SYNTHESIS, CHARACTERIZATION, STRUCTURAL, AND OPTICAL PROPERTIES OF ZINC OXIDE
NANOSTRUCTURES EMBEDDED IN SILICON BASED SUBSTRATES

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Structural and optical properties of ZnO nanostructures synthesized by low energy ion implantation technique were examined. ZnO molecular ions were implanted into Si/SiO₂ substrates at room temperature and then furnace annealed under different temperatures and environments. In all as-implanted samples only Zn nanostructures with varying diameters distributed into the Si/SiO₂ matrices were observed. No trace of ZnO was found. The distributions of Zn nanostructures in Si/SiO₂ closely matched results from Stopping and Range of Ions in Matter (SRIM) simulations. During annealing at 750 °C, Zn diffused both toward and away from the surface of the substrate and combine with oxygen to form ZnO nanostructures. At higher annealing temperatures ZnO bonding started to break down and transfer to zinc silicate (Zn₂SiO₄), and at 900 °C the ZnO was completely converted into Zn₂SiO₄. The average sizes of Zn/ZnO nanostructures depended on the ion fluence. If the fluence increased the average sizes of nanostructures also increased and vice versa. For room temperature photoluminescence (RT-PL), band-edge emission in the ultraviolet (UV) region was observed from all samples annealed at 700 °C/750 °C and were slightly blue shifted as compare to bulk ZnO. Donor-bound exciton (D,X) and acceptor-bound exciton (A,X) transitions were observed in low temperature photoluminescence (PL). The lifetime of both donor-bound excitonic emission (D, X) and acceptor-bound excitonic emission (A, X) were found to be in the picosecond (ps) range.
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1.1 Introduction and Motivation

The invention of first semiconductor transistor by the scientists from Bell Lab in 1947 opened the door of the semiconductor industry. Nowadays, the semiconductor industry is all over the world and has changed the world beyond anything that could have been imagined. It has integrated deeply into our daily life and we can’t imagine life without semiconductor devices. From the beginning of the semiconductor era, silicon (Si) became the first choice among the various competing semiconductors due to their relatively simple processing and low raw material cost. As semiconductor technology has matured, Si has kept the dominant place for fabrication of discrete devices and integrated circuit for computers, communication and data storage. Since Si is an indirect band-gap semiconductor, for optoelectronic devices such as light emitting diodes (LEDs) and laser diodes Si is being replaced by gallium arsenide (GaAs). GaAs is a better option for optoelectronic devices because it has higher carrier mobility and higher effective carrier velocity than Si and also is a direct band-gap semiconductor. As semiconductor technologies continue to progress, however, ultraviolet (UV)/blue light emitter applications have become more and more important and are exceeding the limits of Si and GaAs. Alternative materials have to be synthesized in order to achieve higher-performance devices. Wide bandgap semiconductors such as SiC, GaN and ZnO, which possess larger bandgap, higher electron mobility and breakdown field strength, fill the blank for high power, high temperature electronic devices and short wavelength optoelectronics applications.
Zinc oxide (ZnO) is a wide-band-gap compound semiconductor having band-gap energy of 3.37 eV that is suitable for short wavelength optoelectronic applications. Some optoelectronic applications of ZnO overlap with those of gallium nitride (GaN), another wide-gap (~3.4 eV) semiconductor which is widely used for the production of green, blue-ultraviolet and white light-emitting devices. However, ZnO has some advantages over GaN, such as availability of fairly high quality bulk single crystals and higher exciton binding energy (~60 meV as compared to ~25 meV for GaN). Due to this large exciton binding energy, brighter room-temperature emission can be achieved from ZnO than GaN. ZnO also has much simpler crystal growth technology, resulting in a potentially lower cost for ZnO-based devices.

ZnO is not a newly discovered material in the semiconductor field, having been studied for many decades. It has gained substantial interest in the research community because of its large exciton binding energy of 60 meV, which stabilizes the excitons even at room temperature. Researchers have synthesized and characterized ZnO since even before 1960. The lattice parameters of ZnO have been investigated for many decades under different conditions, and its vibrational properties have been studied using Raman scattering. Its optical properties have also been investigated by different groups.

Because of these exceptional properties, and because ZnO nanostructures are expected to have even stronger exciton emission than bulk ZnO, where deep level emission dominates the exciton emission, ZnO nanostructures have attracted much interest due to their possible optoelectronic applications in devices such as light emitting diodes, random lasers, self-formed cavity lasers, and high performance spintronics devices. Nanostructures with different morphologies and dimensions have been synthesized by various techniques.
Among these different techniques, ion implantation is considered to be one of the best methods to fabricate metal and semiconductor nanoparticles (NPs).\textsuperscript{33} Using ion implantation, nanoparticles can be controllably synthesized at a desired depth, composition and thickness in a substrate. Ion implantation has been used to fabricate semiconductor devices since 1950’s. Since the last decade many research groups have started to study ZnO nanostructure formation using ion implantation combined with thermal oxidation.

The very first study on Zn implanted samples was done by researchers at Fisk University and Oak Ridge National Laboratory (ORNL) in 1998. They synthesized ZnO nanoparticles (NPs) in SiO\textsubscript{2} by ion implantation combined with thermal oxidation.\textsuperscript{29} Zn ions of 160 keV were implanted into SiO\textsubscript{2} up to a fluence of 1.0×10\textsuperscript{17} ions/cm\textsuperscript{2} and annealed in an oxygen atmosphere at 700 °C. An annealing temperature 700 °C was chosen because it has been found from experiment that Zn metal NPs are no longer stable when annealed at 800°C in vacuum. Unfortunately, the Fisk and ORNL group didn’t obtain any clear evidence of ZnO formation, possibly due to too short an annealing time. Even though Zn metal NPs become unstable at 800 °C, Zn atoms can stay in the implanted layer by forming ZnO NPs. In 2006, H. Amekura et al.\textsuperscript{28} annealed Zn-implanted Si in oxygen gas at 800°C for 1 h and generated ZnO NPs.

In another study, a high fluence of 3×10\textsuperscript{17} ions/cm\textsuperscript{2} of Zn ions with energy of 160 keV was implanted into SiO\textsubscript{2} by researchers at Changchun and Fisk Universities.\textsuperscript{25,27} X-ray diffraction (XRD) peaks from ZnO were observed after annealing the sample in air at 700 °C for 2h. UV photoluminescence around 377 nm was detected. X-ray photoelectron spectroscopy (XPS) results showed a large increase in the ZnO signal at the surface of the SiO\textsubscript{2} substrate. From the XPS results and the XRD signal, it was concluded that the SiO\textsubscript{2} surface was fully covered by a
ZnO layer instead of ZnO NPs. The formation of a ZnO layer on the SiO₂ surface was later confirmed by using cross-sectional transmission electron microscopy (XTEM).²⁵

H. Amekura et al.²⁶, ²⁸ implanted 60 keV of Zn ions in SiO₂ up to a fluence of 1×10¹⁷ ions/cm². The samples were annealed in an oxygen atmosphere at 400 – 900 °C for 1 h. Changes in the absorption spectra and the XRD results showed that the transformation from Zn metal NPs to ZnO NPs occurred around 700 °C. XTEM result confirmed the formation of droplet-like ZnO NPs on the SiO₂ surface.

In addition to these studies, several other groups have also reported successful synthesis of ZnO NPs by ion implantation.²³, ²⁴, ³⁰-³² In most of the studies on the formation of ZnO NPs by ion implantation, Zn ions were implanted in a dielectric matrix. However, recent trends for smaller and smaller devices require an implantation range on the order of a few nanometers. To implant ions into such a shallow depth, ions of lower energy are required. Molecular ion implantation is the another viable approach to achieve this goal.³⁴ Hence molecular ion implantation technique is now fast adopted for doping in nanometer device applications. Recently, ZnO molecular ions with an energy of 50 keV were implanted into SiO₂ at a fluence of 7 × 10¹⁶ ions/cm² to form ZnO NPs.³¹ Optical absorption (OA) measurements were utilized to confirm the formation of the NPs. To evaluate this low energy molecular beam ion implantation technique fully as a new way to synthesize ZnO NPs, a detailed and systematic investigation of properties such as uniformity of the implantation, implant depth profile, size and structure of NPs has to be conducted. For future spintronic and optoelectronic device applications, carrier recombination processes in ZnO nanostructures and the role of defects have to be understood. Motivated by the promise of future device application, optical
properties of ZnO nanostructures have been studied theoretically and experimentally by many research groups. Despite different explanations presented, the exact mechanisms for UV photoluminescence and carrier recombination processes in ZnO nanostructures are still not clear. Different research groups have suggested different processes for UV emission from ZnO nanostructures such as donor-bound exciton, donor-acceptor pair, or confined exciton recombination. Material quality and device performance are related to excitonic recombination lifetime. This lifetime in ZnO nanostructures depends on their size and the method of synthesis. To integrate optoelectronic applications in semiconductor devices, carrier dynamics and recombination processes for ZnO nanoparticles have to be understood. In Chapter 4 of this dissertation, we report on an experiment designed to create ZnO NPs at a depth of few nanometers from the surface of the substrate and study their structural and optical properties. ZnO nanostructures were synthesized by using ZnO⁺ molecular ions implanted into thermally grown SiO₂ to a fluence of 5 × 10¹⁶ ions/cm², followed by thermal annealing in an oxygen environment at a temperature 750 °C for 2 h. The structure of the synthesized ZnO nanoparticles is analyzed with the help of XPS, TEM, and FTIR measurements; and light emitting properties are explored with the help of RT-PL and low temperature PL, and, for lifetime, TRPL measurements.

Also, nanometer size metal particles embedded in a dielectric matrix exhibit optical effects such as a strong third order nonlinear optical susceptibility and surface plasmon resonance (SPR), which are absent in the bulk material. Due to these properties, metal NPs in dielectric matrices are of great interest in nanoscience and nanotechnology. To be able to use Zn and ZnO nanoparticles in future applications, detailed and systematic investigation of
properties such as formation depth, size and structure of NPs has to be conducted. In Chapter 5 of this dissertation, we report on an experiment designed to create ZnO and Zn or Zn$_2$SiO$_4$ and Zn NPs at a depth of few nanometers from the surface of the substrate and study their structural and optical properties. These NPs were synthesized by implantation of ZnO$^-$ molecular ions into Si at room temperature, followed by thermal annealing. ZnO NP structure is analyzed with the help of XPS, TEM, and XRD measurements; and light emitting properties are explored with the help of RT-PL and low temperature PL measurements.

In the thermal oxidation process, oxygen diffuses into Si or SiO$_2$ at a rate dependent on the temperature.$^{30,40}$ To increase the rate of oxidation, the temperature must be increased. It has been found that if the temperature exceeds $800\,^\circ$C, ZnO bonding starts to break down, and at a temperature of $900\,^\circ$C, Zn$_2$SiO$_4$ forms.$^{28}$ Also, in this technique the sample must be annealed in an oxygen environment at all times. To anneal the sample in a different environment or in vacuum, and to make the oxidation process faster, alternative routes must be employed. One of the alternative routes is dual implantation of Zn and O ions. In this process oxygen is implanted before thermally annealing, so that during annealing O is already available in the matrix to combine with Zn, and any annealing environment or vacuum can be used to form ZnO. Lee et al.$^{24}$ have earlier reported dual beam implantation of Zn (100 keV) and O (50 keV) into SiO$_2$ to form ZnO. Their implanted samples were annealed in oxygen and in vacuum. It is not clear which atmosphere was used when ZnO was formed. It is important to understand the role of implanted oxygen for its potential as an alternative fabrication method for future device applications. In Chapter 6 of this dissertation, we report on a new experimental technique to create Zn, ZnO and Zn$_2$SiO$_4$ NPs at the depth of few nanometers from the surface
of the substrate, and we study their structural and optical properties. Zn, ZnO and Zn$_2$SiO$_4$ NPs were synthesized by dual beam implantation of ZnO$^-$ molecular ions and O$^-$ ions into Si at room temperature to produce overlapping distributions, followed by thermal annealing. Different characterization techniques were used to study the structural properties and optical properties. ZnO NP structure is analyzed using the results of XPS, TEM, and XRD measurements; and light emitting properties are analyzed using the results of RT-PL and low temperature PL measurements, and, for lifetimes, TRPL results.

