicknesses, ion fluences, together with ion beams. Taking into consideration, ITO and ZnO thin film thicknesses (Table 3.1 Column 5) in all cases, the ion beam energies were selected to give calculated projected range, R_p , recorded in Colum 6 of Table 3.1. Moreover, incorporating the discussion in Section 2.5.1 one can determine that the R_p of 100 keV Co^+ ions in ITO thin films is equal to 46 nm, R_p of 170 keV Co^+ ions in ZnO thin films is 69.56 nm and the R_p of 170 keV V^+ ions in ZnO thin films is 73.98 nm. These estimated ranges were less than ITO and ZnO thin film thicknesses, hence, most of the Co^+ and V^+ ions were implanted within ITO and ZnO thin films, and modification was expected from defects produced in the films. The implantation fluence, F , can be determined using Equation 3.1 given as [109]

$$F = \frac{I \times t}{A} \times \frac{1}{q \times c}, \quad (3.1)$$

where t represents implantation time (seconds), I is equal to current (amperes), A is equal to area of the thin film (cm^2), q represents charge state of the ion and c is equal to the charge state of electron given as 1.6×10^{-19} *Coulombs*.

Table 3.1: SRIM calculated Co^+ and V^+ ion beam, implantation energies, thin film thicknesses, ion fluences, together with projected ranges, R_p in ITO and ZnO thin films

TCO thin film	Substrate	Ion beam	Energy (keV)	Thickness (nm)	Range, R_p , (nm)	Fluence ($\times 10^{15}$ ions/cm ²)
ITO	PET	Co^+	100	100	46.40	0.1
ITO	PET	Co^+	100	100	46.40	1
ITO	PET	Co^+	100	100	46.40	10
ITO	PET	Co^+	100	100	46.40	30
ITO	PET	Co^+	100	100	46.40	50
ZnO	borosilicate glass	Co^+	170	120	69.56	5
ZnO	borosilicate glass	Co^+	170	120	69.56	10
ZnO	borosilicate glass	Co^+	170	120	69.56	50
ZnO	borosilicate glass	V^+	170	120	73.98	5
ZnO	borosilicate glass	V^+	170	120	73.98	10
ZnO	borosilicate glass	V^+	170	120	73.98	50

As discussed in Section 2.5.1, Figures ?? show the created ion paths and displaced ions (Co^+ and V^+) and the surrounding collision cascades. When an ion travels deep into the target at keV energies, it will leave ion track along its path. By considering the approximation made in the software, it can be seen from Figures 3.1 (a), (b) and (c) that the ions travelled in straight free-paths between collisions (binary collision). Furthermore, the ion tracks were terminated, which may be because energy is reduced to a value below a pre-determined value. The nuclear energy loss and electronic energy loss were determined from TRIM calculations [44]. Thus, Co^+ ion and V^+ ion interactions with ZnO thin films, Co^+ ion interaction with ITO thin films and modes of their energy losses were simulated to determine dopant concentrations implanted fluences, total atom displacement, replacement collisions, critical energy and vacancy density as a result of implantation in this work.

3.2.1 Co^+ ion implantation into ITO thin films on PET substrates

TRIM calculations were performed for 100 keV Co^+ ion implantation into ITO on PET substrates. During the simulation, the displacement energy was 4.82 %. The electronic and nuclear energy losses were independent. In addition, it can be seen from Figure 3.1 (a) that a Co^+ ion travels in a random path as it penetrates the ITO film. As a result, it loses energy by electronic and nuclear collisions. It can be seen from Figure 3.2 and Table 3.5 that the calculated electronic energy loss and nuclear energy loss were 33.69 % and 61.49 %, respectively. Indicating that the nuclear part is the dominant mechanism of the energy loss per unit thin film thickness in the ITO crystal.

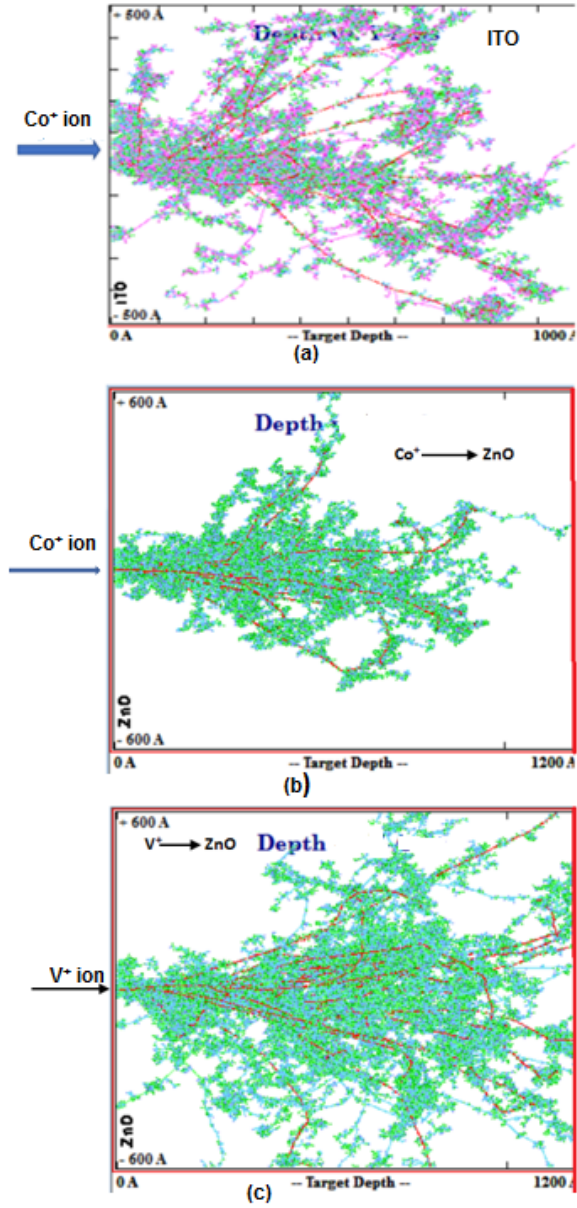


Figure 3.1: (a) Co⁺ ion implanted ITO, collision cascade within the ITO thin films and modes of energy loss (b) Co⁺ ion implanted ZnO, collision cascade within the ZnO thin films and modes of energy loss (c) V⁺ ion implanted ITO, collision cascade within the ZnO thin films and modes of energy loss

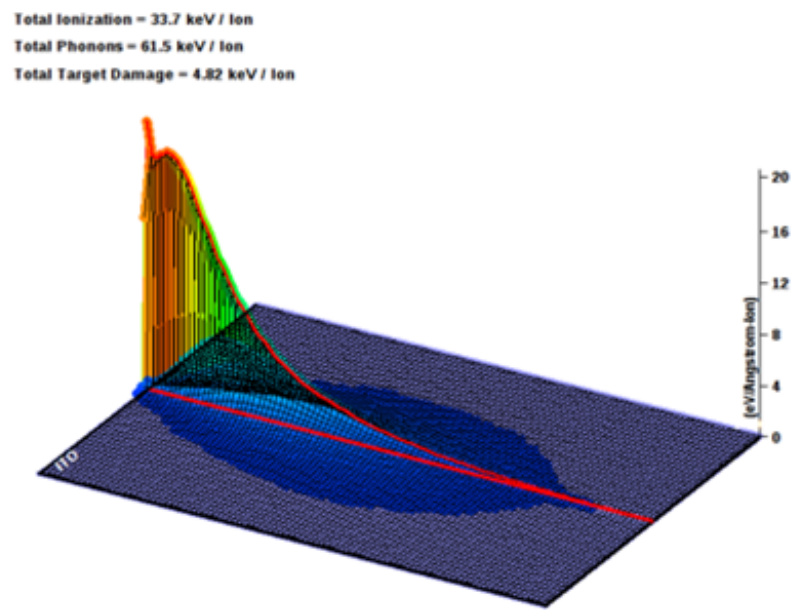
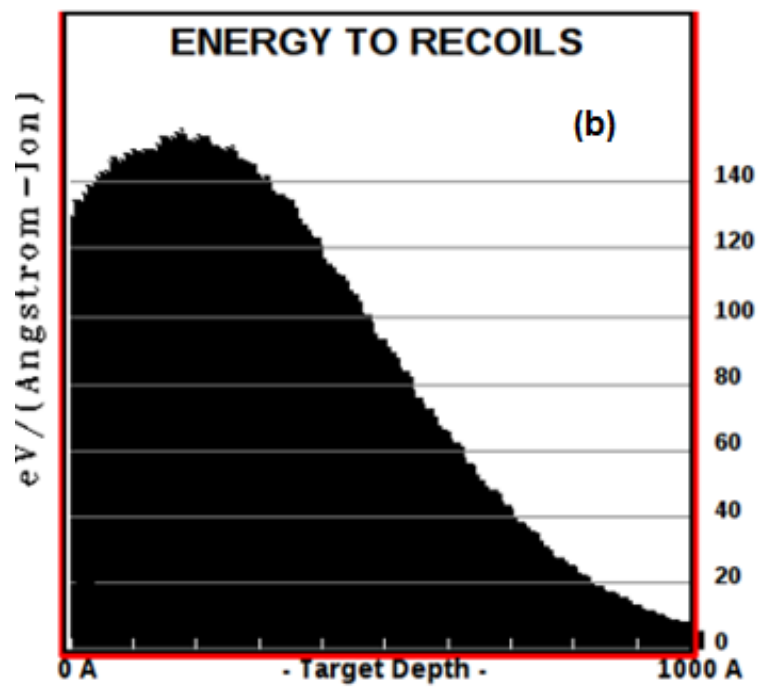


Figure 3.2: 3-D TRIM-2013 plots for Co^+ ion implanted ITO at 100 keV
 Co^+ ion showing mode of energy loss



Ion Distribution

Ion Range = 464 A Skewness = 0.156
Straggle = 229 A Kurtosis = 2.253

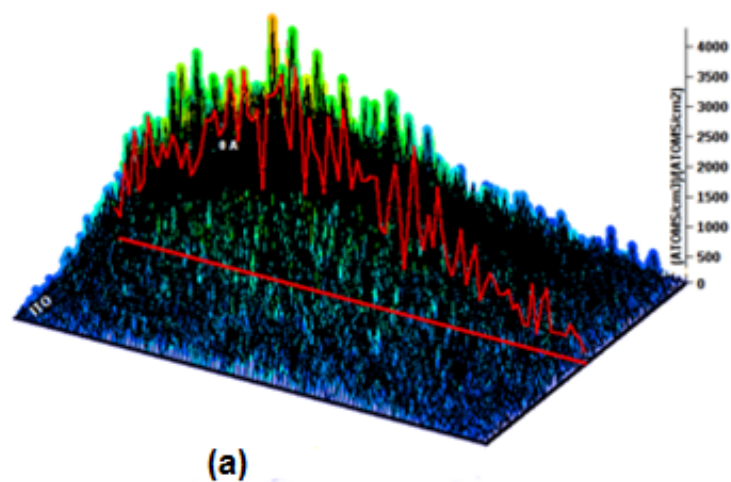
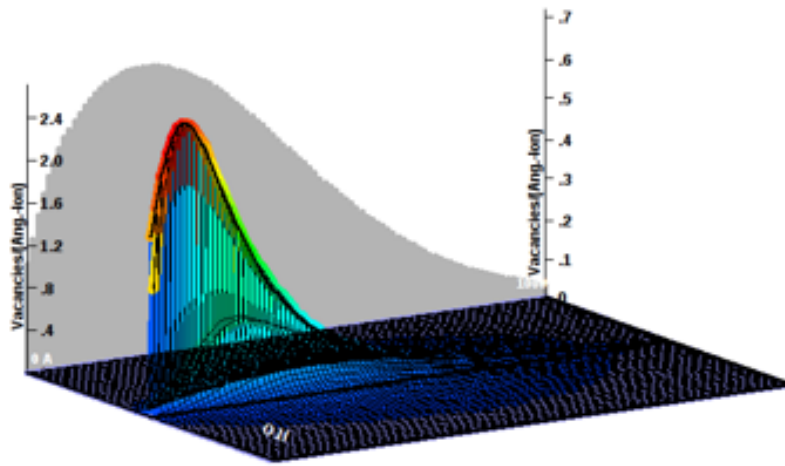


Figure 3.3: 2-D and 3-D TRIM-2013 plots for Co^+ ion implanted ITO at 100 keV (a) Co^+ ion distribution (b) Energy to recoil atom

Total Displacements = 1592 / Ion
Total Vacancies = 1557 / Ion
Replacement Collisions = 35 / Ion



(e)

Figure 3.4: 2-D and 3-D TRIM-2013 plots for Co^+ ion implanted ITO at 100 keV collision events showing total displacements, vacancies and replacement collisions

Furthermore, a simulation of 99999 ions results in the ion distribution observed in Figure 3.3 (a), where the R_p , which accounted for the average depth of the implanted ions, is found to be 46.40 nm with straggling of 22.9 nm in the X axis (depth axis). In Figure 3.3 (a), the Y axis was normalised by ion fluences. The dopant concentration, in Table 3.2 Column 2, was determined from Equation 3.2 given as,

$$\text{dopant conc.} = \text{fluence} \times \text{peak value of the ion distribution plot.} \quad (3.2)$$

Moreover, the collision events of Co^+ ion implanted ITO are shown in Figure 3.4. When ions penetrate a target, they collide with the target atoms and displaces them causing the creation of vacancies. In addition, another collision cascade may be started by recoiling target atoms with enough energy. As shown in Figure 3.4, this collision results in displacement collision (the total displacement collisions are the addition of the vacancies and replacement collisions), replacement collision, vacancy production and interstitial atoms. Consequently, the extended defects such as dislocation loops can be formed due to movement of vacancies and interstitial atoms in the target material [109].

Figure 3.4 shows a maximum vacancy of 2.8 vacancies per Co^+ ion. The vacancy concentration or vacancy density presented in Table 3.2 Column 3 was determined by using Equation 3.3,

$$\text{vacancy Conc.} = 2.8 \times \text{fluence.} \quad (3.3)$$

In addition, the critical energy density presented in column 4 of Table 3.2 is calculated from the energy to recoil atoms plot shown in Figure 3.3 (b), by applying Equation 3.4

$$\text{critical energy density} = \text{fluence} \times \text{maximum peak energy to recoil.} \quad (3.4)$$

To quantify the level of modification produced by the Co^+ ion beam, we calculated the displacement per atom (dpa), which is the fraction of atoms displaced from lattice sites by the incident ions. In this work, the density of ITO used is 5.17×10^{22} atoms/cm³. Hence, the dpa presented in Table 3.2 Column 5 is arrived at by using Equation 3.5,

$$dpa = \frac{\text{vacancy density}}{\text{material density}}. \quad (3.5)$$

It can be observed from Figure 3.5 that the vacancy concentration increased linearly with increased Co^+ ion beam dopant concentration.

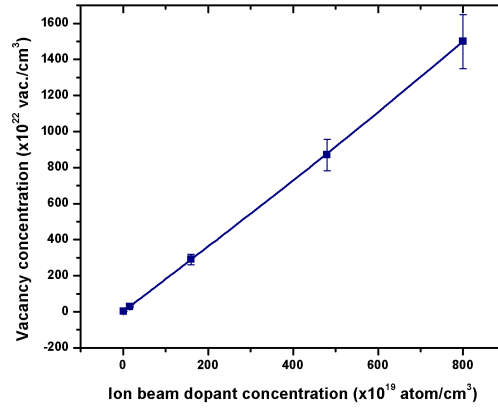


Figure 3.5: Vacancy concentration as a function of Co^+ ion beam dopant concentration for Co^+ ion implanted ITO on PET substrate at 100 keV

Table 3.2: TRIM-2013 calculated parameters for Co^+ ion implanted ITO on PET substrates at 100 keV

Fluence ($\times 10^{15}$ ions/cm ²)	Dopant conc. ($\times 10^{19}$ atom/cm ³)	Vacancy conc. ($\times 10^{22}$ vac./cm ³)	Critical energy dens. ($\times 10^{16}$ eV/cm ³)	dpa
0.1	1.6	2.9	1.6	0.56
1	16	29	16	5.60
10	160	290	160	56.0
30	480	870	480	170
50	800	1500	800	280

3.2.2 Co^+ and V^+ ion implantation into ZnO thin films on glass substrates

The 2-D and 3-D ion distributions for Co^+ and V^+ ion implanted ZnO thin films on borosilicate glass substrates are shown in Figures 3.6, 3.7 and 3.8. A simulation of 99999 ions resulted in the ion distributions observed in Figures 3.6, 3.7 and 3.8. Moreover, the R_p accounted for the average depths of implanted Co^+ and V^+ ions. Thus, TRIM-2013 calculated R_p for implanted Co^+ and V^+ ions were 69.56 nm and 73.98 nm, respectively, with stragglings of 26.79 nm and 26.97 nm, respectively, in the X axis. In Figures 3.6 and 3.8, the Y axis was normalised by ion fluences. The dopant concentrations in column 2 in Table 3.3 and column 2 in Table 3.4, were determined from Equation 3.2.

Furthermore, the critical energy densities presented in column 4 in Table 3.3 and column 4 in Table 3.4 are calculated from the energy to recoil atoms

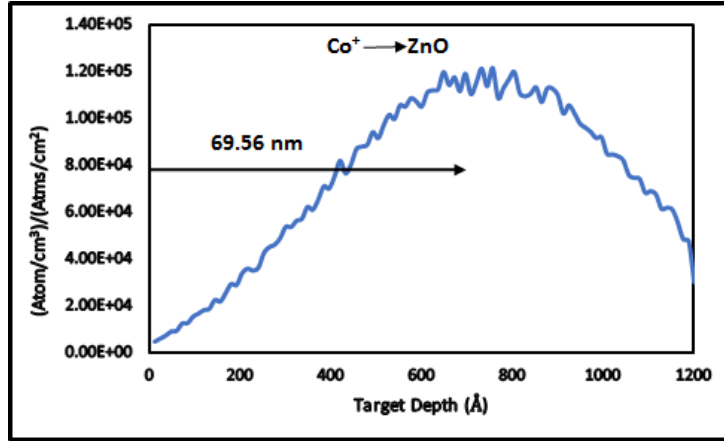


Figure 3.6: 2-D ion distribution for Co⁺ ion implanted ZnO at 170 keV

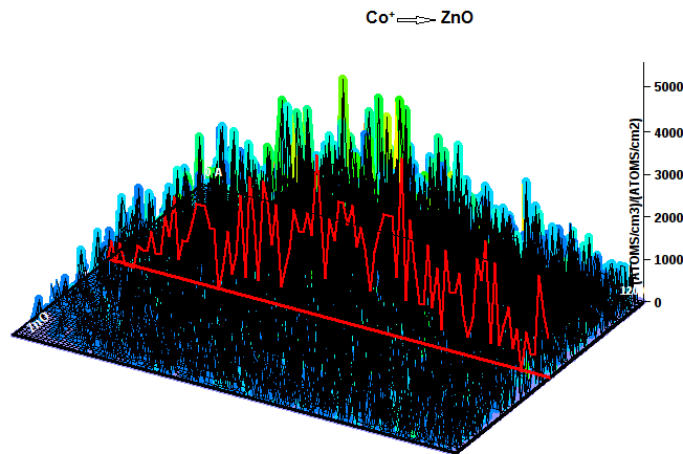


Figure 3.7: 3-D ion distribution for Co⁺ ion implanted ZnO at 170 keV

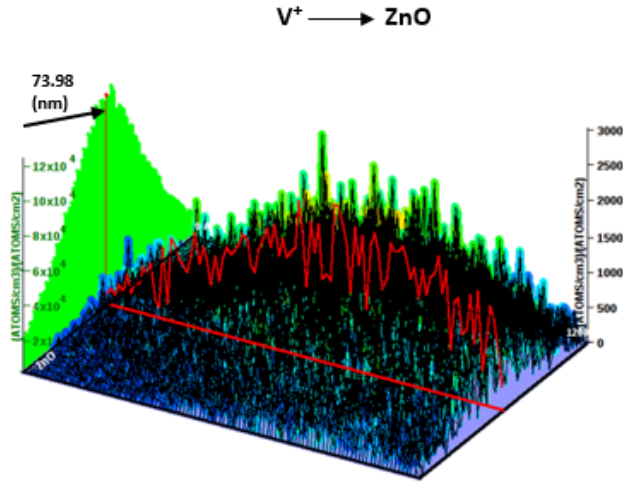


Figure 3.8: 2-D and 3-D ion distributions in V^+ ion implanted ZnO at 170 keV

plot shown in Figures 3.9 and 3.10, using Equation 3.4.

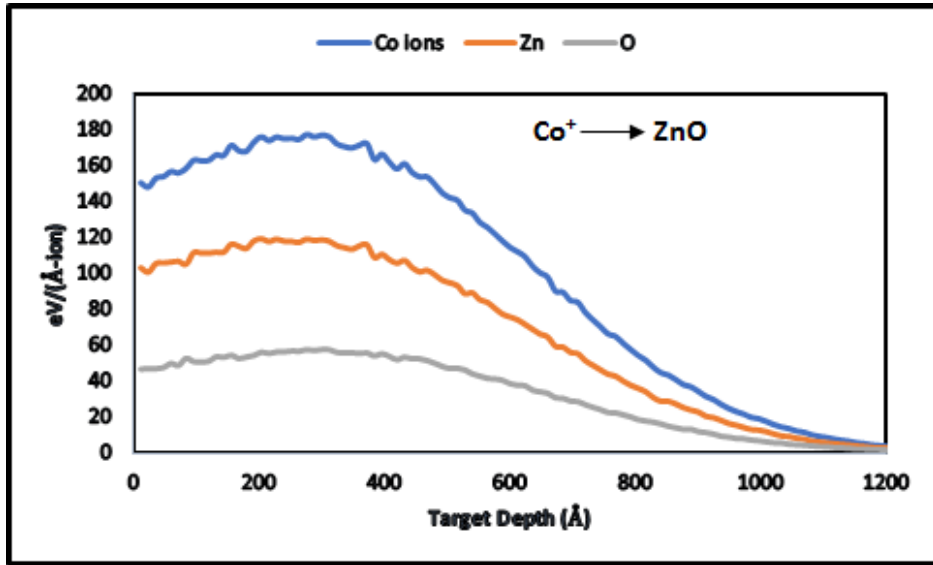


Figure 3.9: TRIM-2013 plot for energy transferred to recoil atoms in Co⁺ ion implanted ZnO thin films at 170 keV

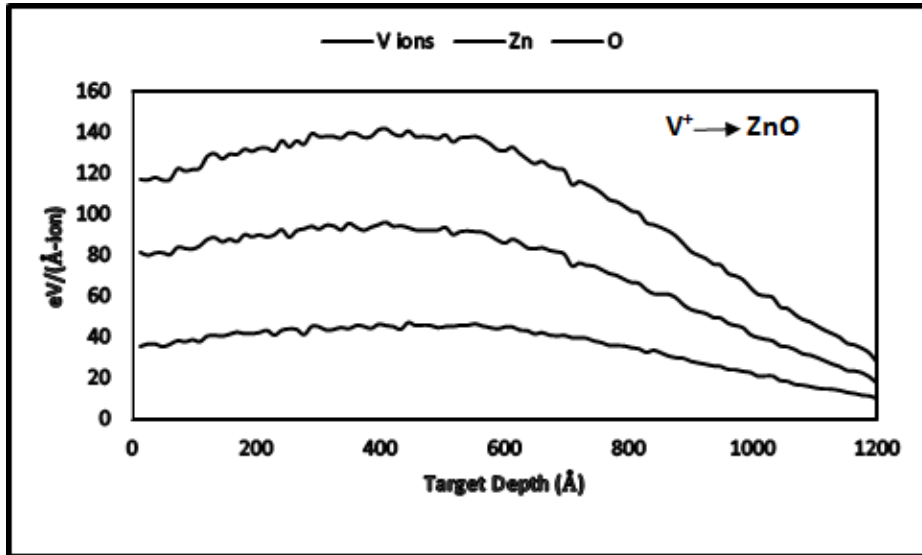


Figure 3.10: TRIM-2013 plot for energy transferred to recoil atoms in V⁺ ion implanted ZnO at 170 keV

Moreover, the collision events of Co^+ and V^+ ion implanted ZnO on borosilicate glass substrates are shown in Figures 3.11 (a) and 3.12 (a). When Co^+ and V^+ ions interact with ZnO, atoms are displaced from their original positions leading to the creation of vacancies. As can be seen (Figures 3.11 (b) and 3.12 (b)), the interactions result in displacement collision, replacement collision, vacancy production and creation of interstitial atoms.

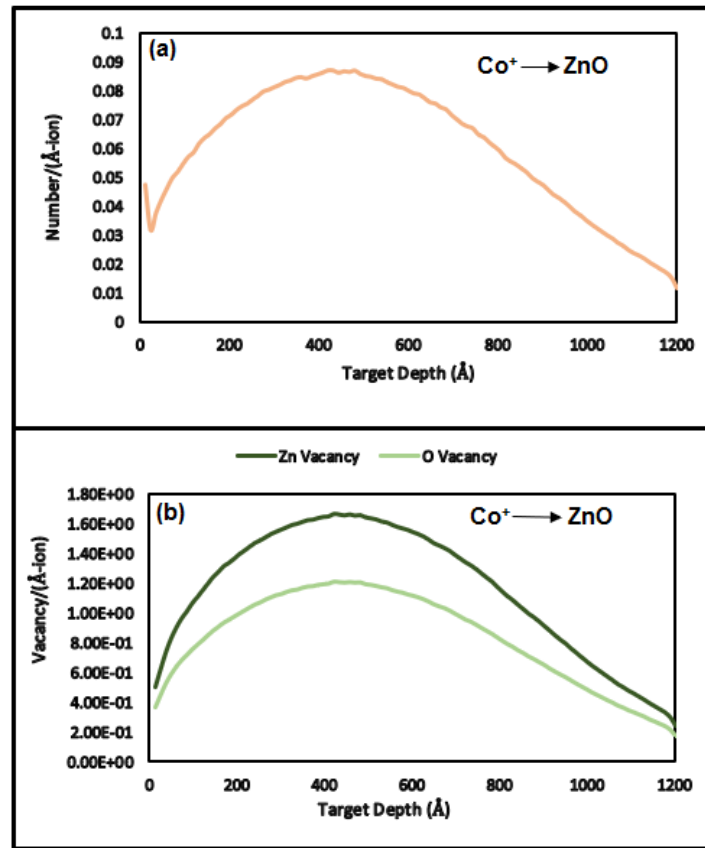


Figure 3.11: TRIM-2013 plots for Co^+ ion implanted ZnO at 170 keV (a) collision events (b) total displacements, vacancies and replacement collisions

Figures 3.11 (b) and 3.12 (b) show maximum vacancies of 1.7 and 1.36 vacancies per Co^+ and V^+ ions, respectively. Therefore, the vacancy densities

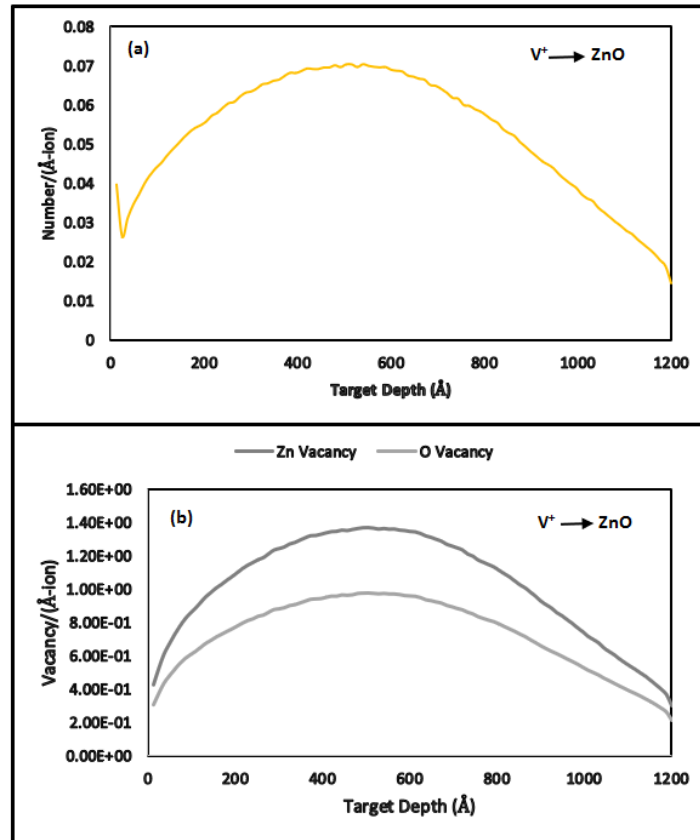


Figure 3.12: TRIM-2013 plots for V^+ ion implanted ZnO at 170 keV (a) Collision events (b) total displacements, vacancies and replacement collisions

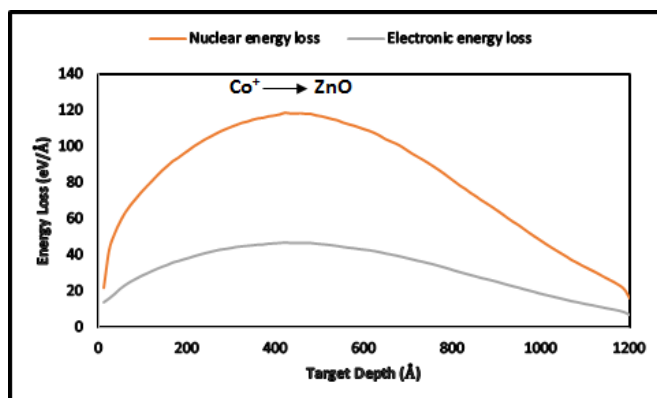


Figure 3.13: TRIM-2013 plots for nuclear and electronic energy losses in Co^+ ion implanted ZnO at 170 keV

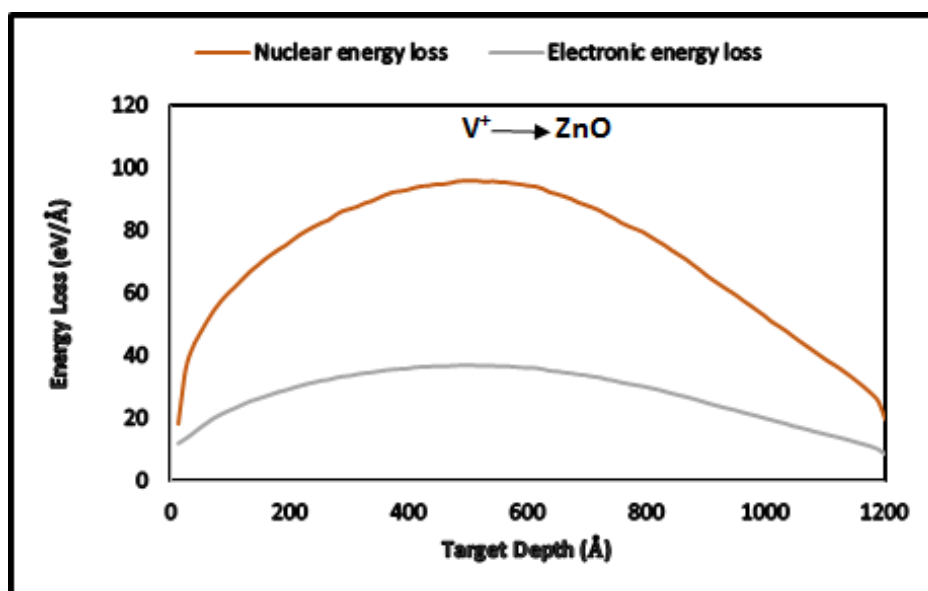


Figure 3.14: TRIM-2013 plots for nuclear and electronic energy losses in V^+ ion implanted ZnO at 170 keV

presented in column 3 in Table 3.3 and column 3 in Table 3.4 were determined by using Equations 3.6 and 3.7 given as,

$$\text{vacancy Conc.} = 1.7 \times \text{fluence}, \quad (3.6)$$

$$\text{vacancy Conc.} = 1.36 \times \text{fluence}. \quad (3.7)$$

Thus, the displacement energies of Co^+ and V^+ ion implanted ZnO on borosilicate glass substrates were 4.38 % and 3.92 %, respectively. Furthermore, it can be seen (Figures 3.1 (b) and (c)) that Co^+ and V^+ ions travel in random paths as they travel deep into the ZnO film. As a result, they lose energy by electronic and nuclear collisions. It can be seen from Table 3.5, Figures 3.13 and 3.14 that Co^+ and V^+ electronic energy losses were equal to 34.64 % and 41.52 %, respectively. However, Co^+ and V^+ nuclear energy losses were 60.92 % and 54.27 %, respectively. Therefore, the nuclear part is the dominant mechanism of energy loss per unit thin film thickness in the ZnO crystal. To quantify the level of modification produced by Co^+ and V^+ ion beams, we calculated the displacement per atom (dpa). In this work, the density of ZnO used is 8.301×10^{22} atoms/cm³. Hence, the dpa presented in column 5 in Table 3.3 and column 5 in Table 3.4 were arrived at by applying Equation 3.5. Therefore, Figures 3.15 and 3.16 show that vacancy concentrations increased linearly with increased Co^+ and V^+ ion beam dopant concentrations. From Figure in 3.15 and Figure in 3.16, it can be seen that the vacancies created in Co^+ and V^+ ion beam implanted ZnO thin films increased rapidly from 1.7×10^{24} to 8.5×10^{24} vac./cm³ and 1.36×10^{24} to 6.8×10^{24} vac./cm³, respectively. These behaviours can be attributed to the increase in implantation fluence.

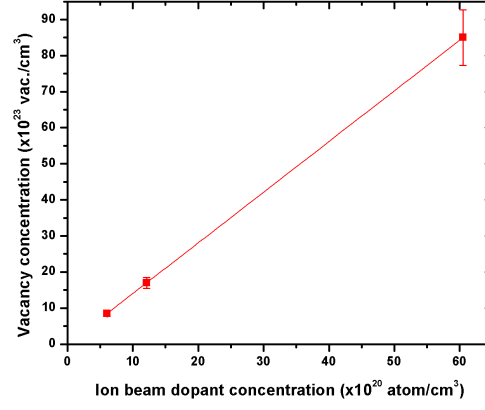


Figure 3.15: Calculated vacancy concentration as a function of Co^+ ion beam dopant concentration in Co^+ ion implanted ZnO on borosilicate glass substrate at 170 keV

Table 3.3: TRIM-2013 calculated parameters for Co^+ ion implanted ZnO on borosilicate glass substrates at 170 keV

Fluence ($\times 10^{15}$ ions/cm ²)	Dopant conc. ($\times 10^{20}$ atom/cm ³)	Vacancy conc. ($\times 10^{23}$ vac./cm ³)	Critical energy dens. ($\times 10^{17}$ eV/cm ³)	dpa ($\times 10^{01}$)
5	6.05	8.5	9	1.02
10	12.1	17	18	2.05
50	60.5	85	90	10.2

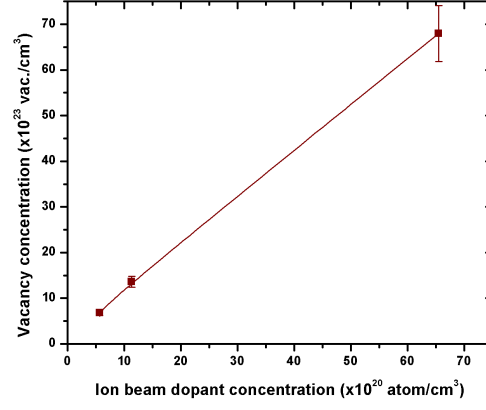


Figure 3.16: Caculated vacancy concentration as a function of V^+ ion beam dopant concentration in V^+ ion implanted ZnO on borosilicate glass substrate at 170 keV

Table 3.4: TRIM-2013 calculated parameters for V^+ ion implanted ZnO on borosilicate glass substrates at 170 keV

Fluence ($\times 10^{15}$ ions/cm ^{2})	Dopant conc. ($\times 10^{20}$ atom/cm ^{3})	Vacancy conc. ($\times 10^{23}$ vac./cm ^{3})	Critical energy dens. ($\times 10^{17}$ eV/cm ^{3})	dpa ($\times 10^{00}$)
5	5.65	6.8	6.95	8.19
10	11.3	13.6	13.9	16.4
50	56.5	68	69.5	81.9

Table 3.5: TRIM-2013 calculated displacement energies, electronic and nuclear energy losses for Co^+ ion implanted ITO and Co^+ and V^+ ion implanted ZnO

TCO thin film	Ion beams	Displacement energy (keV/ion)	Nuclear energy loss (keV/nm)	Electronic energy loss (keV/nm)
ITO	Co^+	4.82	6.15	3.37
ZnO	Co^+	7.45	10.37	5.89
ZnO	V^+	6.66	9.28	7.06

Chapter 4

Experimental Techniques

4.1 Introduction

Chapter 3 has presented SRIM and TRIM-2013 calculations of Co^+ and V^+ ion beam implantations. In the second part of this work, ZnO thin films were synthesised on borosilicate glass substrate. The deposition of ZnO thin films on borosilicate glass substrate was carried out using physical vapour deposition (PVD) method. Thereafter, ITO and ZnO thin films were implanted with Co^+ and V^+ ions using the 200 keV in implanter at NRF-iThemba LABS, Gauteng, South Africa. Lastly, the characterization of Co^+ ion beam implanted ITO thin films on PET substrate, Co^+ ion beam implanted ZnO on borosilicate glass substrate and V^+ ion beam implanted ZnO on borosilicate glass substrate was done at different institutions such as the University of South Africa (Unisa) and Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa, using various characterization techniques discussed in Section 4.4.

4.2 Synthesis of Zinc Oxide

PVD is a deposition process using physical means, such as evaporation and sublimation to create a vapor of atoms or plasma, and it enables the atoms to move from a solid target onto a substrate. There is no chemical reaction applicable in the PVD method. Sputtering and evaporation are the most popular PVD methods [123]. Radio frequency (RF) magnetron sputtering is a desirable method for thin films growth, because it is easy to control [123]. Furthermore, RF magnetron sputtering is suitable for the deposition of large-scale thin film [123].

In this work, ZnO thin films were deposited on borosilicate glass substrate using RF magnetron sputtering at the university of the Witwaterand, Johannesburg, South Africa. Prior to the deposition of ZnO thin films, the borosilicate glass surface was sequential cleaned using acetone, ethanol and ultrapure water in an ultrasonic bath for 10 min each. After the borosilicate glass surface had been thoroughly cleaned, it was dried using high-purity nitrogen gas. The sputtering chamber was evacuated utilizing a turbomolecular pump to a base pressure of about 8×10^{-6} Torr prior to film synthesis. The ambient gas was Ar, and the working pressure was fixed at 2 mTorr. The deposition of ZnO thin films was carried out at room temperature with the ZnO sputtering power maintained at 250 W. The deposition time was varied from 20 to 40 min. A 99.99 % pure ZnO semiconductor was used as a metal target. The metal target was placed at a distance of approximately 8 cm from the borosilicate glass substrate, and it was pre-sputtered for at least 20 min to eliminate contaminants from its surface. Then, ZnO thin films of thickness of about 120 nm were sputtered onto the borosilicate glass substrate.

4.3 Ion implantation in ITO and ZnO thin films

Commercial ITO thin films of thickness 100 nm were implanted with Co^+ ions of energy 100 keV, and the synthesized ZnO thin films were implanted with Co^+ ions of energy 170 keV and another set of synthesized ZnO thin films was implanted with V^+ ions of energy 170 keV. The ion implantation was carried out at different fluences ranging from 0.1×10^{15} to 50×10^{15} ions/cm² (Column 7 in Table 3.1). The Co^+ and V^+ ion beams were focused and carefully scanned over a 1 cm² area, in order to achieve homogeneous implantation. Based on SRIM simulation results (Chapter 3), the range of V^+ and Co^+ ion beams were less than the film thickness. Thus, V^+ and Co^+ ion beams were not allow to travel deep into the substrates. The SRIM simulated ranges were 69.56, 73.98 and 46.40 nm (Column 6 of Table 3.1) for Co^+ and V^+ ion implantation into ZnO and Co^+ ion implantation into ITO thin films, respectively. Therefore, modification in ITO and ZnO thin films were expected from the defects produced in the films.