In this dissertation, Chapter 2 gives a brief review of the structure and properties of ZnO. In Chapter 3, different structural and optical characterization techniques are introduced. Chapters 4, 5 and 6 are devoted to the experimental details and results of our work. Finally, the dissertation ends with some concluding remarks and outlooks for the future in Chapter 7.

1.2 References


CHAPTER 2

ZnO STRUCTURE AND OPTICAL PROPERTIES

2.1 Structure

The most stable structure of ZnO at atmospheric pressure and temperature is hexagonal wurtzite (B4 type) structure (Fig. 2.1) with lattice parameters $a = 0.3295$ and $c = 0.52069$ nm$^1$. It belongs to the space group $C_{4h}^4$ in the Schoenflies notation$^2$ and $P6_3mc$ in Hermann-Mauguin notation$^2$. It is characterized by two interconnecting sublattices of Zn$^{2+}$ and O$^{2-}$ ions stacked tetrahedrally along the c-axis. The tetrahedral co-ordinate in ZnO results in a non-central symmetric structure which is responsible for piezoelectricity and pyroelectricity. Another important characteristic of ZnO is its polar surface. There are two common polar face terminations in wurtzite ZnO, Zn terminated (0001) and O terminated (000$\bar{1}$) faces, which results in normal dipole-moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. Besides these two polar faces, there are two most commonly observed non-polar faces, (2 1 0) and (0 1 1 0), which have equal numbers of Zn and O atoms. They have lower energy than the (0001) faces.

The Zincblende and rocksalt or Rochelle salt (NaCl) structures (shown in Fig. 2.2) are the other two crystalline phases of ZnO besides the wurtzite phase. ZnO zincblende forms can be stabilized by growing ZnO on a cubic structure$^{3-5}$. The rocksalt structure is a high-pressure metastable phase that forms at ~10 GPa and cannot be epitaxially stabilized$^6$. Theoretical calculations suggest that for ZnO a cubic cesium chloride phase may be possible at extremely high temperature$^7$. This phase has not been observed experimentally yet.
2.2 Basic Physical Parameter for ZnO

Basic physical parameters of ZnO are compiled and shown in Table 2.1\textsuperscript{8,9}. Some of these values still are uncertain. For example, the hole mobility and effective mass are still in debate for p-type ZnO. Also, the values for thermal conductivity show some spread due to the influence of defects such as dislocations\textsuperscript{10}. 
Table 2.1: Physical Parameters of ZnO

<table>
<thead>
<tr>
<th>Physical Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>$a_0$</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>$c_0$</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>$c_0 / a_0$</td>
<td>1.602 (ideal hexagonal structure shows 1.633)</td>
</tr>
<tr>
<td>$U$</td>
<td>0.375 (in an ideal wurtzite structure)</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm$^3$</td>
</tr>
<tr>
<td>Linear expansion coefficient ($/ ^\circ$C)</td>
<td>$a_0$: 6.5 ×10$^{-6}$</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 $^\circ$C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1–1.2 W cm$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>&lt;106 cm$^3$</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type conductivity</td>
<td>200 cm$^2$/V s</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
</tbody>
</table>
Hole Hall mobility at 300 K for low p-type conductivity 5–50 cm²/V s

2.3 Nano-size and Optical Properties

The physical properties of a material are normally determined by studying pure macroscopic samples. In such bulk samples, large numbers of molecules are present and physical properties of that material represent averages over those large collections of molecules. It is often assumed that these results should be true for any amount of the material. But this is not true for many materials because for samples with dimensions on the nanometer scale, quantum and surface effects can play a prominent role. Specifically, effects that can be of particular importance for nano-materials are tunneling, quantum confinement (electrons are confined in space), quantization of energy (electrons can only exist at discrete energies), random molecular motion (e.g., Brownian motion), and increased surface to volume ratio (increased relative surface area).

![Fig. 2.3 The images compare the bandgap energy in bulk semiconductor, in a quantum dot and in an atom. As the size decreases bandgap energy increases.](image-url)
Quantum confinement causes the energy of the bandgap to increase as shown in fig 2.3. As the size of the material decreases the bandgap increases. Due to this effect some metals at nanometer sizes have band overlaps that transform into bandgaps and behave as semiconductors. An increase in bandgap energy means more energy is needed to promote valence charge carriers to the conduction band of the material. For radiative excitation, higher energy of course means shorter wavelength (blue shift). So by controlling the size of the semiconductor (in nanometer scale) optical properties (emission and absorption) of nano-sized semiconductors can be tuned over a range of wavelengths, with the result that the same material emits different colors depending on its size.

2.4 Optical Properties of ZnO

Being a direct band semiconductor, the lowest point of the conduction band and the topmost point of the valance band are at the same point in the Brillouin zone, namely at k = 0 for ZnO as shown in Fig. 2.4.

The conduction band originates due to empty 4s states of Zn$^{2+}$ whereas the valance band forms from the occupied 2p orbitals of O$^{2-}$. The valance band splits into three band states A, B, and C under the influence of spin-orbit and crystal-field interaction. The A and C sub-bands possess $\Gamma_{7}$ symmetry and the middle band, B, has $\Gamma_{9}$ symmetry.

For optoelectronic devices applications, optical properties of the material have to be understood. In semiconductors, optical properties can be classified into two types: intrinsic and extrinsic. An intrinsic transition is a transition between an electron in the conduction band and a hole in valance band, in which exciton effects due to the coulomb attraction between the electron and the corresponding hole are also included. Extrinsic transitions are related to the
electronic levels created in the bandgap by defects or dopants. In ZnO, the valance band is split into three bands, and the near-band-gap intrinsic absorption and emission are dominated by transitions from these three valence bands. The free exciton transitions from conduction to the three valance bands or vice versa are A (heavy hole), B (light hole), and C (crystal-field split band).

Fig. 2.4 Band structure and symmetries of hexagonal ZnO. The valance band is split into three bands.

Bound excitons manifest an extrinsic optical transition in which an electron hole pair is localized near an imperfection in the crystal. These are due to the defects and dopants that create discrete electronic state in the band gap and therefore influence both optical absorption and emission processes. The recombination of bound excitons is typically observed as sharp line
optical transitions in photoluminescence. In ZnO, sharp lines in a narrow range from 3.348 to 3.374 eV have been reported for donor and acceptor bound excitons.$^1$

2.5 References


CHAPTER 3
SAMPLE SYNTHEISIS AND CHARACTERIZATION TECHNIQUES

All the samples in these studies were synthesized by using low energy ion implantation followed by thermal annealing. After the sample was prepared, different characterization techniques were used to investigate the structure of nanoparticles and optical properties. In this section, the various characterization techniques along with the low energy ion implantation technique are briefly introduced.

3.1 Ion Implantation

Ion implantation, a technique for modifying the surface and near surface properties of materials, is considered to be one of the preferred methods to fabricate metal and semiconductor nanoparticles (NPs). Using ion implantation, nanoparticles can be controllably synthesized at a desired depth, composition and thickness in a substrate. Ion implantation has been used to fabricate semiconductor devices since the 1950’s. It is also used as a surface treatment technique in enhancing corrosion resistance and other metallurgical processes. The ions introduced by this method can produce chemical change (ions can be of a different element than the target) and structural change (the crystal structure of the target can be damaged or even destroyed) in the target. The implanted ions undergo a series of collisions, both nuclear and electronic, before coming to a rest within the target material. Since the last decade many research groups have extensively utilized ion beam techniques to grow nanostructures.

Fig 3.1 shows a schematic diagram of IBMAL main lab with the low energy implantation line at the University of North Texas. The ion implantation line consists of an ion source,
extraction optics, initial accelerator, mass analyzer, beam raster scanning system, target chamber, Faraday cup and sample changing vacuum interlocks. A National Electrostatics Corporation Source of Negative Ions by Cesium Sputtering (SNICS-II) was used to produce the ions\(^3\) for the implantation, which was done at a pressure of \(1 \times 10^{-7}\) Torr. The desired element or compound for producing a beam is used as the ion source cathode.

Fig. 3. 1 IBMAL main laboratory with ion implantation line (I-1). (b) Low energy ion implantation line from 90° magnet to the target.
Positive cesium ions are produced through thermal ionization of cesium vapor by a high temperature ionizer. The cesium vapor is supplied to the ionizer by heating a reservoir of cesium and allowing the vapor to travel to the ionizing region via a transfer tube. The cesium ions are attracted to and focused on a target cathode which is biased at a negative voltage (-5 to -10kV). The cathode surface is sputtered by the cesium ions, and the sputtered particles that are negatively charged (negative ions) are accelerated away from the cathode due to its bias. The negative ion beam is then focused, and accelerated further by an extractor voltage. The negative ions then receive their final acceleration from the source bias applied to the entire source cage.

The accelerated beam of ions passes through another lens and into the mass analyzer (30° magnet). During tuning, the magnetic field is scanned while monitoring ion beam current in the Faraday cup after the analyzer to determine the magnetic field setting for the peak beam current. To find the magnetic setting for the correct ion species, we use simple magnetic force and kinetic energy equations for ions of charge $q$ moving at speed $v$ along a trajectory of radius $r$ perpendicular to a magnetic field of magnitude $B$:

$$qvB = \frac{mv^2}{r}, \quad E = \frac{1}{2}mv^2, \quad \text{and} \quad E = qV.$$  

Solving for $B$ and comparing to a reference field $B_{\text{ref}}$ gives

$$\frac{B}{B_{\text{ref}}} = \sqrt{\frac{mV}{m_{\text{ref}}V_{\text{ref}}}}$$ \hspace{1cm} (3.1)

Where $B$ is the required field setting, $B_{\text{ref}}$ is the setting of a previously used cathode (known ion); $m$, $V$ and $m_{\text{ref}}$, $V_{\text{ref}}$ are the ion mass and source bias of the new cathode and previously used cathode, respectively.
After leaving the 30° magnet, the ions drift through a 90° magnet (not energized) and on to the target chamber. To maintain uniform implantation over the area of interest the beam is scanned across the sample by using a high voltage electrostatic X-Y raster scanner. To avoid sample heating during ion implantation, low current density around or less than 500 nA/ cm² was maintained.

The distribution of implanted atoms was simulated by using a Monte Carlo simulation code Stopping and Range of Ions in Matter (SRIM). In the case of molecular ion implantation, the implanted profile of each atomic species was calculated independently. When molecular ions of energy \( E_0 \) impinge on the substrate, each component atom of abundance \( k_i \) has energy \( E_i \) proportional to its atomic mass \( m_i \), namely,

\[
E_i = \frac{m_i}{\sum_{j=1}^{n} k_j m_j} E_0.
\] 3.2

The implantation fluence is calculated by using the current integration technique. The target holder is connected through a BNC (Bayonet Neill-Concelman connector) vacuum feedthrough cable to the SHV (super high voltage) input connector of an Ortec digital current integrator. The output pulses from the current integrator are sent to a counter/timer. The fluence calculation is given by

\[
F = \frac{N_C}{eA}.
\] 3.3

Where,

\( F = \) total implanted ion fluence (atoms/ cm²)

\( N = \) Total number of pulses in the counter.

\( C = \) Total charge per pulse (coulombs per pulse).
\[ e = \text{electronic charge (coulomb)}. \]

\[ A = \text{surface area of implanted region on the sample (cm}^2) \]

3.2 X-ray Diffraction (XRD)

XRD is a powerful non-destructive analytical technique primarily used for phase identification of crystalline material. It is also used to study the orientation of single crystals and find shape, size and strain of particles. In this technique, x-rays are produced when a target metal is bombarded with high-energy electrons. Electrons in the x-ray tube are produced by thermionic emission. Emitted electrons are accelerated towards the target by maintaining a high potential difference between the emitter and the target. When these fast moving electrons hit the target, x-rays are produced. Metals like copper, cobalt, chromium and molybdenum are commonly used as the target in x-ray production. In our experiments we used copper as the target.

Intensity and wavelength of the x-rays can be controlled easily in the x-ray tube. The intensity of the x-rays depends on the number of electrons striking on the target per second. Since the number of electrons given out by the emitter is proportional to its temperature, therefore the intensity of x-rays can be controlled by changing the filament current. The frequency of emitted x-rays depends on the voltage between the emitter and the target. If \( V \) is the potential difference between emitter and the target and \( e \) is the electronic charge, the work done on the electron in moving from emitter to target should be equal to \( eV \). This work done will be converted into the energy of the x-rays having maximum frequency \( f \), so

\[ hf = eV. \]
Thus, the minimum wavelength of the x-rays produced is

\[ \lambda = \frac{c}{f} = \frac{hc}{eV}. \]

Hence by changing the potential difference between the emitter and target, wavelength can be controlled.

![Fig. 3. 2 Schematic representation of XRD](image)

These x-rays produced from the x-ray tube are directed onto the sample (Fig. 3.2). The x-rays that impinge on the sample undergo diffraction in all different directions and each atom in the crystal acts as a source of scattering radiation. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). When constructive interference occurs, a relation between the
incident x-rays, crystal structure and sample orientation is formed. British physicists W. H. Bragg and W. L. Bragg first formulated this relation in 1912 and it is called Bragg’s law of diffraction.7

Because each different crystalline material has a unique atomic structure, it will diffract x-rays in a unique characteristic pattern. Peak identification of our experimental diffraction patterns was performed by using the powder diffraction file (PDF) of the International Centre for Diffraction Data (ICDD). In the PDF most of the standard powder diffraction parameters such as Miller indices (hkl) of diffracting planes, integrated peak intensities, diffraction angles (2θ), plane spacing (d), the crystal system, and the corresponding phase for the characteristic peaks of various crystalline materials are reported. The experimental diffraction patterns were compared with standard PDF data to assign the phase of the nanoparticles.

3.2.1 Bragg’s Law of Diffraction

To derive the Bragg’s law consider a set of successive parallel planes of atoms as shown in Fig. 3.3. Assume a parallel monochromatic x-ray beam of wavelength λ to be incident on the first and second crystalline layer. Let one part of the beam interact with the atom at O and another interact with the atom at B. The second beam must travel the extra distance AB + BC if the two beams are to continue traveling parallel and in phase. The path difference between two beams must be equal to an integral (n) multiple of the wavelength λ, i.e.,
Fig. 3. Illustration of Bragg’s law of diffraction occurring in a crystalline material.

\[ n \lambda = AB + BC. \]

Since \( AB = BC \),

\[ n \lambda = 2AB. \] \hspace{1cm} 3.4

From triangle OAB,

\[ AB = OB \sin \theta = d \sin \theta. \] \hspace{1cm} 3.5

From 3.1 and 3.2,

\[ n \lambda = 2d \sin \theta. \] \hspace{1cm} 3.6

Thus, measuring the angle of diffraction and the wavelength of incident x-ray, the interplanar spacing \( d \) of the diffracting plane can be calculated.

The crystal lattice parameters (group of lattice constants) can be determined by the relation between lattice parameters and interplanar spacing \( d \). In the case of a cubic crystal, the lattice parameter is same as the lattice constant \( (a) \), and if the Miller indices \( (hkl) \) of the
diffracting planes are known, then the lattice parameter can be determined by using the following relation:

\[ d^2 = \frac{a^2}{h^2+k^2+l^2}. \]  

### 3.2.2 Particle Size Determination

Scherrer formula\(^8\) can be applied to x-ray diffraction patterns to calculate the average particle size of a crystal (thickness of the crystallite):

\[ t = \frac{0.9 \lambda}{B \cos \theta_B}. \]  

Here, \( \lambda \) is the wavelength of the x-ray source. For our experiment we use Cu K\(\alpha \) x-rays, for which \( \lambda = 1.542 \, \text{Å} \). \( B \) is the full width at half maximum (FWHM) of a diffraction peak. The FWHM can be obtained by using curve fitting. In our calculation, the peak broadening was determined by a Gaussian curve fit of the measured XRD peak using Origin 8.5 software. \( \theta_B \) is the diffraction angle that can be obtained from the diffraction pattern. After determining all parameters, average particle size can be calculated. XRD equipment at the Center for Advanced Research and Technology (CART) facility at the UNT, a Rigaku Ultima-III model with Cu K\(\alpha \) 1.542 Å radiation, was used to record the diffraction patterns from the specimens.

### 3.3 Transmission Electron Microscopy (TEM)

TEM is a powerful analytical technique used for phase identification and analysis; determination of crystal structure, symmetry, and orientation relationships; defect, strain, and chemical analysis; and many more things\(^9\). The resolution (smallest distance between two
discernible points) of the human eye is about 0.1-0.2 mm. In the case of the optical microscope, the image resolution is given by Rayleigh’s criterion, i.e.,

\[ \delta = \frac{0.61 \lambda}{\mu \sin \beta} \]  

where \( \delta \) the smallest distance resolvable, \( \lambda \) is the wavelength of radiation, \( \mu \) is the refractive index of the viewing medium, and \( \beta \) is the semi-angle of collection of the magnifying lens. For simplicity we can approximate \( \mu \sin \beta \) to unity and the resolution is then equal to about half the wavelength of light. Green light, which is in the middle of the visible spectrum, has a wavelength of 500 nm (~1000 atomic diameters), so optical resolution is limited to 300 nm, due to the limitations of wavelength of light. The wavelength of electrons is much less than visible light and related to their energy. If relativistic effects are ignored then de Broglie’s famous equation becomes

\[ \lambda \sim \frac{122}{E^{1/2}} \]  

where \( E \) is the electron energy in eV and \( \lambda \) is in nm. For 100 keV electron energy the wavelength will be .004 nm. Using the Rayleigh criterion (Eq. 3.9) the image resolution will be 0.0024 nm. So, the resolution of a TEM instrument is ~1000 times that of an optical microscope.

The first electron microscope was built and publically demonstrated by Max Knoll and Ernst Ruska in 1931. In 1936 the first commercial TEM was developed in the UK. It didn’t work very well and production was stopped. The regular production of TEMs was started by Siemens and Halske in Germany in 1939. At present several companies are producing TEMs and they are widely available.
Fig. 3. 4 Schematic representation of a TEM.

In TEM, an image is formed from electrons transmitted through a specimen that have interacted with the specimen during transit. The image is then magnified and focused onto an imaging device. Fig. 3.4 represents the schematic diagram of a TEM. In TEM electrons are
produced by either a thermionic emission source (electrons produced when heated) or field-emission source (electrons produced due to electric field). Electrons ejected from the electron gun accelerate towards the two condenser lenses and a condenser aperture and then impinge on the sample. Transmitted electrons from the sample then pass through the objective lens. Since the transmitted electrons have undergone different types of interaction in the sample i.e. no scattering, elastic and inelastic scattering—objective and selective area apertures are used to choose among those transmitted electrons. Selected electrons are then pass through the first and second intermediate lenses and projector lens. A final image is formed on either a fluorescent screen or a monitor by using an electron-sensitive charge coupled device (CCD) camera.

Fig. 3.5 TEM sample preparation technique.

TEM samples were prepared by either a focused ion-beam (FIB) technique or the steps explained in Fig. 3.5. For the FIB technique, samples were prepared by a lift-out technique in
which a platinum strip was deposited over the region of interest, ion milling was used to cut the sample, and finally an Omni Probe instrument (nanomanipulator in FIB machine) was used to lift the specimen from the sample. Using the technique illustrated in Fig. 3.5, samples were prepared by performing the following steps. First, a TEM copper grid having a diameter of 3 mm was attached to the sample by using an M-Bond 200 adhesive kit. The sample was then ground by using different grits of sand paper until the thickness became 150-200 nm. After the thickness reached between 150 nm to 200 nm, the sample was ground in a dimple grinder. The edge of the sample was then trimmed to make a circular shape. For the final step, the sample was milled in an ion miller.

When accelerated electrons interact with a sample many signals will be generated. These signals are shown schematically in Fig. 3.6. In TEM for imaging only transmitted electrons that consist of unscattered electrons, elastically scattered electrons and inelastically scattered electrons are used. The unscattered portion of transmitted electrons is used to determine the internal morphology such as size, shape and arrangement of the sample. The number of transmitted electrons depends on the thickness of the sample, i.e., if the sample is thick fewer electrons are transmitted and if the sample is thin more electrons are transmitted. So, for better imaging the thickness of the sample should be suitably thin (~100 nm). Elastically scattered electrons are used to determine crystallographic information about the specimen. These electrons follow Bragg’s law of diffraction, discussed in Section 3.2.1, where in this case $\lambda$ is the de Broglie wavelength of the electrons.

All the incident electrons have same wavelength and energy. After interaction with the sample, the interaction being elastic, the scattered electrons still have the same energy and
wavelength. When these electron waves interfere, constructive interference occurs in certain directions and a diffraction pattern results. For a single crystal, the diffraction pattern consists of dots but for polycrystalline material a series of ring can be observed. Each of the dots corresponds to specific atomic planes and can provide the information about the crystalline orientation and the phase of the material.

Fig. 3.6 Interactions of electron with matter are schematically illustrated.

Besides these transmitted electrons, the interaction between the sample and the electrons in the beam produces Auger electrons, backscattered electrons, secondary electrons, characteristic X-rays and visible light. Other electron microscopy techniques, such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and electron energy loss spectrometry (EELS), use these signals for materials analysis. In our experiments, the TEM
measurements were performed by using a high resolution TEM (FEI Co. Tecnai G2 F20 S-twin machine operated at 200 keV) in the CART facility at UNT.

3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is based on the photoelectric effect. XPS is widely used to identify the elements contained in a sample, and for analysis of the chemical state of elements, quantification of chemical composition, and chemical imaging.

Fig. 3. 7 Schematic representation of XPS.

In the XPS technique, monochromatic x-rays are directed to the sample surface in ultra-high vacuum with sufficient energy to eject electrons from the sample. The ejected electrons are analyzed by an energy analyzer as shown in Fig. 3.7. This technique is highly surface sensitive due to the short range of the photoelectrons that are produced in the solid. XPS
measurements have to be performed in ultra-high vacuum to avoid scattering of the low energy electrons (generally in the range of 20-2000 eV) due to residual gas molecules in the chamber, which results in a decrease in spectral intensity and ultimately increases the noise level in the spectrum.\textsuperscript{10} In XPS measurements, Mg K\(\alpha\) radiation (1253.6 eV) or Al K\(\alpha\) radiation (1486.6 eV) are often the source of x-rays.

When an x-ray beam is directed to the sample surface, the energy of an x-ray photon can be adsorbed completely by the core electron of an atom. If the photon energy, \(h\nu\), is large enough, the core electron will then escape from the atom and be emitted from the surface. If \(E_k\) is the kinetic energy of the emitted photoelectron, then the binding energy of the core electron is given by the Einstein relationship:

\[ B.E. = h\nu - E_k - W. \]  

where \(W\) is the work function of the spectrometer. Since \(h\nu\) and \(W\) are known, measurement of \(E_k\) gives the \(B.E.\). \(B.E.\) peaks in XPS spectra are characteristic of each element and based on the element’s final state configuration. The composition of the material surface can be determined by using the areas under the peaks in the spectrum. Depending on the chemical state of the sample, the shape of each peak and \(B.E.\) can be slightly changed which makes XPS useful to determine bonding information for the sample. The process of photoemission is shown schematically in Fig 3.8. In Fig 3.8, a 1s electron is ejected from the atom.
Fig. 3. Schematic representation of a photoemission process.

XPS is mostly used as a surface analysis technique but it can be used to study the chemical composition as a function of depth. Depth information can be obtained in two different ways. One is destructive and the other is nondestructive. The nondestructive technique, which is also called angle-resolved electron spectroscopy, involves changing the depth analyzed by changing the geometry of the experiment. This technique is mostly sensitive to the near surface region, up to 10 nm from the surface of a solid sample. If the depth profile has to be measured beyond 10 nm this technique is not useful so the other (destructive) technique has to be implemented. In the destructive technique, layers of the sample surface are removed by ion sputtering. In the beginning of the experiment XPS analysis is done on the surface of the sample. The sample then undergoes a period of ion sputtering, after which the sample is analyzed at this new depth. This process is continued until the required depth range is reached. In our experiments, the XPS measurements were performed using a PHI 5000 VersaProbe™ Scanning XPS Microprobe, in the CART facility at UNT.
3.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a non-destructive technique that uses infrared radiation to measure the absorption spectrum and reflection properties over a broad spectral region of a solid, liquid or gas\textsuperscript{11, 12}. It is a powerful tool for identifying chemical bonding states in molecules. This technique is also used to identify unknown materials, quality, and amount of components in a sample. FTIR spectroscopy measures the characteristic vibrational frequency of molecular bonding in the sample. Since molecules absorb specific frequencies that are characteristic of their structure, by using FTIR it is possible to identify chemical bonding in the sample.