4.4 ITO and ZnO thin film characterization techniques

With reference to all the previous studies discussed in Section 2.7, it should be noted that in this work pristine and ion implanted samples were characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), UV-Visible Spectroscopy (UV-Vis), Vibrating Sample Magnetometry (VSM), Fourier Transform Infrared (FTIR) and Current Voltage (I-V) technique. As discussed in Section 2.6, these ma-

terial characterisation techniques revealed the specific information required from these experiments.

4.4.1 Scanning Electron Microscopy (SEM)

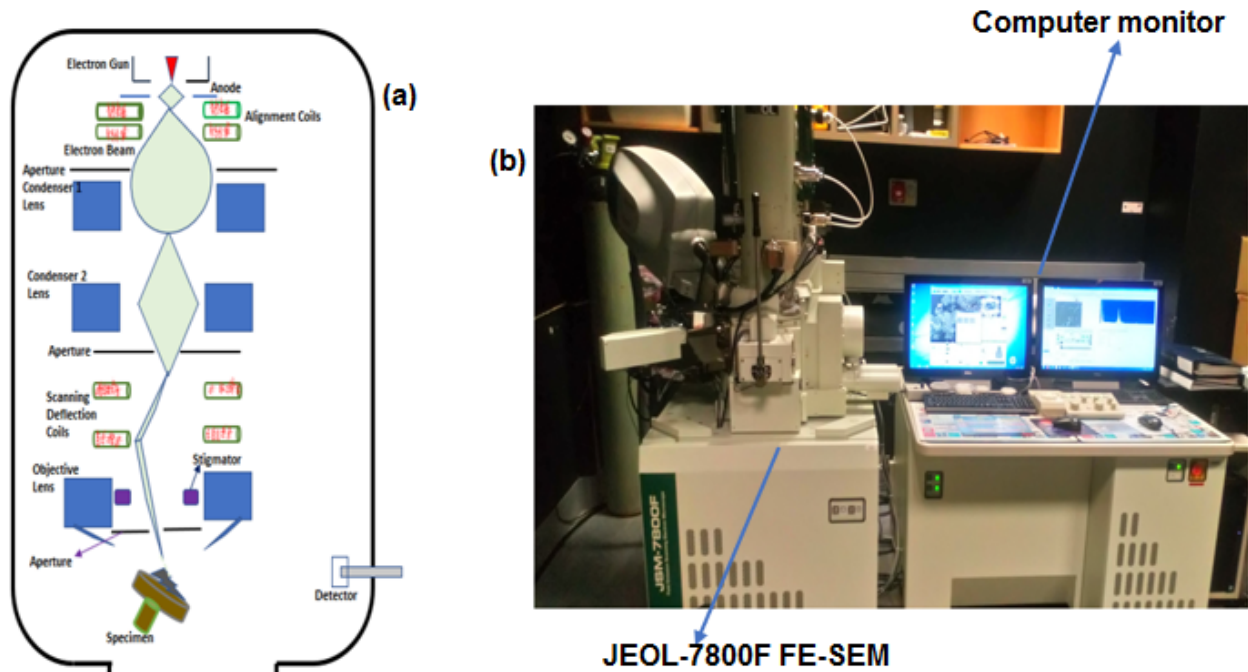


Figure 4.1: (a) Typical SEM schematic diagram showing its main components
(b) JEOL-7800F FE-SE Microscopy used for morphology study

A scanning electron microscopy produces an image, which appears different from the usual human interpretation of images viewed by the eye formed by light. In SEM, an electron beam is scanned over the surface of sample or specimen to form an image. Figure 4.1 (a) shows an electron column and

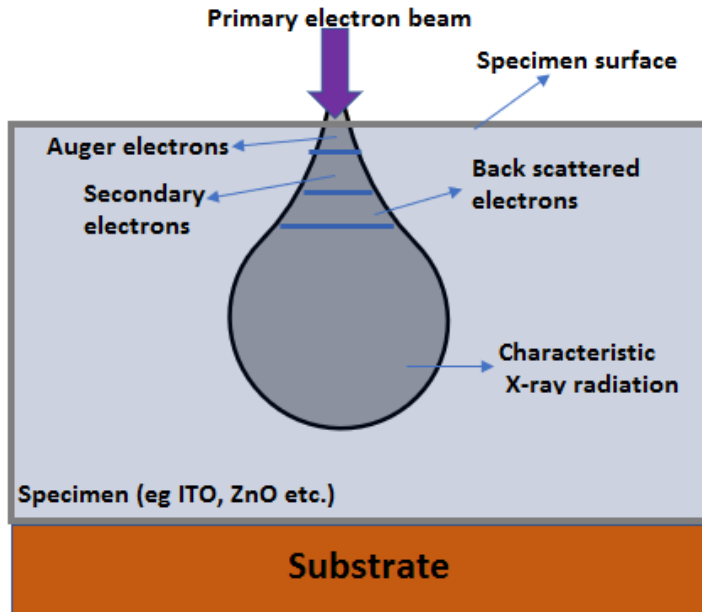


Figure 4.2: Specimen interaction volume

specimen chamber that constitute the main components of a typical SEM. An electron column consists of an electron gun, objective and condenser lenses. The electron gun serves as a source of a free electron beam, which is accelerated through a series of apertures down the column. The electron beam energy can be varied from 1 to 30 keV [124]. The objective and condenser lenses control the diameter of the beam and focus the beam onto a sample. Basically, the electron beams interacts with the sample in a so-called interaction volume (Figure 4.2), and it may interact with the sample to a depth of approximately $1\mu\text{m}$ [124]. The dimension of the interaction volume depends on the mean atomic number of sample, acceleration voltage and the density. For the generation of image, the electron beam is focused onto a fine probe, which is scanned across the surface of the sample. Thus, several types of signals, such as secondary and backscattered electrons, can be collected and processed by a detector positioned perpendicular to the sample surface

in electro-optical path. The resulting signal is amplified and displayed on a computer monitor (Figure 4.1 (b)). All the above discussed processes are maintained at high vacuum level.

In this work, a JEOL-7800F Field Emission-Scanning Electron Microscopy (FE-SEM) (Figure 4.1(b)) was used. The microscope employs a field emission electron gun and is equipped with secondary electron detectors and backscattered electron detectors. The microscope is further equipped with an in-lens secondary electron detector, which is highly surface sensitive, and its efficiency improves as the acceleration voltage decreases to lower voltages. In this study, the in-lens secondary electron detector was employed to study the change in the morphologies of Co^+ and V^+ ion implanted ZnO thin films, and Co^+ ion implanted ITO thin films. Furthermore, the top surfaces as well as inclusions in the layers of the thin films were studied. The results are discussed in Chapters 5 and 6.

4.4.2 Atomic Force Microscopy (AFM)

The Atomic Force Microscope was invented in 1986 by Gerd Binnig et al. based on existed (since 1981) Scanning Tunneling Microscope [125]. However, the AFM working principle is based on interactions between a tip and a sample or specimen surface to produce a topographical image (Figure 4.3 (a)). Typical AFM features are shown in Figure 4.3 (a). It consists a tip of length 3 μm to 15 μm made of silicon attached to the end of cantilever of length 100 to 500 μm . Other AFM components include photodiode, laser and piezo scanner. Generally, a tip is used for imaging. The tip travels through a specimen and based on the topography of specimen the tip moves up and down. A laser beam is directed onto a cantilever, as shown in Figure 4.3 (a), and is reflected towards a positioned sensitive photodiode, which allows the

precise measurement of the bending of the cantilever. Moreover, the negative or positive bending of cantilever is because of the attractive and repulsive forces on the surface due to interactions between the tip and the specimen. However, the cantilever deflection is due to atomic force differences between the tip and the specimen. By using a detector, the cantilever deflection is detected and thereby a topographical image is obtained and displayed on a computer monitor.

Contact mode AFM measurements were carried out in this work. In contact mode, the tip was in soft physical contact with surfaces of ion implanted films. By using AFM, the topography properties of the thin films were investigated with resolution within the range of $100\text{ }\mu\text{m}$ to less than $1\text{ }\mu\text{m}$. The tip was moved above the surfaces of the thin films under a constant force. Therefore, changes in the topography properties of Co^+ and V^+ ion implanted ZnO thin films, Co^+ ion implanted ITO thin films were recorded.

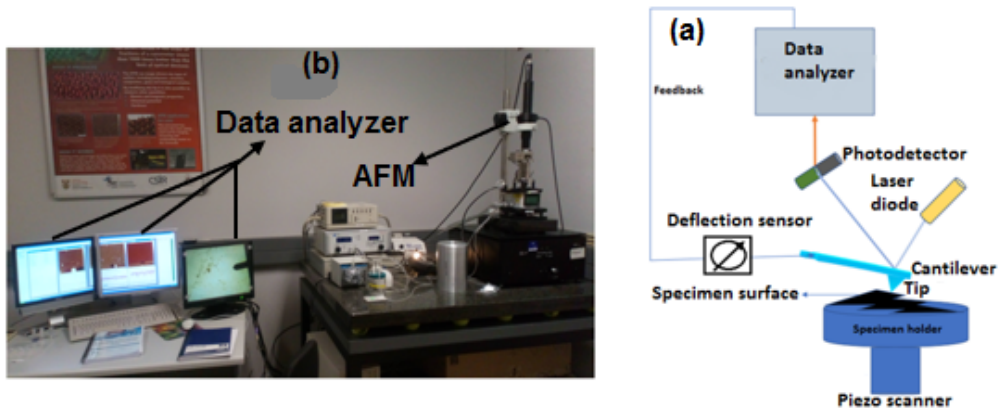


Figure 4.3: (a) Atomic force microscopy working principle schematic diagram
(b) Atomic force microscope used to study the surface characteristics of as-deposited and ion implanted samples

4.4.3 X-Ray Diffraction (XRD)

XRD can be used to determine the crystal structure of a material [126]. From diffraction patterns of material, some qualitative information on the crystal system, unit cell contents, crystallite size, micro-strain and extended defects. can be obtained. Thus, XRD is based on the phenomenon that the atomic planes of a crystal make an incoming beam of X-ray radiation to interfere with one another as they are reflecting from a single crystal. This phenomenon can be understood from Bragg's law [127]. Bragg's law is the most popular law in diffraction which describes the interference pattern of X-ray scattered by crystals as follows:

$$n\lambda = 2d\sin\theta, \quad (4.1)$$

where n is an integer which characterizes the order of reflection, λ is wavelength and d is distance. $2d\sin\theta$ is the path difference between the X-rays reflected from the crystal, which is directly proportional to the integral multiple ($n\lambda$) of wavelengths. Thus, $2d\sin\theta$ as a function of wavelength defines the Bragg's law condition for constructive interference [127]. Therefore, for reflection of X-rays to occur, the condition for constructive interference must be satisfied.

In this work, the structural analyses of Co^+ and V^+ ion implanted ZnO thin films, and Co^+ ion implanted ITO thin films were performed using an X-ray diffractometer (XRD) with model number

PW3373/00CULFFDk184487, where Copper $\text{K}\alpha$ radiation (composed of $\text{Cu K}\alpha_1 = 1.5405980 \text{ \AA}$ and $\text{Cu K}\alpha_2 = 1.5443 \text{ \AA}$; the weighted average of the two is $\text{Cu K}\alpha_{avg} = 1.54184 \text{ \AA}$, 45kV, 40 mA) was used as an X-ray source. Thus, the X-ray diffraction patterns of the samples were recorded in 2θ range. For the estimation of crystal imperfections such as crystallite size distribu-

tion and micro strain analysis, the Williamson-Hall method was used. The Williamson - Hall equation is given as [128]

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D^2} + \frac{4\varepsilon \sin \theta}{\lambda}, \quad (4.2)$$

where, θ equal to the Bragg's angle, D = grain size in nm, ε is the strain and β is the FWHM in radian. Equation 4.2 was used to separate the contributions of crystallite size and strain to the broadening in XRD diffraction peak. In addition, the crystallite size (D) was further estimated by using the Debye-Scherrer formula [129, 130]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (4.3)$$

where, λ represents X-ray wavelength, 1.54060 Å, β represents full width at half aximum in radian and θ is equal to the Bragg's angle.

The strain (ε) and dislocation density (δ) were estimated by using equations 4.4 and 4.5 [129].

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (4.4)$$

$$\delta = \frac{1}{D^2} \quad (4.5)$$

GSAS-II crystallography software package [131] was used for indexing, structure solution and refinement. For the measurement of crystallite size D , dislocation δ , and strain ε , the integral breadth B is corrected against instrument broadening b by using the following equation [132],

$$\beta = B - \frac{b^2}{B}. \quad (4.6)$$

Where, β is the FWHM (radian). By implementing equation 4.6 in GSAS-II crystallography software, the peak shape is somewhat between Lorentzian and Gaussian leading to more accurate results.

4.4.4 Ultraviolet-Visible Spectroscopy (UV-Vis)

Effects such as reflection, absorption and transmittance arise as a result of interaction of light (photons) with materials. Photon interaction effects on the ion implanted thin films were explored in this work using UV-Vis Spectroscopy [133]. The effect produced during photon interactions with thin films depends on the type of thin films and the energy (E) of incoming photon, given as :

$$E = h\nu = \frac{hc}{\lambda}, \quad (4.7)$$

where c is speed of light, h is the Plank's constant, ν is photon frequency and λ is the photon wavelength.

The working principle of a UV-Vis Spectrometer is relatively straightforward. Figure 4.4 shows typical UV-Vis Spectrometer components. A diffraction grating is used to separate a beam of light from a UV or visible light source into its component wavelengths. By using a half-mirrored device, each monochromatic beam is then split into two equal intensity beams attributed to the sample and the reference sample beams. The sample beam passes through a cuvette containing the sample to be studied, and the second beam which is reference sample beam, passes through an identical cuvette containing a reference sample. Therefore, the intensity of the reference beam (I_i) and the intensities of ion implanted thin film beams (I) were recorded by electronic detectors, and the beam intensities were compared. The spectrometer auto scanned the thin film wavelengths within a short period of time. The spectrometer scanned the thin films within the range 200-400 nm wavelength attributed to the ultraviolet (UV) region, and within the range 400-800 nm wavelength attributed to visible region.

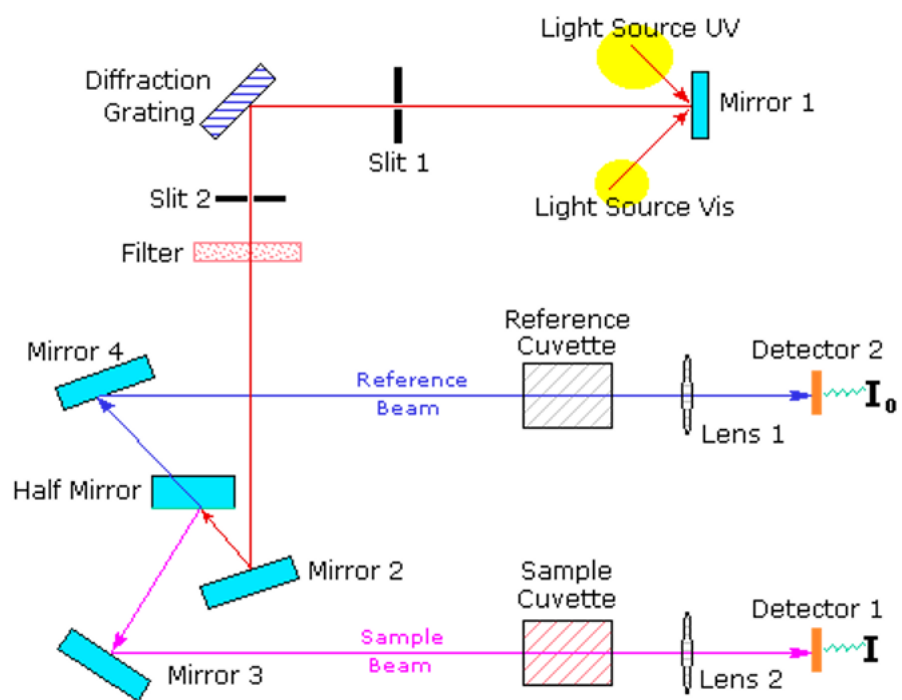


Figure 4.4: UV-Vis working principle [3]

Furthermore, a Lambda 750S UV-Vis spectrometer (Figure 4.5) was used to study the optical properties of ion implanted thin films. The Lambda 750S UV-Vis spectrometer is a high-performance spectrometer equipped with double-monochromator design producing excellent data quality. It gives the highest possible consistency coupled with the highest accuracy and lowest stray-light performance [3]. It can precisely measure transmittances (T) of Co^+ and V^+ ion implanted ZnO and Co^+ ion implanted ITO thin films over a wide range of wavelengths, from the near-infrared region to the ultraviolet region [3]. This spectrometer is now a well-improved and adaptable optical properties instrument popularly used for a wide variety of transparent conducting oxide matrices. The relation between absorbance (A) and transmittance T % was used to determined optical band gap by using Tauc's relation (Section 2.4.2), and the results are discussed in Chapte 5.

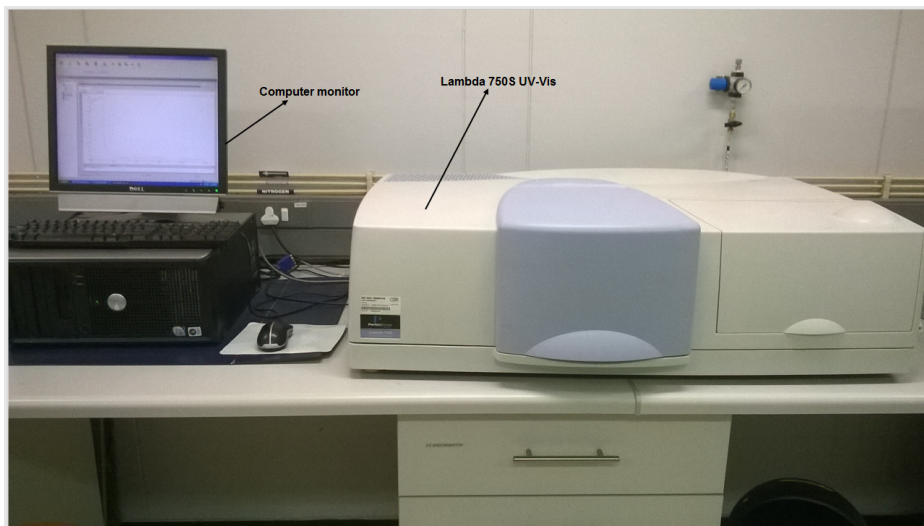


Figure 4.5: Optical characterization tools used in this study: Lambda 750S UV-Vis

4.4.5 Vibrating Sample Magnetometry (VSM)

The magnetic behavior of Co^+ ion implanted ITO thin films on PET substrate, at fluences of 1×10^{14} , 1×10^{15} and 1×10^{16} ions/cm², was probed using a quantum design physical properties measurement system (PPMS) in vibrating sample magnetometry (VSM) mode, with a helium cooling system. The Co^+ ion implanted ITO and as-grown thin films were cut to approximately 0.5 cm², and the thin film weight of 0.011 g was recorded. The weight was used to determine the horizontal component of hysteresis loops at room temperature. Sample magnetizations were, thereafter, collected as a function of applied field within the range -5000 Oe-5000 Oe at 300 K.

Moreover, VSM is capable of recording magnetic moment and hysteresis at temperatures from 2 to 400 K and applied fields from -9 to +9 T. The magnetometer uses electromagnetic induction and lock-in principle of data collection, and it can be configured in vibration parallel to the field or in vibration transverse to the field [134]. In a longitudinal arrangement, the detection coils are surrounded by a superconducting drive coil. The detection coils are used to measure variations in the applied field due to the sample inserted into the space within the coils by using a long thin rod. However, thin films are placed in a predetermined position on the long thin rod before inserting into the system.

For accurate data collection and background noise reduction, calibration coils are built into the system together with a non-magnetic thermometer to measure temperature. Moreover, Model 6000 shown in Figure 4.6 is connected directly to the set up and it controls the components, thus it performs series of measurement. Between Model 6000 and user, a computer system is used as an interface.

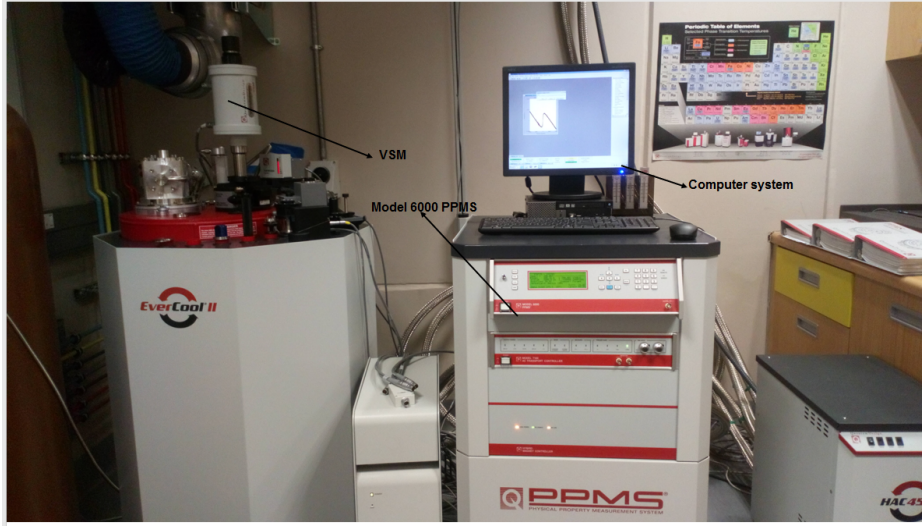


Figure 4.6: Physical properties measurement system (PPMS) utilized in this study to measure the magnetic properties of Co^+ ion implanted ITO thin films

4.4.6 Current Voltage (I-V) Characterization

Current Voltage (I-V) characteristic technique popularly used to understand the basic electrical parameters of a conducting component or device, and their behavior within an electronic circuit.

In this work, two-point probe I-V characteristics were measured with a Keithley 4200 semiconductor characterization system (Figure 4.7) to determine changes in basic electrical parameters, such as conductivity and resistivity, after Co^+ and V^+ ion implantations.

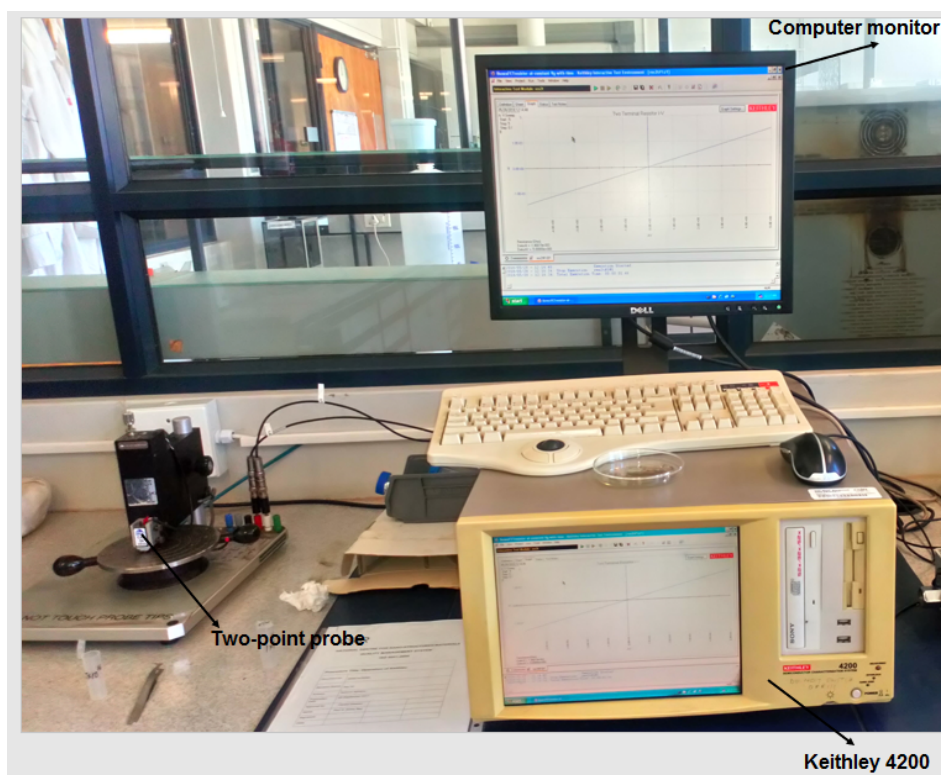


Figure 4.7: Keithley 4200 semiconductor characterization system utilized in this study to measure changes in basic electrical parameters

Chapter 5

Results and Discussion I: Co^+ and V^+ Ion Implanted ZnO Thin Films

5.1 Introduction

The effects of ion implantation on the structural and morphological properties of ZnO thin films have been analyzed using XRD, AFM and SEM techniques. These techniques have been discussed in detailed in Sections 4.4.1, 4.4.2 and 4.4.3. By inducing structural modification on ZnO thin films, it results in modification of other properties such optical and electrical properties. This chapter discusses the modification of structural, optical and electrical properties of V^+ and Co^+ ion implanted ZnO thin films. The analysis of ion implanted ZnO thin film chemical bonds using Fourier Transform Infrared Spectroscopy (FTIR) have also been discussed.

5.2 Structural modification of V^+ ion implanted ZnO thin films

The lattice structures of as-grown and V^+ ion implanted ZnO thin films have been studied. As-grown XRD patterns (Figure 5.1) reveal four peaks at $2\theta = 43.19^\circ, 45.66^\circ, 60.10^\circ$ and 80.21° correspond to (011), (002), (102) and (112) planes, respectively, and it is attributed to the diffraction of ZnO hexagonal crystalline structure (hcp) [135]. From Figure 5.1, it can be observed that the XRD peak intensities of thin films implanted from 5×10^{15} to 5×10^{16} ions/cm² suddenly decrease to very low intensities (Table 5.2 Column 7) and not clearly visible indicating an amorphous structure in V^+ ion implanted ZnO thin films. The reason for this observation could be due to implantation produced defects in the ZnO crystal and as ion fluence increases the structure does not re-crystallize. This indicates that V^+ ion implanted ZnO atoms are randomly distributed in 3-dimensional space, and there is a range of interatomic distances.

As can be seen from as-grown and V^+ ion implanted ZnO thin films spectra, XRD patterns reveal multiphase with the amorphous phase of substrate (glass) observed from $2\theta = 0^\circ$ to 30° . This means that diffracting amorphous material will scatter X-rays in many directions giving very broad diffraction peaks in a wide 2θ range instead of high narrow peaks. However, it is clearly shown on Figure 5.1 that the degree of crystalline of the as-grown is higher than that of V^+ ion implanted ZnO thin films. There are no peaks corresponding to V^+ ions observed, which means implanted V^+ ions have been incorporated well in the ZnO matrix.

The degree of preferred orientation has been observed to change with fluence, this is shown on the bases of variation of the intensity ratio, $100(I/I_{max})$, as

Table 5.1: Degree of preferred orientation (I/I_{011}) parameters of V^+ ion implanted ZnO thin films in comparison with as-grown

Fluence ($\times 10^{15}$ ions/cm ²)	Intensity (I)	Intensity Max. (I_{011})	Intensity Ratio
0	570.00	1958.00	44.08
5	13.00	21.00	62.00
10	9.00	25.00	36.00
50	2.00	25.00	8.00

a function of fluence which was recorded in Table 5.1 and illustrated in Figure 5.2. From Figure 5.2, it was showed that preferred orientation decreases from 5×10^{15} to a maximum ion fluence of 5×10^{16} ions/cm² due to implantation. Indicating that the crystallization of ZnO thin films is optimum before implantation. It can be attributed to the agglomeration of crystals are frequently decomposing.

From Table 5.2 Column 7, changes in the magnitude of XRD intensities of the as-grown and V^+ ion implanted ZnO thin films as a function of fluence (Table 5.2 Column 1) are pronounced from the fluences of 5×10^{15} to 5×10^{16} ions/cm². Therefore, V^+ ion implanted ZnO thin film optimum crystallization was observed at a fluence of 5×10^{15} ions/cm².

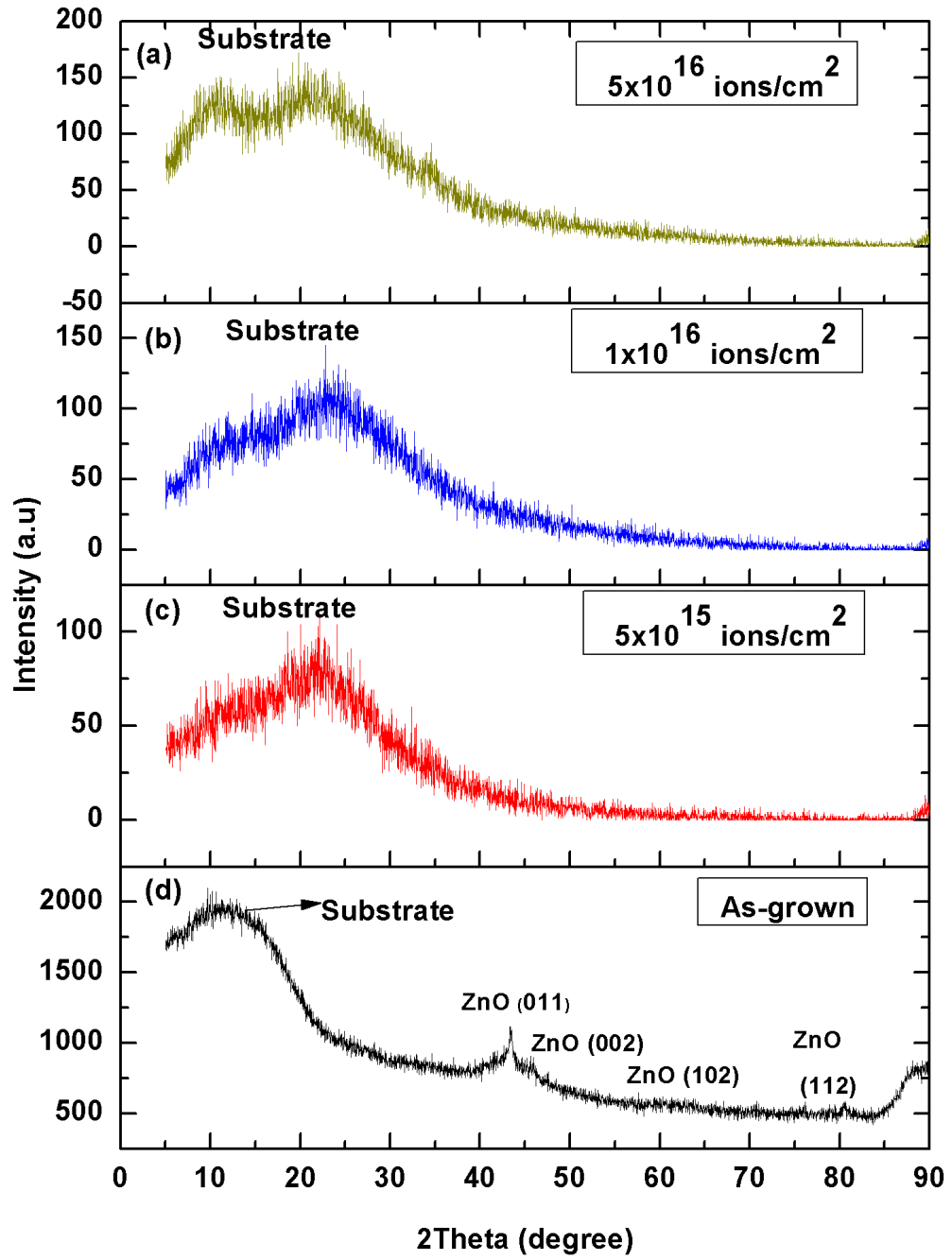


Figure 5.1: XRD spectral of (a) as-grown and V⁺ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

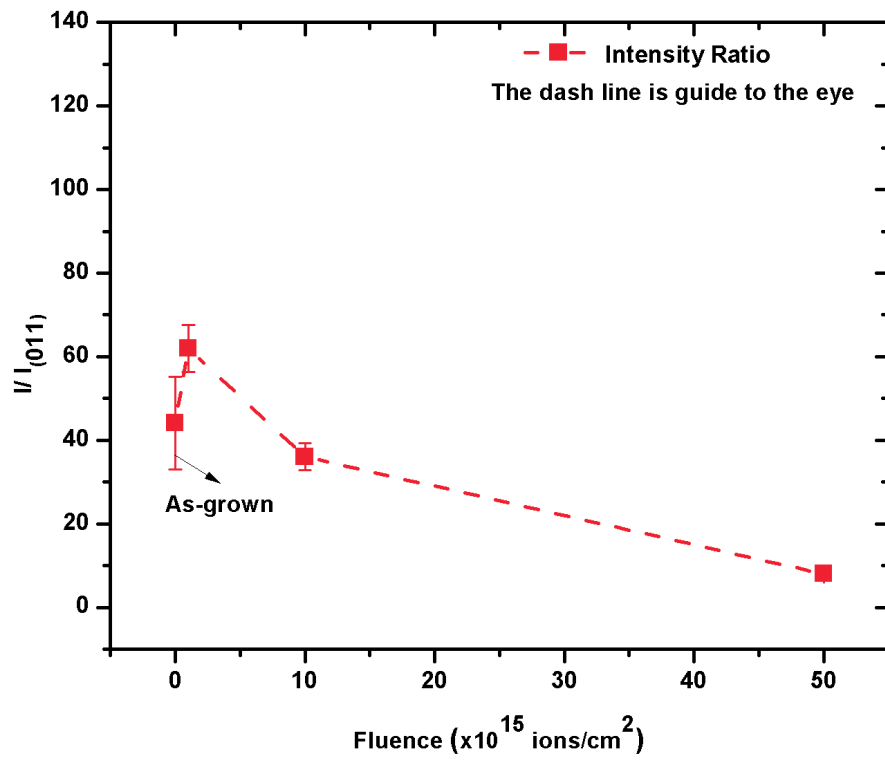


Figure 5.2: Effect of ion fluences on degree of preferred orientation (I/I_{max}) of V^{+} ion implanted ZnO thin films in comparison with as-grown

5.2.1 Crystallite size and strain

As-grown and V^+ ion implanted ZnO crystals are finite as can be seen from Table 5.2 and Figure 5.1, therefore, small deviation from the Bragg angle will not always cause destructive interference (Subsection 4.4.3)) leading to a finite broadening of the observed peak. Figure 5.1 and Table 5.2 Column 5 show some finite broadening of as-grown and V^+ ion beam implanted ZnO peaks. The broadening was calculated as Full Width at Half Maximum (FWHM). The FWHM can be related to crystallite size, D , by the Scherrer formula (Equation 4.3). Equation 4.3 shows that the smaller the crystallite size, the greater the FWHM of the peak. The calculated FWHM and grain size using Equation 4.3 are recorded in Table 5.2 Column 5 and Table 5.3 Column 4, respectively. Figure 5.3 shows the effects of ion fluence on average FWHM and grain size of V^+ ion implanted ZnO thin films in comparison with as-grown films. From Figure 5.3, it can be observed that as ion fluence increases the FWHM increases progressively from 5×10^{15} to 5×10^{16} ions/cm² by 26.52 %. However, the grain size decreases gradually from 5×10^{15} to 5×10^{16} ions/cm² by 27.02 % as ion fluence increases. Therefore, there is good agreement with Equation 4.3, and it shows that as grain size decreases hardness of V^+ ion beam implanted ZnO thin films increases, peaks become broader and peak intensity decreases due to reduction in crystallinity.

Table 5.2: Structural parameters of as-grown and V⁺ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	2θ (deg)	d _{hkl} -space observed (Å)	d _{hkl} -space calculated (Å)	FWHM (deg)	h k l	Intensity (a.u)	W-H (nm)
0	43.19	2.0842	2.0839	1.1012	011	1958.00	5.37
	45.66	1.9880	1.8977	2.0000	002	863.00	
	60.10	1.5424	1.5428	2.0000	102	570.00	
	80.21	1.1963	1.2074	1.2219	112	491.00	
5	43.38	2.0928	2.0922	1.7475	011	21.00	3.89
	45.59	1.9852	2.0002	2.0000	002	13.00	
	59.92	1.5381	1.5374	2.0000	101	3.00	
	80.16	1.1966	1.1966	1.7567	112	2.00	
10	43.24	2.0904	2.1024	2.0904	011	25.00	3.06
	45.92	1.9745	1.9730	2.0000	110	18.00	
	60.18	1.5363	1.5366	2.0000	020	9.00	
	80.99	1.1863	1.1869	1.6070	210	2.00	
50	43.30	2.0880	2.0879	2.0000	011	25.00	3.02
	45.03	2.0115	2.0115	2.0000	110	22.00	
	59.52	1.5517	1.5516	2.0000	020	11.00	
	80.17	1.1962	1.1962	2.0000	201	2.00	

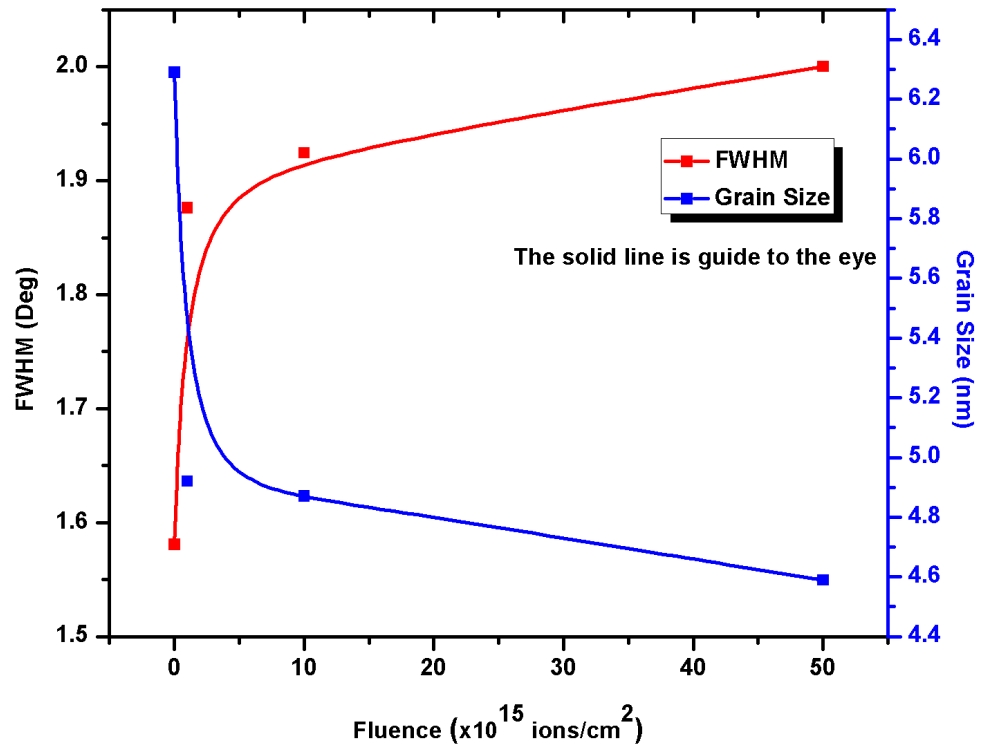


Figure 5.3: Variation of ion fluences with grain size and FWHM of V^+ ion implanted ZnO thin films in comparison with as-grown and in relation with Equation 4.3

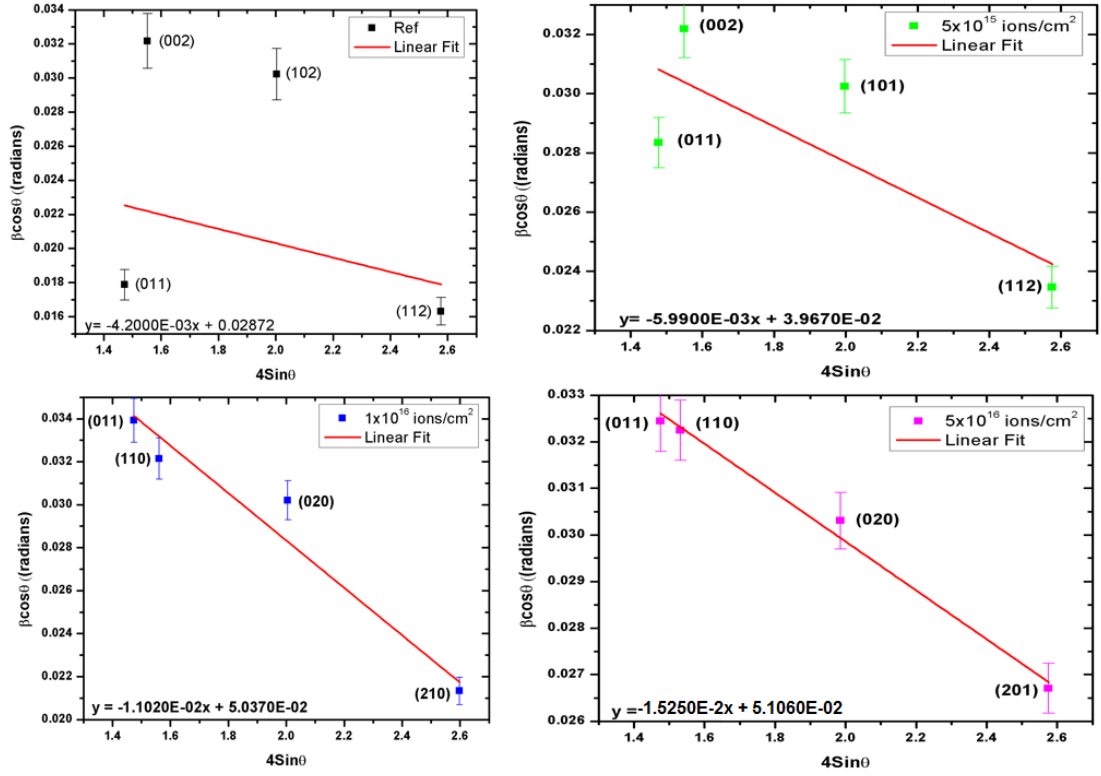


Figure 5.4: Williamson-Hall analysis for the deconvoluting size and strain broadening by considering the peak broadening of reflection as a function of 2θ of the as-grown and V^+ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm²

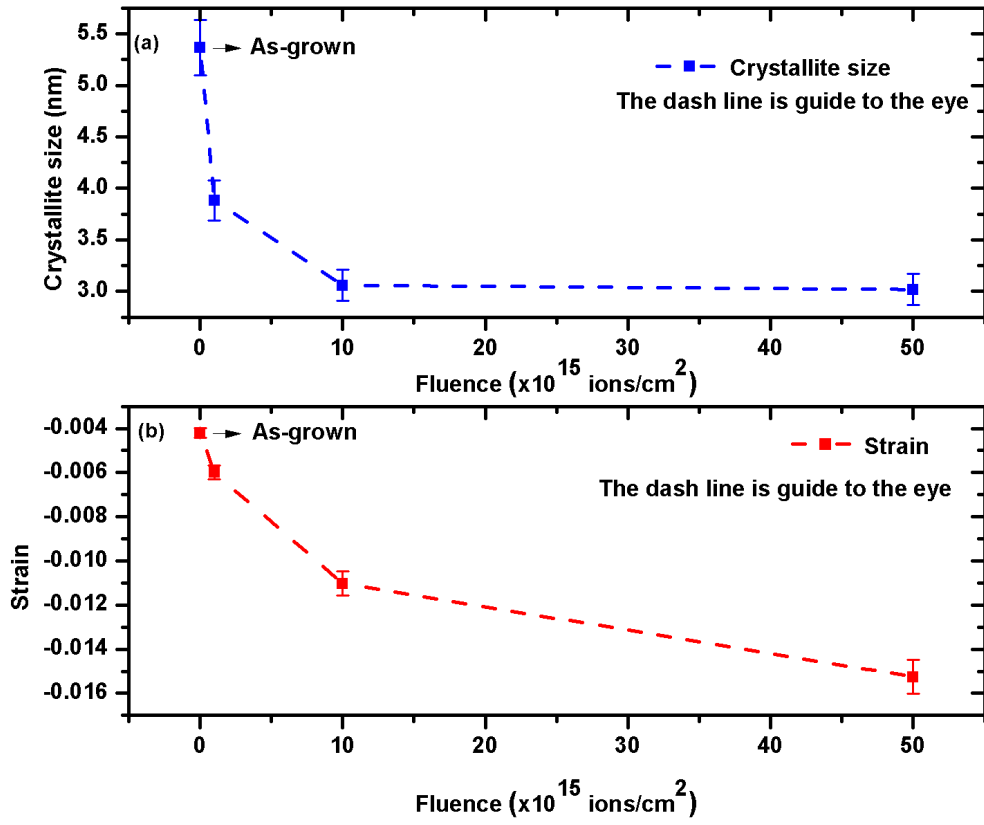


Figure 5.5: Variation of ion fluences with (a) crystallite size and (b) strain of V⁺ ion implanted ZnO thin films in comparison with as-grown using Williamson-Hall method

The shape of diffraction peaks is usually determined by structural effects such as crystallite size and strain within crystals containing lattice defects [128]. By using Equation 4.2 and diffraction planes (011), (002), (102), (101), (020), (110), (210), (201) and (112) characterizing the XRD diffraction peaks of as-grown and V^+ ion implanted ZnO thin films, one can be able to determine the contributions of crystallite size and strain to the broadening in diffraction peaks of both as-grown and V^+ ion implanted ZnO thin films. Figure 5.4 shows linear fitting of the Williamson-Hall (W-H) plots of as-grown and V^+ ion implanted ZnO thin films at different fluences. From Figure 5.4, it is clear that crystallite size and strain contributed to the broadening in diffraction peaks. Moreover, the W-H plots exhibited negative slope indicating that the contribution of strain to the broadening is very small.

The average crystallite size recorded in Table 5.2 Column 8 and illustrated in Figure 5.5 (a) as a function of ion fluence were calculated from the inverse intercept of the W-H plots, and the slope of the plot represent average strain (Figure 5.5 (b)) based on Equation 4.2. The average crystallite sizes estimated from W-H plots show exponential decrease with upper limit approximately 4.00 nm for the thin film implanted at a fluence of 5×10^{15} ions/cm². From both Scherrer and W-H methods, a considerable decrease of crystallite size was observed as expected (Figures 5.3 and 5.5 (a)). Therefore, the observed decrease in grain size of V^+ ion implanted ZnO thin films may be explained in terms of a columnar grain size growth [8].

The variation of strain using W-H method with fluence is illustrated in Figure 5.5 (b) which confirms that as ion fluence increases strain gradually becomes small. This observation may be due to decrease in crystallinity or decrease in the degree of preferred orientation as confirmed quantitatively by XRD pattern.

5.2.2 d -value

As-grown and V^+ ion implanted ZnO crystals consist of atoms that are separated at distances d apart, which have been resolved into many planes and recorded in Table 5.2 Columns 3 and 4 as observed and calculated d_{hkl} -spacings, each with a unique d_{hkl} -spacing. In order to investigate the effect of ion fluence on the observed d_{hkl} -spacings, the average observed d_{hkl} -spacings between planes of atoms were determined for as-grown and ion implanted thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm² as 1.7027, 1.7032, 1.6969 and 1.7118 Å, respectively, together with the orientation of a single crystal. Figure 5.6 shows the effect of fluence on the average observed d_{hkl} -spacings between the planes of atoms of the V^+ ion implanted ZnO thin films in comparison with as-grown. From Figure 5.6, it can be seen that at a fluence of 1×10^{16} ions/cm² the observed d_{hkl} -spacing approximately shifted towards as-grown d_{hkl} -value, however, as the fluence increases to 5×10^{16} ions/cm² it shifted away from the as-grown d_{hkl} -value. This d_{hkl} -spacing shift can be explained by an increased relaxation of V^+ ion implanted ZnO thin films as the fluence increases, with more relaxation due to high d_{hkl} -value recorded at higher fluence [136].

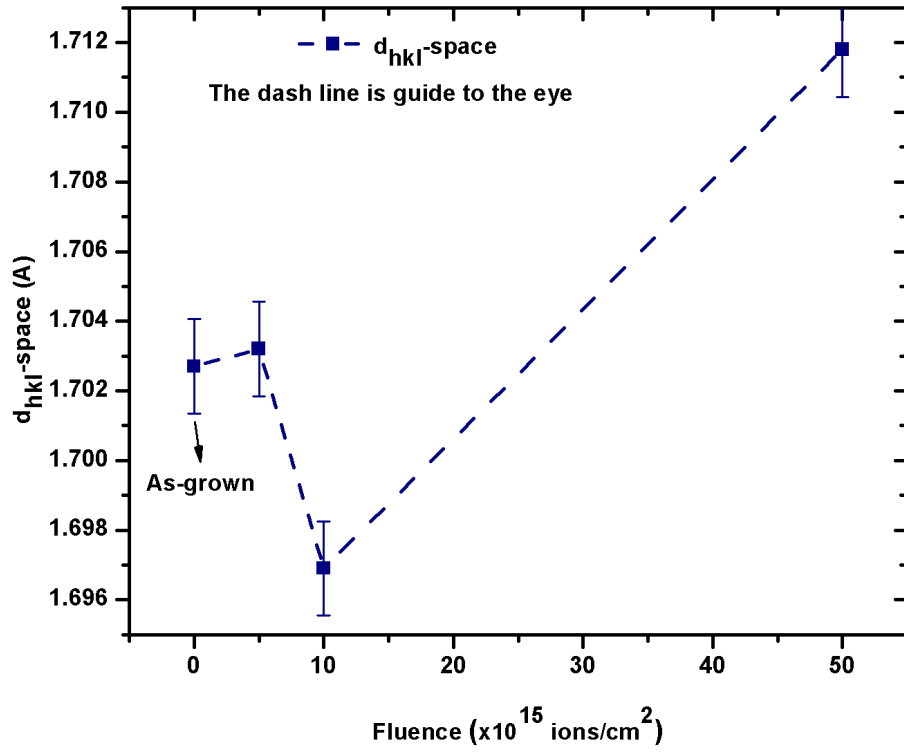


Figure 5.6: Variation of d_{hkl} -spacings of as-grown and V^+ ion beam implanted ZnO thin films as a function of fluence

5.2.3 Lattice constants

As discussed earlier, the crystal structure of ZnO is described as hexagonal close pack (hcp) with two different phase angles of $a = b = 90^\circ$ and $c = 120^\circ$ [135]. As a result, the lattice constants a and c have been determined by the relations [135]:

$$a = d_{hkl} \sqrt{(h^2 + k^2 + l^2)}; \text{ and} \quad (5.1)$$

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}, \quad (5.2)$$

where hkl are Miller indices, a and c are lattice constants and d as defined in subsection 5.2.2.

By using Equations 5.1 and 5.2, the variation and estimated lattice constants a and c are shown in Figure 5.7 and recorded in Table 5.3 Columns 5 and 6. As can be seen from Figure 5.7, the average values of a and c are 3.2276 ± 0.07156 and 5.1041 ± 0.11433 Å, respectively.

It can be observed that as ion fluence increases there is a gradual decrease in the lattice constant up to a fluence of 1×10^{16} ions/cm² in comparison with as-grown, beyond it there is a slight decreasing, where it reaches to a minimum value of 2.89 and 4.83 Å at 5×10^{16} ions/cm² for lattice constants a and c , respectively (Figure 5.7). Therefore, as shown in Figure 5.7, this suggests that lattice constant shrinks with increasing ion fluence. It also suggests that V^+ ions enter substitutionally into the ZnO lattice, upon implantation. Similar decrease in lattice constant has been observed in Co-doped ITO films by Stankiewicz et al. [136].

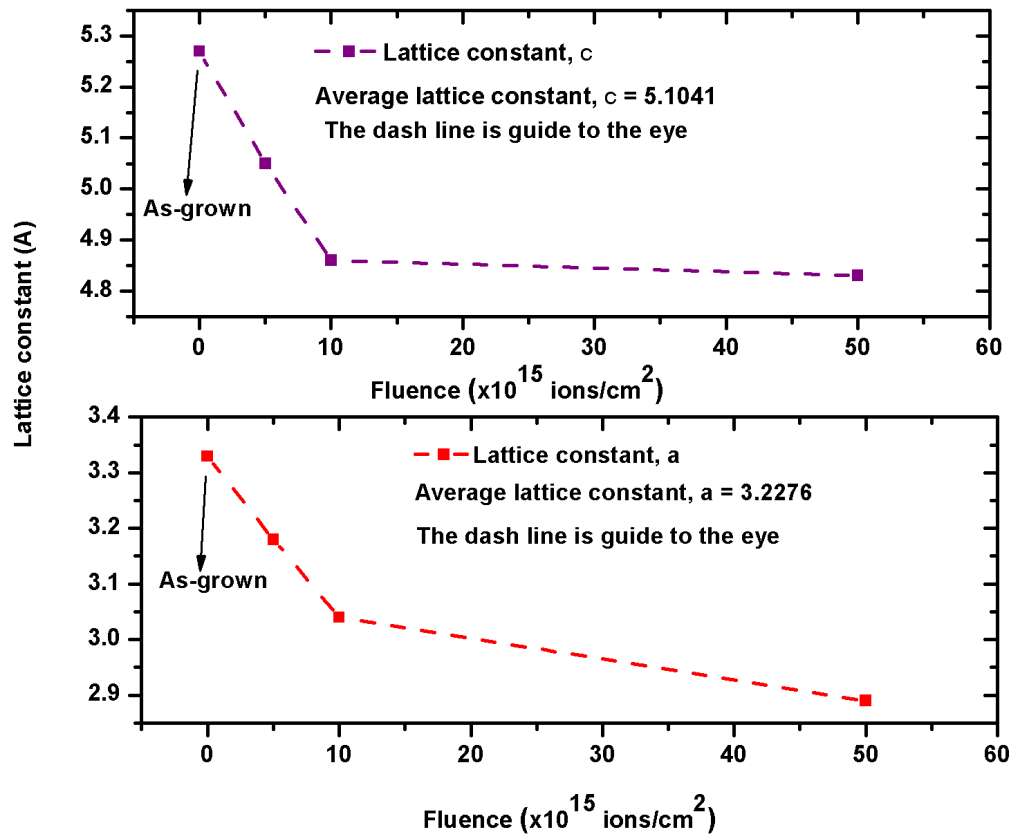


Figure 5.7: Variation of lattice constants c and a of as-grown and V^+ ion implanted ZnO thin films as a function of ion fluence

Table 5.3: Structural parameters such as strain, dislocation density, crytallite size and lattice constant of as-grown and V⁺ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	strain, ε ($\times 10^{-3}$)	Dislocation density, δ ($\times 10^{-11}$ line/m ²)	Crytallite size (nm)	Lattice constant, a ($\text{\AA}$)	Lattice constant, c ($\text{\AA}$)
0	4.4676	1.6603	7.76	2.9475	5.2727
	8.0430	5.3810	4.31	3.9760	5.6229
	7.5537	4.7462	4.59	3.4489	5.0944
	4.0779	1.3833	8.50	2.9303	5.0755
Average	6.0356	3.2927	6.29	3.33	5.27
5	7.0805	4.1756	4.89	3.6248	3.9708
	8.0451	5.3838	4.31	3.9704	5.6150
	7.5605	4.7548	4.59	2.1752	5.3281
	5.8649	2.8612	5.91	2.9311	4.1451
Average	7.1389	4.2939	4.92	3.18	5.05
10	8.4794	5.9808	4.09	3.6207	2.8046
	8.0353	5.3707	4.32	2.7924	5.9235
	7.5506	4.7424	4.59	3.0726	5.3219
	5.3323	2.3651	6.50	2.6527	4.5945
Average	7.3459	4.6148	4.87	3.05	4.86
50	8.1110	5.4724	4.28	2.9529	3.6165
	8.0615	5.4058	4.30	2.8447	5.6894
	7.5757	4.7739	4.58	3.1030	5.3746
	6.6767	3.7081	5.19	2.6748	4.6329
Average	7.6062	4.8401	4.59	2.89	4.83

5.2.4 Dislocation density

Dislocation is a misregistry of lattice, which results in imperfection in a crystal matrix, i.e. it is the length of dislocation line/cm². The dislocation densities have been calculated using Equation 4.5 and estimated dislocation densities for as-grown and V⁺ ion implanted ZnO thin films are recorded in Table 5.3 Column 3 and shown in Figure 5.8. As can be seen from Figure 5.8, there is a rapid increase in the dislocation density with ion fluence up to a fluence of 5×10^{15} ions/cm² in comparison with as-grown. Thereafter, there is a slight increase, up to 5×10^{16} ions/cm².

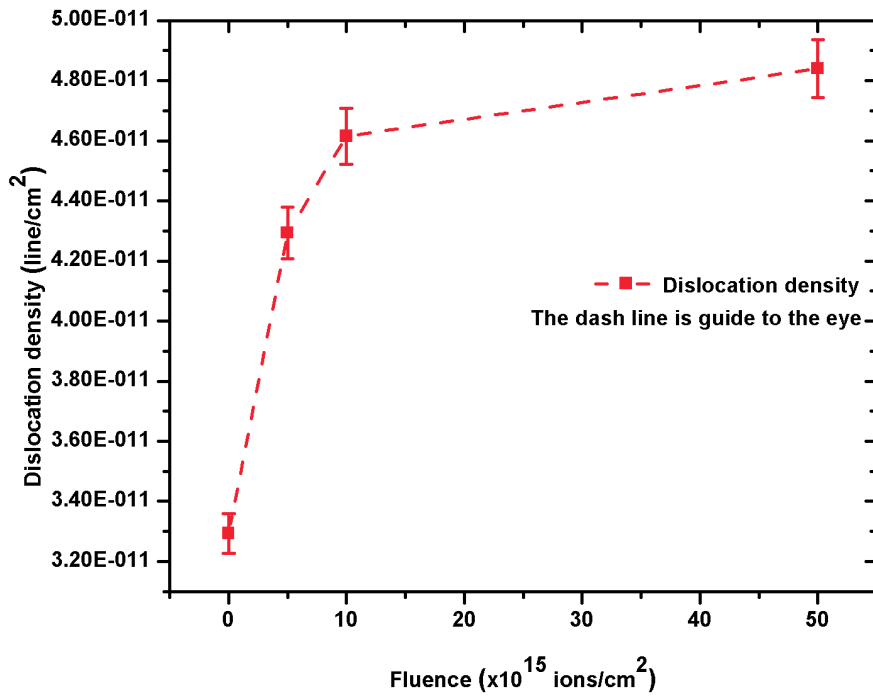


Figure 5.8: Variation of dislocation densities of as-grown and V⁺ ion implanted ZnO thin films as a function of ion fluence

5.2.5 Thermal and chemical stability

By implementing Equation 2.8 in EXPO-2014 software, the thermal factors or B-factors and mean square displacement amplitude U (Section 2.4.4) of as-grown and V^+ ion implanted ZnO thin films have been determined, and they are as recorded in Table 5.4 and shown in Figure 5.9. From Figure 5.9, it can be seen that the vibrational motion of different parts of the V^+ ion implanted ZnO thin film structures, induced by thermal motion, decreases rapidly from a fluence of 5×10^{15} to 5×10^{16} ions/cm². This shows that atoms of thin film implanted to 5×10^{16} ions/cm² are stable as a result of the low B-factors of 15.70 %. However, atoms of thin film implanted at a fluence of 5×10^{15} ions/cm² are flexible due to the high B-factors of 94.29 %. In addition, mean square displacement amplitude was observed to decrease from low fluence to high fluence.

Table 5.4: Isotropic (iso) refined thermal parameters (B and U) of as-grown and V^+ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ^{2})	B-factor $\text{\AA}^2$	U ($\times 10^{-1} \text{\AA}^2$)
0	9.985	1.9784
5	9.415	1.1924
10	3.308	0.4189
50	1.568	0.1986

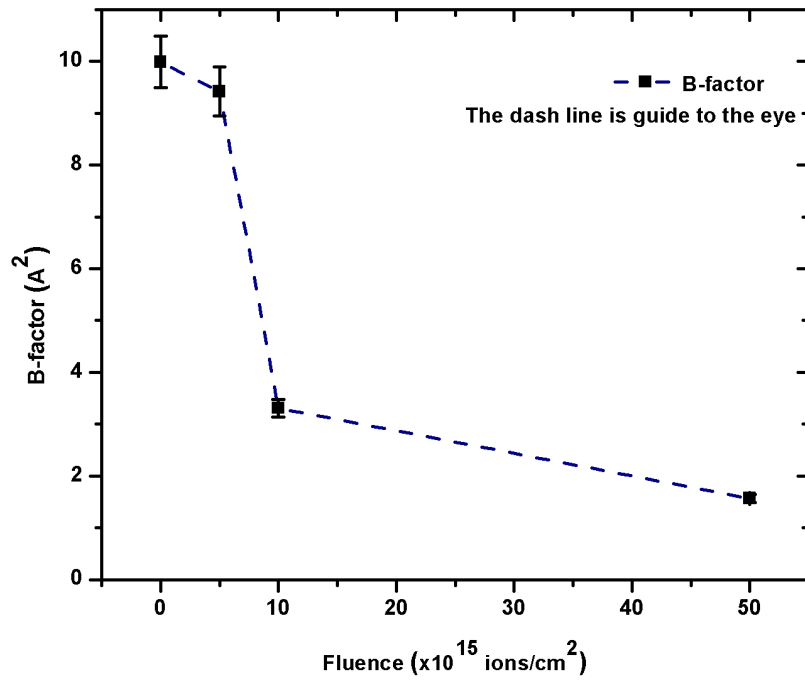


Figure 5.9: Variation of thermal factors (B-factors) of as-grown and V^+ ion implanted ZnO thin films as a function of ion fluence

5.2.6 Morphological properties

The effects of ion fluences (5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm²) on the surface morphological properties of V⁺ ion implanted ZnO thin films have been studied using FE-SEM and AFM techniques (4.4.1 and 4.4.2). It has been observed that there are pronounced changes in the morphology of V⁺ ion implanted ZnO thin films in comparison with as-grown as a result of ion implantation.

5.2.6.1 AFM scans

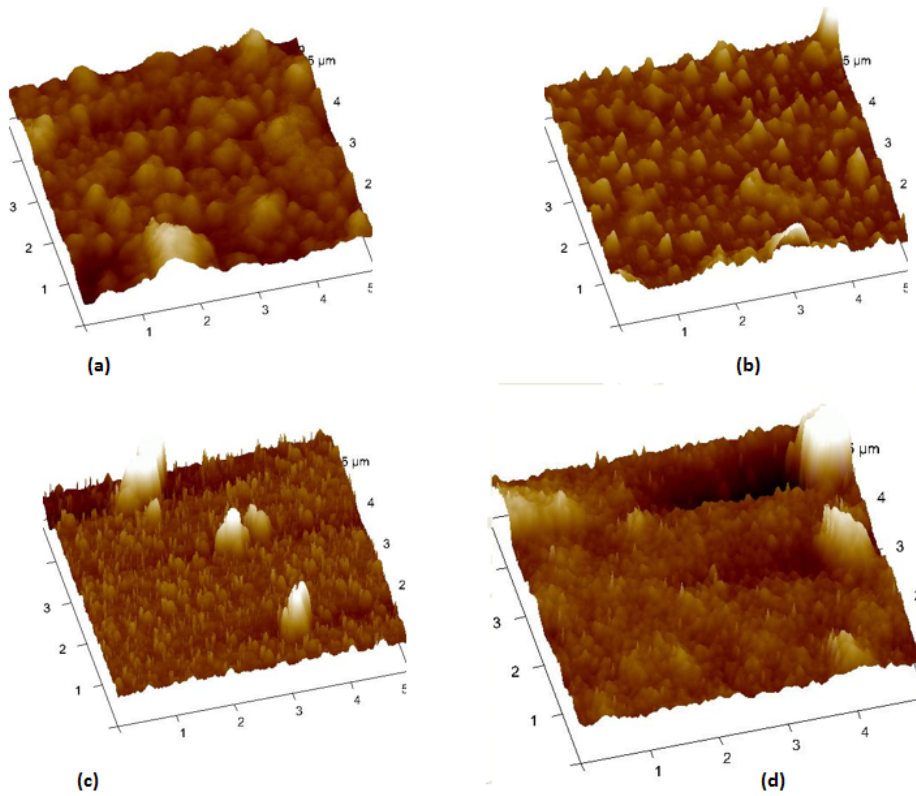


Figure 5.10: AFM 3-D images of (a) as-grown and V⁺ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

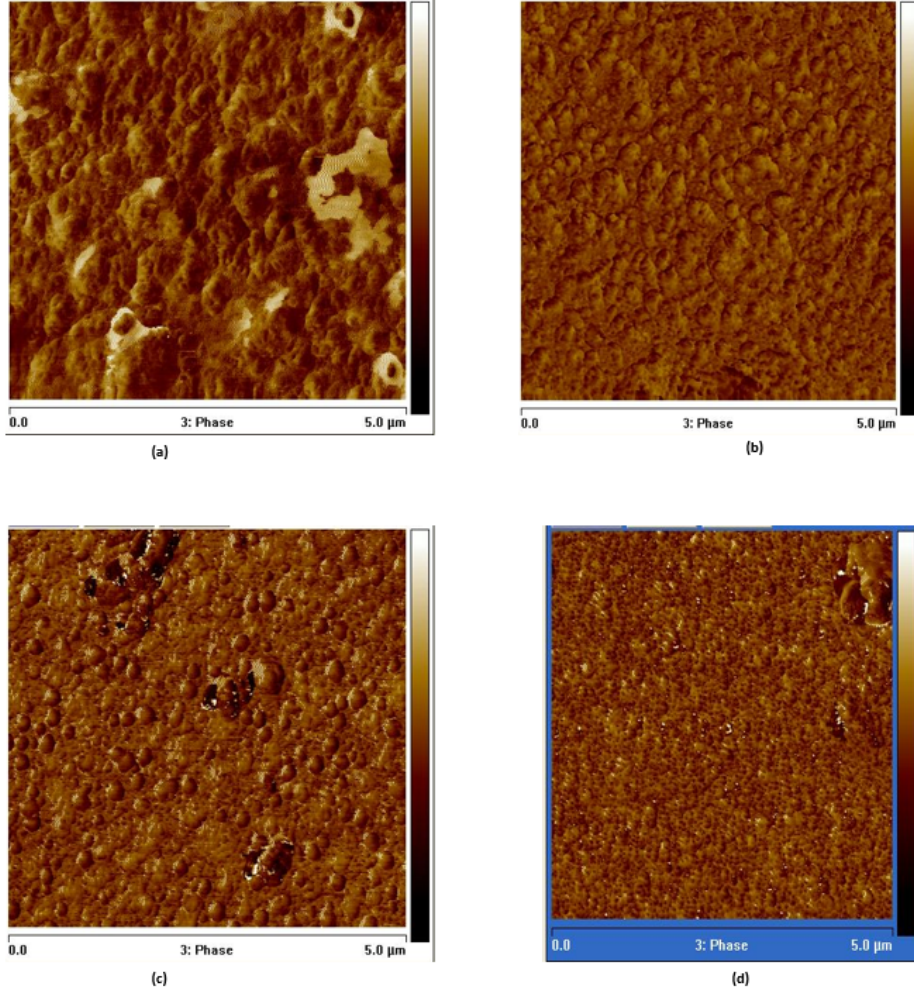


Figure 5.11: AFM 2-D images of (a) as-grown and V^+ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

Figures 5.10 and 5.11 show 3-D and 2-D AFM scans of as-grown and those of V^+ ion implanted ZnO thin films at different ion fluences. The calculated

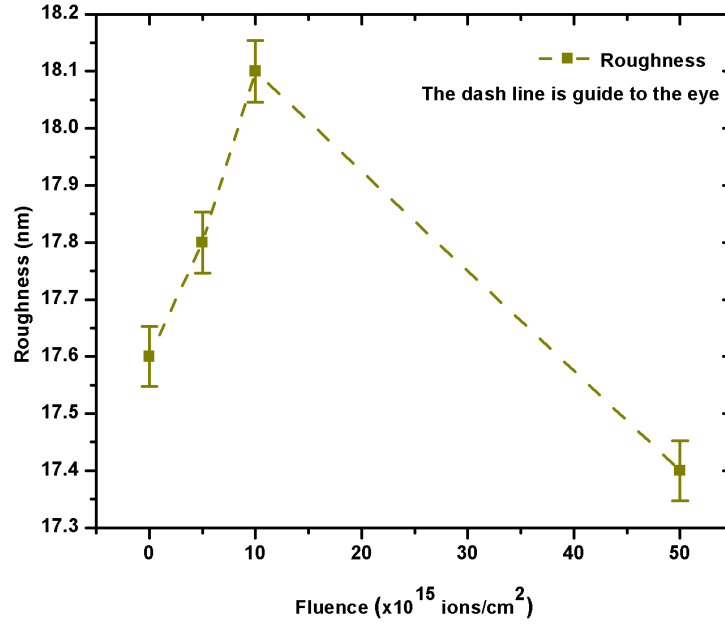


Figure 5.12: Surface roughness as a function of fluence for as-grown and V^+ ion implanted ZnO thin films

Table 5.5: Optical band gaps, average roughnesses (Ra) at different ion fluences, together with root mean squares, wavelengths and corresponding absorbance edges of V^+ ion implanted ZnO thin films

Fluence ($\times 10^{15}$ ions/cm ^{2})	Wave- length (nm)	Absor- bance (au)	Band gap (eV)	RMS (Rq) (nm)	Ave. Ra (nm)
0	415	0.31	3.20	17.6	12.6
5	456	0.23	3.40	17.8	12.6
10	368	0.12	4.10	18.1	9.35
50	589	0.56	2.40	17.4	9.07

root mean squares and average roughnesses are listed in Table 5.5 as function of ion fluence. It can be observed from Table 5.5 and Figure 5.12 that the surfaces of thin films implanted from 5×10^{15} to 5×10^{16} ions/cm² have been modified upon implantation. The AFM image of the thin film implanted to 5×10^{16} ions/cm² showed a sharp decrease in roughness with root mean square (Rq) roughness of approximately 17.4 nm, and the grain size decreased to 4.59 nm while the estimated grain size and roughness of the as-grown have been found to be 6.29 and 17.6 nm, respectively.

The decrease could be attributed to implantation induced defects [29]. Thus, the decrease in grain size made the thin films show no regular distribution of granular shaped crystallites (Figure 5.1). Furthermore, the decrease in RMS roughness observed in the thin films established a relatively smooth surface [137]. However, the roughness of thin film implanted at a fluences of 1×10^{16} ions/cm² increased by 2.84 %. This increase in surface roughness may be due to the increase in amount of implanted V⁺ metal particles on the surface of ZnO thin films [138].

5.2.6.2 FE-SEM micrographs

Figure 5.13 depicts FE-SEM micrographs of as-grown and V⁺ ion implanted thin films. The micrographs were carefully taken at higher magnifications and 3 kV, which resulted in clear images of the thin film surface morphologies. FE-SEM micrographs reveal unarranged particles in a disorder manner after implantation. It is obvious that the average particle sizes decreased gradually from as-grown thin films (6.29 nm) to the thin films implanted at high fluence (4.59 nm). This is in good agreement with the AFM and XRD (figure 5.5) results. Therefore, this shows that V⁺ ion implantation induced modification on the surface morphology of ZnO thin films.

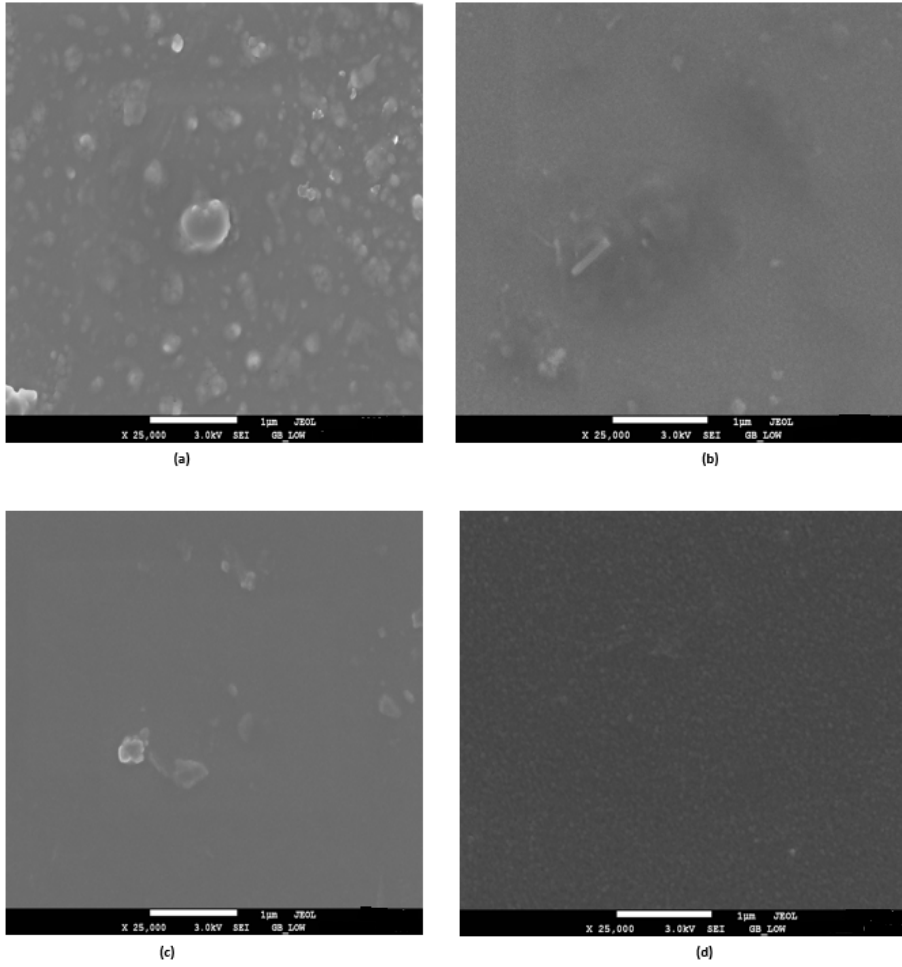


Figure 5.13: FE-SEM micrographs of (a) as-grown and V^{+} ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

5.2.7 Chemical bond analysis

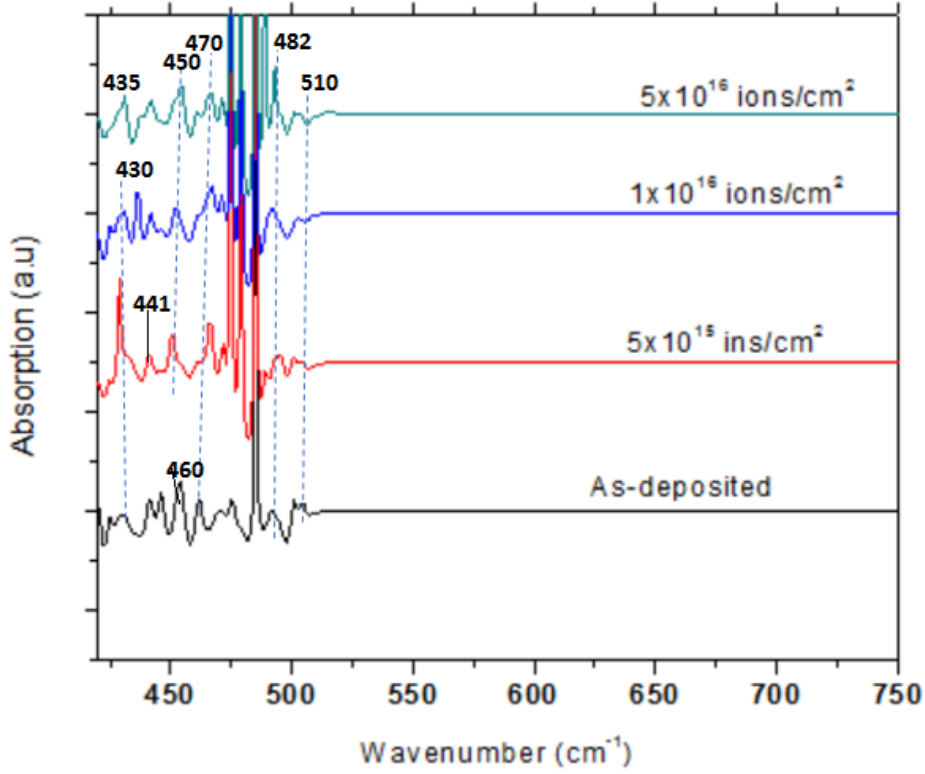


Figure 5.14: FTIR spectra in the wavenumber range 420-750 cm⁻¹ at room temperature of as-grown and V⁺ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm²

Fourier Transform Infrared Spectroscopy (FTIR) is a popular tool to probe vibrational properties of materials. FTIR is based on the absorption of photons by molecules of the material. However, the absorption peak and band positions depend on the morphology, structure and chemical composition of

the material [139, 140]. Figure 5.14 shows the compositional analysis of both as-grown and V^+ ion implanted ZnO thin films at different fluences (5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm²), using FTIR measurement at 300 K in the range 420-750 cm⁻¹. As can be seen from the spectrum, the presence of ZnO thin film stretching vibrations was confirmed by peaks in the range 470-482 cm⁻¹ for as-grown and in the range 435-482 cm⁻¹ for V^+ ion implanted ZnO thin films [140]. The presence of vanadium oxide is not found in the thin film by FTIR, which indicates that upon implantation vanadium metal incorporated well in ZnO lattice structure, and probably there is no formation of oxide of the vanadium.

It can also be seen from Figure 5.14 that most of as-grown peaks are doublets, and the doublets changed to single polycrystalline in V^+ ion implanted ZnO thin films. The observed absorption shoulder at 430 cm⁻¹ was not observed at high fluence. The absorption peak shifted to high wavenumber 435 cm⁻¹ for thin film implanted to 5×10^{16} ions/cm² corresponding to single polycrystalline phase of the films. In addition, the absorption shoulder at 510 cm⁻¹ was observed to shift to lower wavenumber 500 cm⁻¹. Therefore, it is believed that the micro structural changes may be the reason for the well resolving of the peaks at 430, 435, 441 and 450 cm⁻¹, and shifting of the peaks to 435 and 500 cm⁻¹ in V^+ ion implanted ZnO thin films. The micro structural changes are also supported by our AFM scan of the surface, SEM and XRD results. Thus, the presence of absorption shoulder and strong peaks in the range 475-479 cm⁻¹ reveals higher population of ZnO in both as-deposited and V^+ ion implanted ZnO thin films.