FTIR is typically based on a Michelson interferometer as shown in Fig. 3.9. The interferometer consists of a beam splitter, a fixed mirror and a moving mirror (scanning mirror). The beam splitter is made of special material that reflects half of the incident radiation and transmits the remaining half. The separated radiation then recombines at the beam splitter after reflecting from the two mirrors. Due to the path difference between the two beams, an interference pattern is generated. The output beam from the interferometer is recorded as a function of path difference. This is called an interferogram. With the use of Fourier transformations this time domain signal can be converted into the frequency domain.
Three components—radiation source, detector and beam splitter—determine the operating frequency range of an FTIR. Infrared detectors are classified into two types: quantum types such as InSb and HgCdTe detectors, where free electrons excited by IR photons create an electrical signal; and thermal types such as Deuterated Tri-Glycine Sulfate (DTGS) detectors where temperature changes in the material due to the absorption of IR photons causes a change in polarization and produces a detectable electric signal. The sensitivity of thermal type detectors is lower than quantum type detector. For the IR source, high temperature ceramic is
commonly used. Ge-coated KBr, Sn$_2$Sb$_3$-coated CaF$_2$, or Mylar thin films are used as beam splitters. The resolution of an FTIR spectrometer is given by

$$\Delta \sim \frac{1}{\delta_{max}}$$  \hspace{0.3cm} (3.12)

where $\Delta$ is the resolution in wavenumber (cm$^{-1}$) and $\delta_{max}$ is the maximum path difference.

This technique also has some limitation. The main drawback of the FTIR technique is that it cannot detect atoms and monoatomic ions because single atomic entities are not chemically bonded, and hence do not undergo characteristic vibrational motion and absorb no infrared radiation. In our experiments, the FTIR measurements were performed using a 750 Nicolet FTIR model with 4 cm$^{-1}$ resolution in the CART facility at UNT.

3.6 Photoluminescence Spectroscopy (PL)

Photoluminescence (PL) is a process in which material spontaneously emits photons (light) under optical excitation$^{13}$. It is a contactless, nondestructive method mostly used to determine the bandgap of a material, measure impurity levels and detect defects, and probe recombination mechanisms. The electronic bandgap of a material can be determined by analyzing the spectral distribution of PL. Mostly in low temperature PL, spectral features associated with impurities can be observed that can help to determine the impurities and defects in the host material, and recombination mechanisms can be explained by measuring the quantity of PL emitted from a material because this quantity is proportional to the recombination rate$^{14}$. 
In the PL technique, a laser or a full-spectrum high-intensity lamp is used to excite the carriers. A schematic representation of a typical PL measurement setup is shown in Fig. 3.10. The laser is focused directly on the sample, the sample absorbs photons and excitations are created. Photons are emitted from the material (sample) when these excited carriers relax. Those emitted photons are passed through a monochromator and then detected by highly sensitive detectors depending on the detection range. The PL spectrum can be collected and analyzed to study various important properties of the material. Carriers in the materials are
excited only when the energy of the incident photons is equal to or greater than the bandgap energy of the material. So, different excitation source have to be used for different materials depending on their bandgap energy. To study the electronic states and bands of a material in detail, PL experiments can be performed by changing different external parameters such as temperature, excitation power, magnetic field, electric field, pressure etc.

In a semiconductor, the gap between the conduction band and valance band is one of two types: direct bandgap or indirect bandgap. A semiconductor is said to be direct bandgap if the lowest energy level of the conduction band and the highest energy level of the valance band are at the same point in the Brillouin zone, namely, at \( k = 0 \). If otherwise then it is called an indirect bandgap semiconductor\textsuperscript{15}. In direct bandgap materials, when an electron is excited by the photon to the conduction band, it is unstable and recombines with a hole in the valence band. During this recombination process the electron releases energy in the form of a photon that corresponds to the bandgap of the material. This process is called a direct transition process or radiative process, shown in Fig. 3.11 (a). If the photon energy is much larger than \( E_g \), then the excited electron is not near \( E_C \) and has to lose the extra energy \( (h\nu - E_g) \) to reach thermal equilibrium. The excess energy is lost to lattice vibrations as heat as the electron is scattered from one atomic vibration to another. In indirect bandgap materials, since the lowest energy level of the conduction band and highest energy level of the valance band are widely separated in momentum space, the transition of an electron occurs with a change in momentum so excess energy is emitted in the form of heat (a phonon) in the semiconductor crystal lattice. This is called an indirect transition process or non-radiative process, shown in Fig. 3.11 (b).
In our experiment, continuous wave photoluminescence (CW-PL) measurements were carried out at an excitation wavelength of 325 nm using a He-Cd laser with a TRIAX 320 spectrometer. When a pulsed laser is used to provide the excitation, the lifetime of the excited state can be obtained and the technique is called Time-Resolved PL (TR-PL). TR-PL measurements were carried out using a mode-locked, frequency-doubled, Ti:sapphire laser (pulse width 80 fs, repetition rate 80 MHz) at an excitation wavelength of 350 nm. The light emitted from the sample was analyzed using a C4334 Streak scope and Bruker 250IS spectrograph.
3.7 Rutherford Backscattering Spectrometry (RBS)

Rutherford backscattering Spectrometry (RBS) is an ion scattering technique that is used for materials characterization. It is also nondestructive and sensitive to all elements in the periodic table. It has good depth resolution, on the order of several nanometers (nm).

![Schematic representation of an elastic collision between an ion and target atom.](image)

Fig. 3.12 Schematic representation of an elastic collision between an ion and target atom.

RBS is named after physicist Lord Ernest Rutherford. In this technique high energy ions are incident on the stationary atoms in a target material. Due to elastic collisions with the target atomic nuclei, the ions are backscattered. These elastically backscattered ions are used to determine the different characteristics of the material. The intensity and the energy of the backscattered ions provide information about the near surface of the target material. When a \(^4\text{He}^+\) beam is used, backscattered ions typically give information up to 5\(\mu\text{m}\) from the surface of the material. Fig. 3.12 is a schematic representation of an elastic collision between an ion and an initially stationary target atom. \(M_1\) and \(M_2\) are the masses of the incident particle and the
atom respectively. $E_0$ and $E_1$ are the initial and backscattered energies of the ion, and $\vartheta$ is the ion scattering angle. Using conservation of momentum and energy in the laboratory frame of reference, the kinematic factor $K$ can be derived as:

$$K = \frac{E_1}{E_0} = \left[\frac{(M_2^2 - M_1^2 \sin^2 \vartheta)^{\frac{1}{2}} + M_1 \cos \vartheta}{M_1 + M_2}\right]^2.$$ 3.13

By knowing the scattered ion energy for the specific beam and the scattering angle, target atom mass can be easily determined.

Quantitative analysis can be done by using the scattering cross section. For example, for a thin layer, the areal density of an element in the material can be determined by using the following formula:

$$n = \frac{N_p}{N_0 \Delta \Omega \frac{d\sigma}{d\Omega}}.$$ 3.14

Here $n$ is number of atoms per cm$^2$, $N_p$ is the number of ions scattered from the element into the detector, $N_0$ is the number of ions incident on the material, $\Delta \Omega$ is the solid angle of the detector as seen from the target, and $d\sigma/d\Omega$ is the differential scattering cross section.

Fig. 3.13 represents the schematic of the RBS setup and data acquisition electronics. A 1.5 MeV He$^+$ beam from a NEC 9SDH-2 Tandem Pelletron accelerator at the Ion Beam Modification and Analysis Laboratory (IBMAL) is passed through the electron trap and aluminum mesh and then impinges on the target material. The scattered beam from the sample is collected by the solid state detector.
The signal from the detector is amplified and sent to a multichannel analyzer, which in our case is interfaced to a computer. Data are plotted as counts as a function of channel number, which corresponds to scattered ion energy. The charge delivered to the target is measured by integrating the beam current on the target holder, which is configured to suppress secondary currents.

3.8 References


4.1 Motivation

The first study on ZnO nanoparticles synthesized by using ion implantation was done in 1998 at Fisk University and ORNL. They synthesized ZnO NPs in SiO₂ by ion implantation combined with thermal oxidation.¹ After the first research result, several other groups have also reported successful synthesis of ZnO NPs by ion implantation.²⁻¹⁰ In most of the studies on the formation of ZnO NPs by ion implantation, Zn ions were implanted in a dielectric matrix. However, recent trends for smaller and smaller devices require an implantation range on the order of a few nanometers. To implant ions into such a shallow depth, ions of lower energy are required. Molecular ion implantation is a viable approach to achieve this goal¹¹. Hence molecular ion implantation techniques are now being rapidly adopted for doping in nanometer device applications. There is only one report on the molecular ion implantation of ZnO for NP synthesis³, but no detailed study on structural and optical properties has been reported. To evaluate this low energy molecular beam ion implantation technique fully as a new way to synthesize ZnO NPs, a detailed and systematic investigation of structural and optical properties the resulting NPs has to be conducted. So in this chapter, we report on an experiment designed to synthesize ZnO NPs in SiO₂ by using molecular ion implantation techniques followed by thermal annealing, and to study their structural and optical properties.

¹ Some part of this chapter is reproduced partially or fully from [B. Pandey, P. Poudel, A. Singh, A Neogi, D.L Weathers, “Ion beam synthesis and carrier dynamics of ZnO nanoparticles embedded in an SiO2 matrix” Applied Physics A 112(3), 801-806 (2013).], with the permission from the Springer.
4.2 Experimental Procedure

A boron-doped p-type <100> silicon wafer with a resistivity on the order of 15 to 25 Ω-cm was thermally oxidized to form an SiO₂ thin film on Si by the dry oxidation technique\textsuperscript{12} (Si thermally oxidized in O₂ environment at 1100 °C for 5 h). The SiO₂ wafer was implanted with low energy 35 keV ZnO⁻ ions to a fluence of 5 × 10\textsuperscript{16} ions/cm\textsuperscript{2} using the ion implantation facilities in the IBMAL\textsuperscript{13} at the University of North Texas. A National Electrostatics Corporation Source of Negative Ions by Cesium Sputter (SNICS-II) was used to produce the ions\textsuperscript{14} for the implantation, which was done at a pressure of 1 × 10\textsuperscript{-7} Torr. To avoid sample heating during ion implantation, low current density was maintained. The typical rastered beam current density was 50 nA/ cm\textsuperscript{2} and current integration techniques were utilized to determine the implantation fluence. The implanted sample was cut into small pieces (5 mm × 5 mm) for thermal annealing. The samples were furnace annealed in flowing oxygen gas at a temperature 750° C for a period of 2 h.

Fig. 4.1 shows the two different simulation techniques used to estimate depth profile and sputtering effect during the implantation of ZnO into SiO₂. The distribution of implanted atoms has been simulated by using a Monte Carlo simulation code (SRIM)\textsuperscript{15} Fig. 4.1(a)). In the case of molecular ion implantation, the implanted profile of each atomic species was calculated independently. Using Eq. 3.2, for the given 35 keV ZnO molecules, each Zn atom had an energy of 28 keV and each O atom 7 keV. Fig. 4.1 shows the SRIM simulation of Zn and O ions implanted with energies of 28 keV and 7 keV, respectively, into SiO₂. The simulated Zn and O distributions (without considering the sputtering effect during implantation) overlap in the 5 to 50 nm depth range. O atoms are distributed from the surface to a depth of 50 nm, whereas Zn
atoms are distributed between 5 and 55 nm from surface. As shown in Fig. 4.1(a), the overlap of the implanted Zn and O distributions could provide favorable conditions to form ZnO even if the sample is annealed in vacuum or other inert gases. The simulated profile peak positions of Zn and O atoms are at depths of 24 nm and 19 nm, respectively. Static SRIM simulation is most valuable for estimating the range of the implanted ions. The detailed shape is less meaningful because sputtering effect are not factored in here. To study the sputtering effect dynamic transportation of ions in matter (T-DYN)\textsuperscript{16} is used. According to T-DYN, Zn and O ions distributed from the surface to 40 nm depth. In the surface, Zn has \(~18\%\) concentration and after 15 nm depth the concentration of Zn decreases slowly.

![Fig. 4.1 Simulation of ZnO ions into SiO\textsubscript{2}. (a) Static SRIM simulation of implanted ZnO constituents in SiO\textsubscript{2}. The simulated Zn and O distributions overlap in the 5 to 50 nm depth range. O atoms are distributed from the surface to a depth of 50 nm, whereas Zn atoms are distributed between 5 and 55 nm from surface. (b) T-DYN simulation of ZnO into SiO\textsubscript{2}. According to the simulation the Zn and O ions distributed from the surface to 40 nm depth.](image)

In order to monitor the formation of NPs at various depths in the substrate and their chemical states XPS measurements were performed by using a VersaProbe 5000 equipped with...
an argon ion sputter depth profiling system on both as-implanted and annealed samples. A monochromatic radiation (1486.9 eV) was used as the x-ray source and was focused to a spot size of about 200 μm. Argon sputtering was performed at a chamber pressure of ~1 × 10⁻⁷ Torr and beam energy of 1keV. The sputtering rate was determined to be about 7 Å/min.

An HRTEM FEI Co. Tecnai G2 S-Twin machine operated at 200 keV was used to characterize the microstructure and the crystalline quality of the implanted and annealed samples. TEM samples were prepared by following the technique explained in section 3.3.

In order to study optical properties, continuous wave photoluminescence (CW-PL) measurements were carried out at an excitation wavelength of 325 nm using a He-Cd laser with a TRIAX 320 spectrometer, while TR-PL measurement were carried out using a mode-locked, frequency-doubled, Ti: sapphire laser (pulse width 80 fs, repetition rate 80 MHz) at an excitation wavelength of 350 nm (C4334 Streak scope and Bruker 250IS spectrograph).

4.3 Results and Discussion:

XPS was used to study the depth profile and formation mechanism of ZnO. Fig 4.2(a) shows composite depth profiles of Zn, O and Si derived from XPS measurements of the as-implanted sample. Zn is almost negligible on the surface and the concentration peaks inside the substrate. The concentration of O is about 70 atomic % on the surface, decreases slightly up to a depth of 36 sputtering cycles (~25 nm), after which it start to increase up to 70 sputtering cycles (~49 nm) and then remains constant at ~ 70 atomic %. Si has a concentration of ~ 30 atomic % on the surface, and as the concentration of Zn increases it starts to decrease and as
the concentration of Zn decreases it increases again to a constant value after approximately 70 sputtering cycle (49 nm).

Fig. 4.2 Atomic concentrations of Zn, Si, and O in (a) as-implanted sample and (b) sample annealed at 750 °C. In the as-implanted sample, Zn is almost negligible, O is about 70 atomic %, and Si is about 30 atomic % on the surface. In the annealed sample, Zn is almost negligible again, O is about 60 atomic %, and Si is about 40 atomic % on the surface. Atomic concentrations of Si and O start to decrease as the atomic concentration of Zn increases with depth in both as-implanted and annealed samples. The sputtering rate was about 7 Å/min.

Composite depth profiles of Zn, O and Si in an annealed sample are shown in Fig 4.2(b). Similarly to the as-implanted sample, Zn is almost negligible on the surface but here it has diffused further into the substrate. Measureable concentrations of Zn can be observed to a depth of ~80 sputtering cycles (~56 nm). The concentration of O reduced to~ 60 atomic % on the surface and increased to a constant value inside the substrate; this could be either due to the diffusion of O inside the substrate or to formation of O₂ and loss through the surface. In the annealed sample, the Si concentration increased to ~40 atomic % on the surface, decreasing with increasing depth until it reached a concentration of ~30 atomic % at 30 sputtering cycle
(~21 nm). From the figure it is observed that during thermal annealing Zn and possibly O atoms diffused in the inward direction.

Fig. 4.3 Atomic concentration of Zn in the as-implanted and annealed samples as a function of depth derived from XPS measurements. In the as-implanted sample the profile peak position is observed at 36 sputtering cycles and Zn is distributed to a maximum depth of 68 sputtering cycles. In the annealed sample, Zn has diffused deeper into the substrate. The sputtering rate was about 7 Å/min.

Fig. 4.3 represents the compositional depth profiles of as-implanted and annealed samples. Zn is seen to be distributed with concentrations ranging from an almost negligible amount at the surface to about 9 atomic % at the profile peak position 36 sputtering cycles (at 1 min./cycle) into the as-implanted sample. The profile peak position corresponds to a depth of about 25 nm. Zn is distributed to a maximum depth of 68 sputtering cycles (~ 48 nm from surface) as shown in Fig. 4.3. In the annealed sample, Zn has diffused deeper into the substrate. Due to this thermal diffusion, the peak Zn concentration is reduced to about 7
atomic %. However, the peak position has not shifted appreciably and remains at essentially the same depth as in the as-implanted sample.

Fig. 4.4 XPS spectra showing Zn $2p_{3/2}$ and Zn $2p_{1/2}$ electron BE for as-implanted and annealed samples at different depths. BE has increased in the annealed sample. (Dotted lines on the fig. are just to show the shift on BE.)

To observe the formation of ZnO, the shifts in BE in XPS spectra of the Zn $2p_{1/2}$ and Zn $2p_{3/2}$ electrons have been utilized. Fig. 4.4 shows the XPS measurements of the Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals, measured at three different depths for as-implanted and annealed samples. The first three curves from the bottom represent the XPS signals from 5 nm, 25 nm, and 40 nm depths in the as-implanted sample, and the fourth through sixth curves from the bottom represent the XPS signals from 5 nm, 25 nm, and 40 nm depths in the annealed sample, respectively. It can clearly be seen that the value of BE has increased in the annealed sample.
This supports the conclusion that a Zn phase was present in the as-implanted sample, and after annealing Zn became incorporated in ZnO in all three different regions.

Fig. 4.5 Zn 2p$_{3/2}$ average BE from fitted XPS spectra as a function of depth in sample annealed at 750 °C. The BE of Zn 2p$_{3/2}$ is observed to be in between 1022.225 ± 0.033 eV and 1022.623 ± 0.010 eV.

For the annealed sample, Zn 2p$_{3/2}$ peaks were fitted for different depths from the surface to 80 sputtering cycles (~56 nm) as shown in Fig. 4.5. The BE of Zn 2p$_{3/2}$ is seen to be between 1022.225 ± 0.033 eV and 1022.623 ± 0.010 eV. This range of BE for Zn is typical of Zn in ZnO$^{17}$. This confirms the formation of ZnO throughout the range of measured depths. More quantitative analysis was done on the formation of Zn and ZnO phase on next pages.
The length of diffusion, $L$, for oxygen during annealing can be estimated by using the formula\(^2\)

$$L = \sqrt{4Dt},$$ \hspace{1cm} 4.1

where $D$ is the diffusion constant of $O_2$ in $SiO_2$ and is given by

$$D = D_0 e^{-\frac{E}{k_BT}}.$$ \hspace{1cm} 4.2

Here, $D_0 = 2 \times 10^{-9} \text{cm}^2\text{s}^{-1}$, $E = 1.3 \text{ eV}$, $T$ is the temperature and $k_B$ is the Boltzmann constant.

Evaluating the diffusion constant gives $D = 8 \times 10^{-16} \text{ cm}^2\text{s}^{-1}$, and using this with the thermal oxidation time, the length of diffusion is found to be 48 nm. This shows that all the Zn NPs could easily interact with indiffused oxygen molecules, and supports the BE result shown in Fig. 4.5.

Fig. 4. 6 Quantitative analysis of Zn and ZnO phases in an annealed sample at 2\textsuperscript{nd} sputtering cycle (1 sputtering cycle $\sim 0.7$ nm). It is observed that at this depth of $\sim 1.4$ nm, the Zn phase is more prevalent than the ZnO phase.
Fig. 4.6 represents the quantitative analysis of Zn phase and ZnO phase in the annealed sample at the second sputtering cycle or ~1.4 nm (1 sputtering cycle ~ 0.7 nm) with fitting parameters. The peak position was kept at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE. Similarly FWHM of the fitting parameter was kept 2.23 eV for both the peaks. The fitted result shows that the amount of Zn phase is greater than the ZnO phase at this depth.

Fig. 4. 7 Quantitative analysis of Zn and ZnO phases in an annealed sample at different sputtering cycles (1 sputtering cycle ~ 0.7 nm). Only at the 2\(^{nd}\) sputtering cycle is the amount of Zn phase greater than ZnO phase. After 3\(^{rd}\) sputtering cycle, the amount of Zn phase is reduced and after the 10\(^{th}\) sputtering cycle no Zn phase is observed till the 67\(^{th}\) sputtering cycle.
For quantitative study the same parameters described in the previous paragraph were used to fit all the Zn 2\(p_{3/2}\) peaks at different depths (the peak positions were kept at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE and FWHM was kept 2.23 eV for both the peaks). The areas under the fitted peaks for both Zn-Zn bonding and Zn-O bonding are plotted for different depth cycles to show the proportion of Zn and ZnO phases in Fig 4.7. It is observed that only at the 2\(^{nd}\) sputtering cycle is the amount of Zn phase greater than the ZnO phase. After the 3\(^{rd}\) sputtering cycle the amount of Zn phase is less than the ZnO phase and starts to decrease with increasing sputtering cycle. After the 10th sputtering cycle no Zn phase is observed and only ZnO phase is present. A small trace of Zn phase is observed at the depth of 67\(^{th}\) and 71\(^{th}\) sputtering cycles. At all depths the ZnO phase is present in the sample; this result support the BE result shown in Fig. 4.5.

![HRTEM images of SiO\(_2\) layer grown by dry oxidation technique and as-implanted sample.](image)

Fig. 4.8 HRTEM images of (a) SiO\(_2\) layer grown by dry oxidation technique (SiO\(_2\) layer ~ 250 nm thick was grown on the Si substrate), and (b) as-implanted sample, where the sizes of these Zn NPs are not uniform and range from 2 nm to 4.5 nm.
Fig. 4.8 (a) shows the HRTEM image of a thermally grown SiO$_2$ layer. A boron-doped p-type <100> silicon wafer with a resistivity on the order of 15 to 25 $\Omega$-cm was thermally oxidized at 1100 °C in an O$_2$ environment at atmospheric pressure for 5 hrs. SiO$_2$ layer ~ 250 nm thick was grown on the Si substrate. In order to study the microscopic structure of the as-implanted and annealed samples, detailed investigations were performed with a TEM apparatus equipped with selective area diffraction (SAD) detector. Fig. 4.8 (b) shows a plan view HRTEM image of the as-implanted sample. Zn NPs are seen to be dispersed within the SiO$_2$ matrix. The sizes of these Zn NPs are not uniform and range from 2 nm to 4.5 nm. A SAD pattern taken from the as-implanted sample shows amorphous rings that confirm the amorphous nature of the as-implanted sample.

Fig. 4.9 HRTEM image of annealed sample shows the annealed sample is crystalline in nature and the inter-planar spacing between the lattice planes of ~0.267 nm.
A plan view HRTEM image taken from the annealed sample is shown in Fig 4.9. Formation of ZnO NPs within the SiO₂ background can easily be observed in the image. The NPs thus formed are crystalline in nature and have diameters of up to 8 nm. The inter-planar spacing between the lattice planes is found to be ~0.267 nm, which matches closely with the spacing expected between the (002) planes of ZnO. This result also supports our XPS results on the formation of ZnO NPs in the annealed sample.

Fig. 4.10 FTIR spectra of the (a) as-implanted sample and (b) annealed sample. The absorption dip around 465 cm⁻¹ observed in the annealed sample is attributed to the stretching vibrational mode of Zn-O.
The formation of ZnO NPs was further characterized by acquiring FTIR spectra. Fig. 4.10 shows the spectra of both as-implanted and annealed samples. In both samples, the absorption dip at 1090 cm\(^{-1}\) is assigned to the stretching vibrational mode of Si-O-Si. Absorption dips in both the samples due to the Si-Si stretching vibrational mode are observed around 620 cm\(^{-1}\). An absorption dip around 465 cm\(^{-1}\) observed in the annealed sample (Fig. 4.10 (b)) is attributed to the stretching vibrational mode of Zn-O.\(^{18}\) No absorption dip is observed in the as-implanted sample at around 465 cm\(^{-1}\). This confirms and supports previous characterization results that no ZnO NPs formed in the as-implanted sample.