5.3 Electrical properties of V^+ ion implanted ZnO thin films

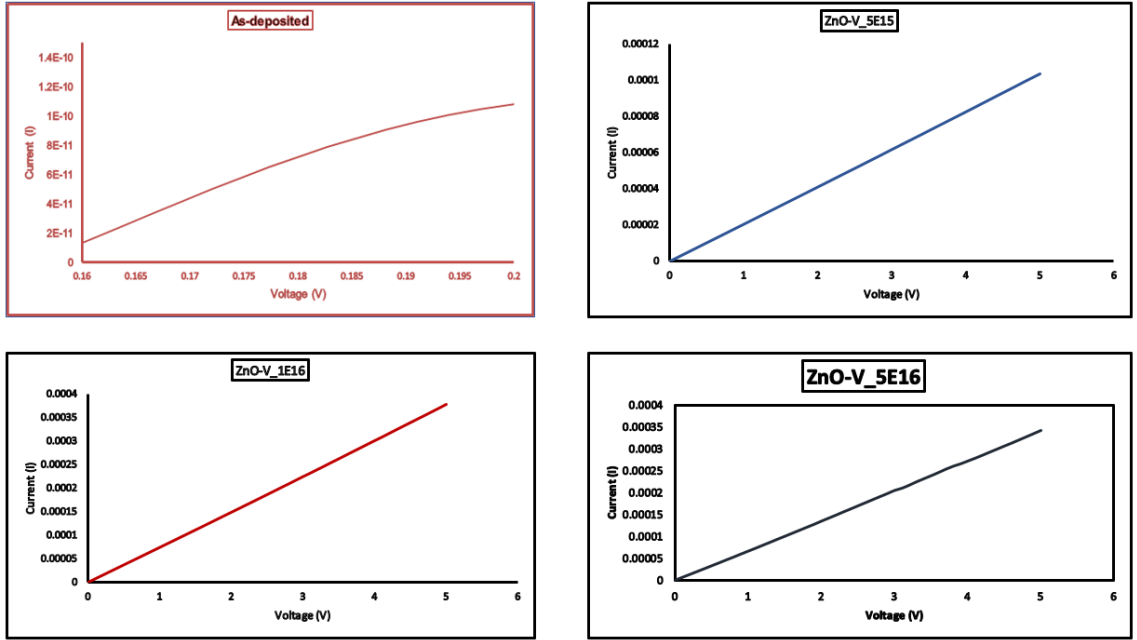


Figure 5.15: I-V response (a) as-grown and V^+ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

The current-voltage response of V^+ ion implanted ZnO thin films has been measured using a two-point probe. Table 5.6 lists calculated conductances and resistances as functions of ion fluence. Figure 5.15 shows the I-V response of as-grown and V^+ ion implanted ZnO thin films at different ion fluences. As can be seen from Figure 5.15, the current increases linearly with voltage as ion fluence increases from 5×10^{15} to 5×10^{16} ions/cm². Due to very

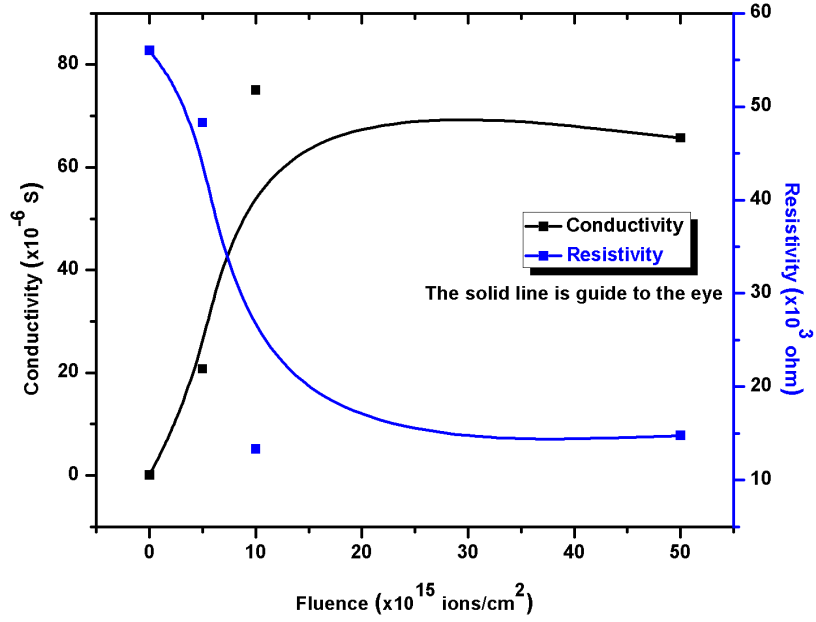


Figure 5.16: Variation of conductivity and resistivity of V^+ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm ^{2} in comparison with as-grown

Table 5.6: Conductances, resistances and transmittances of V^+ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ^{2})	Conductance ($\times 10^{-6}$ S)	Resistance ($\times 10^3$ ohm)	Transmittance (%)
0	0.07	56.00	72.14
5	20.71	48.30	78.50
10	75.05	13.33	82.34
50	65.70	14.77	45.26

high resistance observed in the as-grown film, Figure 5.15 (a) was recorded by varying V from 0 to 0.2 V with a step of 0.005 V. Figures 5.15 (b), (c) and (d) were recorded by varying V from 0 to 6 V with a step of 1 V. At a fluence of 1×10^{16} ions/cm², a sharp increase in conductance was observed. The effects of ion fluence on conductivity and resistivity in comparison with the as-grown ZnO thin films are illustrate in Figure 5.16. Figure 5.16 shows that the resistivity of thin films is inversely proportional to conductivity, and a 99 % decrease in resistivity was recorded for the thin film implanted to 1×10^{16} ions/cm². The observed electrical behavior was expected according to Equation 4.9.

5.4 Optical properties of V^+ ion implanted ZnO thin films

The UV-Vis spectroscopy spectral properties of the as-grown and V^+ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm² are shown in Figures 5.17, 5.18, 5.19 and tabulated in Tables 5.5 and 5.6. As can be seen from Figure 5.17 different transmittance behaviors were observed at different fluences upon ion implantation.

UV-Vis spectra in Figure 5.18 were used to determine the optical band gap energy E_g using Tauc relation (Equation 2.6) discussed in Section 2.4.2. Figure 5.19 shows estimated optical band gap energies which are listed in Table 5.5. Thus, the calculated optical direct band gaps vary between 2.4 and 4.1 eV. Figure 5.20 (a) shows effects of ion fluence on the band gaps of V^+ ion implanted ZnO thin films in comparison with as-grown. As can be seen from Figure 5.20 (a), there are significant changes in the band gap enegies due to implantation. An increase in band gap energy was observed with in-

crease in ion fluence from as-grown to 1×10^{16} ions/cm². This could arise due to the quantum size effect or could be that at a fluence of 1×10^{16} ions/cm² the defect energy levels might have been eliminated. As the ion fluence increased further, the optical band gap was observed to decrease. The effects of ion fluence on absorbance and transmittance of V⁺ ion implanted ZnO thin films in comparison with as-grown are illustrated in Figure 5.20 (b) and (c), respectively. From Figure 5.20 (b), lowest absorbance of 0.12 % was estimated for the thin film implanted at a fluence of 1×10^{16} ions/cm², and its absorbance edge was observed to shift toward a low wavelength of 368 nm (Figure 5.18). This means that the wavelength of absorption in this region shows a blue shift for the film implanted at 1×10^{16} ions/cm² with respect to the as-grown sample. However, from Figure 5.20 (c), transmittance increases progressively from as-grown to 1×10^{16} ions/cm². The highest average transmittance of 82.34 % was estimated at a fluence of 1×10^{16} ions/cm².

On the other hand, the highest absorbance of 0.56 % and transmittance of 45.26 % have been observed in the thin film implanted to 5×10^{16} ions/cm². The sharp decrease in the transmittance can be attributed to the production of defects by V⁺ ions, which resulted in high absorbance related to the development of intermediate energy levels [33]. However, the wavelength of absorption in the regions 456 and 589 nm shows a red shift for the film implanted at fluences 5×10^{15} and 5×10^{16} ions/cm² with respect to the as-grown sample. Within the wavelength range 280-380 nm (ultraviolet region), the observed transmittance shoulders in the thin films implanted from 5×10^{15} to 5×10^{16} ions/cm² may be due to reflection from the substrate [33].

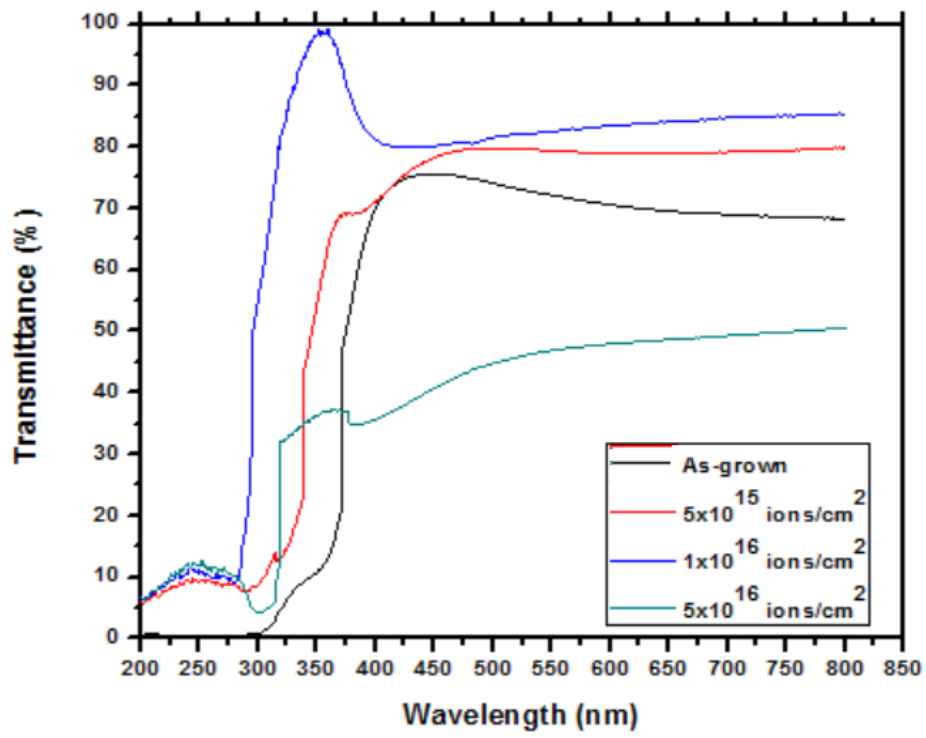


Figure 5.17: Optical transmittance of as-grown and V^+ ion implanted ZnO thin films at different fluences

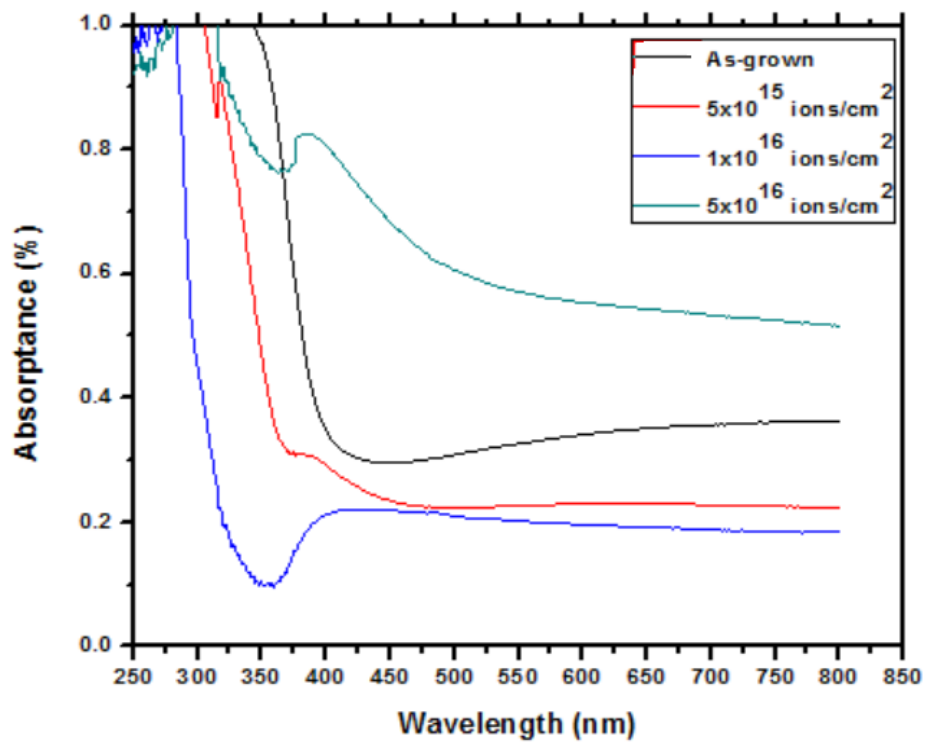


Figure 5.18: Optical absorbance of as-grown and V^+ ion implanted ZnO thin films at different fluences

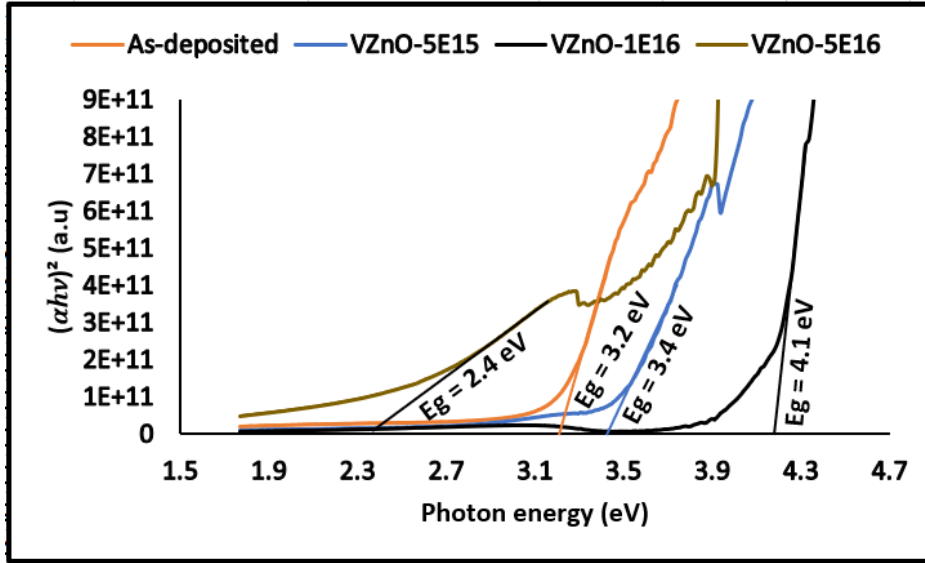


Figure 5.19: Calculated optical band gap E_g of as-grown and V^{+} ion implanted ZnO thin films at different fluences using Tauc relation

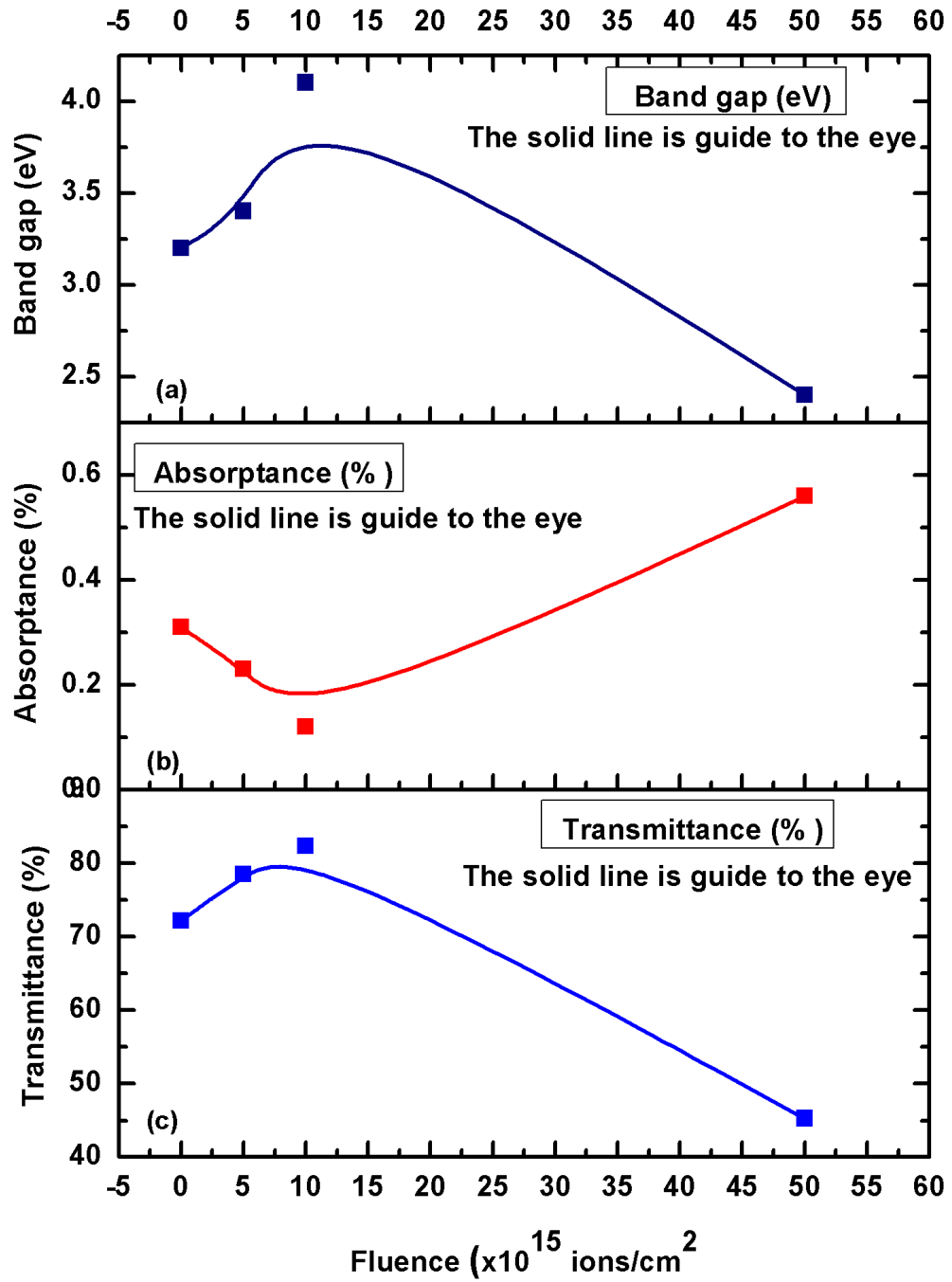


Figure 5.20: Variation of (a) optical band gap E_g , (b) absorbance, (c) transmittance of V^+ ion implanted ZnO thin films as a function of fluence in comparison with as-grown thin film

5.5 Effect of structural modification on the properties of V^+ ion implanted ZnO thin films

Changes in structural parameters such as, surface roughness and crystallite size due to ion implantation have significant effects on the optical band-gap, transmittance and conductance of V^+ ion implanted ZnO thin films. As can be seen from Figures 5.21 (a), (b) and (c), as the RMS roughness increases, it results in increased optical band-gap, transmittance and conductance to 4.11 eV, 82.34 % and 75.05×10^{-6} S, respectively. From the figures, it can be observed that optical band-gap, transmittance and conductance gradually increase up to a fluence of 1×10^{16} ions/cm², thereafter there is decrease in conductance to 65.70×10^{-6} S for the thin film implanted at 5×10^{16} ions/cm² with low value of RMS roughness (17.4 nm), but this conductance is higher than that of the as-grown. Therefore, the observed increase in optical band-gap, transmittance and conductance due to increased surface roughness may be attributed to the reduction of inter-sheet electron scattering on the Fermi surface, possibly due to induced surface roughness [182].

On the other hand, Figures 5.22 (a), (b) and (c) showed a contrast behavior, i.e., the effects of induced-crystallite size on the optical band-gap, transmittance and conductance of V^+ ion implanted ZnO thin films. It can be observed from Figure 5.22 (a), (b) and (c) that optical band-gap, transmittance and conductance gradually increase up to a fluence of 1×10^{16} ions/cm² as the crystallite size decreases. However, from the figure, it can be observed that at the lowest value of crystallite size a sharp decrease in transmittance and band gap to 45.26 % and 2.40 eV, respectively, together with slight decrease in conductance for the thin film implanted to 5×10^{16} ions/cm². The

reason for this observed effects of induced-surface roughness and induced-crystallite size could be that, as ion fluence increased the structure did not re-crystallize and V^+ ion implanted ZnO atoms were randomly distributed in 3-dimensional space, and there was a range of interatomic distances. Therefore, there is good agreement between UV-Vis results, I-V behaviour and XRD and AFM results.

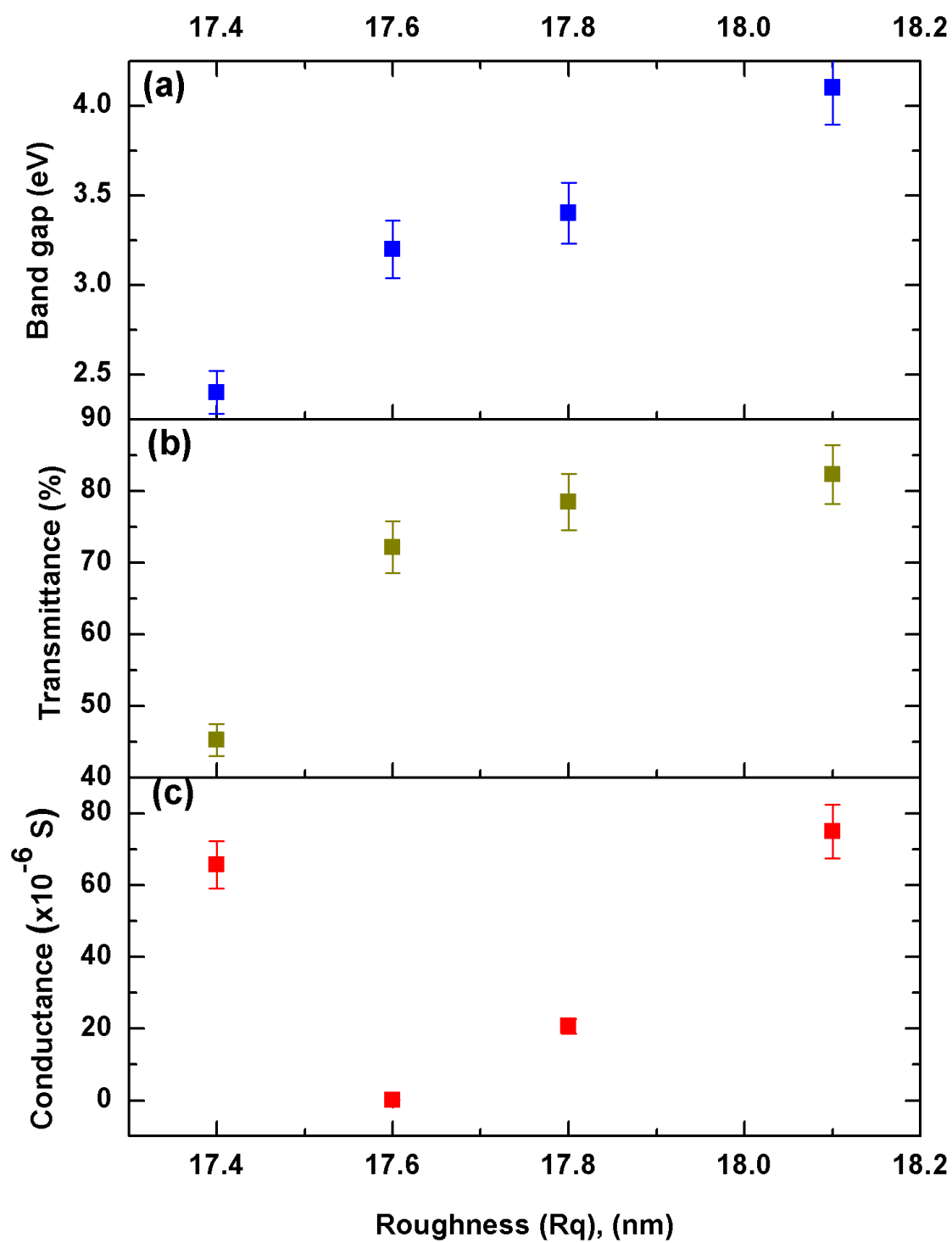


Figure 5.21: Effects of surface roughness on the (a) optical band gap, (b) transmittance and (c) conductance of V^+ ion implanted ZnO thin films

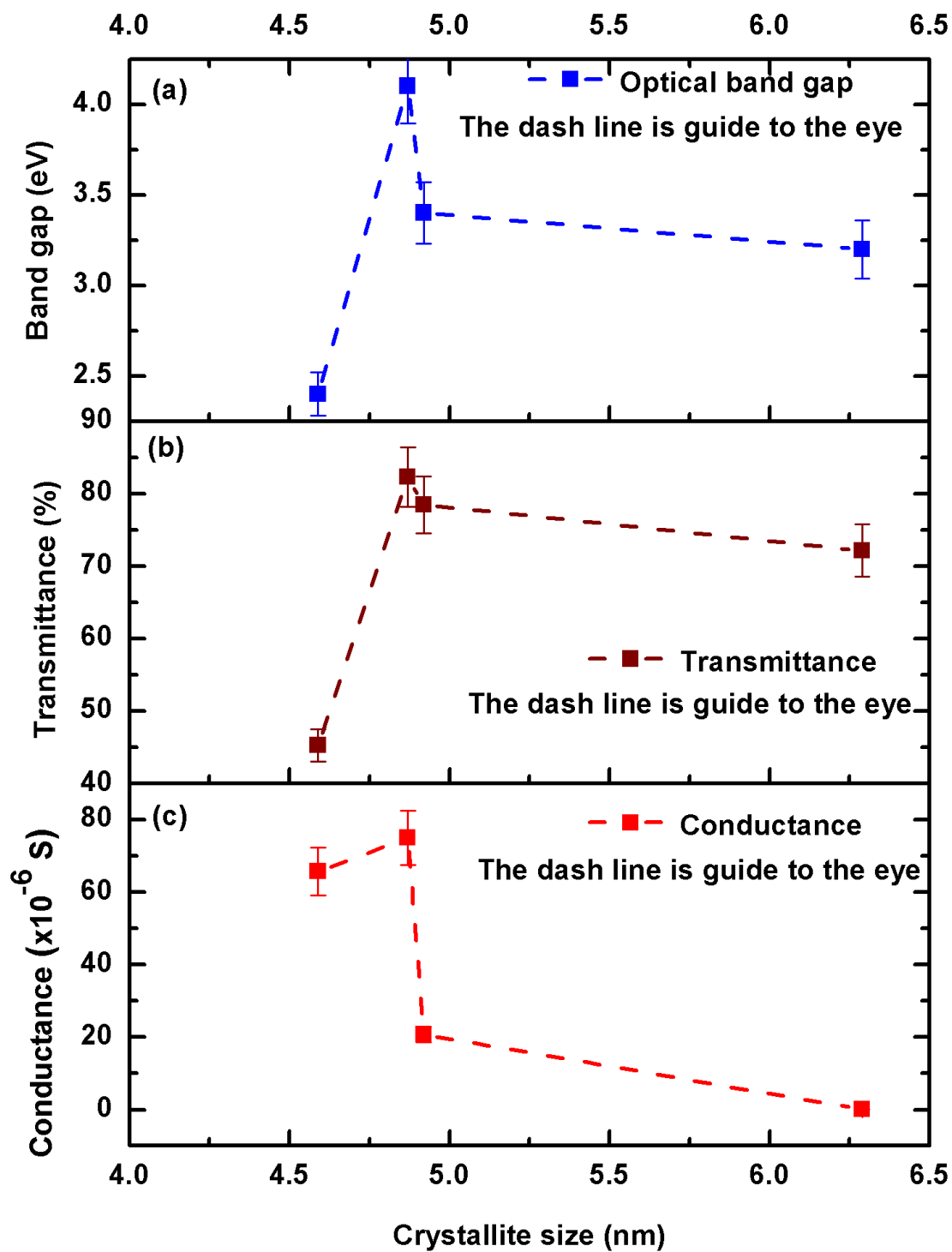


Figure 5.22: Effects of crystallite size on the (a) optical band gap, (b) transmittance and (c) conductance of V^+ ion implanted ZnO thin films

5.6 Structural modification of Co^+ ion implanted ZnO thin films

Figure 5.23 shows XRD spectra of Co^+ ion implanted ZnO thin films at fluences of (a) 5×10^{16} , (b) 1×10^{16} and (c) 5×10^{15} ions/cm² in comparison with the XRD spectrum of the (d) as-grown sample. As discussed earlier (Subsection 5.2), it can be observed that the diffraction spectrum of the as-grown reveals four peaks at $2\theta = 43.19^\circ$, 45.66° , 60.10° and 80.21° identified as ZnO peaks when compared with literature [135]. It can also be observed that ZnO thin films are polycrystalline in nature, because the diffraction spectrum of the as-grown reveals more than one peak. It can be clearly seen that the as-grown four peaks decrease to very low intensity (Table 5.8 Column 7) and not visible after ion implantation at a fluence of 5×10^{15} ions/cm². The peak of ZnO at $2\theta = 89.35^\circ$ corresponding to the (011) plane was revealed at a fluence of 5×10^{15} ions/cm². This behavior reflects the reduction of thin film crystallinity at relatively low fluences. By increasing ion fluence to 1×10^{16} ions/cm², one peak of Co at $2\theta = 35.23^\circ$ corresponding to the (100) plane was observed. All the ZnO peaks were visible as the ion fluence increases to 5×10^{16} ions/cm², which indicates that the crystal structures are in regular pattern. This behavior might be as a result of the restoration of crystal phases and structural re-crystallization after ion implantation at high fluence [141]. Furthermore, it could be that as ion fluence increases thermal spikes produced resulted in grain boundaries being directly affected [142]. In addition, the amorphous phase of the substrate (glass) was observed in as-grown and Co^+ ion implanted ZnO thin films from 2θ angles of 0° to 20° . The intensity ratio as a function of fluence recorded in Table 5.7 and illustrated

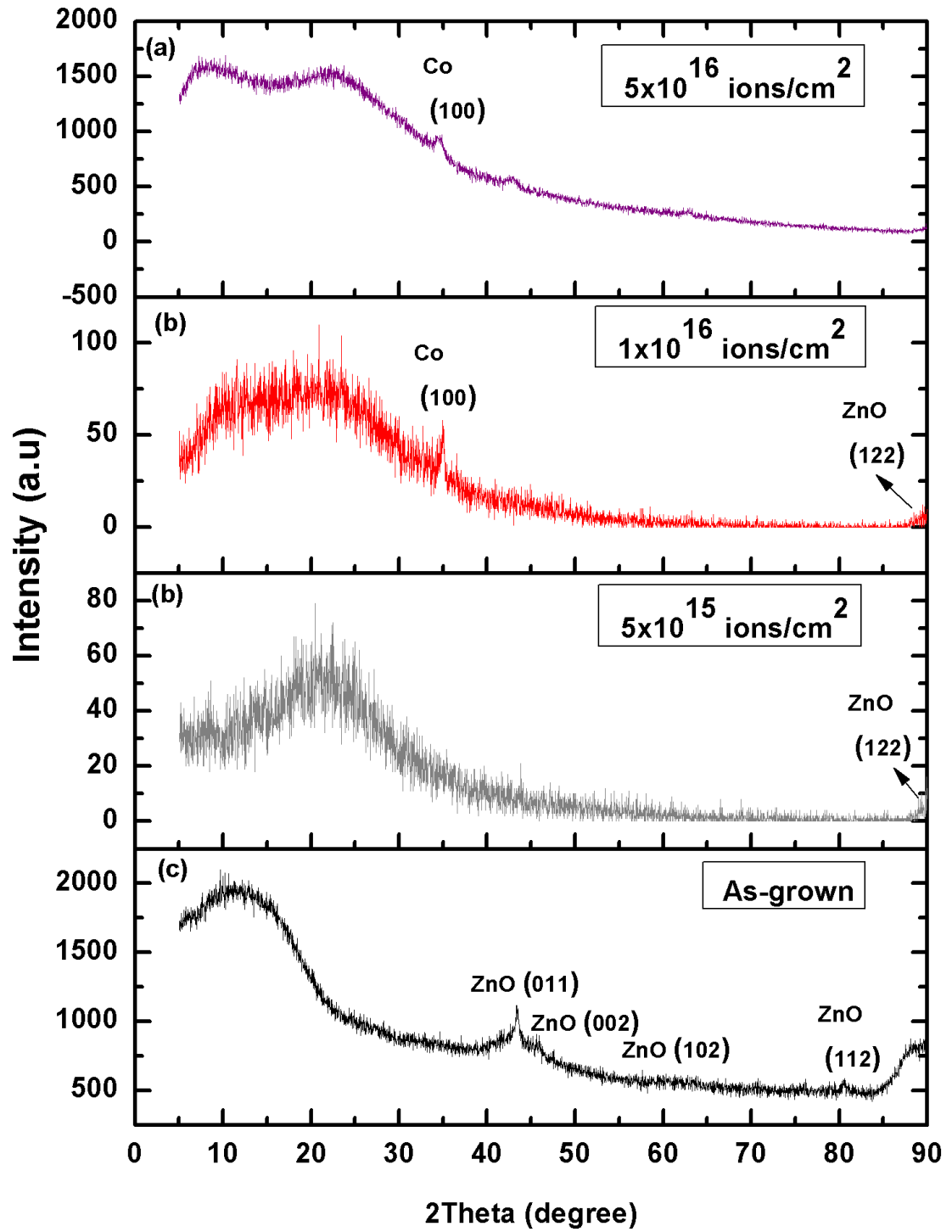


Figure 5.23: XRD spectral of Co^+ ion implanted ZnO thin films at fluences of (a) 5×10^{16} , (b) 1×10^{16} and (c) 5×10^{15} ions/cm² and (d) as-grown

in Figure 5.24 shows that preferred orientation decreases from 5×10^{15} to 5×10^{16} ions/cm². This means that the crystallization of ZnO thin films and degree of preferred orientation have been changed, which resulted in some of the ZnO phases not visible and new phases such as, Co⁺, being revealed. By increasing fluence to 5×10^{16} ions/cm², gradual increase of preferred orientation was observed which can be attributed to the agglomeration of crystals.

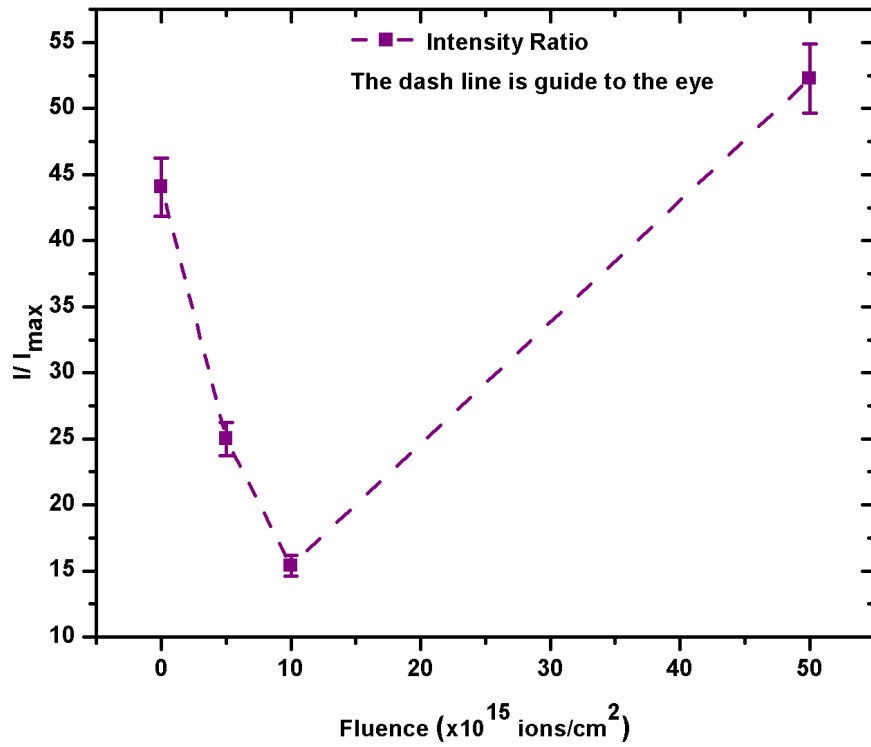


Figure 5.24: Variation of degree of preferred orientation (I/I_{max}) of Co⁺ ion implanted ZnO thin films with ion fluence

Table 5.7: Effect of fluence on degree of preferred orientation (I/I_{max}) of Co^+ ion implanted ZnO thin films in comparison with as-grown

Fluence ($\times 10^{15}$ ions/cm ²)	Intensity (I)	Intensity Max. (I_{max})	Ratio
0 (as-grown)	570.00	1958.00	44.08
5	2.00	8.00	25.00
10	4.00	26.00	15.38
50	461.00	882.00	52.27

From Table 5.8 Column 7, it can be seen that the changes in magnitude of XRD intensities of the as-grown and Co^+ ion implanted ZnO thin films as a function of fluence (Table 5.8 Column 1) are very pronounced in the fluence range 5×10^{15} to 1×10^{16} ions/cm². For Co^+ ion implanted ZnO thin films crystallization enhancement, the optimum fluence enhancement was observed at a fluence of 5×10^{16} ions/cm².

5.6.1 Crystallite size and strain

Table 5.8 and Figure 5.23 show polycrystalline nature and finite broadening of as-grown and Co^+ ion implanted ZnO peaks. As recorded in Table 5.8 Column 5, broadening was estimated as Full Width at Half Maximum (FWHM). As discussed earlier, FWHM is related to crystallite size, D , by Equation 4.3. Thus, Equation 4.3 shows that the bigger the crystallite size of as-grown and Co^+ ion implanted ZnO peaks the smaller the broadening of the peaks. The estimated FWHM and grain size using Equation 4.3 are listed in Table 5.8 Column 5 and Table 5.9 Column 4, respectively. Furthermore, the effects of fluence on FWHM and grain size of Co^+ ion implanted

Table 5.8: Structural parameters of as-grown and Co⁺ ion implanted ZnO thin films at different fluences

Fluence ($\times 10^{15}$ ions/cm ²)	2θ (deg)	d _{hkl} -space observed (Å)	d _{hkl} -space calculated (Å)	FWHM (deg)	h k l	Intensity (a.u)	W-H (nm)
0 (as-grown)	43.19	2.0842	2.0839	1.1012	011	1958.00	
	45.66	1.9880	1.8977	2.0000	002	863.00	6.29
	60.10	1.5424	1.5428	2.0000	102	570.00	
	80.21	1.1963	1.2074	1.2219	112	491.00	
5	42.90	2.1062	2.1057	2.0000	011	8.00	
	45.40	1.9961	1.9965	2.0000	002	5.00	4.92
	60.23	1.5351	1.5352	2.0000	102	5.00	
	80.22	1.1956	1.1955	1.9601	112	2.00	
	89.35	1.0955	1.1279	2.0000	122	2.00	
10	35.23	2.1450	2.5440	1.0116	100	26.00	
	43.06	2.0989	2.0969	2.0000	011	16.00	6.52
	59.66	1.5486	1.5484	2.0000	102	2.00	
	80.03	1.1979	1.1978	1.3216	112	2.00	
	88.28	1.1060	1.1072	1.5386	122	4.00	
50	34.74	2.5804	2.5762	0.9455	100	882.00	
	42.72	2.1149	2.1112	1.0683	011	547.00	7.24
	45.03	2.0115	2.0132	2.0000	002	461.00	
	59.76	1.5461	1.5489	2.0000	102	261.00	
	62.31	1.4889	1.4902	0.9684	200	250.00	
	80.48	1.1924	1.1922	1.4216	112	95.00	

Table 5.9: Structural parameters such as strain, dislocation density, crytallite size and lattice constant of as-grown and Co⁺ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	strain, ε ($\times 10^{-3}$)	Dislocation density, δ ($\times 10^{-11}$ line/m ²)	Crytallite size (nm)	Lattice constant, a ($\text{\AA}$)	Lattice constant, c ($\text{\AA}$)
0 (as-grown)	4.4676	1.6603	7.76	2.9475	5.2727
	8.0430	5.3810	4.31	3.9760	5.6229
	7.5537	4.7462	4.59	3.4489	5.0944
	4.0779	1.3833	8.50	2.9303	5.0755
	Average	6.0356	6.29	3.33	5.27
5	8.1222	5.4876	4.27	2.9786	5.1591
	8.0507	5.3913	4.30	3.9922	5.6458
	7.5487	4.7400	4.59	3.4326	4.0084
	6.5411	3.5590	5.30	2.9286	4.1417
	6.2056	3.2033	5.58	3.2865	6.5730
	Average	7.2937	4.81	3.09	5.10
10	4.2070	1.4722	8.24	2.5450	5.2542
	8.1178	5.4815	4.27	2.9682	5.1412
	7.5704	4.7673	4.58	3.4628	5.9977
	4.4165	1.6225	7.85	2.9342	5.0823
	4.8178	1.9308	7.19	3.3180	4.6924
	Average	5.8259	6.43	3.05	5.50
50	1.2896	8.81	2.5804	8.9388	
	4.3412	1.5676	7.99	2.9909	5.1804
	8.0615	5.4058	4.30	4.0230	5.6894
	7.5656	4.7625	4.58	3.4572	5.9880
	3.6160	1.0877	9.58	2.9778	5.1577
	4.7378	1.8671	7.31	2.9208	5.0598
	Average	5.3767	7.10	3.16	6.00

ZnO thin films in comparison with as-grown are shown in Figure 5.25. From Figure 5.25, it can be seen that as ion fluence increases from 0 (as-grown) to 5×10^{15} ions/cm² there is a sharp increase in the FWHM, which results in grain size decreasing by 23.53 %. However, at ion fluences higher than of 5×10^{15} ions/cm², it was observed that the grain size increased progressively from 1×10^{16} to 5×10^{16} ions/cm² by 12.88 %. On the other hand, FWHM decreases by 11.40 % from 1×10^{16} to 5×10^{16} ions/cm². Therefore, there is good agreement with Equation 4.3, and it shows that as grain size increases crystallinity of Co⁺ ion implanted ZnO thin films improves, peak broadening decreases and peak intensity increases due to re-crystallization at high ion implantation fluences.