To investigate the optical properties of the implanted samples, PL measurements were performed on both as-implanted and annealed samples and also bulk ZnO powder. No PL signal was observed from the as-implanted sample. Bulk ZnO powder shows the sharp UV emission at 3.232 eV (384 nm) (Fig 4.11 (b)). The full width at half maximum (FWHM) of the emitted peak is 140 meV. Fig. 4.11 (a) shows the RT-PL spectrum of the annealed sample. Sharp near-band-edge UV emission is observed at 3.252 eV. The observed UV emission matches well with data in the literature for RT-PL of ZnO nanocrystals and is attributed to acceptor-bound excitons.\(^{19}\) The peak at 3.252 eV (381 nm) for the ZnO NPs is slightly blue shifted compared to the emission from bulk ZnO. The blue shift could be attributed to the quantum confinement effect in ZnO NPs.\(^{2}\) The FWHM of the PL emission band is observed to be 121 meV at RT. This agrees well with the FWHM of high purity ZnO grown by plasma-assisted molecular beam epitaxy (117 meV)\(^{20}\) and of ion beam synthesized ZnO NPs (113 meV).\(^{10}\) A small peak related to the defect on the sample can be observed on 2.6 eV.\(^{21}\)
Fig. 4.11 Room temperature PL measurements: (a) sample annealed at 750 °C, (b) ZnO powder. Sharp UV emission is observed in both ZnO Powder and ZnO NPs at 3.232 eV and 3.252 eV respectively.

Low-temperature PL spectra of the annealed sample are presented in Fig. 4.12 (a). Donor-bound excitonic emission (D, X), acceptor-bound excitonic emission (A, X), and donor-acceptor-pair (DAP) transitions are observed at low temperature. Fig 4.12 (b) shows a Gaussian fit of the PL spectrum of the annealed sample taken at 15 K. It is observed that along with the D, X [at about 3.363 ± 4.7 × 10^{-5} eV] and A, X [at about 3.317 ± 4.1 × 10^{-5} eV], and DAP [a broad peak at 3.249 ± 9.2 × 10^{-4} eV] two small peaks are also present in the spectrum. The peak having energy of 3.3776 ± 1.5 × 10^{-4} eV is attributed to free excitons transition\textsuperscript{22} and the peaks
having energy $3.31244 \pm 3.2 \times 10^{-4}$ eV couldn’t be identified at this point but it could be related to the excitons bound to structural defects.\textsuperscript{22}

Fig. 4.12 PL measurements: (a) Low temperature PL measurement of annealed sample. (D, X), (A, X), and (DAP) transitions are observed at low temperature.(b) Deconvolution of PL spectrum taken at 15 K for annealed sample.

Fig 4.13 shows the peak energy of both donor-bound excitonic emission and acceptor-bound excitonic emission at different temperatures. The donor-bound excitonic energy and acceptor-bound excitonic energy both decrease with temperature $T$ according to the Varshni law\textsuperscript{23},

$$E(T) = E(0) - \frac{\alpha T^2}{T-\theta_D}, \quad 4.3$$
where $E(0)$ is the energy at temperature $T = 0$ K, $\alpha$ is a parameter and $\theta_D$ is the Debye temperature. By keeping the value of $\theta_D = 920$ K $^{24}$, the value of $\alpha$ and $E(0)$ are determined by solving the equation 4.3 for two different temperatures. After calculation, the values of $\alpha$ and $E(0)$ for A, X are found to be 0.77 meV/K and 3.316 eV, respectively. For the donor-bound excitonic emission (D, X) peak, the value of $\alpha$ is 1.05 meV/K and $E(0)$ is 3.365 eV.

Fig. 4.13 Peak excitonic emission energies vs. temperature for the annealed sample. Solid lines are fits using the Varshni law. Using Varshni law the value of $\alpha$ and $E(0)$ for acceptor-bound excitonic emission (A, X) are found to be 0.77 meV/K and 3.316 eV, respectively. For the (D, X) peak, the value of $\alpha$ is 1.05 meV/K and $E(0)$ is 3.365 eV.

The Internal Quantum Efficiency (IQE) of the annealed sample was estimated. IQE can be calculated in different ways; one of the methods is to assume the IQE at low temperature is equal to 100% and compare with other excitation conditions. Assuming all the carriers
radiatively recombine at 15K, i.e., that at 15 K IQE is 100%, and then IQE at 200 K can be calculated from integral intensity ratio $I_{200 K} / I_{15 K} \times 100\%$. The IQE for ZnO at 200K is estimated to be 6%.

![Streak images of the annealed sample taken at three different temperatures](image)

Fig. 4.14 Streak images of the annealed sample taken at three different temperatures. The lifetime of both (D,X) and (A,X) can be observed in all three different temperatures.

Fig. 4.14 shows streak images of the annealed sample at three different temperatures (4 K, 20 K, and 40 K). The lifetimes of both donor-bound excitonic emission at around 366 nm and acceptor-bound excitonic emission at around 373 nm can be observed in all three images.

One important parameter related to material quality and device performance is excitonic lifetime. Fig. 4.15 (a) shows a PL lifetime measurement for donor-bound excitonic emission of the annealed sample at 4 K. The ZnO NPs exhibit a single exponential decay. A lifetime of 160 ps was measured at 4 K, which is shorter than the excitonic radiative lifetime of bulk ZnO (322 ps)$^{25}$ and longer than that of ZnO quantum dots (QDs) having an average diameter of 5 nm embedded in an SiO$_x$ matrix (65 ps)$^{26}$. PL lifetime measurement of acceptor-bound excitonic emission of the annealed sample at 4K is shown in Fig 4.15 (b). The decay of the acceptor-bound excitonic emission is found to be bi-exponential with time constants of $\tau_1 =$
43 ps and the $\tau_f = 620$ ps. The fast decay constant is most probably due to the non-radiative recombination and the slow decaying component is attributed to the radiative life time.\cite{22}

Fig. 4.15 PL lifetime measurement of the annealed sample at 4 K: (a) donor-bound excitonic emission. A single exponential decay was observed and a lifetime of 160 ps was measured. (b) acceptor-bound excitonic emission. Bi-exponential decay with time constants of $\tau_s = 43$ ps and the $\tau_f = 620$ ps was measured.
To confirm whether our sample exhibits radiative or non-radiative recombination processes, lifetimes at different temperatures were measured. For the non-radiative recombination process, the lifetime would decreases with increasing temperature. Fig. 4.16 presents the relation between lifetime and temperature. It is observed that below 20 K lifetime remains constant and above 20 K lifetime changes with temperature. From our result we conclude that below 20 K the recombination process is due to radiative recombination and the lifetime measured below 20 K is the exciton radiative lifetime. The decay time of our sample lies
between the two results for bulk ZnO and ZnO QDs. This could be due to the size of our ZnO NPs (up to 8 nm), which is bigger than the QDs (5 nm) and smaller than bulk, and it is well known that lifetime depends on the crystal size.

4.4 Summary and Conclusions

ZnO nanostructures were synthesized successfully by the implantation of low energy (35 keV) ZnO molecular ions into thermally grown SiO2 to a fluence of $5 \times 10^{16}$ ions/cm². Implanted samples were annealed in an oxygen environment to allow the growth of ZnO precipitates. XPS results verified that Zn atoms were implanted up to a depth of 50 nm with peak concentration at 25 nm. After annealing, Zn atoms were observed to have diffused in both directions from the depth of peak concentration. XPS BE spectra acquired at different depths confirmed the presence of ZnO regions after annealing. Quantitative analysis suggested that very few Zn NPs were present in the annealed sample. HRTEM showed the formation of amorphous nanostructures having diameters up to 5 nm in the SiO2 for the as-implanted sample. In the annealed sample, NPs up to 8 nm in diameter were observed that were crystalline in nature and for which the d spacing of the lattice plane closely matched with the d spacing of ZnO (002) planes. RT-PL measurement showed band-edge emission in the UV region with a FWHM of 121 meV. TR-PL measurements performed at 4K revealed an excitonic lifetime of donor-bound excitonic emission (D, X) of 160 ps, and two acceptor-bound excitonic emission (A, X) lifetimes of 43 ps and 620 ps. It was observed that below 20 K the recombination process was due to radiative recombination, and above 20 K the recombination was dominated by non-radiative processes.
4.5 References


CHAPTER 5
SYNTHESIS AND CHARACTERIZATION OF ZnO NPs BY ZnO MOLECULAR ION IMPLANTATION INTO Si

5.1 Motivation

In the thermal oxidation process, oxygen diffuses from the surface into Si or SiO₂ at a rate dependent on the temperature\(^1\,\,^2\). Thus, to increase the rate of oxidation of Si or implanted Zn by oxygen from the surface, the temperature must be increased. It has been found that if the temperature exceeds 800 °C, ZnO bonding starts to break down, and at a temperature of 900 °C, \(\text{Zn}_2\text{SiO}_4\) forms\(^3\). Also, in this technique the sample must be annealed in an oxygen environment at all times. To anneal the sample in a different environment or in vacuum, and to make the oxidation process faster, alternative routes must be employed to get oxygen beneath the surface. So in this chapter, we report on an experiment designed to create ZnO NPs synthesized by using ZnO molecular ion implantation into Si to provide the oxygen, followed by thermal annealing in a mixture of 96% Ar and 4% H\(_2\) gases at different temperatures. We also report on the structural and optical properties of the resulting NPs.

5.2 Experimental Procedure

Boron doped Si (100) wafer (p-type with resistivity on the order of 10 to 20 Ω-cm) was implanted with low energy (35 keV) ZnO\(^-\) molecular ions to a fluence of \(1 \times 10^{17}\) ions/cm\(^2\). Similar technique and same facility explained in Chapter 4.2 were adopted for the ion implantation. The implantation fluence was determined by current integration techniques. The implanted sample was cut into small pieces (5 mm × 5 mm) for thermal annealing. The samples
were furnace-annealed in a flowing gas mixture of 96% Ar and 4% H₂ at different temperatures for a period of 1 h.

![Graph showing ZnO in Si](image)

Fig. 5.1 Simulation of ZnO ions into Si. (a) Static SRIM simulation of implanted ZnO constituents in Si. The simulated Zn and O distributions overlap in the 5 to 55 nm depth range. O atoms are distributed from the surface to a depth of 55 nm, whereas Zn atoms are distributed between 5 and 60 nm from surface. (b) T-DYN simulation of ZnO into Si. According to the simulation the Zn and O ions distributed from the surface to 50 nm depth.

Fig. 5.1 shows the two different simulation techniques used to estimate the depth profile and sputtering effect during the implantation of ZnO into Si. The distribution of implanted atoms has been simulated by using a Monte Carlo simulation code (SRIM)⁴. Using Eq. 3.2,⁵ for the given 35 keV ZnO molecules, each Zn atom had an energy of 28 keV and each O atom 7 keV. Fig. 5.1 (a) shows the SRIM simulation of Zn and O ions implanted with energies of 28 keV and 7 keV, respectively, into Si. The simulated Zn and O distributions overlap in the 5 to 55 nm depth range. O atoms are distributed from the surface to a depth of 55 nm, whereas Zn atoms are distributed between 5 and 60 nm from surface. As shown in Fig. 5.1(a), the overlap of the implanted Zn and O distributions could provide favorable conditions to form ZnO even if the sample is annealed in vacuum or other inert gases. The simulated profile peak positions of
Zn and O atoms are at depths of approximately 25 nm and 19 nm, respectively. As it is discussed in chapter 4.2, static SRIM simulation is used to estimating the range of the implanted ions. The detailed shape is less meaning full because sputtering effect are not factored in here. To study the sputtering effect dynamic transportation of ions in matter (T-DYN) is used. According to T-DYN, Zn and O ions distributed from the surface to 50 nm depth (Fig 5.1 (b)). In the surface, Zn has 23% concentration and after 20 nm depth the concentration of Zn decreases slowly.