It is of interest to determine the contributions of crystallite size and strain to the broadening in diffraction peaks of both as-grown and Co⁺ ion implanted ZnO thin films. The contributions were estimated using Equation 4.2 together with diffraction planes (011), (002), (102), (102), (112), (122), (100), (002) and (200). Figure 5.26 shows the linear fitting of Williamson-Hall (W-H) plots of as-grown and Co⁺ ion implanted ZnO thin films at different fluences. Furthermore, the average crystallite sizes listed in Table 5.9 Column 5 and shown in Figure 5.27, as a function of fluence, were calculated

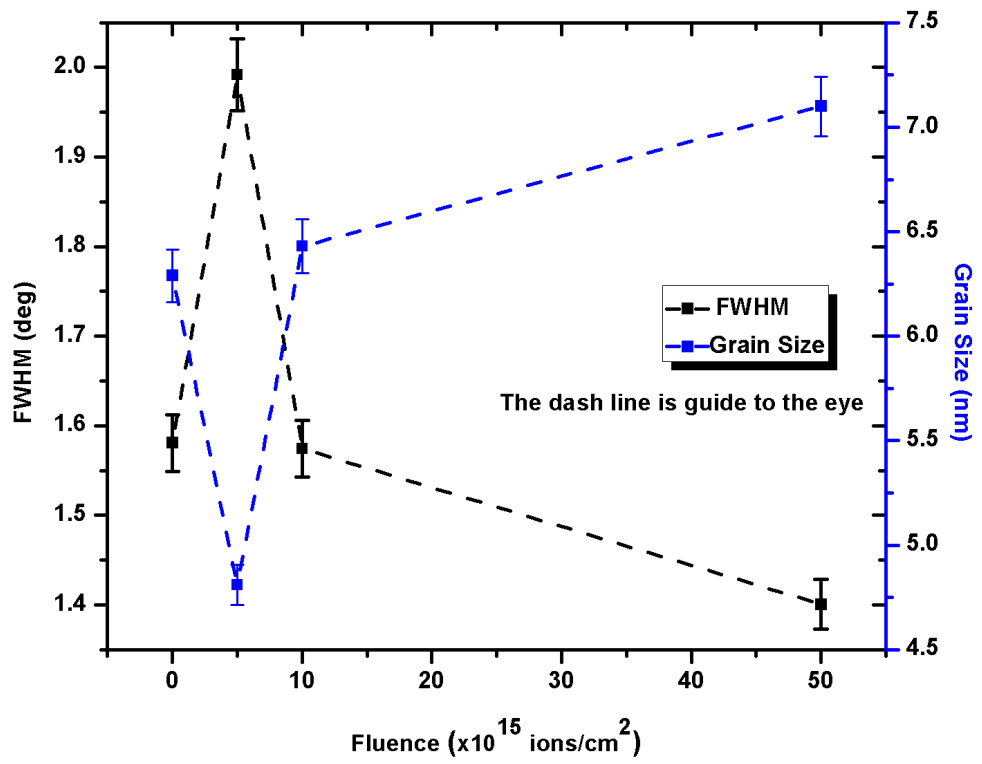


Figure 5.25: Variation of grain size and FWHM of Co^+ ion implanted ZnO thin films with ion fluence and in relation with Equation 4.3

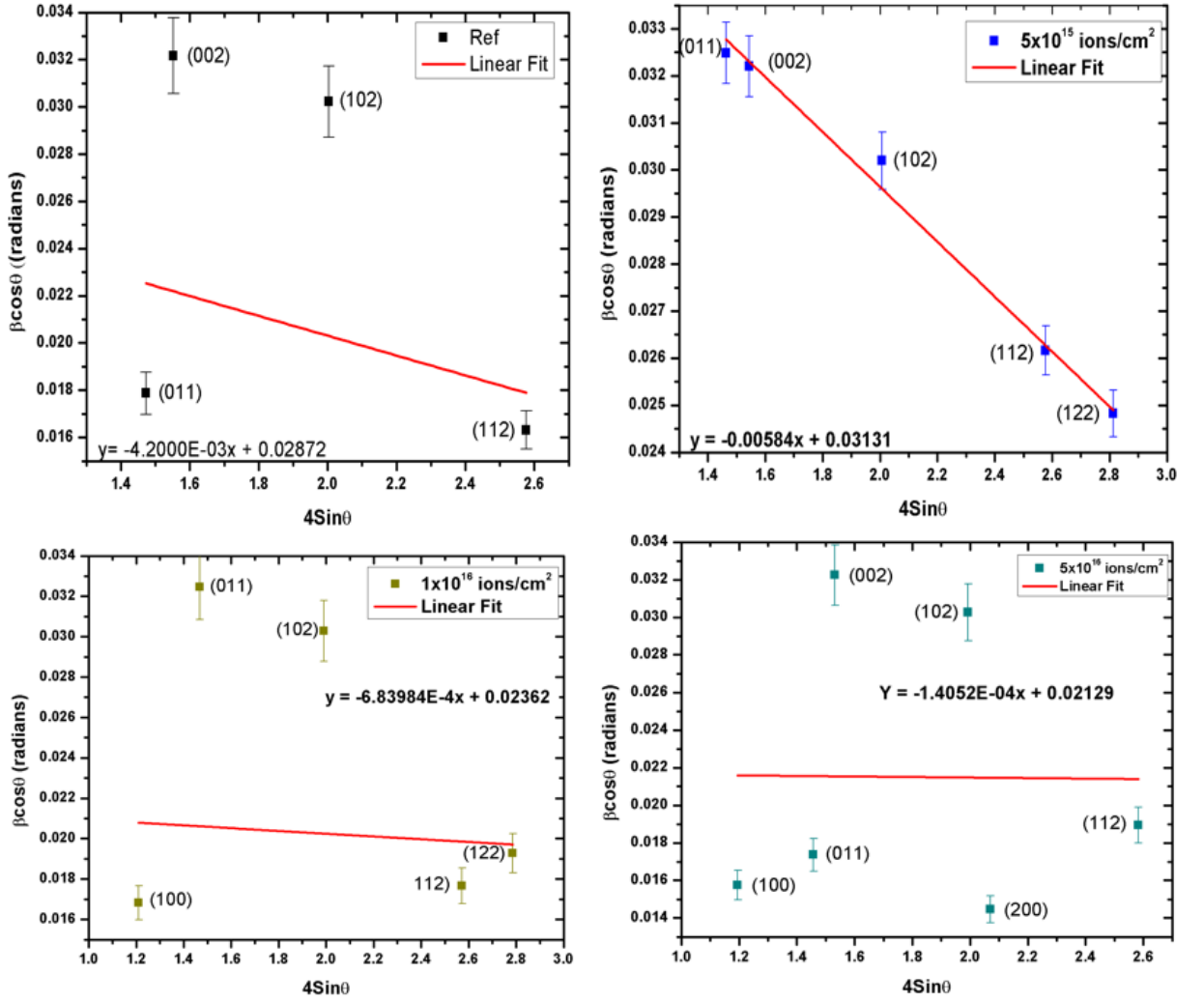


Figure 5.26: Williamson-Hall analysis for the deconvoluting size and strain broadening by considering the peak broadening of reflection as a function of 2θ of the as-grown and Co^+ implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm²

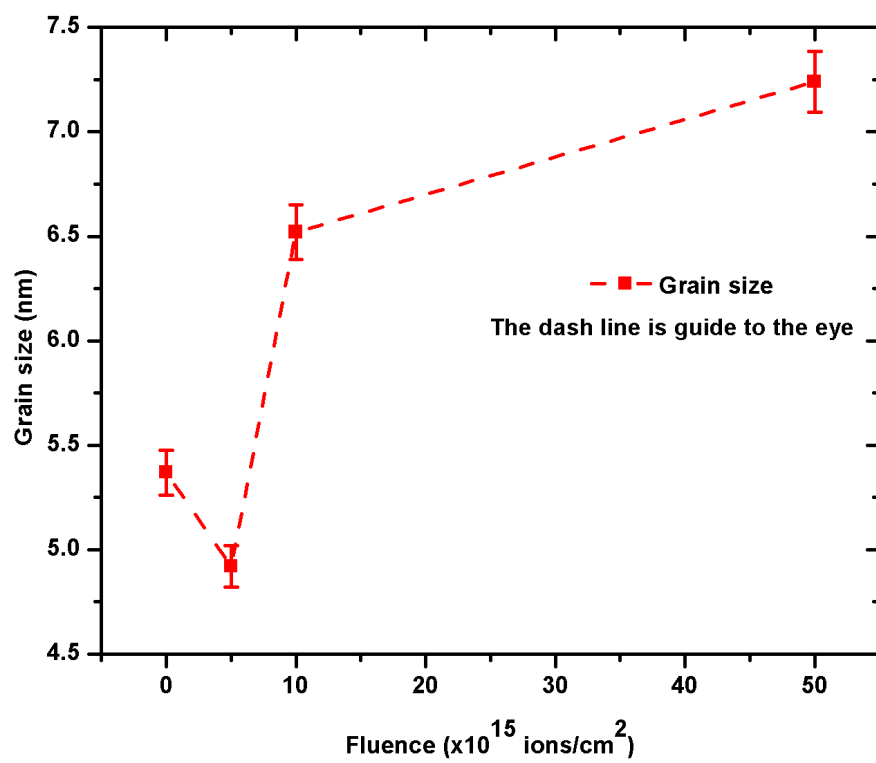


Figure 5.27: Variation of crystallite size of Co^+ ion implanted ZnO thin films with ion fluence using Williamson-Hall method

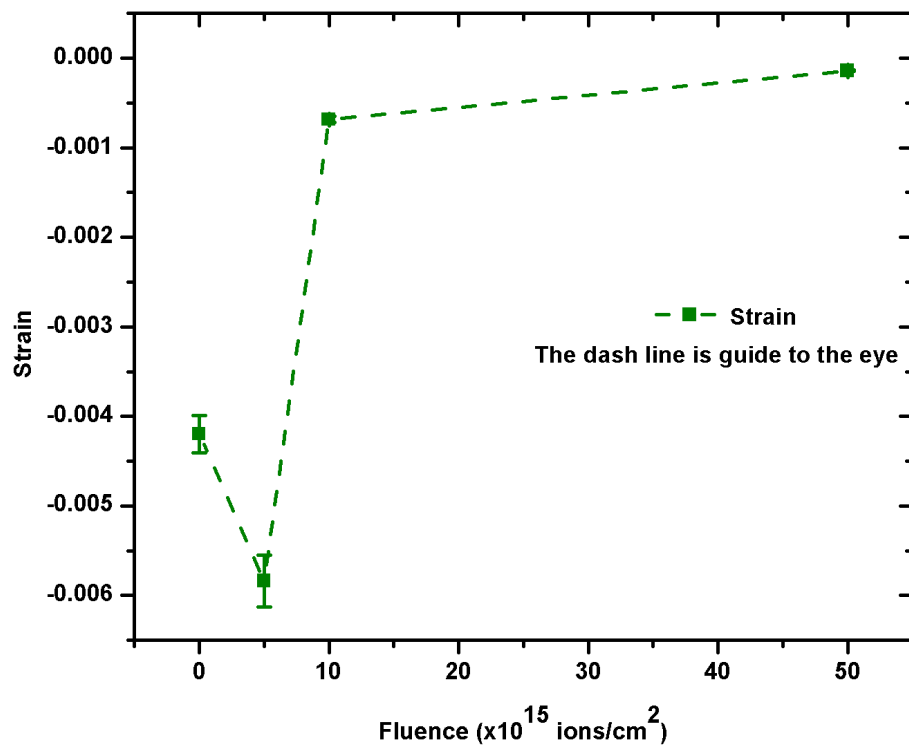


Figure 5.28: Variation of strain of Co^+ ion implanted ZnO thin films with ion fluence using Williamson-Hall method

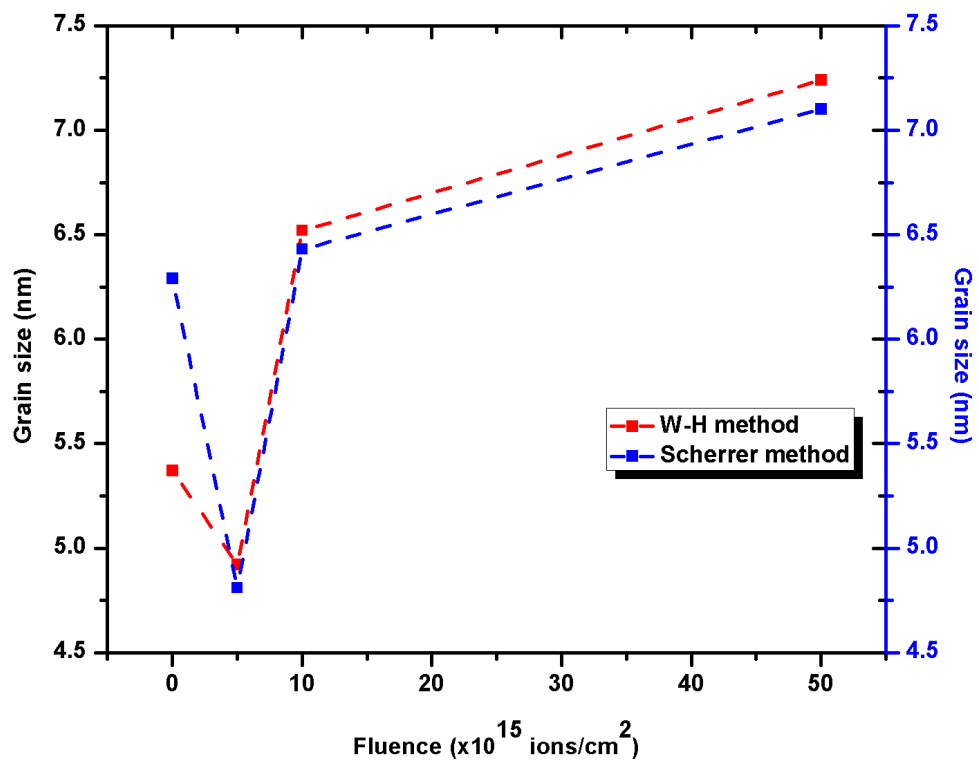


Figure 5.29: Comparison between Williamson-Hall and Scherrer methods in estimating crystallite grain size of Co^+ ion implanted ZnO thin films

from the inverse of intercepts of the W-H plots while the slope of the plot represents average strain (Figure 5.28) according to Equation 4.2.

Average crystallite sizes estimated from Figure 5.27 show a slight decrease in grain size with estimated limit 4.92 nm for the thin film implanted at a fluence of 5×10^{15} ions/cm². At high fluence, a rapid increase in grain size was observed for the thin films implanted to 5×10^{16} ions/cm² with increment of 34.82 %. Therefore, the behavior of W-H estimated crystallite size agree with that of the Scherrer estimated crystallite size (Figures 5.29), which indicates good agreement between the two methods. The agreement between the Scherrer and W-H methods in estimating grain size confirms the quality of the data. The decrease in grain size of Co⁺ ion implanted ZnO thin films at a fluence of 5×10^{15} ions/cm² can be attributed to columinar grain size growth [8]. Also, the enhancement of crystallite size for the thin films implanted from 1×10^{16} to 5×10^{16} ions/cm² can be attributed to low strain observed in the lattice crystal.

From Figure 5.26, both crystallite size and strain contributed to the broadening of XRD diffraction peaks. W-H plots exhibited negative slope (Figure 5.26) indicating that the contribution of strain to the broadening is very low with small magnitude of 10^{-4} at high fluence in comparison with contribution of grain size. The effect of fluence on strain using W-H method is shown in Figure 5.28. From Figure 5.28, strain follows the behavior of grain size in negative direction indicating how small the effect of strain on broadening is compared to the effect of grain size at different fluences. The strain behavior may be due to increase in crystallinity or increase in the degree of preferred orientation as confirmed by XRD diffraction peaks [8].

Table 5.10: Effect of fluence on the observed d_{hkl} -spacings of Co^+ ion implanted ZnO thin films in comparison with as-grown

Fluence ($\times 10^{15}$ ions/cm ²)	Ave. d_{hkl} -spacings observed
0 (as-grown)	1.7027
5	1.5857
10	1.6193
50	1.8224

5.6.2 d -value

From XRD analysis, observed and calculated d_{hkl} -spacings were resolved into many planes and listed in Table 5.8 Columns 3 and 4. To study the effect of ion fluence on the observed d_{hkl} -spacings in Co^+ ion implanted ZnO films in comparison with as-grown, the average observed d_{hkl} -spacings between planes of atoms were determined for as-grown and Co^+ ion implanted ZnO thin films at different fluences, together with the orientation of a single crystal (Table 5.10). As recorded in Table 5.10 and depicted in Figure 5.30, it can be seen from Figure 5.30 that at a fluence of 5×10^{15} ions/cm² d_{hkl} -spacing decreases in comparison with as-grown d_{hkl} -value, however, as ion fluence increases from 1×10^{16} to 5×10^{16} ions/cm² d_{hkl} -spacing increases to 1.8224. The d_{hkl} -spacing behavior can be explained as the decrease in relaxation of Co^+ ion implanted ZnO thin films at low fluence [136]. The relaxation of thin film increases at high fluence.

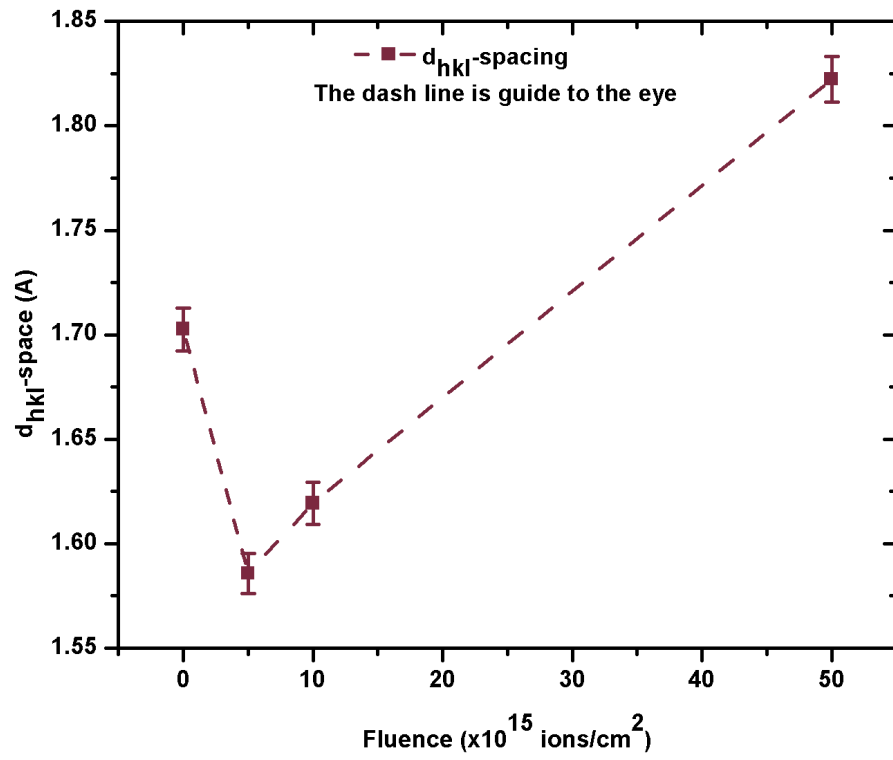


Figure 5.30: Variation of d_{hkl} -spacings of as-grown and Co^+ ion implanted ZnO thin films as a function of fluence

5.6.3 Lattice constants

By using Equations 5.1 and 5.2, the variation and estimated lattice constants a and c for hexagonal close pack (hcp) ZnO crystal structure are shown in Figure 5.31 and recorded in Table 5.9 Columns 5 and 6. The calculated average values of a and c were 3.1678 ± 0.0963 and $5.2084 \pm 0.1070 \text{ \AA}$, respectively. It can be observed that there is no significant difference between the estimated average lattice constant and the lattice constant reported in the literature (3.2429 and $5.2069 \text{ \AA}$).

As ion fluence increases there is a gradual decrease in the lattice constant, c , up to a fluence of $5 \times 10^{15} \text{ ions/cm}^2$ in comparison with as-grown, beyond it there is a sharp increase, where it reaches a maximum value of $6.0022 \text{ \AA}$ at a fluence of $5 \times 10^{16} \text{ ions/cm}^2$ (Figure 5.31). However, the lattice constant, a , was observed to decrease up to a fluence of $1 \times 10^{16} \text{ ions/cm}^2$ with notable decrease at a fluence of $5 \times 10^{15} \text{ ions/cm}^2$ in comparison with as-grown, thereafter there is increase, reaching a maximum value of $3.1584 \text{ \AA}$ at a fluence of $5 \times 10^{16} \text{ ions/cm}^2$. This implies that lattice constant shrinks at low implantation fluence, and it relaxes at high fluence. It also suggests the behavior of Co^+ ions in ZnO matrix. Similar behavior in lattice constant has been observed in Co-doped ITO films by Stankiewicz et al. [136].

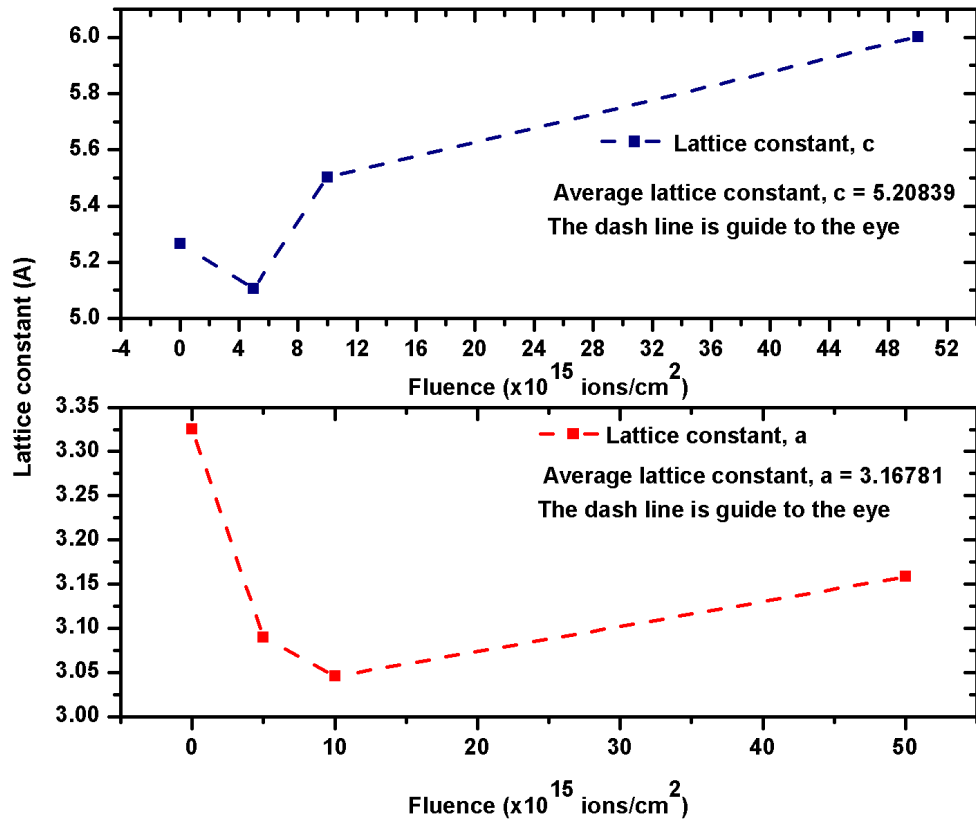


Figure 5.31: Variation of lattice constants c and a of as-grown and Co^+ ion implanted ZnO thin films as a function of fluence

5.6.4 Dislocation density

The dislocation densities of as-grown and Co^+ ion implanted ZnO thin films were estimated using Equation 4.5. As listed in Table 5.9 Column 3 and shown in Figure 5.32 as a function of fluence, it can be seen that dislocation density increases to maximum $4.4762 \times 10^{-11} \text{ line/m}^2$ at a fluence of 5×10^{15} . This suggests that at a fluence of 5×10^{15} Co^+ ion implanted ZnO thin films recorded high imperfection of lattice structure. However, as ion fluence increases to $5 \times 10^{16} \text{ ions/cm}^2$, the dislocation density decreases to minimum in comparison with as-grown. This shows that lattice structure has been improved as a result of dislocation reduction. Therefore, there is good agreement with what has been observed from XRD diffraction patterns.

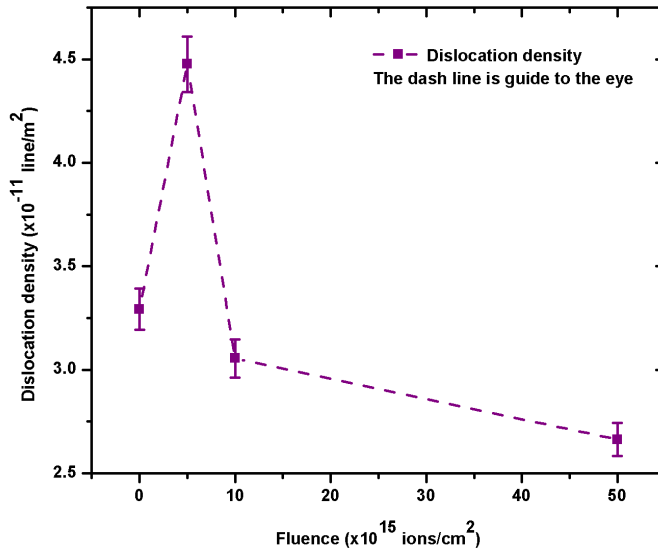


Figure 5.32: Variation of dislocation density of as-grown and Co^+ ion implanted ZnO thin films as a function of fluence

Table 5.11: Isotropic (iso) refined thermal parameters (B and U) of as-grown and Co⁺ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	B-factor $\text{\AA}^2$	U ($\times 10^{-1} \text{\AA}^2$)
0 (as-grown)	9.985	1.9784
5	4.707	0.5962
10	8.814	0.1116
50	9.234	0.0985

5.6.5 Thermal and chemical stability

By using EXPO-2014 software together with Equation 2.8, the thermal factors or B-factors and mean square displacement amplitude U (Section 2.4.4) of as-grown and Co⁺ ion implanted ZnO thin films have been determined, and they are recorded in Table 5.11 and shown in Figure 5.33. From Figure 5.33, it can be seen that the vibrational motion of different parts of Co⁺ ion implanted ZnO thin film structures, induced by thermal motion, decreases rapidly by 52.86 % at a fluence of 5×10^{15} ions/cm² in comparison with as-grown. This shows that atoms of the thin film implanted at a fluence of 5×10^{15} ions/cm² are stable as a result of low B-factor. However, the B-factor of the thin film implanted to 5×10^{16} ions/cm² decreases by 7.52 %, meaning that the atoms have become flexible. It can be observed (Table 5.11) that the mean square displacement amplitude decreased from ion fluence of 5×10^{15} to 5×10^{16} ions/cm².

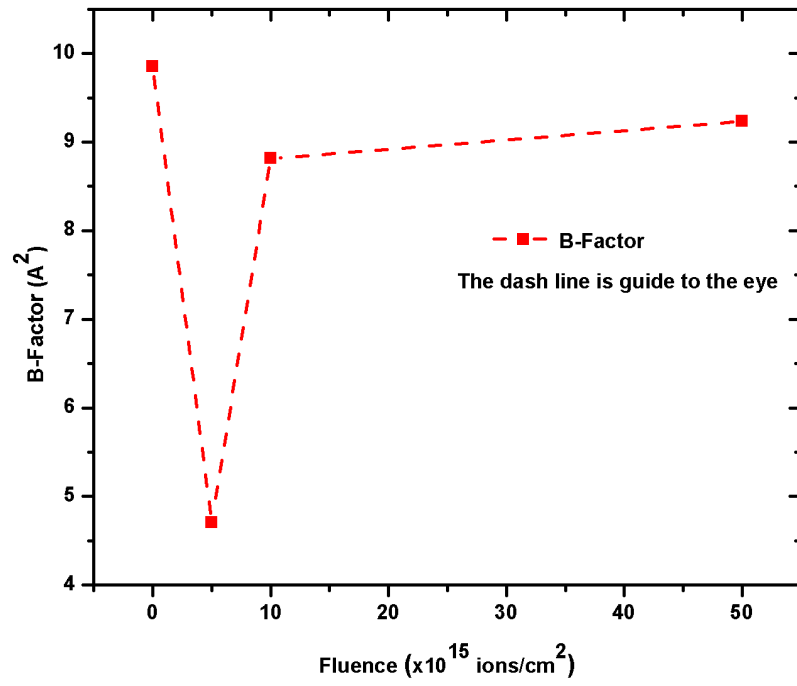


Figure 5.33: Variation of thermal factors (B-factors) of as-grown and Co^+ ion implanted ZnO thin films as a function of fluence

5.6.6 Surface Morphology properties

The surface morphological properties of as-grown and Co^+ ion implanted ZnO thin films have been investigated using AFM and FE-SEM. The effects of ion implantation on the surface morphology of the thin films at different ion fluences are discussed below.

5.6.6.1 AFM scans

Figures 5.34 and 5.35 depict 3-D and 2-D AFM scans of as-grown and Co^+ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/ cm^2 .

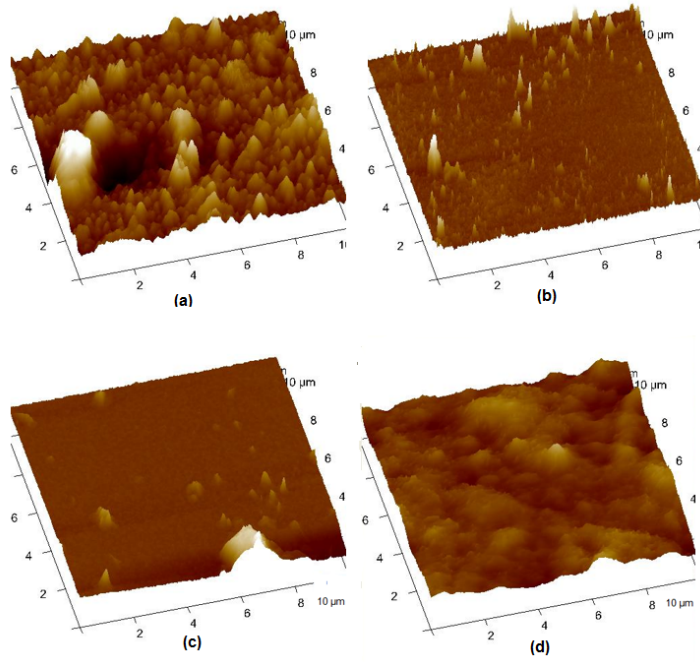


Figure 5.34: AFM 3-D images of (a) as-deposited and Co^+ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/ cm^2

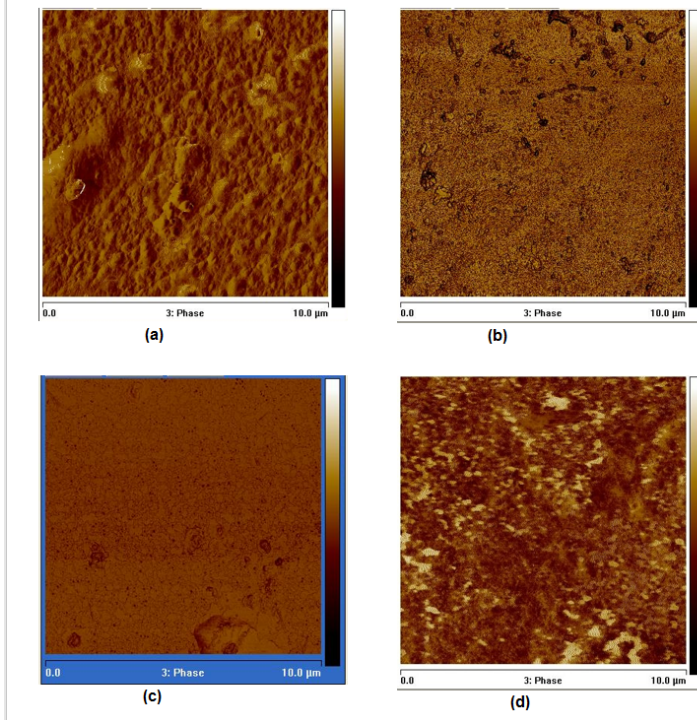


Figure 5.35: AFM 2-D images of (a) as-deposited and Co^+ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/ cm^2

The estimated root mean square and average roughness are recorded in Table 5.13 as a function of fluence. It can be seen from Table 5.13 and Figure 5.36

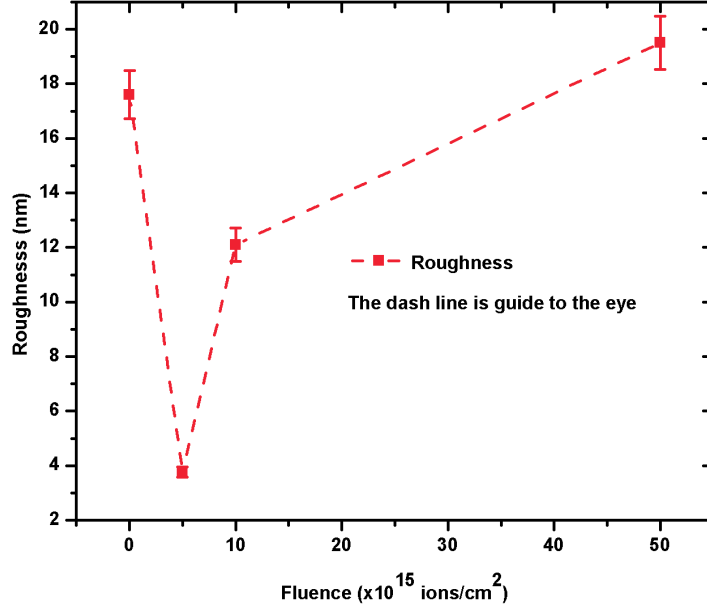


Figure 5.36: Surface roughness of as-grown and Co^+ ion implanted ZnO thin film as a function of fluence

that ion implantation induced modifications on the surface of Co^+ ion implanted ZnO thin films. The AFM image of the thin film implanted at a fluence of 5×10^{15} ions/cm ^{2} shows that the thin film surface roughness decreased by 92.13 %, and its grain size decreased to 4.81 nm while the estimated grain size and roughness of the as-grown were 6.29 and 17.6 nm, respectively. However, the roughness of the thin film implanted at 5×10^{16} ions/cm ^{2} increased by 10.79 %. As discussed earlier, the increase in the amount of metal ion on the surface of Co^+ ion implanted ZnO thin films may be the reason for observed surface roughness at high fluence.

5.6.6.2 FE-SEM micrographs

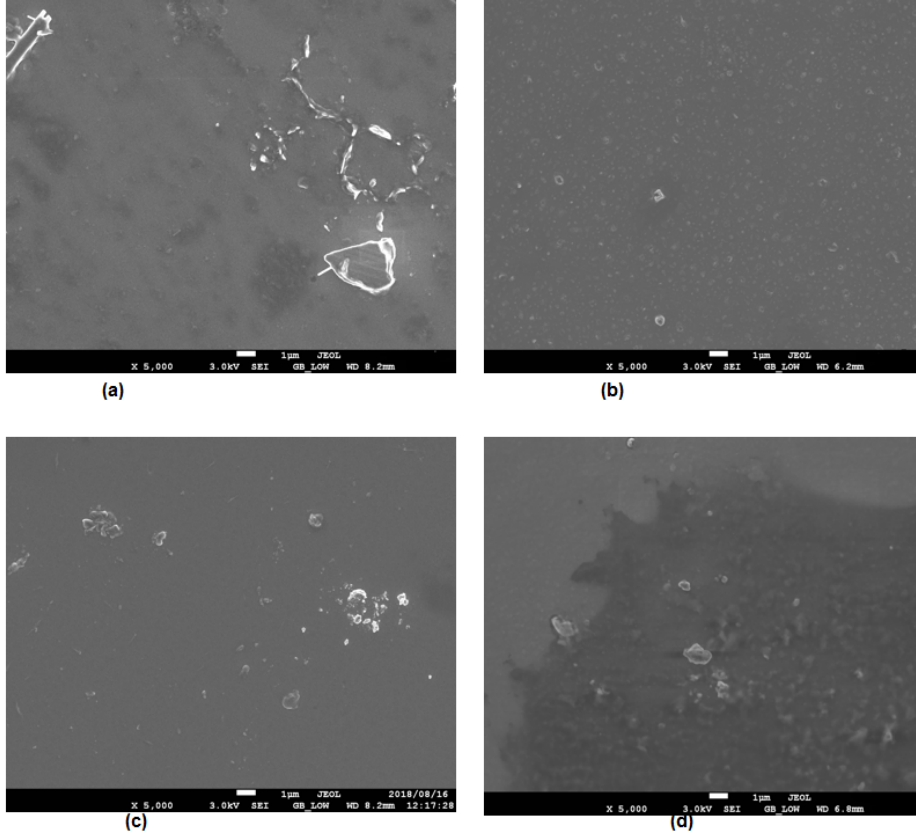


Figure 5.37: FE-SEM micrographs of (a) as-grown and Co^+ ion implanted ZnO thin films at fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

Figure 5.37 depicts FE-SEM micrographs of as-grown and Co^+ ion implanted ZnO thin films. The micrographs were taken with high resolution FE-SEM at 3 kV. By carefully examining the thin film surface morphologies, it can be observed that the micrographs reveal smooth surfaces and decrease in grain size for the thin film implanted at a fluence of 5×10^{15} ions/cm²

in comparison with as-grown. However, the average particle sizes appear to increase in a regular pattern at high fluence. There is good agreement with AFM and XRD results. Therefore, there was profound change in the morphology of Co^+ ion implanted ZnO thin films.