RBS results were obtained using a 1.5 MeV He beam from the NEC 9SDH-2 Pelletron accelerator at the IBMAL. The active area of the surface barrier detector used was 0.441 cm, the distance from the sample to detector was 7.62 cm and the angle θ was 155°. The charge delivered to the target was measured by integrating the beam current on the target holder, which was configured to suppress secondary currents.

To observe the different sample phase formations, XRD analysis was done on as-implanted and annealed samples. A RigaKu Ultima- III instrument having Cu Kα (1.542 Å) radiation was used to analyze the samples. XRD patterns were obtained using 2θ scans from 30° to 70°. The grazing angle was fixed to 0.5°, scan speed was 0.4°/min, and step size was 0.05°.

XPS, TEM and PL analysis were performed on both as-implanted and annealed samples using the same devices explained in Chapter 4.2. The only difference in the XPS analysis was the argon sputtering rate, which was about 38 Å/min, and HRTEM samples were prepared by focused ion beam (FIB) milling using a lift out technique explained in section 3.3.
5.3 Results and Discussion

Fig. 5.2 shows the measured RBS spectrum of the as-implanted sample with SIMNRA fit. The presence of Zn, Si and O can be observed in the spectrum. From the RBS results, it was determined that the areal density of Zn in the as-implanted sample was $6.4 \times 10^{16}$ atoms/cm$^2$ (calculated using a surface energy approximation), which is 36% less than the areal density of $1 \times 10^{17}$ atoms/cm$^2$ determined by current integration during implantation. This result shows that a significant amount of Zn was lost due to sputtering during implantation. From the RBS results the areal densities of O in the as-implanted sample was found to be $7.0 \times 10^{16}$ atoms/cm$^2$. Similarly to Zn, around 30% of O was lost due to sputtering during implantation.

![RBS spectrum of the as-implanted sample with SIMNRA fit](image)

Fig. 5.2 RBS spectrum of the as-implanted sample with SIMNRA fit. Using the surface energy approximation the areal densities of Zn and O in the as-implanted sample were found to be $6.4 \times 10^{16}$ atoms/cm$^2$ and $7.0 \times 10^{16}$ atoms/cm$^2$, respectively.
The areal density of Zn and O is also calculated by using SIMNRA. For SIMNRA simulation 11 different layers were considered and the value of Si, Zn and O were changed till the best possible fit with the RBS data was achieved. After fitting the simulation data with RBS data, the layer areal densities of Zn and O were added to find the total areal density of Zn and O. According to SIMNRA the areal density of Zn is $6.1 \times 10^{16}$ atoms/cm$^2$ which is close to the surface energy approximation result, but the areal density of O is $1.25 \times 10^{17}$ atoms/cm$^2$ which is greater than that of surface approximation technique. The Zn and O profiles obtained from SIMNRA are presented in Fig. 5.6.

The XRD spectrum of the as-implanted is shown in Fig. 5.3(a). A diffraction peak at a scattering angle of 43.2° corresponding to reflection from the (101) plane of crystalline Zn (JCPDS No. 40-831) and a broad peak from 45° to 60° corresponding to amorphous Si are present for the as-implanted sample. This confirms the presence of Zn NPs in the as-implanted sample, and no diffraction related to a ZnO phase is observed. Fig. 5.3(b) shows the XRD pattern of a sample annealed at 700 °C. Diffraction peaks at scattering angles of 34.4°, 36.3°, 43.2°, 47.5°, 53.1°, 56.6°, 62.8°, and 67.9° indicate the polycrystalline structure. According to the JCPDS data card no. 40-831, diffraction peaks corresponding to scattering at 43.2° and 53.1° are reflections from the (101) and (102) planes of Zn, respectively. Diffraction at the scattering angles 34.4°, 36.3°, 47.5°, 56.6°, 62.8°, and 67.9° correspond to reflections from the (002), (101), (102), (110), (103) and (112) ZnO planes (JCPDS No. 36-1451), respectively.

These sharp diffraction peaks indicate the formation of ZnO NPs with high crystallinity. For a sample annealed at 800 °C for an hour, a diffraction peak at 43.2° corresponding to Zn (101) can be observed in the XRD spectrum [Fig. 5.3(c)]. The ZnO diffraction peaks are very
small in this case and diffraction peaks at scattering angles of 31.6°, 34.1°, and 57.8° appear. According to the JCPDS data card no. 37-1485, diffraction peaks corresponding to scattering angles of 31.6°, 34.1°, and 57.8° are reflections from the (113), (410), and (710) planes of zinc silicate (Zn$_2$SiO$_4$), respectively.

This result shows that at 800 °C, ZnO is not stable and it has started to transform to zinc silicate (Zn$_2$SiO$_4$)\textsuperscript{8}. Fig. 5.3(d) shows the XRD pattern of a sample that was annealed at 900 °C. Sharp diffraction peaks at scattering angles of 31.6°, 34.1°, 38.8°, 43.2°, 49.1°, 57.8°, 65.6°, and
68.5° indicate a polycrystalline structure. According to the JCPDS data card no. 37-1485, diffraction peaks corresponding to scattering at 31.6°, 34.1°, 38.8°, 43.2°, 49.1°, 57.8°, 65.6°, and 68.5° are reflections from the (113), (410), (223), (333), (710), (713) and (633) planes of Zn₂SiO₄, respectively. A diffraction peak at scattering angle 43.2° corresponds to reflection from the (101) plane of crystalline Zn (JCPDS No. 40-831), which also confirms the present of Zn NPs when the sample is annealed at 900 °C.

Fig. 5. 4 Gaussian fit of an XRD peak, for ZnO (200) in the sample annealed at 700 °C in this case. The peak is fitted to find the peak position and the FWHM with uncertainties in those parameters. For this given peak the FWHM is 0.47934 ±0.027° and peak position is at 35.524 ±0.008°
The sizes of the crystalline Zn and ZnO NPs were estimated from the diffraction peak FWHM and peak position using the Scherrer equation (Eq. 3.5). Fig. 5.4 shows the Gaussian fit to calculate the peak position (angle 2θ) and FWHM and their corresponding values with errors for peak for ZnO (200) in the sample annealed at 700 °C. For this given peak the FWHM is 0.47934 ±0.027° and peak position is at 35.524 ±0.008°. Using Eq. 3.5, the average sizes of ZnO NPs in the sample annealed at 700 °C were found to be 17.2 nm. Using the same technique to calculate FWHM and peak position (angle 2θ) and equation 3.5, the average size of Zn NPs in the sample annealed at 700 °C were found to be 19.8 nm. By using same method, the average sizes of Zn and Zn$_2$SiO$_4$ NPs in the sample annealed at 900 °C were found to be 18.7 nm and 14.5 nm, respectively.

Fig. 5.5 (a) shows the compositional depth profile of Zn, O and Si in an as-implanted sample. The concentration of Zn increases from 1 atomic % at the surface to 32 atomic % at 6 sputtering cycles (~23 nm). This depth for the maximum concentration of Zn is around ~25 nm. According to the SRIM results, the maximum depth of Zn atoms occurs at 60 nm beneath the Si surface. However, according to the XPS result the maximum depth of the Zn distribution is 13 cycle (~50 nm). These discrepancies may be due to the simulation not including recession of the surface associated with sputtering; as such, the SRIM results should be regarded as approximate.
Fig. 5.5 Atomic concentrations as a function of depth derived from XPS measurements of (a) the as-implanted sample, (b) sample annealed at 700 °C and (c) sample annealed at 900 °C. In as-implanted sample Zn, and O distributed from surface to 13 sputtering cycle. In samples annealed at 700 °C and 900 °C, Zn diffused in both directions. The sputtering rate was about 38 Å/min.

Fig. 5.5 (b) is the compositional depth profile of Zn, O and Si in a sample annealed at 700 °C. It is observed that after annealing, Zn has diffused in both directions from the profile peak position in the as-implanted sample. Thermal diffusion caused the Zn profile to reach a depth of 20 sputtering cycles (~76 nm) after annealing and the maximum concentration moved
deeper than for the as-implanted sample to 8 cycles (~31 nm). Fig. 5.5 (c) is the compositional depth profile of a sample annealed at 900 °C. It is observed that after annealing at 900 °C for an hour, Zn has diffused farther inside and outside compared to the sample annealed at 700 °C. The Zn spectrum has profile peak positions at 2 sputtering cycles (~7.6 nm) and 20 sputtering cycles (~76 nm) respectively. Thermal diffusion caused the Zn profile to reach a depth of 30 sputtering cycles (~114 nm).

Fig. 5.6 Elemental depth profiles of (a) Zn and (b) O in an as-implanted sample extracted from XPS and SIMNRA. Zn profile is closely matched up to 30 nm in both techniques. O also matches up to 20 nm depth after that no match is observed.

Fig. 5.6 shows the comparison of depth profile of Zn and O in as-implanted sample extracted by using two different techniques (XPS and SIMNRA). To find the depth in nm from XPS data, sputtering time is multiplied by approximate sputtering rate (38 Å/min). For SIMNRA the atomic concentration (atoms/cm²) is converted into nm. The value of densities 7.14 g cm⁻³, 1.141 g cm⁻³, and 2.239 g cm⁻³ were used for Zn, O and Si, respectively for the calculation of depth in nm. After using those parameters the depth in nm with corresponding concentration are plotted. Fig 5.6 (a) shows the depth profile of Zn obtained from the two different
techniques. It is observed that up to 30 nm the profiles of zinc closely match but after 30 nm depth XPS results showed the sharp decrease in Zn and the trace of Zn can only be found up to 50 nm depth. On the other hand, SIMNRA result suggested the slow decrease on Zn and its trace can be found up to a depth of 80 nm. The difference could be due to the assumptions for densities in the RBS analysis, a change in sputtering rate after 30 nm in the XPS analysis, or uncertainties in fitting parameters obtained from SIMNRA. Fig 5.6 (b) shows the depth profile of O obtained from two different techniques. It also matches up to 20 nm depth after that no match is observed on the depth profile O. it could be due to the same reasons as for Zn, or other reasons that are yet to be determined.

Fig. 5.7 XPS spectra showing the BE of Zn 2p_{3/2} and 2p_{1/2} electrons at different depths for the as-implanted sample. The dotted lines are to suggest the mean BE values.
In order to monitor the formation of Zn and ZnO NPs at different depths, the binding energies (BE) of Zn 2p\(_{1/2}\) and Zn 2p\(_{3/2}\) electrons were measured using XPS. Fig. 5.7 presents XPS signals for Zn 2p\(_{1/2}\) and Zn 2p\(_{3/2}\) electrons, measured at different depths (numbered in the figure) ranging from the surface to 10 sputtering cycles for the as-implanted sample. It can clearly be observed that the BE remained constant for all different depths. The peak position of the Zn 2p\(_{1/2}\) signal was found to be 1021.64 ± 0.23 eV. This BE for Zn is attributed Zn-Zn bonding\(^{10}\), which supports the XRD results and confirms the presence of a Zn phase in the as-implanted sample.

Fig. 5.8 XPS spectra showing the BE of Zn 2p\(_{1/2}\) and 2p\(_{3/2}\) electrons at different depths for the sample annealed at 700 °C. The dotted lines are to suggest the mean BE values.
Fig. 5.8 shows XPS Zn 2p\textsubscript{1/2} and Zn 2p\textsubscript{3/2} signals from 5 different depths in the sample annealed at 700 °C. The depths at 2, 3, 8, 10, and 12 sputtering cycles were used to represent the nature of the BE at different depths. It is observed that as the depth increases the BE starts to decrease and after 10 sputtering cycle it becomes constant. The peak position of the Zn 2p\textsubscript{1/2} signal was found to be 1022.53 ± 0.13 eV after the 2\textsuperscript{nd} sputtering cycle and 1021.62 ± 0.19 eV after the 12\textsuperscript{th} sputtering cycle. One can conclude from this that at the surface and to a depth of a few nanometers most of the Zn NPs converted to ZnO NPs during annealing, but at depths below a few nanometers both the Zn and ZnO phases are present, with the Zn phase increasing and the ZnO phase decreasing with increasing depth. This shift continues to a depth of about 10 sputtering cycles, at which point the Zn phase completely dominates ZnO phase. This result matches the XRD result, which indicates the presence of both Zn and ZnO NPs in the annealed sample. More quantitative analysis on the ZnO and Zn phase is done in next pages.