5.6.7 Chemical Bond Analysis

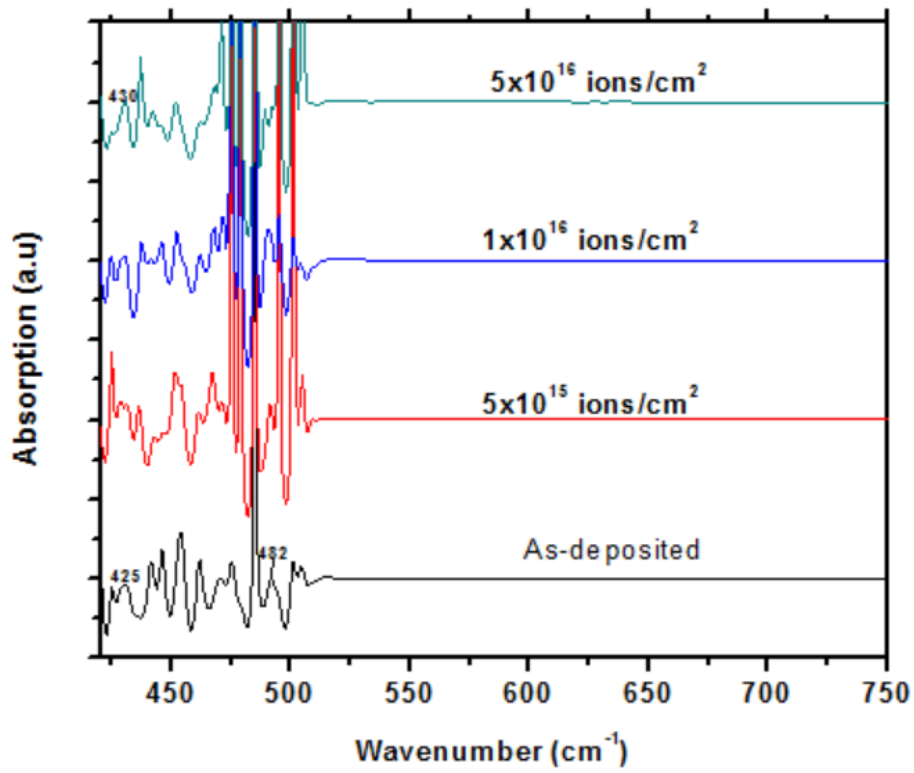


Figure 5.38: FTIR spectra in the wavenumber range 420-750 at room temperature of as-deposited and Co^+ ion implanted ZnO thin films at fluences of 5×10^{15} , 1×10^{16} and $5 \times 10^{16} \text{ ions/cm}^2$

FTIR spectrar of as-grown and Co^+ ion implanted ZnO thin films recorded

at room temperature are shown in Figure 5.38. A distinct characteristic absorption peak around 482 cm^{-1} is assigned to the stretching vibration of ZnO bonds [140]. The absorption peaks in the range $425 - 482\text{ cm}^{-1}$ can be attributed to the stretching vibration of ZnO [140]. In the as-grown film, a strong peak was observed around 476 cm^{-1} while in Co^+ ion implanted ZnO thin films similar strong peaks were observed in the range $473\text{-}512\text{ cm}^{-1}$. The observed strong peaks can be attributed to high concentration of ZnO in the region in both as-grown and Co^+ ion implanted ZnO thin films. It can be seen from the spectrum that the number of doublets observed in the as-grown sample decreases to three doublets in the thin films implanted from 5×10^{15} to $1 \times 10^{16}\text{ ions/cm}^2$. The doublets further decrease to one in the thin film implanted at $5 \times 10^{16}\text{ ions/cm}^2$. This decrease in the number of doublets can be attributed to morphological and structural changes in Co^+ ion implanted ZnO thin films. The observed morphological and structural changes are also supported by the AFM scans of the surface, SEM and XRD results. However, the presence of cobalt oxide is not found in the thin films by FTIR studies, which indicates that upon implantation Co^+ ions are incorporated well into the ZnO matrix, and possibly there is no formation of oxide of the cobalt.

5.7 Electrical properties of Co^+ Ion Implanted ZnO Thin Films

The current-voltage (I-V) responses of as-grown and Co^+ ion implanted ZnO thin films at different ion fluences are listed in Table 5.12 and depicted in Figure 5.39 (a), (b), (c) and (d). From Figure 5.39, it can be seen that current increases linearly with voltage as ion fluence increases from 5×10^{15} to $5 \times 10^{16}\text{ ions/cm}^2$ in the voltage range 0 to 6 V. However, Figure 5.39 (a)

was recorded by varying V from 0 to 0.2 V with a step of 0.005 V, due to very high resistance observed in the as-grown thin film. It can be observed that at high ion fluence conductivity increased to 156.92×10^{-6} S from nearly zero conductivity recorded for the as-grown thin film. Therefore, high implantation fluence improves the conductivity of Co^+ ion implanted ZnO thin films, (see Figure 5.40). As can also be seen on Figure 5.40, as ion fluence increases the resistivity of Co^+ ion implanted ZnO thin films decreases, which indicates that ion implantation enhances the conductivity of implanted ZnO thin films in the ion fluences range 5×10^{15} to 5×10^{16} ions/cm² by 98.87 %.

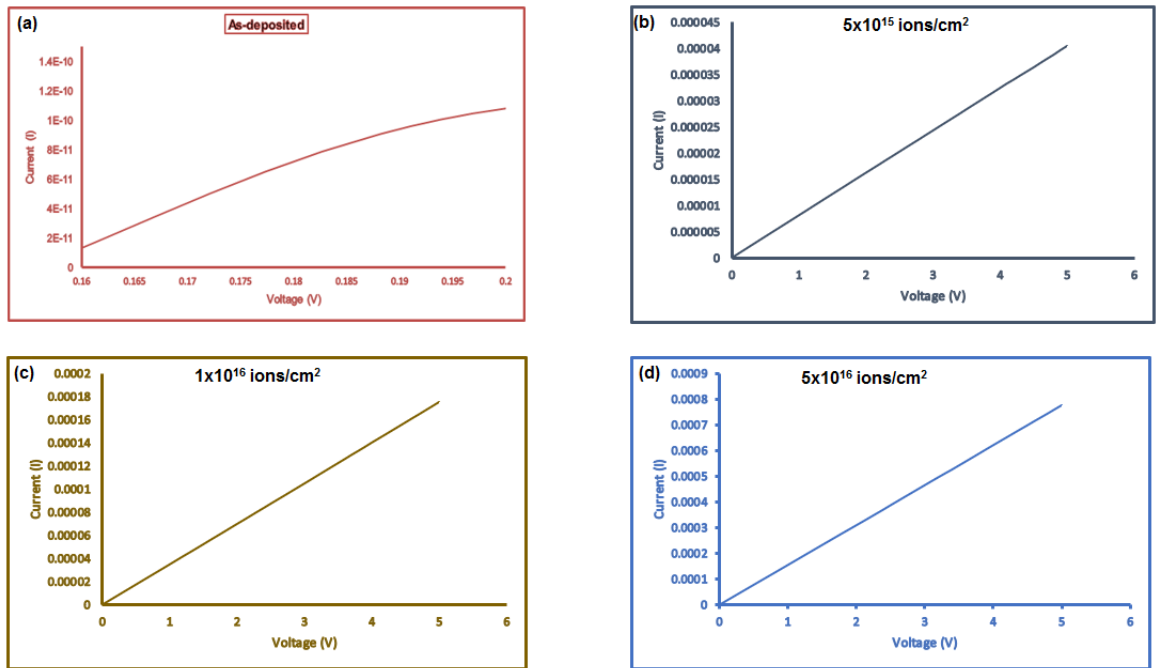


Figure 5.39: I-V responses of (a) as-grown and Co^+ ion implanted ZnO thin films at ion fluences of (b) 5×10^{15} , (c) 1×10^{16} and (d) 5×10^{16} ions/cm²

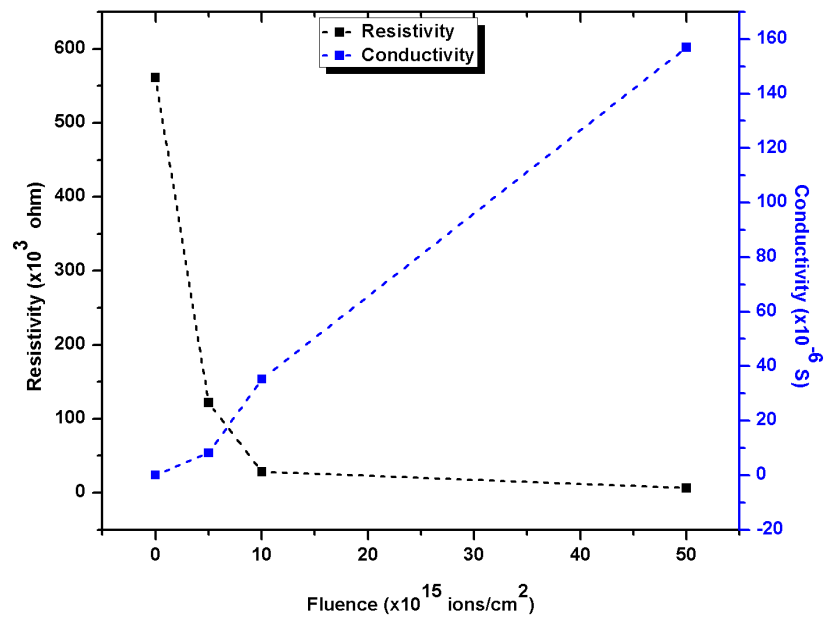


Figure 5.40: Variation of conductivity and resistivity of Co^+ ion implanted ZnO thin films at ion fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm ^{2} in comparison with as-grown

5.8 Optical properties of Co^+ Ion Implanted ZnO Thin Films

As discussed in Section 4.4.4, the optical properties of as-grown and Co^+ ion implanted ZnO thin films at different fluences have been investigated using UV-Vis spectroscopy. Upon ion implantation at fluences of 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm², the observed changes transmittance, absorbance and optical band gap in relation to wavelength are shown in Figures 5.41, 5.42, 5.43 and listed in Tables 5.12 and 5.13.

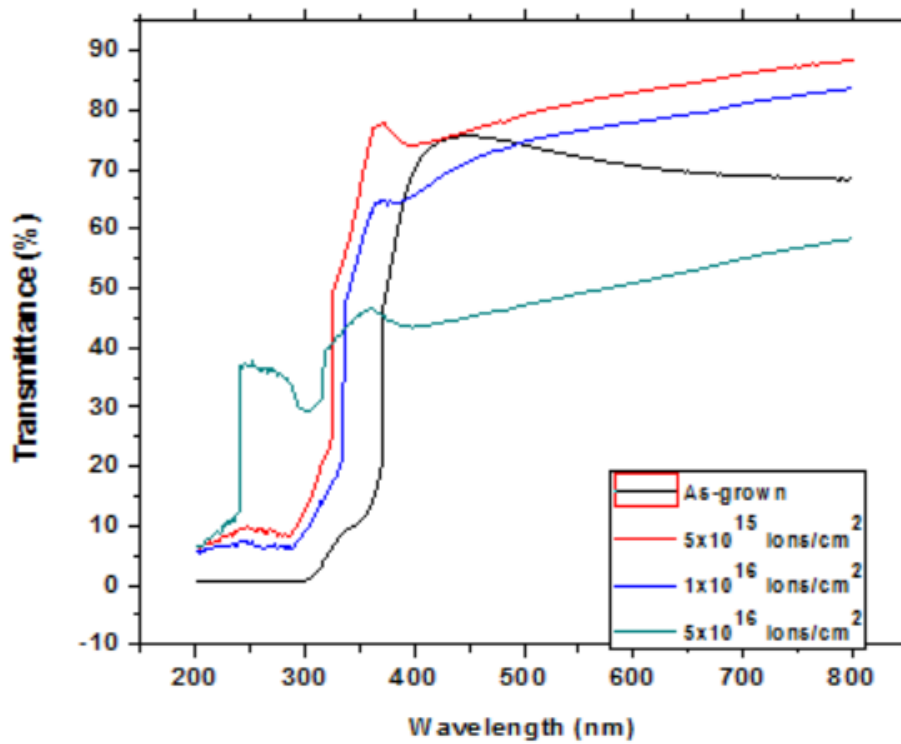


Figure 5.41: Optical transmittances of as-grown and Co^+ ion implanted ZnO thin films at different ion fluences

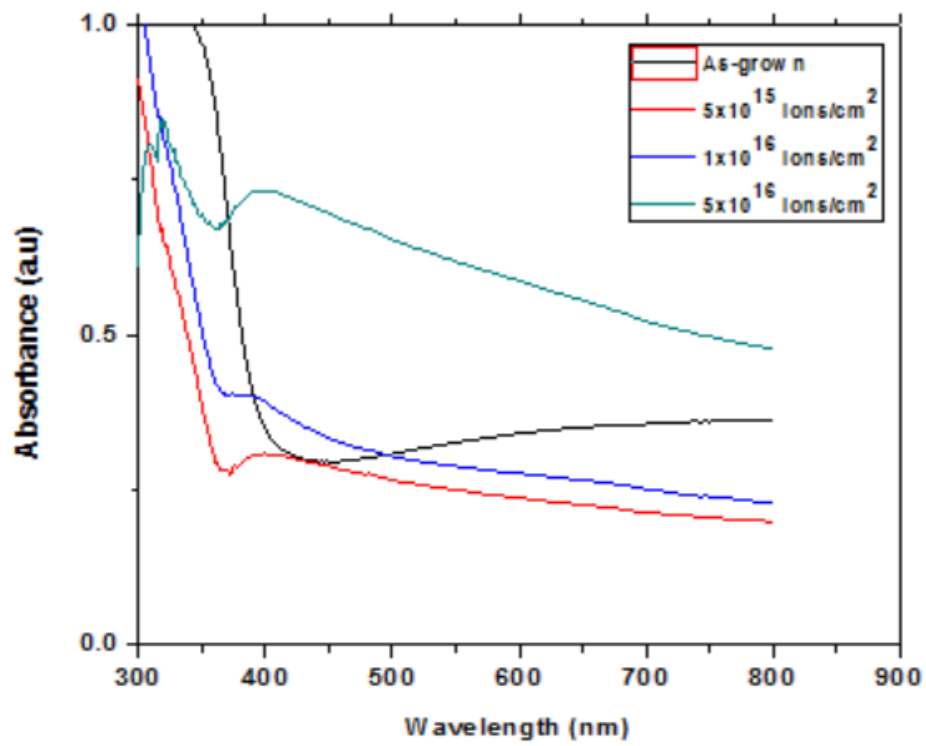


Figure 5.42: Optical absorbance of as-grown and Co^+ ion implanted ZnO thin films at different ion fluences

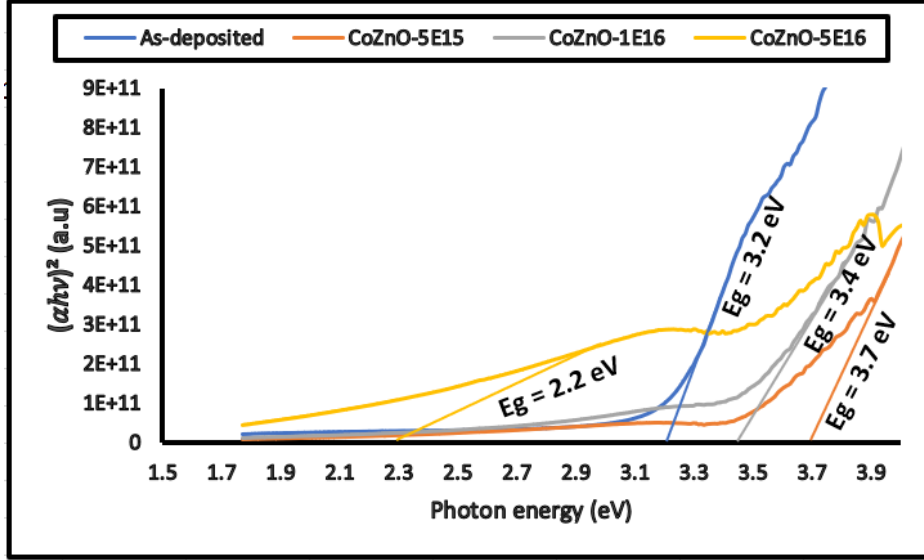


Figure 5.43: Calculated optical band gaps E_g of as-grown and Co^+ implanted ZnO thin films at different ion fluences using Tauc relation

Table 5.12: Conductances, resistances and transmittances of Co^+ ion implanted ZnO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	Conductance ($\times 10^{-6}$ S)	Resistance ($\times 10^3$ ohm)	Transmittance (%)
0 (as-grown)	0.07	561.00	72.14
5	8.21	121.86	80.69
10	35.27	28.35	75.52
50	156.92	6.37	49.00

Table 5.13: Optical band gap, average roughnesses (Ra) and transmittances at different ion fluences, together with root mean squares, wavelengths and corresponding absorbance edges of Co⁺ ion implanted ZnO thin films.

Fluence ($\times 10^{15}$ ions/cm ²)	Wave- length (nm)	Absor- bance (au)	Band gap (eV)	RMS (Rq), (nm)	Ave. Ra (nm)
0 (as-grown)	410	0.37	3.20	17.6	12.6
5	365	0.28	3.70	3.76	2.16
10	514	0.30	3.40	12.10	4.84
50	367	0.68	2.20	19.50	15.6

In addition, the variation of transmittance and absorbance of Co^+ ion implanted ZnO thin films in comparison with the as-grown ZnO are illustrated in Figures 5.44 (a) and (b), respectively. It is clear from figure 5.44 (a)

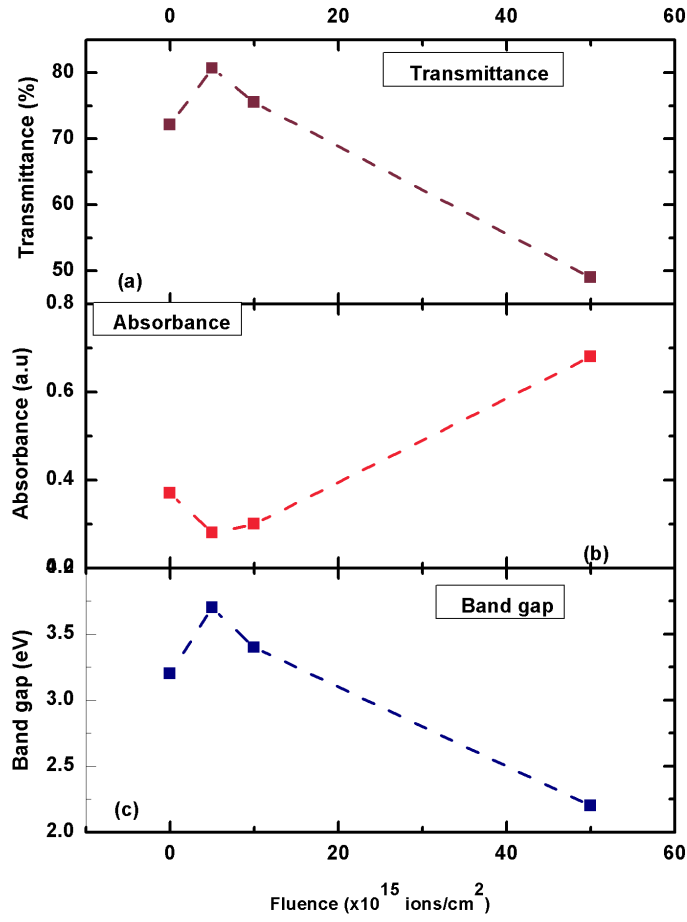


Figure 5.44: Variation of (a) transmittance, (b) absorptance, (c) optical band gap E_g of Co^+ ion implanted ZnO thin films as a function of ion fluence in comparison with as-grown

that transmittance has been enhanced, with average transmittances of 80.69 % and 75.52 % recorded, for the thin films implanted at fluences of 5×10^{15} and 1×10^{16} ions/cm², respectively. Figure 5.44 (b) shows the lowest absorbance of 0.28 at a fluence of 5×10^{15} ions/cm², and its absorbance edge shifted toward low wavelength of 365 nm (Figure 5.42). However, a high absorbance of 0.68 and low transmittance of 49 % have been observed in the thin film implanted at 5×10^{16} ions/cm². As shown on Figures 5.41, the decrease in transmittance can be attributed to the production of defects by Co⁺ ions, which resulted in high absorbance related to the development of intermediate energy levels [33]. The wavelength of absorption in both 365 and 367 nm regions shows a blue shift respect to the as-grown. While, absorbance edge of the thin film implanted to 1×10^{16} ions/cm² shifted toward high wavelength of 514 nm. Thus, the wavelength of absorption in the region 514 nm shows a red shift with respect to the as-grown film.

Furthermore, Figure 5.42 together with the Tauc relation (Equation 2.6), discussed in Section 2.4.2, have been used to determine the optical band gap energy E_g . Figure 5.43 shows estimated optical band gaps which are listed in Table 5.13. Thus, the estimated optical band gaps vary between 2.20 and 3.70 eV. Figure 5.44 (c) shows variation of the band gap of Co⁺ ion implanted ZnO thin films with ion fluence in comparison with the as-grown. As can be seen from Figure 5.44 (c), the band gap energy was observed to increase at a fluence of 5×10^{15} ions/cm². This can be attributed to the quantum size effect or could be that at a fluence of 5×10^{15} ions/cm² the defect energy levels might have been eliminated [33]. However, at high fluences, a decrease in the optical band gap was observed.

5.9 Effect of structural parameters on the properties of Co^+ ion implanted ZnO thin films

The observed changes in structural parameters such as surface roughness and crystallite size due to ion implantation have notable effects on resistivity, transmittance and optical band-gap of Co^+ ion implanted ZnO thin films (Figures 5.45 and 5.46).

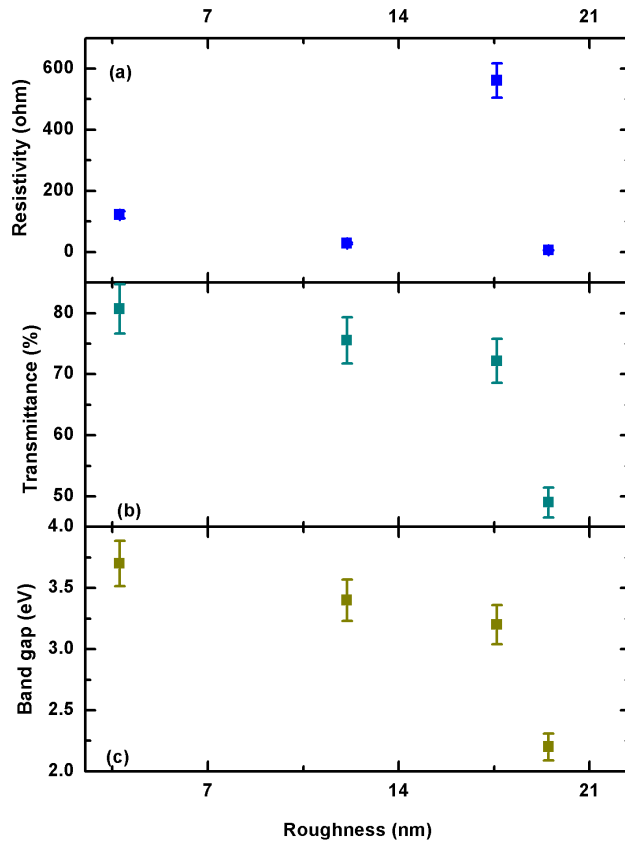


Figure 5.45: Effects of surface roughness on the (a) resistivity, (b) transmittance and (c) optical band gap of Co^+ ion implanted ZnO thin films

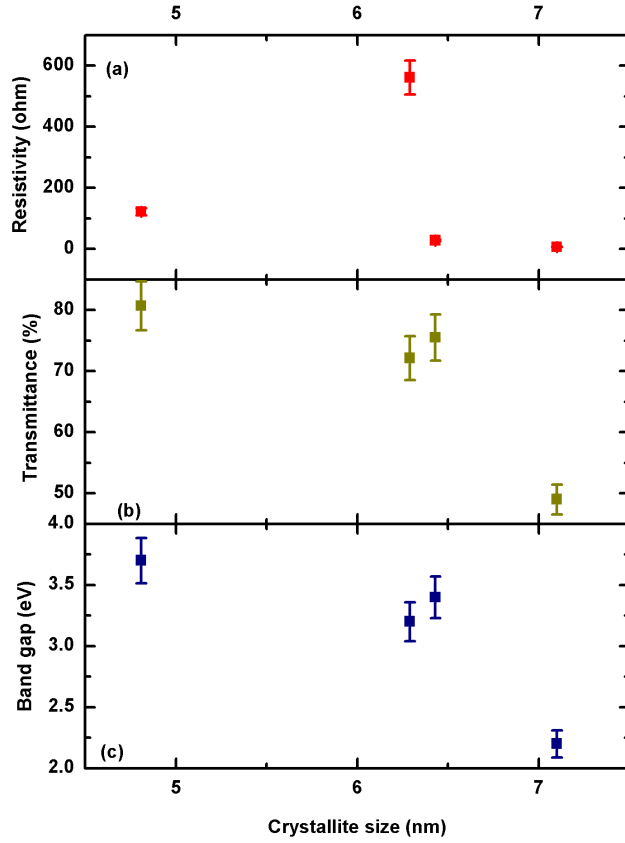


Figure 5.46: Effects of crystallite size on the (a) resistivity, (b) transmittance and (c) optical band gap of Co^+ ion implanted ZnO thin films

It can be seen from Figures 5.45 (a), (b) and (c) that as the roughness decreases by 78.64 % resulting in decreased resistivity by 78.28 % and hence increased in optical band gap and transmittance by 15.63 % and 11.85 %, respectively, in comparison with as-grown. Thereafter, it can be observed

that resistivity, transmittance and optical band gap decrease as the roughness increases. The observed effects of induced surface roughness on resistivity, transmittance and optical band gap can be attributed to the behavior of inter-sheet electron on the Fermi surface [143].

Figures 5.46 (a), (b) and (c) show the effects of induced-crystallite size on the resistivity, transmittance and band gap of Co^+ ion implanted ZnO thin films. From Figures 5.46 (a), (b) and (c), as the crystallite size increases, it can be observed that resistivity, transmittance and band gap decrease to 98.87 %, 32.08 % and 31.25 %, respectively. At low fluence, high band gap, transmittance and high resistivity values were recorded while the induced-crystallite size decreases by 23.53 %. The reason for the observed effects of induced-crystallite size could be that, as ion fluence increases the structure re-crystallizes and interatomic distance reduces. Therefore, there is good agreement between UV-Vis results, I-V behavior, XRD and AFM results.

Chapter 6

Results and Discussion II: Co^+ ion implanted ITO Thin Films

6.1 Introduction

The results of Co^+ ion implantation into indium tin oxide (ITO) thin films on PET substrates at different fluences are presented in this chapter. The previous chapter discussed the modification of ZnO thin films by V^+ and Co^+ ions of energy 170 keV, which was the first study undertaken to explore the effects of transition metal, such as V^+ and Co^+ ions, on ZnO and ITO thin film properties. The results obtained here have provided additional information and insight into transition metal ion implantation effects in TCO thin films, in particular ITO, establishing the physical mechanism underlying modification of ITO thin film properties such as lattice structure, chemical bond, magnetic, electrical and optical properties. This chapter further discusses structural changes in ITO thin films following 100 keV Co^+ ion implantation which resulted in modification of transmittance, conductivity, band gap, together with exchange bias field of the as-grown and Co^+ ion implanted ITO

thin films.

6.2 Structural modification of Co^+ ion implanted ITO thin films

The lattice structure of as-grown and Co^+ ion implanted ITO thin films was analyzed using X-ray diffraction (XRD) (Section 4.4.3). Figure 6.1 shows XRD spectra of as-grown and Co^+ ion implanted ITO thin films on PET substrates at ion fluences of 1×10^{14} , 1×10^{15} and 1×10^{16} ions/cm².

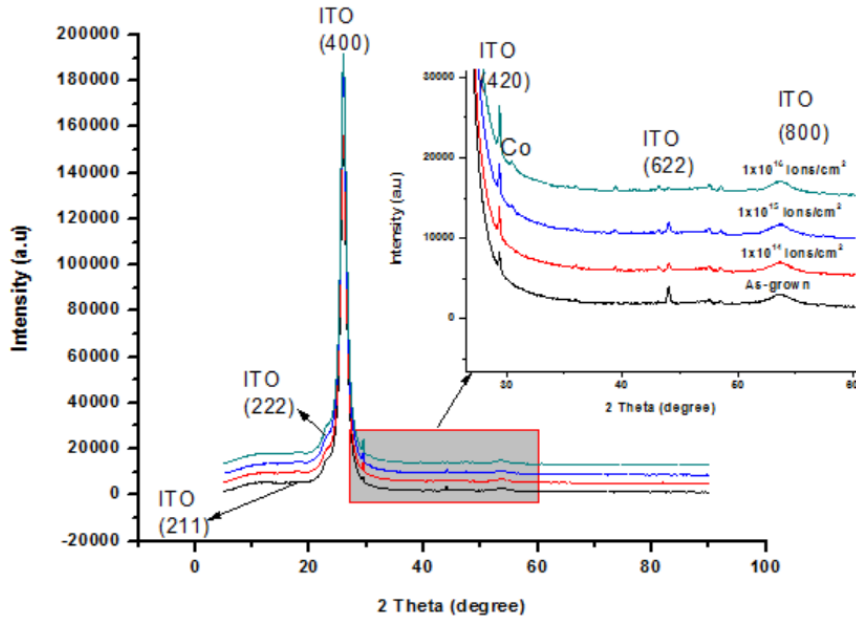


Figure 6.1: XRD spectra of as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

Structural studies were carried out to investigate the modification in crystallinity in implanted thin films as compared with as-grown. All thin films

show preferential growth of (4 0 0) plane, with small (2 2 2), (2 1 1), (6 2 2) and (8 0 0) diffraction peaks, indicating the polycrystalline nature of the thin films. As can be seen in Figure 6.1 each peak also has an intensity which differs from other peaks in the pattern and reflects the relative strength of the diffraction. The diffraction peaks were properly indexed and well in agreement with that of standard data of [JCPDS No. 71-2194] corresponding to cubic structure (bcc) with space group Ia-3 [17, 131]. The XRD patterns show one additional peak at approximately 2θ value of 30.55° corresponding to (2 2 0) peak of cubic Co metal in addition to the diffraction peaks corresponding to ITO thin films. In addition, no significant diffraction peak shifts could be observed in the X-ray diffraction patterns.

The effect of ion fluence on degree of preferred orientation (I_{420}/I_{400}) of as-grown and Co^+ ion implanted ITO thin films are listed in Table 6.1 and shown in Figure 6.2.

Table 6.1: Degree of preferred orientation (I_{420}/I_{400}) of Co^+ ion implanted ITO thin films in comparison with as-grown

Fluence ($\times 10^{15}$ ions/cm ^{2})	Intensity (I_{420})	Intensity Max. (I_{400})	Ratio
0 (as-grown)	8208	150467	5.46
0.1	13810	155993	8.85
1.0	19306	184733	10.45
10	26627	191424	13.91

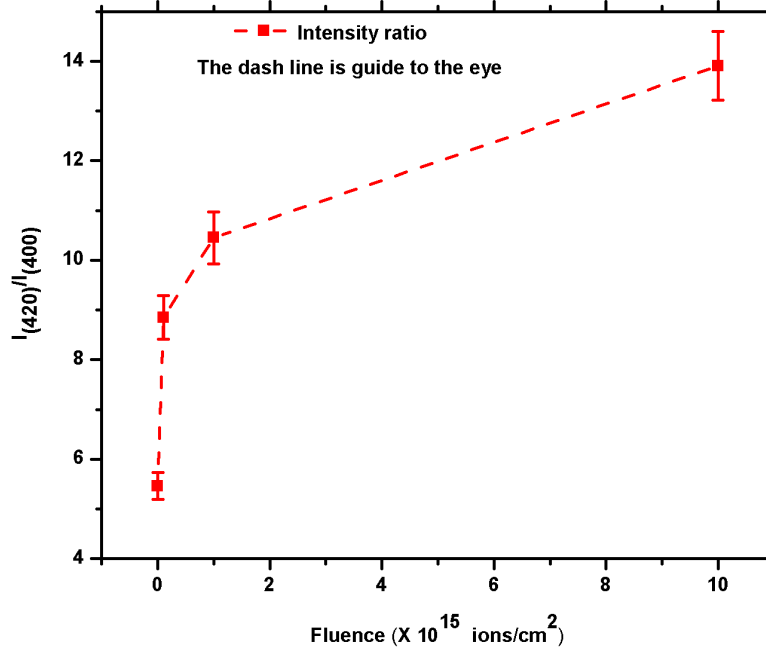


Figure 6.2: Effect of ion fluence on degree of preferred orientation (I_{420}/I_{400}) of Co^+ ion implanted ITO thin films in comparison with as-grown

By convention in a diffraction pattern, the strongest peak is assigned an intensity value of 100 %, and other peaks are scaled relative to that value [131]. Following this, the diffraction peak intensity ratio I_{420}/I_{400} of as-grown was found to be very small (5.5). However, as can be seen from Figure 6.2, the diffraction peak intensity ratio increased as a function of Co^+ ion fluence. It was nearly three times higher (13.90) at a fluence of 1×10^{16} ions/cm² when compared to the as-grown film. This suggests that implantation at low Co^+ ion fluence results in increased density of the thin films, preferred growth of the (4 0 0) plane and a small diffraction peak on the (4 2 0) plane. This can be attributed to the role of the implanted Co^+ ions in the nucleation process which determines the ITO thin films crystal orientation [19].

6.2.1 Crystallite size and strain

Table 6.2 Columns 2 and 4 show calculated strain and grain sizes at different ion fluences. The structural modification can be discussed in relation to total energy deposited in electronic excitations in the ITO thin films by implanted energetic ions. Therefore, the increased intensity of the peaks could be attributed to implantation induced crystallization because of increase in grain size [8] as recorded in Table 6.2 Column 4 and shown in Figure 6.3 (a). Interestingly, as can be seen from Figure 6.3 (a), as ion fluence increases, grain size increases, indicating that there is a significant improvement in the crystalline quality of ITO thin films after ion implantation. A similar increase in grain size has been reported in Ag^{+9} ion irradiated SnO_2 thin films [8].

By using the Debye-Scherrer formula (Equation 4.3) [144, 145], the estimated grain size D of the as-grown thin film is about 25.29 nm. Ion implantation

Table 6.2: Structural parameters such as strain, dislocation density, crytallite size together with intensity and crystallite structure of as-grown and Co⁺ ion implanted ITO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	strain, ε ($\times 10^{-3}$)	Dislocation density, δ ($\times 10^{-11}$ line/m ²)	Crytallite size (nm)	Intensity (a.u)	Crystallite structure
0 (as-grown)	8.5574	6.0914	4.05	17035	BCC cubic
	4.2337	1.4910	8.19	150467	
	0.5001	0.0208	69.33	8208	
	0.8835	0.0649	39.24	1987	
	6.1516	3.1479	5.64	2856	
Average	4.0653	2.1632	25.29		
0.1	0.06949	0.0402	49.90	14491	BCC cubic
	3.4268	0.9768	8.20	155993	
	0.6190	0.0319	56.01	13810	
	8.0905	5.4448	36.23	2591	
	5.8484	2.8452	5.93	2890	
Average	3.7359	1.8677	31.25		
1.0	8.5549	6.0877	4.05	16940	BCC cubic
	4.2166	1.4789	8.22	184733	
	0.4246	0.0150	81.66	19306	
	0.4293	0.0153	80.76	5475	
	1.0955	0.0998	31.65	3428	
	5.9266	2.9218	5.85	2994	
Average	3.4412	1.7698	35.37		
10	5.440	2.4689	6.36	12875	BCC cubic
	4.1334	1.4211	8.39	191424	
	0.4005	0.0143	86.56	26627	
	0.4056	0.0136	85.48	4958	
	6.2209	3.2191 159	5.57	3005	
Average	3.3217	1.4272	38.47		

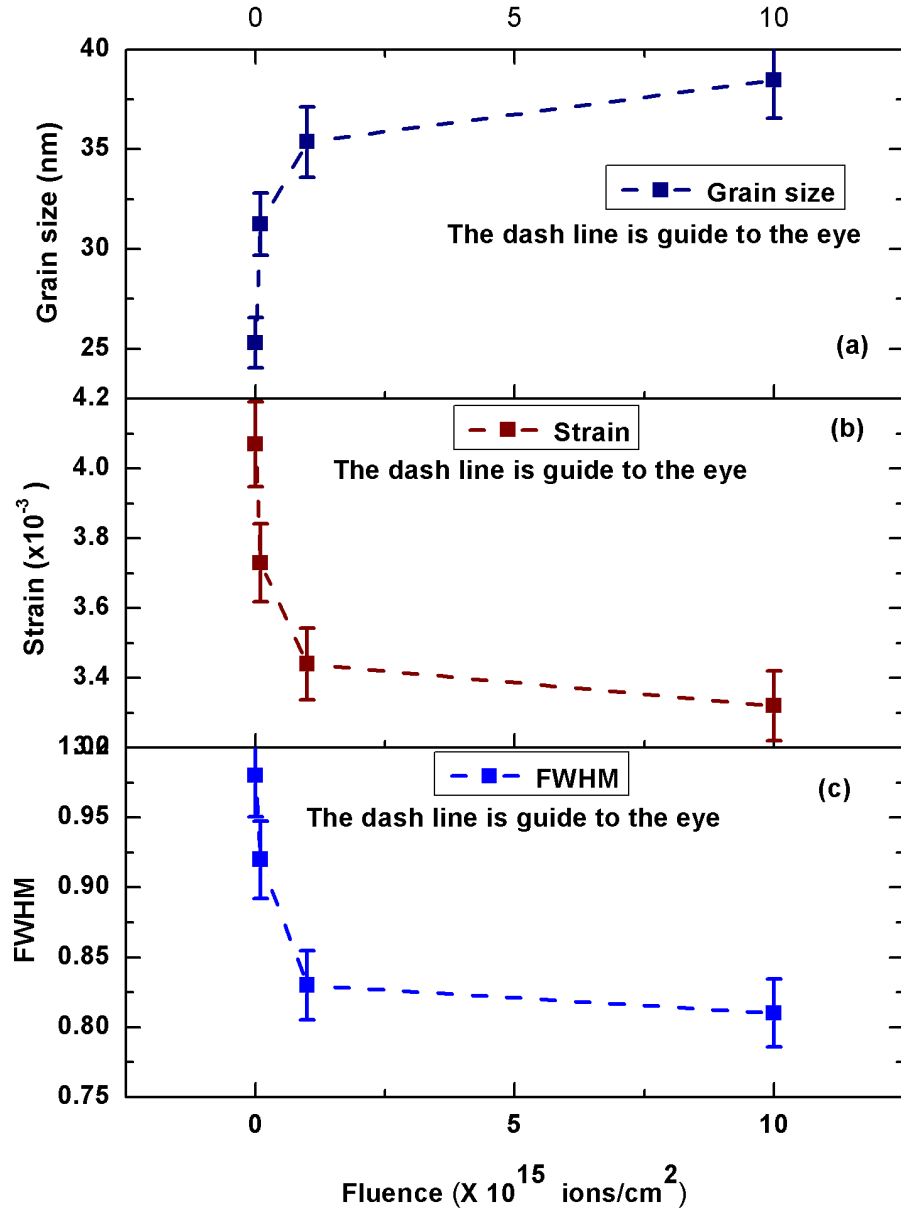


Figure 6.3: Variation of grain size, strain and FWHM of Co⁺ ion implanted ITO thin films as a function of fluence in comparison with as-grown

resulted in increase in grain sizes to 31.25 nm and 35.37 nm for thin films implanted at fluences of 1×10^{14} and 1×10^{15} ions/cm², respectively. And a maximum grain size of 38.37 nm was estimated for thin films implanted at 1×10^{16} ions/cm². Therefore, the observed increase in crystallinity indicates the agglomeration of small grains as more ions impacted the crystal lattice and increased the concentration of nucleation centers. Furthermore, the increased concentration of nucleation centers resulted in increase in vacancy concentration as estimated from TRIM (Table 3.2 Column 3 and Figure 3.5). This shows good agreement with the XRD results.

However, the variation of strain, using the Debye-Scherrer method, with ion fluence is illustrated in Figure 6.3 (b) which confirms that as fluence increases strain decreases to 3.3217×10^{-3} for the thin film implanted at 1×10^{16} ions/cm². This observation can be attributed to the quality of crystallinity and degree of preferred orientation, indicating that the contribution of strain to the broadening in diffraction peaks of as-grown and Co⁺ ion implanted ITO thin films is very small [17]. In addition, Co⁺ ion implantation produces local strain and improves the formation of grain boundaries [146]. As can be seen from Figure 6.3 (c), the full width at half maximum (FWHM) of the diffraction peaks decreases as ion fluence increases. This means that, in the process of implantation, as fluence increases the grain size increases due to recrystallization caused by self-annealing from 100 keV incident Co⁺ ions [8]. Consequently, the crystalline quality of the ITO thin films was getting enhanced by implantation as ion fluence increased [146].

6.2.2 *d*-value, lattice constant and dislocation density

The resolved planes and unique d_{hkl} -spacings of as-grown and Co⁺ ion implanted ITO thin films are recorded in Table 6.3 Columns 3 and 4, together

with the orientation of a single crystal in Column 6 of the Table. Figure 6.4 shows the variation of average observed d_{hkl} -spacings between the planes of atoms of the Co^+ ion implanted ITO thin films in comparison with as-grown. As can be seen from the figure, the observed d_{hkl} -spacing of the thin film implanted at a fluence of 1×10^{14} ions/cm² shifted below that of the as-grown d_{hkl} -value. However, as ion fluence increases to 1×10^{16} ions/cm² the observed d_{hkl} -spacing shifted away from the as-grown d_{hkl} -value. This observation can be attributed to relaxation of Co^+ ion implanted ITO thin films as ion fluence increases, with 6.47 % increase in relaxation of the thin film observed at higher fluence. However, at low ion implantation fluence, relaxation decreases by 0.26 % in comparison with as-grown.

As shown in Table 6.2 Column 6, the crystal structure of ITO is described as cubic structure (bcc) with space group Ia-3 and phase angles $a = b = c = 90^\circ$ [17, 131]. By using Equation 5.1, the variation and estimated lattice constant a , together with average lattice constant a are shown in Figure 6.4 and recorded in Table 6.3 Column 7. From Figure 6.4, it can be observed that as ion fluence increases, lattice constant slightly decreases by 0.23 % at a fluence of 1×10^{14} ions/cm² in comparison with as-grown, thereafter there is a sharp decreasing, where it reaches low values of 12.74 and 12.61 Å for the thin films implanted at 1×10^{15} and 1×10^{16} ions/cm², respectively. Therefore, this suggests that lattice constant decreases with increasing ion fluence. This also implies that there is a perfect incorporation of Co^+ ions into the ITO matrix. Stankiewicz et al. [136] have reported similar behavior of lattice constant in Co-doped ITO thin films.

The behavior of dislocation densities have been investigated in as-grown and Co^+ ion implanted ITO thin films. Using Equation 4.5, the estimated variation of dislocation densities with ion fluences are listed in Table 6.2 Column

Table 6.3: Structural parameters of as-grown and Co⁺ ion implanted ZnO thin films at different fluences

Fluence ($\times 10^{15}$ ions/cm ²)	2θ (deg)	d _{hkl} -space observed (Å)	d _{hkl} -space calculated (Å)	FWHM (deg)	h k l	Lattice constant (Å)
0 (as-grown)	22.60	3.9302	3.9316	2.0000	222	13.6146
	25.84	3.4450	3.4087	0.9955	400	13.7799
	29.42	3.0338	3.0454	0.1185	420	13.5677
	43.89	2.0611	2.0611	0.2183	622	13.6718
	53.60	1.7085	1.7024	1.5795	800	13.6679
Average		2.8357		0.9824		13.6604
0.1	22.63	3.9260	3.9107	0.1624	222	13.6001
	26.01	3.4228	3.3868	0.8060	400	13.6912
	29.48	3.0270	3.0292	0.1467	420	13.5372
	43.95	2.0583	2.0423	2.0000	622	13.6532
	53.62	1.7079	1.6934	1.5018	800	13.6632
Average		2.8284		0.9234		13.6290
1.0	22.78	3.9012	3.9299	0.6632	222	13.5141
	25.86	3.4425	3.4034	0.9915	400	13.7698
	29.38	3.03760	3.0441	0.1006	420	13.5847
	30.55	2.9228	2.9024	0.1020	220	8.2669
	44.01	2.0559	2.0523	0.2708	622	13.6373
	53.60	1.7084	1.7017	1.5217	800	13.6672
Average		2.8447		0.8311		12.7400
10	22.21	3.9993	3.9938	1.2724	222	13.8540
	25.84	3.4450	3.4587	0.9719	400	13.7800
	29.40	3.0350	3.0936	0.0949	420	13.5729
	30.69	2.9106	2.8240	0.0964	220	8.2324
	53.64	1.7071	1.7294	1.5976	800	13.6568
Average		3.0194	163	0.8066		12.6192

3 and shown in Figure 6.4. As can be seen from Figure 6.4, the dislocation densities decrease with increasing ion fluence from 1×10^{14} to 1×10^{16} ions/cm² in comparison with as-grown. Therefore, the observed behavior of dislocation densities may suggest the improvement in perfection imperfection and quality of ITO thin films lattice structure due to implantation.

6.2.3 Thermal and chemical stability

As discussed in Section 2.4.4, the EXPO-2014 software [100] was used together with Equation 2.8 to determine thermal factor and mean square displacement amplitude U of as-grown and Co⁺ ion implanted ITO thin films. Table 6.4 lists thermal factors and mean square displacement amplitude parameters. As can be seen from Figure 6.5, after implantation there is evidence of disorder in the films, as confirmed by the increase in B-factors for Co⁺ implanted films. The vibrational motion of different parts of the Co⁺ ion implanted ITO thin film structures, induced by thermal motion, increased by 22.94 % at a fluence of 1×10^{14} , and by 27.18 % at high fluence. This means that atoms of Co⁺ ion implanted ITO thin films become flexible due to the high B-factors observed. In addition, the mean square displacement amplitude was observed to increase at fluences of 1×10^{14} and 1×10^{16} ions/cm².

6.2.4 Morphological properties

6.2.4.1 AFM scans

The surface morphology of Co⁺ ion implanted ITO thin films was studied using AFM (4.4.2). Figures 6.6 and 6.7 show 2-D and 3-D AFM scans of as-grown and Co⁺ ion implanted ITO thin films at different ion fluences.

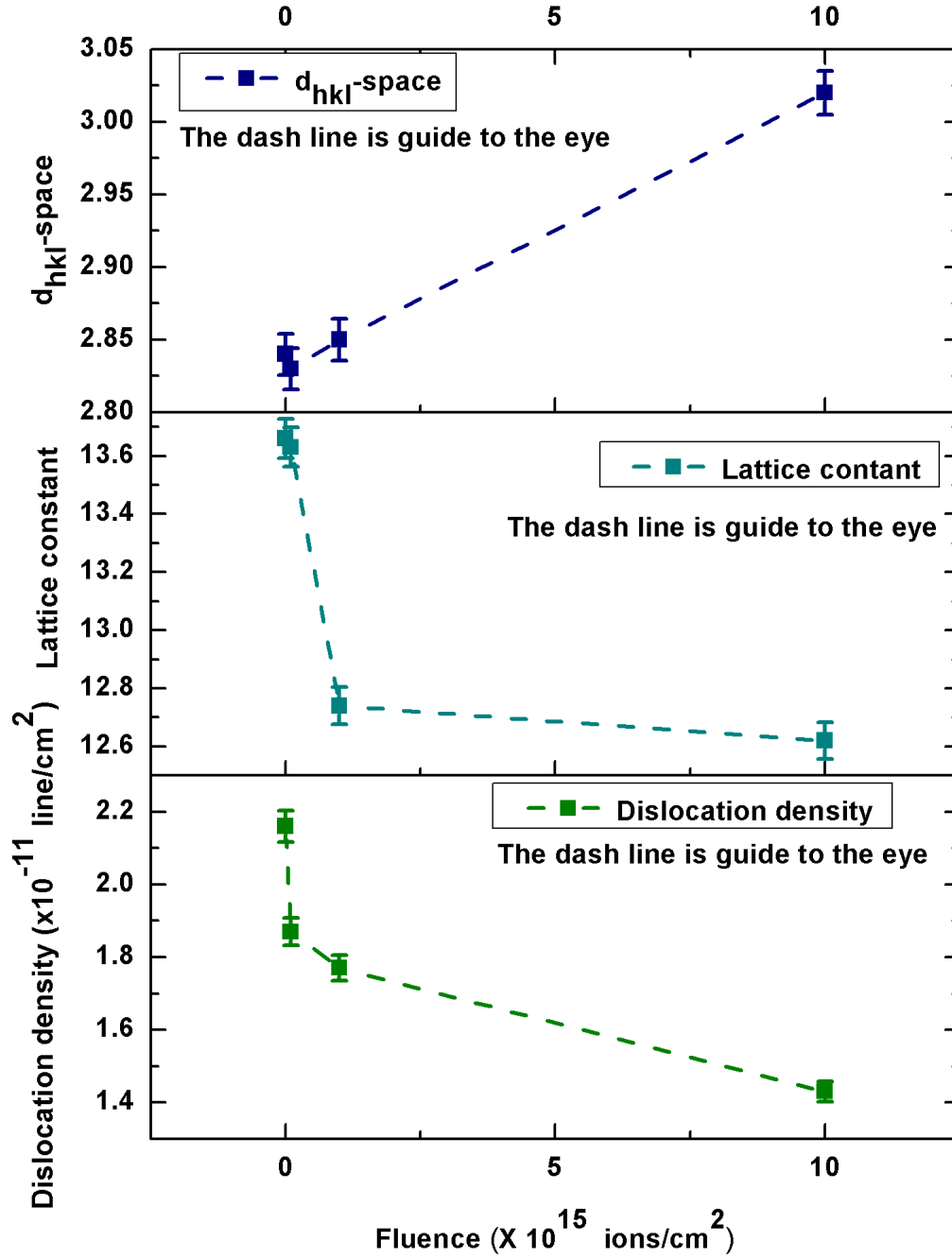


Figure 6.4: Variation of d_{hkl} -spacings, lattice constant and dislocation density of Co⁺ ion implanted ITO thin films as a function of fluence in comparison with as-deposited

Table 6.4: Isotropic (iso) refined thermal parameters (B and U) of as-grown and Co^+ ion implanted ITO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/ cm^2)	B-factor $\text{\AA}^2$	U ($\times 10^{-1} \text{\AA}^2$)
0 (as-grown)	4.816	0.6100
0.1	5.921	0.7500
1	5.289	0.6099
10	6.125	0.7757

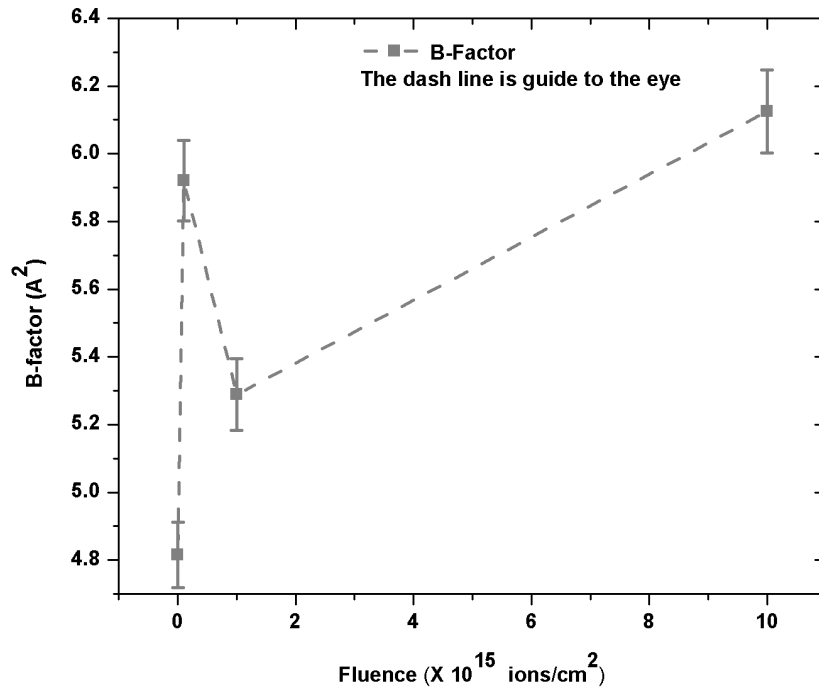


Figure 6.5: Variation of thermal factors (B-factors) of Co^+ ion implanted ITO thin films as a function of fluence

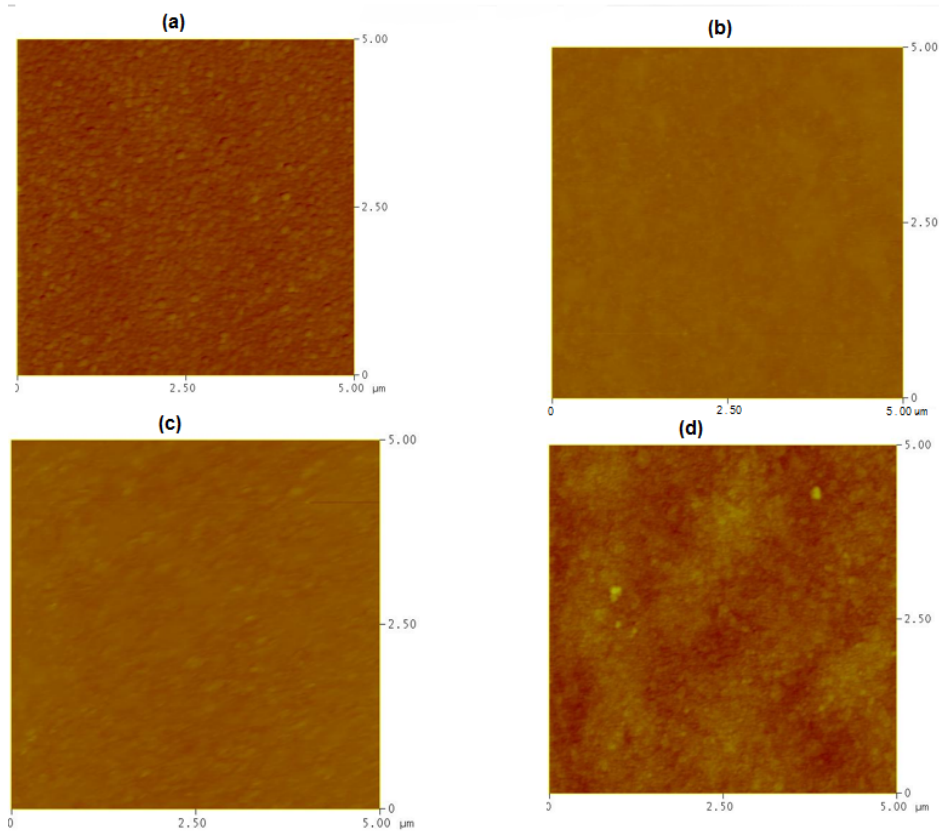


Figure 6.6: AFM 2-D images of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

The calculated average roughnesses (R_a) at different ion fluences, together with root mean squares are listed in Table 6.7 Columns 5 and 6. The AFM image of the as-grown shows a regular distribution of granular shaped crystallites with root mean square (R_q) roughness of approximately 2.10 nm. As can be seen from Figure 6.8, the roughnesses of thin films implanted at fluences of 1×10^{14} and 1×10^{15} ions/cm² were found to be 1.54 and 1.56 nm, respectively.

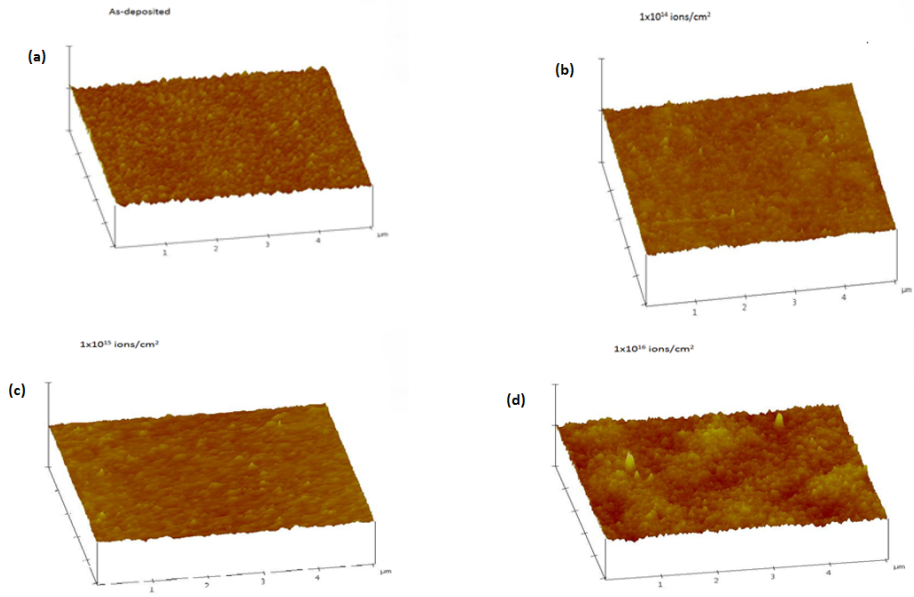


Figure 6.7: AFM 3-D images of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/ cm^2

The sharp decrease in RMS roughness observed in the thin films validated a relatively smooth surface and improved crystallinity [99]. The decrease could be attributed to intermittent tracks and implantation induced defects [29]. This makes the thin films to appear more transparent as is evident from UV-Vis results (Figure 6.17). Comparable decrease in surface roughness has been reported in ion irradiated CdO thin films [28]. However, the increase in surface roughness to 2.30 nm at higher ion fluence of 1×10^{16} ions/ cm^2 may be due to the amount of metal particles on the surface of ITO thin films, high electronic excitations induced by implantation and increase in density [137].

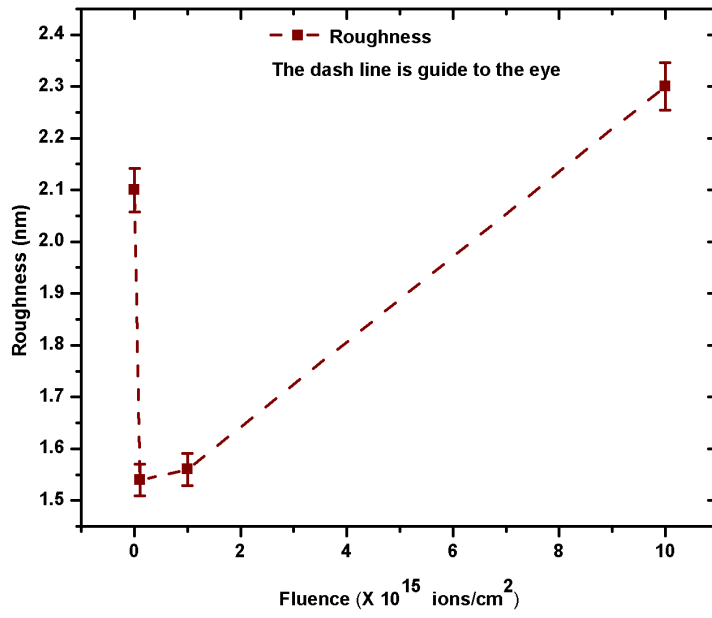


Figure 6.8: Variation of surface roughness of Co^+ ion implanted ITO thin films as a function of ion fluence in comparison with as-grown

6.2.4.2 FE-SEM micrographs

Figure 6.9 depicts FE-SEM micrographs of as-grown and Co^+ ion implanted ITO thin films. The micrographs reveal well-arranged particles in a regular pattern after ion implantation. It is clear that the average particle sizes increased from as-grown thin films (25.29 nm) to the thin films implanted at higher fluences (38.37 nm). This is in good agreement with the AFM results. Therefore, this shows that the morphology of ITO thin films changed after Co^+ ion implantation.

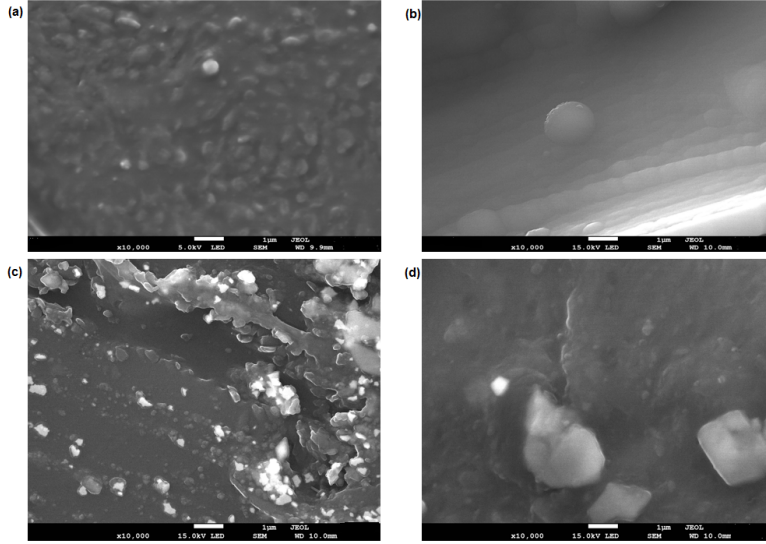


Figure 6.9: FE-SEM micrographs of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

6.2.5 Chemical bond analysis

FTIR spectra recorded in the visible region (400–800 nm) from as-grown and Co^+ implanted ITO thin films are shown in Figure 6.10. The FTIR technique is popularly used to probe bonding and certain functional groups in ITO thin films [138, 30], based on the absorption of photons by the particles constituting the thin films. The absorption bands in the wavenumber range 426–620 cm^{-1} are attributed to O-Sn-O stretching vibration of antisymmetric functional groups of SnO_2 [138, 147]. Strong and weak absorption bands at 440 and 557 cm^{-1} are related to In-O stretching vibration in bcc- In_3O_2 thin film bonds [147], while the absorption peaks between 426 and 620 cm^{-1} are ascribed to the Sn-O bond of SnO_2 [138]. In ITO thin films, the absorption bands normally occur below 700 cm^{-1} , which can be attributed to interatomic vibration [138, 30]. However, the absorption band at 410 cm^{-1} observed in Co^+ implanted ITO thin films was not observed in as-grown ITO thin films. Furthermore, bands between wavenumber 482–539 cm^{-1} are ascribed to stretching vibrating Co-O bonds [148, 149]. Usually, changes in the relative intensities of these FTIR vibrational peaks means that there may be some morphological or structural changes during implantation at different ion fluences [150]. This can be seen clearly from AFM scans of the surface and FE-SEM micrographs.

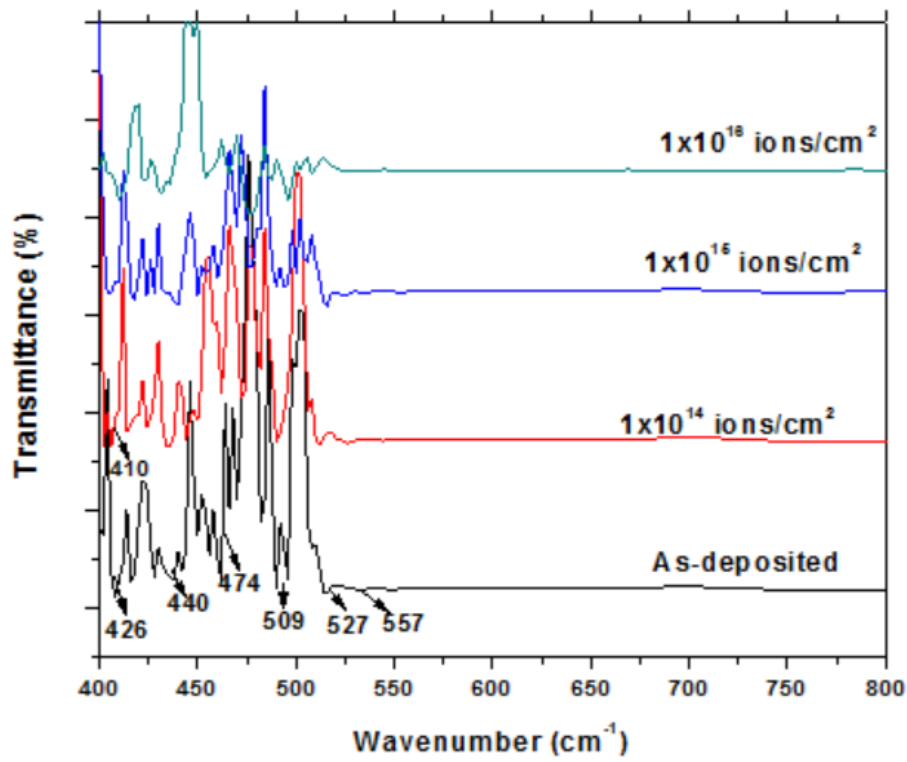


Figure 6.10: FTIR spectra in the wavenumber range from 400 to 800 cm^{-1} at room temperature of as-grown and Co^+ ion implanted ITO thin films at fluences of 1×10^{14} , 1×10^{15} and 1×10^{16} ions/cm^2

6.3 Magnetic properties of Co^+ ion implanted ITO thin films

As discussed in Subsection 4.4.5, the magnetic properties of Co^+ ion implanted ITO thin films in comparison with as-grown were studied using vibrating sample magnetometry (VSM). Figure 6.11 shows the variation of magnetization with applied field and magnetic moment M_s , coercivity H_c , exchange bias H_{ex} and retentivity are presented in Table 6.5.

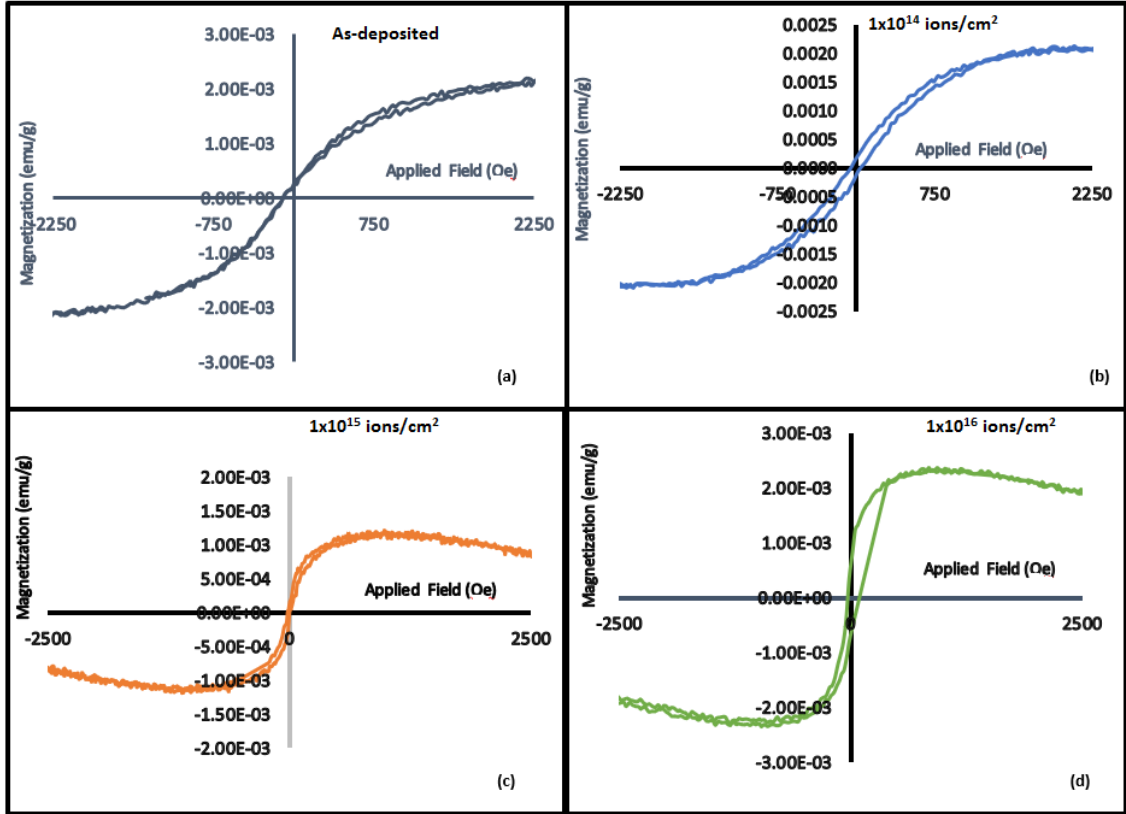


Figure 6.11: Hysteresis loops at 300 K of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

Table 6.5: Magnetization M_s , coercivity H_c , exchange bias H_{ex} and retentivity of Co^+ ion implanted ITO thin films on PET substrates

Fluence ($\times 10^{15}$ ions/cm ²)	Grain size (D) (nm)	H_{c2} (Oe)	H_{c1} (Oe)	H_{ex} (Oe)	H_c (Oe)	M_s ($\times 10^{-3}$ emu/g)	Retentivity ($\times 10^{-4}$ emu/g)
0 (as-grown)	25.29	0.00	0.00	0.00	0.00	2.19	0.00
0.1	31.25	1.54	-19.97	-9.215	45.31	2.08	1.50
1.0	35.37	44.98	-45.63	-0.325	10.76	1.18	2.25
10	38.37	76.00	-49.45	13.275	62.73	2.33	3.35

Figure 6.11 (a), (b), (c) and (d) show the hysteresis loops at room temperature of as-grown and Co^+ ion implanted ITO thin films at fluences of 1×10^{14} , 1×10^{15} and 1×10^{16} ions/cm². It can be observed that the loops have different s-shapes and magnetization reversals. Co^+ ion implanted ITO thin films exhibited magnetization M_s , coercivity H_c , exchange bias H_{ex} and retentivity, as presented in Table 6.5 while Figure 6.11 (a) reveals that the as-grown ITO film was composed of a superparamagnetic phase which appeared in a small ferromagnetic nanoscale structure of the film. The shift in the hysteresis loop away from the ($H_c = 0$, $M_s = 0$) point, which is attributed to exchange bias (Subsection 6.3.1), confirms the multi-phase nature of the as-grown and Co^+ ion implanted ITO thin films. This type of magnetic behavior may result in blocking magnetic moments of varying orientations. Consequently, it will require a finite threshold (HT) applied field to bring all these moments to a net zero magnetization. Above such a HT applied field, the moments align with the applied field and a finite amount of magnetization emerges in the thin films. Thus, as discussed earlier, the observed

magnetic behavior of the as-grown thin films can be attributed to intrinsic properties of ITO thin films [31, 136].

Figure 6.12 shows the magnetization of Co^+ ion implanted ITO thin films as a function of fluence.

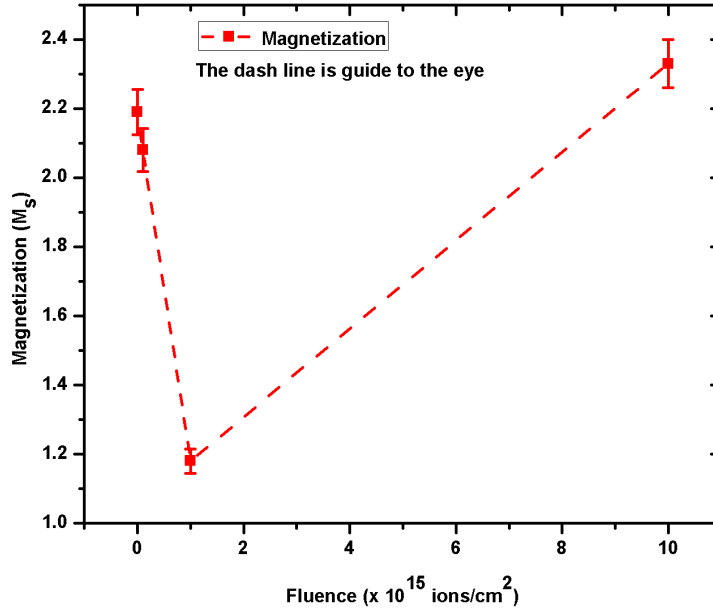


Figure 6.12: Variation of saturation magnetization of Co^+ ion implanted ITO thin films as a function of ion fluence in comparison with the as-grown thin film

As can be seen from Figure 6.12, the extent to which the thin film implanted at 1×10^{16} ions/cm ^{2} exhibited maximum saturation magnetization is high with almost all its magnetic domains aligned at a value of 2.33×10^{-3} emu/g and at maximum field of 2250 Oe. However, the thin film implanted at 1×10^{15} ions/cm ^{2} exhibited the lowest saturation magnetization value of 1.18×10^{-3} emu/g. Moreover, the level of residual magnetism in the thin films increased at an average of 35 % (in Table 6.5 Column 8). This means that the

Co⁺ implanted ITO thin films have good ability to retain a certain amount of residual magnetic field at zero magnetizing force, as ion fluence increases. Moreover, the net coercivity increased in the thin film implanted at a fluence of 1×10^{16} ions/cm² indicating the enhancement of ferromagnetic behavior which suggests more Co⁺ ion incorporation in the thin film. Comparative magnetic behavior has been reported in Co doped ZnO [33]. As discussed in Chapter 1 and Subsection 2.4.1, Co dopant is of special interest because the ionic radius difference between tin (Sn) (0.69 Å) and Co (0.75 Å) is small enough to allow Co to substitute for Sn in the crystal lattice structure of SnO₂ [17, 18, 19]. Thus, Co, as a ferromagnetic ion characterized by electronic structure [Ar] 3d⁷4s², is found to play a crucial role in the observed magnetic behavior of Co⁺ ion implanted ITO thin films. Furthermore, it can be clearly observed in Figure 6.11 (b), (c) and (d) in comparison with Figure 6.11 (a) that the observed room temperature ferromagnetism in Co⁺ ion implanted ITO thin films was induced by implanted Co⁺ ions as a result of the exchange coupling between the localized 3d electrons in cobalt metal atoms and the free carriers mediated mechanism generated from Co⁺ ion implantation in the ITO matrix and defects [151].

However, Co⁺ ion implantation was not carried out in oxygen environment as a result Co oxidation (CoO) was not expected, though there might have been oxidation of implanted Co from the oxygen in ITO. From XRD results, peaks corresponding to cubic Co (220) were detected, while peaks corresponding to CoO (311) are absent which indicates that other phases of Co oxides are not present in ITO matrix. This shows that Co metal is properly incorporated into the ITO lattice structure, hence, CoO could probably not have played a significant role.

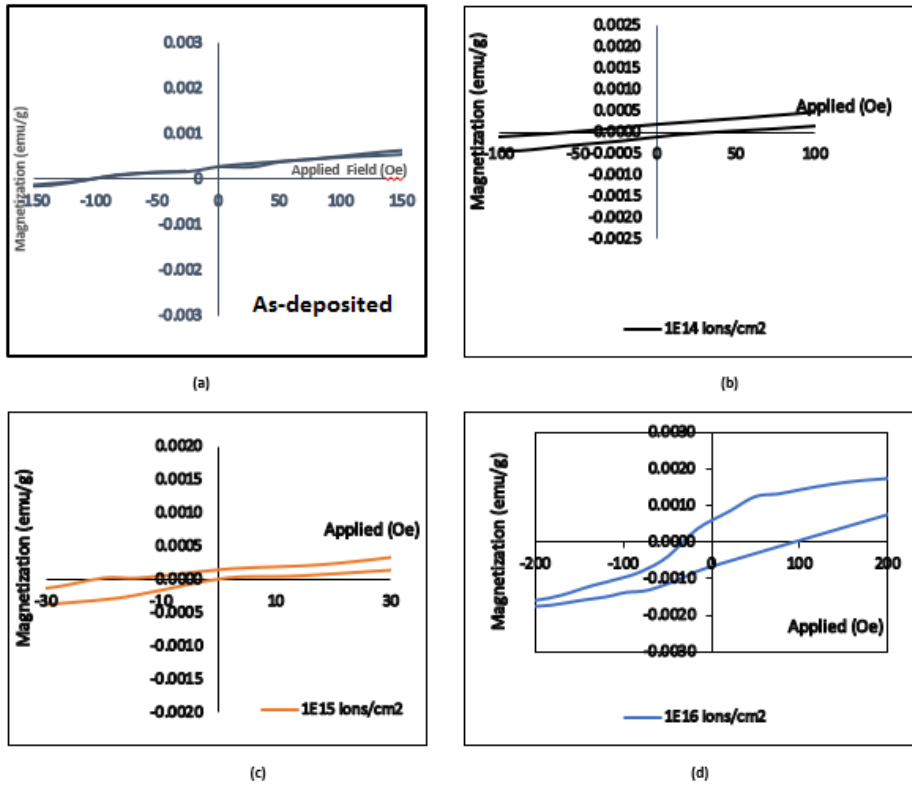


Figure 6.13: Zoom in of hysteresis loops at 300 K of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

6.3.1 Influence of grain size on the exchange bias field

Exchange bias and coercivity are identified as the most crucial magnetic properties that could affect the magnetization of as-grown and Co^+ ion implanted ITO thin films [17, 152]. Shifting of the hysteresis loops along the magnetic field axis was observed in coreshell ferromagnetic (FM)-antiferromagnetic (AntiFM) thin films. This type of hysteresis loop shifting is called the exchange bias effect due to exchange coupling at the FM-AFM interfaces [17, 152]. However, the origin of the exchange bias is yet to be fully understood, and it is still the subject of investigation [153]. Various studies have investigated the exchange bias in thin films and nanoparticles in order to understand its source [154, 155, 156]. Based on these earlier reports, it is generally believed that the exchange coupling between the FM-AntiFM interfaces is the source of the exchange bias [157]. Therefore, the multi-phase nature of the as-grown $\text{In}_2\text{O}_3/\text{SnO}_2$ and Co^+ ion implanted ITO thin films, $\text{In}_2\text{O}_3/\text{SnO}_2\text{:Co-metal}$, together with non-magnetic defects and the exchange coupling at the FM-AntiFM interfaces of the films could be the possible sources of the observed exchange bias in both as-asgrown and Co^+ ion implanted ITO thin films.

Moreover, a good understanding of exchange bias, coercive and hysteretic properties of magnetic thin films is particularly believed to be highly significant in magnetic sensor and spin valves applications [158]. Furthermore, Co^+ ion implanted ITO thin films with high coercivity are potential candidates for the next generation ultra-high-density magnetic recording media [33].

As discussed earlier, the thickness of the ITO thin films used in this study were in nanometer scale (100 nm), therefore, the lattice structure of the films became the main parameter in defining its physical properties. Thus, grain size distribution, average grain size and crystallinity are the most important

of these lattice structural properties. In order to understand the magnetic behavior of as-grown and Co^+ ion implanted ITO thin films in relation to grain size, the variation of average grain size D (in Table 6.5 Column 2) estimated using Debye-Scherrers equation on the exchange bias, H_{ex} , and coercivity was investigated. It can be seen from Figure 6.13 that there is a clear difference between the coercivity of the thin films having the smallest grain size and those with larger grain sizes. In addition, the loop is highly asymmetric and shifted away from the $[0,0]$ point in the case of as-grown and towards negative magnetic field values for the thin films implanted at fluences of 1×10^{14} and 1×10^{15} ions/cm². This shift switches sign to positive upon increasing the ion fluence to 1×10^{16} ions/cm². This can be attributed to H_{ex} effects [17, 152]. Upon implanting Co^+ ions, and by convention, AntiFM is induced from an imprint of the FM during Co^+ ion implantation through non-magnetic defects, and the exchange coupling at the FM-AFM interfaces resulting in a shift of the hysteresis loop, defined as H_{ex} [159].

6.3.2 Room temperature exchange bias H_{ex}

It is interesting to realize room temperature H_{ex} on as-grown and Co^+ ion implanted ITO thin films. This can be explained as follows. As discussed earlier, exchange bias is traditionally due to existence of FM and AntiFM domains in the bulk material. It is the unequal distribution of these domains that makes the M-H hysteresis loop to be asymmetric about the H axis. However, in these bulk systems, this exchange bias gets destroyed above the Neel temperature. Therefore, one can observe exchange bias phenomenon only at low temperature in bulk materials. When a material is reduced to nanoscale, the AntiFM domains compete so well with the FM-domains. Through the exchange bias mechanism, AFM coupled to FM and make the surface atoms

of the FM in as-deposited and Co^+ ion implanted ITO thin films to align with the surface atoms of the AntiFM in as-grown and Co^+ ion implanted ITO thin films. This resulted in the pinning of the orientation of the FM in the films at 300 K. Furthermore, the temperature at or above which an AntiFM phase loses its capability to pin the magnetization order of a neighboring FM phase is referred to as the blocking temperature, T_B , of that phase, and the T_B could be increased by the observed exchange bias [152, 160]. As a result, exchange bias phenomenon can be observed at room temperatures (Figure 6.11). In other words, the T_B can be above room temperature, as a result of exchange bias. In addition, the observed superparamagnetism is a size effect (Table 6.5 column 2) of the as-grown and Co^+ ion implanted ITO thin films [161]. As can be seen from Table 6.5 column 6 and Figure 6.11, the coercivity changes with the particle size and at small size of 25.29 nm, the coercivity became zero with zero retentivity and saturation magnetization of 2.19×10^{-3} emu/g which indicates superparamagnetic phase of as-grown thin films. The non-smoothness of M-H curves of as-grown and Co^+ ion implanted ITO thin films (Figure 6.11) is related to microstructural roughness of the AntiFM-FM interfaces [162]. As can be seen from Figures 6.11 (b), (c) and (d), the magnetization curve of Co^+ ion implanted ITO thin films show minor hysteresis loop behavior in low field region. The saturation magnetization occurred at the maximum applied fields of 2250 Oe in the ion implanted and as-grown thin films. Although the ferromagnetic component saturates at very low applied field, the antiferromagnetic component increases linearly resulting in magnetic saturation at maximum applied field. The minor hysteresis loops observed can also be explained by antiferromagnetic coupling with ferromagnetic behavior of thin films having different grain sizes [163]. However, the exchange bias has been estimated by considering horizontal

shift of the loops. From Figure 6.11, the exchange biasfield, H_{ex} , and the coercivity, H_c , were estimated for as-grown and all Co^+ implanted ITO thin films at different fluences using the following equations [153].

$$H_{ex} = \frac{(H_{c1} + H_{c2})}{2}, \quad (6.1)$$

$$H_c = \frac{(H_{c1} - H_{c2})}{2}, \quad (6.2)$$

where H_{c1} is the coercive field of descending branch of the M-H hysteresis loop including its sign and H_{c2} represents the coercive field of ascending branch of the M-H hysteresis loop including its sign. The H_{ex} effect in thin films or nanoparticles is inversely proportional to D [164]. By taking reciprocal of the grain size, D , it implies that H_{ex} will decrease when grain size increases and vice versa, as shown in Figure 6.14. Peng et al. [165, 166, 167] observed a similar trend on oxide coated Co/CoO particles.

Furthermore, as can be seen from Table 6.5, as ion fluence increases, H_{ex} changes from negative to positive in comparison with as-grown. This means when the maximum field of 2250 Oe is applied at 300 K after Co^+ ion implantation, the hysteresis loop shifted towards the estimated negative values of -9.22 and -0.33 Oe for the thin films implanted at fluences of 1×10^{14} and 1×10^{15} ions/cm², respectively (negative exchange bias). The negative H_{ex} is attributed to the interfacial FM and AntiFM spins aligned in the positive and negative directions, respectively [167]. However, upon increasing ion fluence to 1×10^{15} ions/cm² at the same maximum applied field of 2250 Oe, at 300 K, the loop shifted towards the estimated positive value of 13.28 Oe (positive exchange bias). Positive H_{ex} is attributed to interfacial interaction in which both FM and AFM spins are aligned in the positive direction [168, 169]. The observed increase in H_{ex} at higher fluence indicates the creation of pinning sites in the AntiFM layer produced by non-magnetic defects [17]. Our results

are well in agreement with that of transformation from negative to positive H_{ex} recently reported for Ho^{3+} doped $\text{YFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ [170]. Moreover, H_{ex} is very sensitive to the interfacial condition of AntiFM-FM [171, 172, 173, 174].

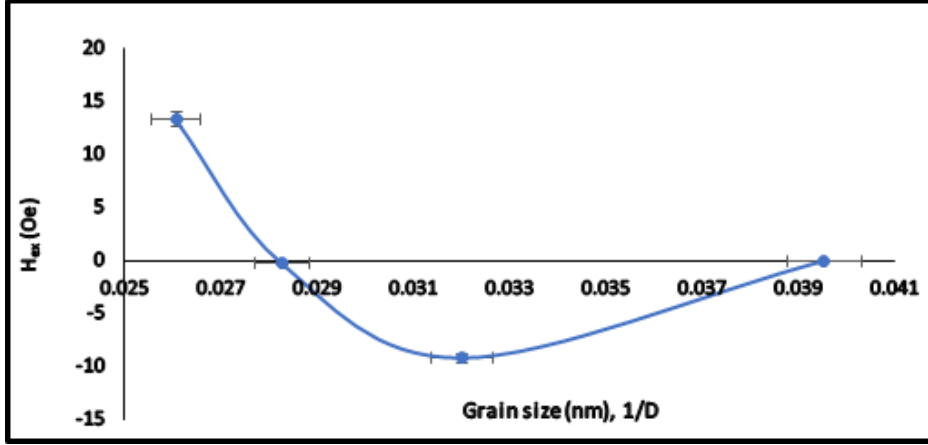


Figure 6.14: Exchange bias, H_{ex} , width as a function of $1/D$ for as-grown and Co^+ implanted ITO thin films

6.4 Electrical properties of Co^+ ion implanted ITO thin films

The current-voltage response of Co^+ ion implanted ITO thin films was measured using a two-point probe. Table 6.6 lists calculated conductances and resistances of Co^+ Ion Implanted ITO Thin Films. Figure 6.15 shows the I-V response of as-grown and Co^+ ion implanted ITO thin films at different ion fluences. The response curve was taken by varying the applied voltage (V) from 0 to 12 V with a step size of 2 V. At a Co^+ ion fluence of 1×10^{14} ions/cm², a 78.49 % decrease in resistance was estimated from Figure 6.15 in comparison with the as-grown sample. As can be seen from Column 3 in Table 6.6, the sample implanted at a fluence of 1×10^{14} ions/cm² exhibits a

Table 6.6: Conductances, resistances and transmittances of Co^+ ion implanted ITO thin films at different ion fluences

Fluence ($\times 10^{15}$ ions/cm ²)	Conductance ($\times 10^{-6}$ S)	Resistance ($\times 10^3$ ohm)	Transmittance (%)
0	22.10	43.490	73.97
0.1	106.86	9.3600	86.53
1.0	35.58	28.110	77.52
10	6.60	147.12	57.09

sharp increase in conductance and the optical band-gap, E_g , increased from 3.01 to 3.26 eV, as shown in Figures 6.16 and 6.19, respectively. However, at a fluence of 1×10^{16} ions/cm² E_g decreased to 2.92 eV.

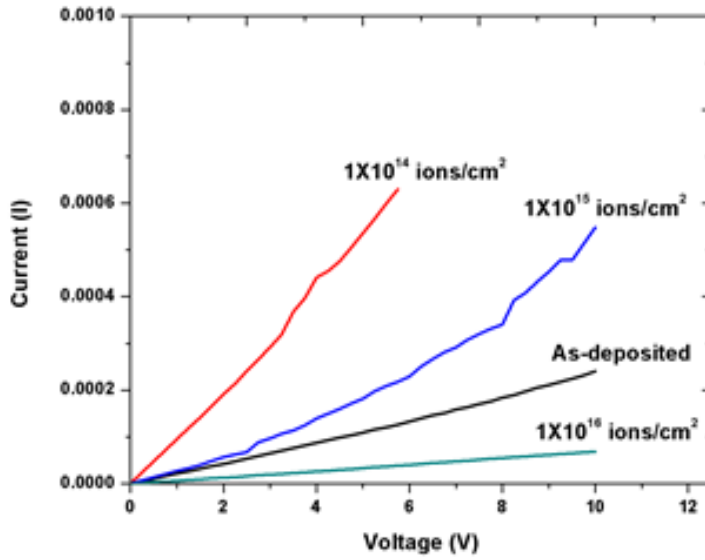


Figure 6.15: I-V response of (a) as-grown and Co^+ ion implanted ITO thin films at fluences of (b) 1×10^{14} , (c) 1×10^{15} and (d) 1×10^{16} ions/cm²

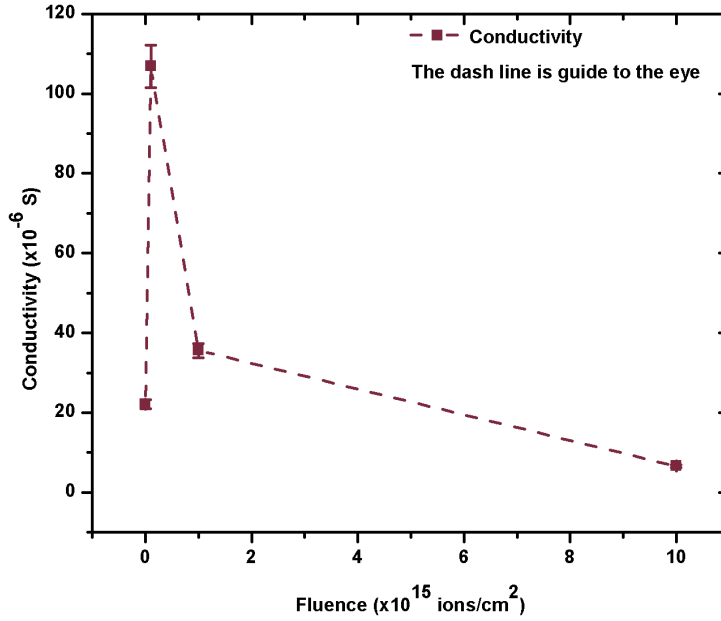


Figure 6.16: Variation of conductivity of Co^+ ion implanted ITO thin films at different fluences in comparison with as-grown

6.5 Optical properties of Co^+ ion implanted ITO thin films

Figure 6.17 shows the optical transmittances of as-grown and Co^+ ion implanted ITO thin films at different ion fluences, together with their absorbances.

The calculated optical band gaps and transmittances at different ion fluences, together with wavelengths and corresponding absorbance edges of Co^+ ion implanted ITO thin films are listed in Tables 6.7 and 6.6. In order to minimize

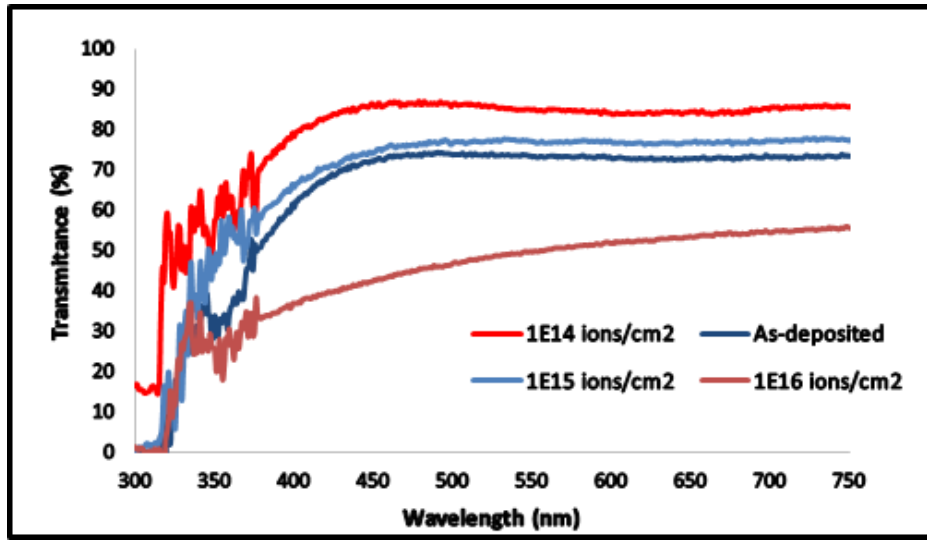


Figure 6.17: The optical transmittance of as-grown and Co^+ ion implanted ITO thin films at different fluences

error in the transmittance (T) data and to ascertain the accuracy of the data, the UV-Vis spectrometer was first run at autozero to configure the spectrometer to 100 % T in the wavelength range 400 - 700 nm with resolution of 0.17 - 5.00 nm. Hence, the configured 100 % T was used as a benchmark against the as-grown and Co^+ ion implanted ITO thin film transmittances. It can be observed that Figure 6.18 shows a strong absorbance at different ion fluences below a wavelength of 450 nm. The ITO film implanted at a fluence of 1×10^{14} ions/cm² was observed to have the lowest absorbance edge of 0.09, and it shifted towards a lower wavelength of 445 nm in comparison with absorbance edge of the as-grown film (Table 6.7). The highest absorbance edge of 0.33 was observed from the sample implanted at a fluence of 1×10^{14} ions/cm².

Changes in the optical properties of the majority of optoelectronic devices are directly proportional to implantation fluences [175, 176]. A transmittance of 86.53 % in the visible region (400 - 700 nm) was observed in the thin film

implanted at a fluence of 1×10^{14} ions/cm², while the as-grown had 73.97 % transmittance. R. Kumaravel et al [116] have reported similar results on Ag irradiated ZnSnO thin films and additional similar results were reported on Xe irradiated Al-doped ZnO films by Fukuoka et al. [177]. As can be seen from Figure 6.18, at a fluence of 1×10^{14} ions/cm² the lowest absorbance was observed leading to increased bandgap, and hence increase in transmittance. The increase in band gap may be due to increased concentration of Co⁺ ions in the ITO thin films during ion implantation, and hence leading to increase in transmittance [178, 179, 180, 181]. However, 57.09 % transmittance was observed in the thin film implanted at 1×10^{16} ions/cm². This sharp decrease in the transmittance can be attributed to the production of defects by Co⁺ ions, which resulted in decreased bandgap and high absorbance related to the development of intermediate energy levels [33]. This agrees with band gap behaviours estimated from Taucs relation presented in Table 6.7 Column 4.

As discussed in Section 2.4.2, the obtained UV-Vis spectra of as-grown and Co⁺ ion implanted ITO thin films were used to determine the optical band gap, E_g , using Tauc's relation [99]. As shown in the insets on Figure 6.19, the value of the band gap energy is given by the value of the intercept of the linear region of the curve on the $h\nu$ -axis [99]. Figure 6.20 ((a), (b) and (c)) shows plots of optical band gap energy, transmittance and absorbance as a function of ion fluence. The estimated optical direct band gaps vary between 2.92 and 3.26 eV. As can be seen from Figure 6.20 (a), an increase in optical band gap was observed with increase in ion fluence from as-grown to 1×10^{14} ions/cm². This could be due to the quantum size effect or it could be that at a fluence of 1×10^{14} ions/cm² the defect energy levels might have been eliminated during ion implantation [33]. Further increase

in the ion fluence resulted in a decrease in the optical band gap energy. Co^+ ion implantation could have resulted in the creation of defect energy levels below the conduction band minimum, consequently, leading to a decrease in the band gap energy at high fluences [33] (Table 6.7 Column 4).

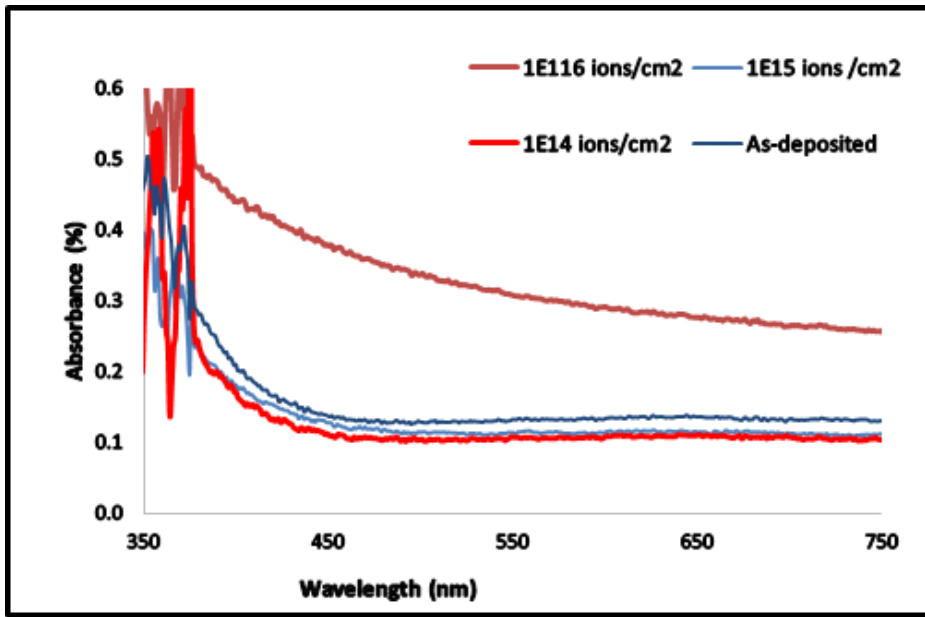


Figure 6.18: The optical absorbance of as-grown and Co^+ ion implanted ITO thin films at different fluences

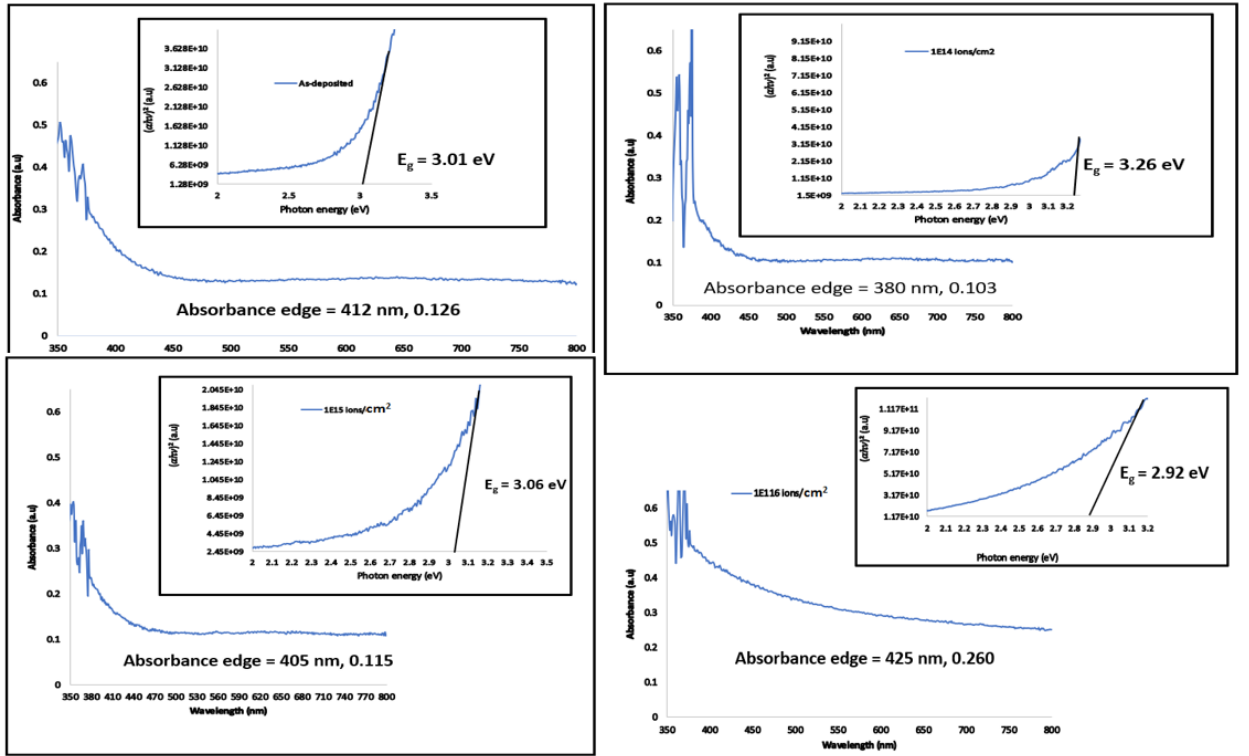


Figure 6.19: The determination of optical band gap E_g values of as-grown and Co^+ ion implanted ITO thin films from Tauc relation

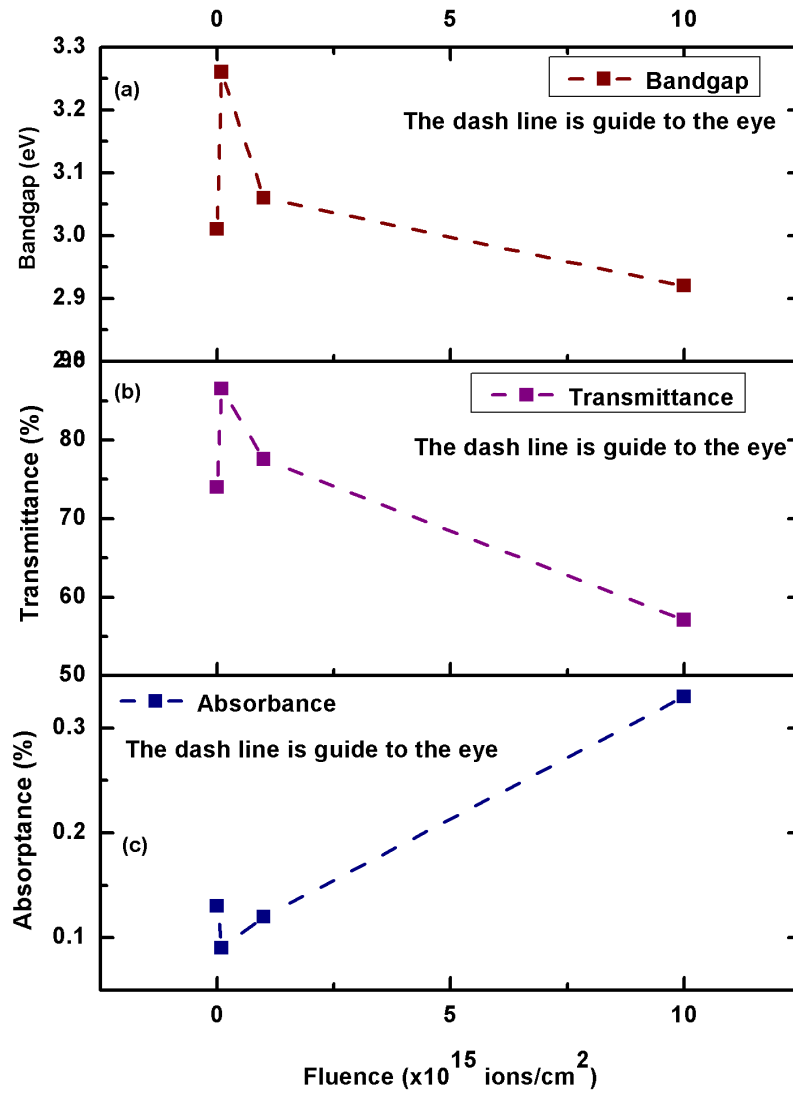


Figure 6.20: Variation of (a) optical band gap E_g , (b) transmittance (c) absorbance of Co⁺ ion implanted ITO thin films as a function of fluence in comparison with as-grown

Table 6.7: Optical band gaps, average roughnesses (Ra) at different ion fluences, together with root mean squares, wavelengths and corresponding absorbance edges of Co⁺ ion implanted ITO thin films

Fluence ($\times 10^{15}$ ions/cm ²)	Wave- length (nm)	Absor- bance (au)	Band gap (eV)	RMS (Rq) (nm)	Ave. Ra (nm)
0	460	0.13	3.01	2.10	1.61
0.1	445	0.09	3.26	1.54	1.23
1.0	449	0.12	3.06	1.56	1.21
10	516	0.33	2.92	2.30	1.82

6.6 Effect of surface roughness on the Properties of Co⁺ Ion Implanted ITO Thin Films

Changes in surface roughness due to ion implantation have significant effects on the conductance, transmittance and optical band-gap of Co⁺ implanted ITO thin films (Figures 6.21, 6.22 and 6.23). As can be clearly seen from Figures 6.21 and 6.22, an increase in RMS roughness above 1.54 nm resulted in a decrease in conductance and transmittance to 35.6×10^{-6} S and 77.5 %, respectively. From Table 6.7 and 6.6, it can be seen that at a fluence of 1×10^{14} ions/cm² the highest conductance, transmittance and optical band-gap were estimated with the lowest value of RMS roughness. However, the lowest conductance, transmittance and optical band-gap were estimated for the thin film implanted at 1×10^{16} ions/cm² with the highest RMS roughness

value. Similar effects of surface roughness on band gap and transmittance properties of CdS thin films have been reported by Maeng jun kim et al. [143]. Furthermore, this observation can be explained from the suggestion made by Kuan and Rossnagel [182] that roughness-induced conductivity reduction may be related to the inter-sheet electron scattering on the Fermi surface, possibly perturbed by surface roughness. Thus, there is good agreement between UV-Vis results, I-V behaviour and structural properties from AFM studies.

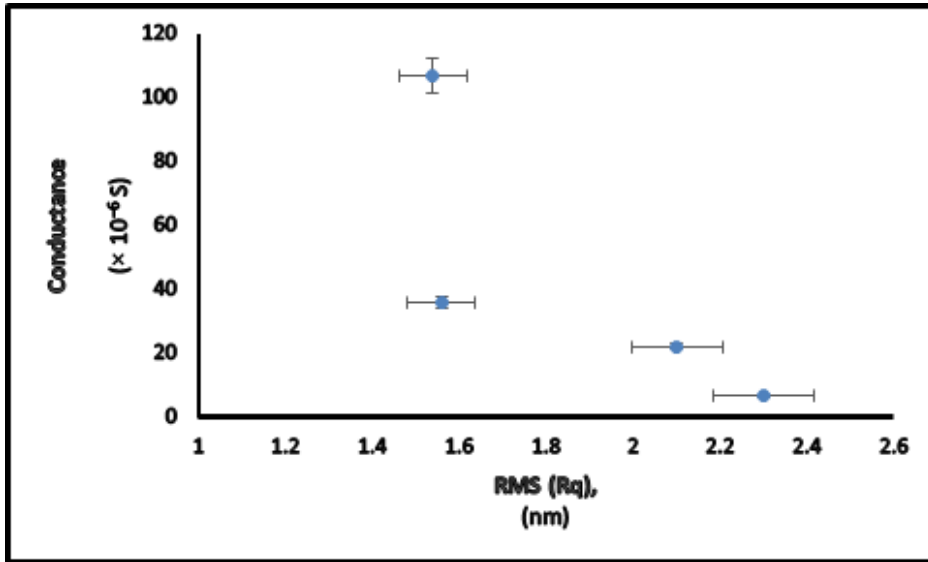


Figure 6.21: Variation of surface roughness with conductance of Co^{+} ion implanted ITO thin films

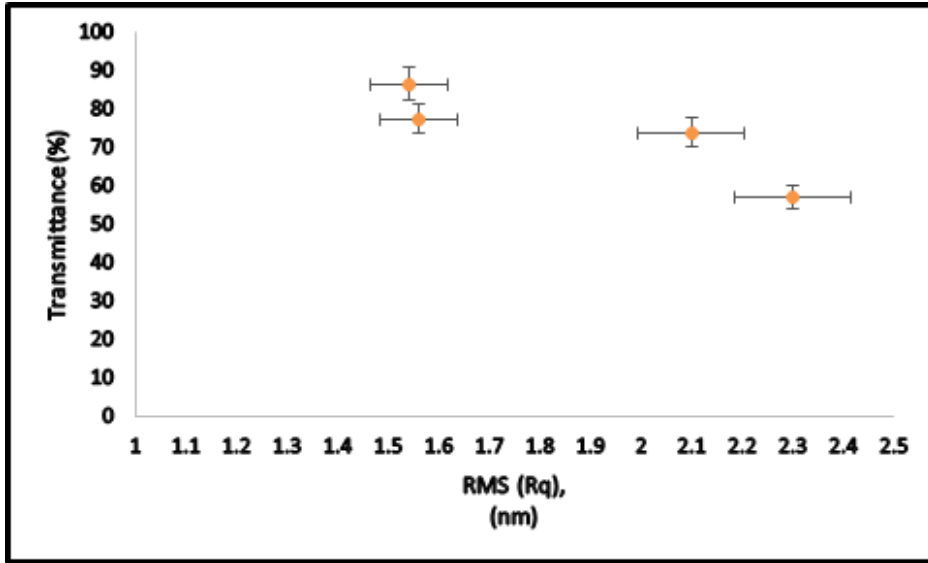


Figure 6.22: Variation of surface roughness with transmittance of Co^+ ion implanted ITO thin films

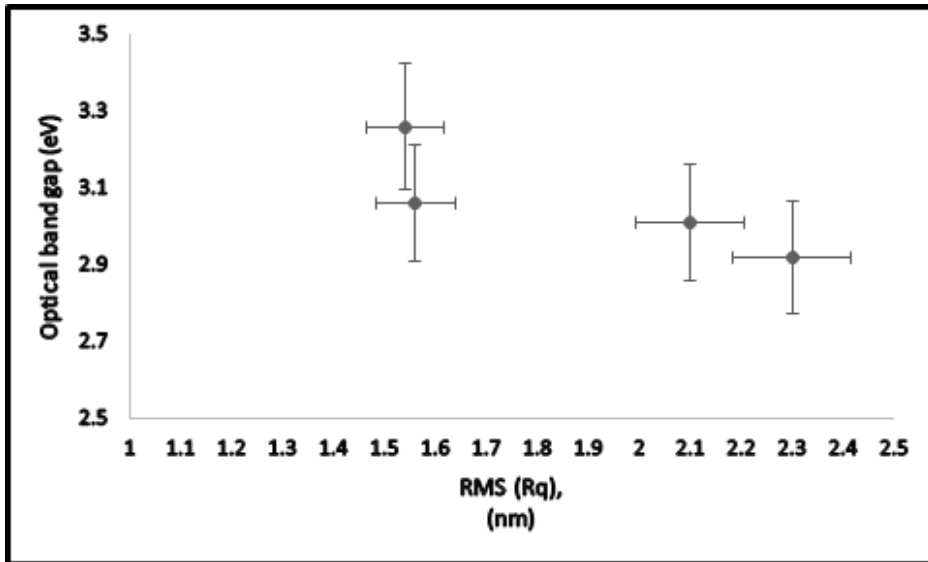


Figure 6.23: Variation of surface roughness with optical band gap of Co^+ ion implanted ITO thin films

Chapter 7

Summary and Concluding Remarks on Major Findings

7.1 Introduction

The overview of the work performed is presented, with the major findings highlighted. The literature review and physics background necessary to understand the basis for ion beam induced modification in TCO thin films, in particular ITO and ZnO thin films have been discussed. An attempt has been made to provide more information on ITO and ZnO thin films and relevant properties under current research interest. SnO_2 , In_2O_3 and ZnO are the traditional transparent conducting oxides. ITO and ZnO are preferred materials due to their non-toxicity, low cost and (environmental friendliness), environmental considerations and cost.

Furthermore, the continuation of development of TCO materials has seen constant discovery of newer novel materials leading to diversity of TCOs. Fundamental principles of ion beams analysis or materials characterization techniques that provide a nondestructive way to investigate the elemental

composition or properties of a material have been discussed, including different techniques available for the characterization of TCO materials. Some previous studies on the modification of the properties of various types of TCO thin film materials by using ion beams have also been discussed. It has been found that ion beams are a powerful tool in the modification of materials. A notable unique feature associated with an ion beam is that it can deposit a large energy density on materials. This makes the material to be driven far from equilibrium. Due to this, unexpected induced changes and novel material properties can be created. Ion beams, therefore, provide flexibility to manipulate changes in the properties of materials, due to the availability of a wide range of ion energies, from keV to TeV and the possibility of controlling ion fluences.

Detailed simulations of Co^+ and V^+ ion implantation in ZnO and Co^+ ion implantation in ITO thin films have been discussed. The simulations show that the nuclear part is the dominant mechanism of energy loss per unit thin film thickness in ITO and ZnO films. In addition, vacancies and displacements per Co^+ and V^+ atoms in ZnO films and ITO thin films increased with increase in dopant concentration.

7.2 Summation

Thereafter, the synthesis of ZnO, Co^+ and V^+ ion implantations and various characterization techniques employed in this work were presented. The RF magnetron sputtering type of PVD method was adopted to grow high quality ZnO thin films. The SRIM-2013 simulated Co^+ and V^+ ion beam parameters (Table 3.1) were used to implant ITO thin films on PET substrates and ZnO thin films on borosilicate glass substrate. Furthermore,

the properties of Co^+ ion implanted ITO thin films on PET substrate, Co^+ ion implanted ZnO on borosilicate glass substrate and V^+ ion implanted ZnO on borosilicate glass substrate have been investigated. The thin films were implanted using the 200 kV ion implanter at iThemba LABS in South Africa. As-grown and ion implanted thin films were characterized using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and UV-Visible Spectroscopy (UV-Vis), Vibrating Sample Magnetometry (VSM), Fourier Transform Infrared (FTIR) (Subsection 5.1.3) and Current Voltage (I-V) Characterization.

The analyses of these implanted thin films showed that they had been modified as expected. Upon implantation, there were profound changes in the structural, optical, electrical properties, together with chemical bond and magnetic properties of V^+ and Co^+ ion implanted ZnO and ITO thin films.

7.2.1 ZnO thin films

The effect of 170 keV V^+ ion implantation on the lattice parameters, resistivity, transmittance together with optical bandgap, surface roughness and thermal parameters of ZnO thin films on borosilicate glass substrate have been studied. It has been found that the implanted V^+ ions were introduced into the ZnO crystal structure as substitutional ions. A 99 % decrease in resistivity was observed for the thin film implanted to 1×10^{16} ions/cm² while lattice parameters such as d-spacing, lattice constant, dislocation, crystallite size and strain showed interesting changes. From UV - Vis spectroscopy, the transmittance of thin film implanted at 1×10^{16} ions/cm² increased to 82.34 % in comparison with that of the as-grown films. However, there was a decrease in transmittance at high ion fluence with sharp increase in absorbance to 0.56 %. The optical band gaps of implanted samples showed

significant changes upon implantation. An increase in bandgap was observed with increase in ion fluence from as-grown to 1×10^{16} ions/cm². The surfaces of implanted thin films showed modification due to ion implantation. The thin film implanted at 5×10^{16} ions/cm² showed decrease in roughness with root mean square (Rq) roughness of approximately 17.4 nm, and the grain size decreased to 4.59 nm while the estimated grain size of the as-grown and roughness have been found to be 6.29 and 17.6 nm, respectively. It has been found that atoms of the thin film implanted at 5×10^{16} ions/cm² were stable as a result of the low thermal factor of 15.70 %. However, atoms of thin film implanted at a fluence of 5×10^{15} ions/cm² were flexible due to the high thermal factor of 94.29 %.

On the other hand, in Co⁺ ion implanted RF - magnetron sputter deposited zinc oxide thin films, the lattice strain was observed to decrease by 10.92 %, while grain size increased by 34.82 % at high ionfluence. Hence, ion implantation enhanced the mechanical strength of ZnO. Williamson-Hall analysis in estimation of grain size and lattice strain showed good agreement with the crystallite size estimated using the Debye-Scherrer method. The optical band gaps of implanted samples showed interesting improvement.

7.2.2 ITO thin films

Lastly, Co⁺ ion implantation induced modifications in the physical properties of ITO thin films have been studied. The grain sizes of the ITO thin films were observed to increase with increase in ion fluence, showing that the crystalline quality of the ITO thin films was getting enhanced. At a fluence of 1×10^{16} ions/cm², a high value of 2.33×10^{-3} emu/g saturation magnetization was estimated. The level of residual magnetism in the Co⁺ ion implanted ITO thin films increased at an average value of 35 % with increase in ion flu-

ence. This means that Co^+ ion implanted ITO thin films have good ability to retain a certain amount of residual magnetic field at zero magnetizing force, as ion fluence increases. Furthermore, the Co^+ ion implanted ITO thin films were found to exhibit clear room temperature ferromagnetism. The shift in hysteresis loops along applied magnetic field axes provides information about the exchange bias on as-grown and Co^+ ion implanted ITO thin films in relation with grain size. The optical band gaps of Co^+ implanted ITO thin films increased from 3.01 to 3.26 eV as ion fluence increased from as-grown to 1×10^{14} ions/cm², but it decreased to 2.92 eV at higher fluences. Changes in the morphology of the ITO thin films were well pronounced after ion implantation. The morphological changes at different ion fluences, and the presence of metal/oxide chemical bonding were confirmed by Fourier transform infrared (FT-IR) spectral analysis. Furthermore, the surface roughness of Co^+ ion implanted ITO thin films was observed to improve at low ion fluences

We can, therefore, conclude that Co^+ and V^+ ion implanted ZnO thin films are suitable for optoelectronics and energy devices. ITO thin films have potential applicability in spin based magnetoelectronic, energy devices and optoelectronic nanodevices.

Conclusively, based on the results presented in this thesis, transition metals, such as Co^+ and V^+ , affect the notable roles and properties of ITO and ZnO thin films in spin based magnetoelectronic and optoelectronic nanodevices. Consequently, the modification of these TCO materials eventually leads to enhanced properties, which could foreseeably extend the useful life of spin based magnetoelectronic, and optoelectronics nanodevices, and as such, greatly benefit the nanotechnology industry.

Appendix A

Publications, Conferences and Awards

A.1 List of publications contributing to this thesis:

- O. Oluwaleye, M Madhuku, B Mwakikunga, SJ Moloi, Studies of lattice structure, electrical properties, thermal and chemical stability of cobalt ion implanted Indium Tin Oxide (ITO) thin films on polymer substrates, Nuclear Instruments and Methods in Physics Research Section B: Beam 450 (2019) 267-273.
- O. Oluwaleye, M Madhuku, B Mwakikunga, SJ Moloi, Investigation of structural and magnetic properties of Co^+ ion implanted indium tin oxide thin films on polyethylene terephthalate ($\text{C}_{10}\text{H}_8\text{O}_4$)_n substrates by 100 keV ions, Nuclear Instruments and Methods in Physics Research Section B: Beam 444 (2019) 96-102.

A.2 Contributions to conferences

A.2.1 Presentations at international conferences

Contributions from this work to international conferences are listed below:

- Poster presentation at the 4th USA International Conference on Surfaces, Coatings and Nanostructured Materials (NANOSMAT-USA 2018), which was held in South Padre Islands, Texas, USA, 29 Oct. - 1 Nov. 2018.
Topic: Modification of RF - magnetron sputter deposited Zinc Oxide thin films by Vanadium ion implantation: Electrical and optical properties;
- Poster and oral presentations at Joint ICTP - IAEA Advanced School on Ion Beam Driven Materials Engineering: Accelerators for a New Technology Era 1 - 5 October 2018, ICTP, Trieste, Italy.
Topic: Modification of Indium Tin Oxide (ITO) thin films on glass substrate by Vanadium keV ion implantation: Structural, electrical and optical properties; ;
- Poster presentation at the 21st International Conference on Ion Beam Modification of Materials (IBMM - 2018), which was held in San Antonio, Texas, USA, June 24 - 29, 2018.
Topic: Investigation of structural, optical, electrical and magnetic properties of Co^+ ion implanted indium tin oxide thin films on Polyethylene terephthalate ($\text{C}_{10}\text{H}_8\text{O}_4$)_n substrates by 100 keV ions;
- Poster presentation at the 23rd International Conference on Ion Beam Analysis (IBA - 2017), organized by Fudan University, in co - operation with the International Atomic Energy Agency (IAEA), Shanghai,

China, 8 - 13 Oct. 2017.

Topic: Studies of lattice structure, electrical properties, thermal and chemical stability of Cobalt ion implanted Indium Tin Oxide (ITO) thin films on polymer substrates; and

- Poster presentation at the International Conference of Young Researchers on Advanced Materials (IUMRS - ICYRAM 2016) 11-15, December 2016, Bangalore, India.

Topic: Ion beam modification of transparent conducting oxide (TCO) thin films by keV to MeV ions .

A.2.2 Presentations at local conferences

Contributions from this work to local conferences are listed below:

- Oral presentation at 64th Annual Conference of the South Africa Institute of Physics (SAIP), 8 - 12 July 2019. Topic: Cobalt ion implantation induced modification in band gap, thermal parameters and lattice strain on RF magnetron sputter deposited Zinc Oxide thin films on borosilicate glass;
- Poster presentation at Surfaces, Coatings and Nanostructured Materials Confrence (NANOSMAT - AFRICA 2018), which was held in Cape Town, South Africa, 19 - 23 Nov. 2018.
Topic: Modification of RF - magnetron sputter deposited Zinc Oxide thin films by Vanadium ion implantation: Electrical and optical properties; and
- Oral presentation at 62nd Annual Conference of the South Africa Institute of Physics (SAIP), 3 - 7 July 2017.

Topic: Investigating the effects of Cobalt keV ion implantation on optical and magnetic properties of Indium Tin Oxide (ITO) thin films on flexible PET substrates.

A.3 Awards

The best research presentation at the Joint ICTP-IAEA Advanced School on Ion Beam Driven Materials Engineering: Accelerators for a New Technology Era 1 - 5 October 2018, ICTP, Trieste, Italy.

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