Fig. 5.9 represents the quantitative analysis of the Zn and ZnO phases in the annealed sample at the 3\textsuperscript{rd} sputtering cycle or ~11.4 nm (1 sputtering cycle ~ 3.8 nm) with fitting parameters. The peak position was kept at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE. Similarly, the FWHM was fixed at 2.47 eV for both the peaks. A small peak corresponding to Zn phase (red in color) and a larger peak corresponding to ZnO phase (green in color) are observed. The areas under the corresponding curves show that in this sputtering cycle, the ZnO phase is more prevalent than the Zn phase at this depth.
Fig. 5.9 Quantitative analysis of Zn and ZnO phases in a sample annealed at 700 °C, at 3rd sputtering cycle (1 sputtering cycle ~ 3.8 nm). It is observed that at this depth of ~ 11.4 nm, the ZnO phase is much more prevalent than the Zn Phase.

To study quantitatively the proportion of Zn phases in the sample, Zn 2p3/2 peaks at different depths were fitted in this manner (holding the peak positions at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE, and FWHM for both the peaks at 2.47 eV). The areas under the BE curves for both Zn-Zn bonding and Zn-O bonding are plotted vs depth cycle to show the proportions of the Zn and ZnO phases, in Fig 5.10. It is observed that up to 4th sputtering cycle the amount of ZnO phase is greater than Zn phase. After the 5th sputtering cycle the amount of Zn phase is greater than that of the ZnO phase, and from the 11th sputtering cycle no trace of ZnO phase is observed. It shows that the Zn doesn’t get sufficient O to form ZnO in the deeper level because most of the O combined with Si to form SiO₂.
Fig. 5.10 Quantitative analysis of Zn and ZnO phases in sample annealed at 700 °C at different sputtering cycles. Up to the 4th sputtering cycle the amount of ZnO phase is greater than Zn phase. After the 5th sputtering cycle amount of Zn phase is greater than the ZnO phase and from 11th sputtering cycle no trace of ZnO phase is observed.

Fig. 5.11 HRTEM images of (a) as-implanted sample and (b) sample annealed at 700 °C. Zn NPs are distributed into the substrate. The sizes of NPs vary from 3 nm to 6 nm in as-implanted sample but after annealing the particle sizes have increased.
Microscopic structure of the as-implanted and sample annealed at 700 °C were investigated by using a TEM equipped with selective area diffraction (SAD) detector. Fig. 5.11 (a) shows a TEM image of the as-implanted sample. Zn NPs can be observed distributed into the substrate. The size of Zn NPs was found to be in the range of 3 nm to 6 nm. Fig 5.11 (b) shows the cross-sectional view of an annealed sample. The top layer (surface) in the cross-sectional image is a protective Pt layer deposited before ion-milling. Compared to the as-implanted sample, NPs with bigger in size can be observed in sample annealed at 700 °C that supports the XRD result to calculate the average sizes of NPs using Scherrer equation.

![Graph showing Room temperature PL measurement of sample annealed at 700 °C. Near-band-edge UV emission is observed at 3.306 eV (375 nm).](image)

Optical properties of the implanted samples were investigated using RT PL. PL measurements were performed on both as-implanted and annealed samples. No PL signal was
observed from the as-implanted sample and sample annealed at 900 °C. Fig. 5.12 shows the RT-PL spectrum of the sample annealed at 700 °C. Sharp near-band-edge UV emission is observed at 3.306 eV (375 nm). This is slightly blue shifted as compare to the UV emission of bulk ZnO [Fig. 4.11(b)]. The full width at half maximum (FWHM) of the PL emission band was measured to be 65 meV at RT. This is slightly greater than the FWHM of ZnO quantum dots (50 meV)\textsuperscript{11} and smaller than the ion beam synthesized ZnO NPs (113 meV)\textsuperscript{12} and bulk ZnO [Fig 4.12 (b)].

![Image of PL measurements](image)

Fig. 5.13 PL measurements: (a) low temperature PL measurement of sample annealed at 700 °C, (b) peak energy vs. temperature of annealed sample (lines represent the theoretical and dots the experimental peak energies).

Low-temperature PL spectra of the annealed sample are presented in Fig. 5.13 (a). Donor-bound excitonic emission (D, X) [at about 3.3659 ± 4.2 × 10⁻⁵ eV] and acceptor-bound
excitonic emission (A, X) [at about 3.30985 ± 5.8 × 10^{-4} eV] are observed at 15 K. The donor-bound excitonic energy and acceptor-bound excitonic energy both decrease with temperature $T$ according to the Varshni law$^{13}$ (Eq. 4.3) [Fig 5.13 (b)]. By keeping the value of $\theta_D = 920$ K$^{14}$ the value of $E(0)$ for acceptor-bound excitonic emission (A, X) was found to be 3.310 eV. For the donor-bound excitonic emission (D, X) peak, the value of $E(0)$ is 3.3661 eV.

Fig. 5.14 PL intensity vs Temperature for both donor-bound excitonic emission (D, X) and acceptor-bound excitonic emission (A, X) peaks. Intensities decrease with increasing temperature.

The PL intensity of donor-bound and acceptor-bound excitonic emission was found to be a function of temperature (Fig 5.14). PL intensity decreased with increasing temperature. No negative thermal quenching effect on donor-bound excitonic emission was observed here,
although it has been reported\textsuperscript{15} for ZnO NCs. The internal quantum efficiency (IQE) of the annealed sample was estimated by using the method explained in Section 4.2. Assuming all the carriers radiatively recombine at 15K, i.e., at 15 K IQE is 100%, and then IQE at 200 K can be calculated from the integral intensity ratio $I_{200\text{ K}} / I_{15\text{ K}} \times 100\%$. Here the IQE for ZnO at 200K is estimated to be 19%.

5.4 Summary and Conclusions

Zn, ZnO and Zn$_2$SiO$_4$ NPs were synthesized successfully by the implantation of low energy (35 keV) ZnO$^{-}$ molecular ions into Si to a fluence of $1 \times 10^{17}$ ions/cm$^2$ at room temperature, followed by thermal annealing in a mixture of 96% Ar and 4% H$_2$ for 1 h. When a sample was annealed at 700 °C, Zn and ZnO NPs could be observed, but when a sample was annealed at 900 °C, ZnO bonding broke down and Zn$_2$SiO$_4$ and Zn NPs formed. XRD patterns showed that in the as-implanted sample, only Zn NPs could be observed. Both Zn and ZnO NPs were observed after thermal annealing at 700 °C and had an average size of at least ~20 nm and ~17 nm, respectively. Also, Zn and Zn$_2$SiO$_4$ NPs having average sizes of 21 nm and 18.5 nm, respectively, were present in the sample annealed at 900 °C. From XPS measurements of the as-implanted sample, it was found that Zn was distributed from the surface to a depth of ~50 nm and electron binding energy measurements indicated that Zn-Zn bonding was dominant at all depths. This shows that a Zn phase was present, consistent with the XRD results. The highest concentration of Zn in the as-implanted sample was ~23 nm beneath the surface. After annealing, broader spatial distributions of Zn were observed, with Zn distributed to a maximum depth of ~76 nm. A quantitative analysis suggested that the ZnO phase was present in the
annealed sample up to the depth of the 10th sputtering cycle, and beyond that no trace of ZnO was observed. This leads to the conclusion that both Zn and ZnO phases were present, also consistent with the XRD results. HRTEM showed the formation of nanostructures having diameters in the range of 3-6 nm in the as-implanted sample. In the annealed sample, NPs of bigger diameter were observed. RT-PL measurement on the sample annealed at 700 °C showed band-edge emission in the UV region with a FWHM of 65 meV. At LT-PL both donor bound exciton (D, X) and acceptor bound exciton (A, X) emission were present and both emissions followed the Varshni law. Using the Varshni law, the values of value of $E(0)$ for the acceptor bound exciton (A, X) and donor bound exciton (D, X) peak were found to be $3.30985 \pm 5.8 \times 10^{-4}$ eV and $3.3659 \pm 4.2 \times 10^{-5}$ eV, respectively.

5.5 References


CHAPTER 6
SYNTHESIS AND CHARACTERIZATION OF ZnO NPs BY DUAL BEAM ZnO- AND O- ION IMPLANTATION INTO Si‡

6.1 Motivation

The experiment described in Chapter 5 was designed to create ZnO NPs synthesized by using a molecular ion implantation technique followed by thermal annealing without oxygen. After studying the NP properties, it was found that most of the implanted oxygen combined with Si to form SiO₂, and less oxygen combined with Zn to form ZnO. So ZnO NPs were fewer in numbers than the Zn NPs in the sample after annealing. New technique has to be developed to increase the concentration of ZnO NPs for future application. In this chapter, we describe an experiment designed to increase the density of ZnO NPs by using dual beam implantation of ZnO and O, followed by thermal annealing in a mixture of 96% Ar and 4% H₂ gases at different temperatures. We also report on the resulting NP structural and optical properties.

6.2 Experimental Procedure

An intrinsic silicon (100) wafer was implanted with low energy (45 keV) ZnO⁻ molecular ions to a fluence of $1 \times 10^{17}$ ions/cm², followed by 15 keV O⁻ ions to a fluence of $2 \times 10^{17}$ ions/cm², using the similar technique and same facility explained in chapter 4.2. The typical rastered beam current density on the target wafer was 100 nA/cm² for the ZnO⁻ ions and 500

‡ Some part of this chapter is reproduced partially or fully from [B. Pandey, P. Poudel, D.L Weathers “Formation of ZnO nanoparticles by ZnO⁻ and O⁻ dual beam ion implantation and thermal annealing”. Japanese Journal of Applied Physics 51, 11PG03 (2012) and B. Pandey, D.L Weathers “Temperature dependent formation of ZnO and Zn₂SiO₄ nanoparticles by ion implantation and thermal annealing” Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 332, 359-363 (2014)], with the permission from the Japan Society of Applied Physics and Elsevier respectively.
nA/cm² for the O⁻ ions. The samples were furnace-annealed in a flowing gas mixture of 96% Ar and 4% H₂ at different temperatures for a period of 1 h.

The distribution of implanted atoms has been simulated using a Monte Carlo simulation code (SRIM).¹ Using Eq. 3.2² for 45 keV ZnO molecular ions, \( E_{Zn} = 36 \) keV and \( E_{O} = 9 \) keV. To calculate the atomic depth profiles resulting from the ZnO implantation, Zn and O atomic ions with the above energies were separately simulated to impinge on Si.

Fig. 6.1 Simulation of ZnO and O ions into Si. (a) Static SRIM simulation of implanted ZnO constituents and O in Si. The simulated Zn trace can be observed up to 75 nm and O up to 100 nm. (b) T-DYN simulation of ZnO and O into Si. According to the simulation the Zn ions distributed to 75 nm and O ions distributed up to 115 nm from the surface.

Fig. 6.1 shows the two different simulation techniques used to estimate the depth profile and sputtering effect during the implantation of ZnO and O into Si. Fig. 6.1 (a) shows the SRIM simulation results for 36 keV Zn ions, and for O ions having energies of 9 keV and 15 keV, incident on Si. According to these results, the distributions of implanted Zn and O atoms in Si should overlap over the depth range from 5 nm to 75 nm. As shown in Fig. 6.1 (a), the (simulated) implanted Zn distribution is everywhere overlapped by a larger concentration of O, which should provide favorable conditions for ZnO formation. According to the SRIM results,
the maximum concentration of Zn atoms occurs at a depth of 35 nm beneath the Si surface. These results should be regarded as approximate because the simulation does not include recession of the surface associated with sputtering.

As it is discussed in chapter 4.2, static SRIM simulation is used to estimating the range of the implanted ions. To study the sputtering effect T-DYN is used. According to T-DYN, Zn ions are distributed up to 75 nm and O ions are distributed up to 115 nm from the surface Fig.(6.1(b)). In the surface, Zn has 10% concentration and the concentration of Zn decreases slowly with depth.

RBS, XRD XPS, TEM, and PL analysis were performed on both as-implanted and annealed sample by using same devices and parameters as describe in sections 4.2 and 5.2.
6.3 Results and Discussion

Fig. 6.2 (a) RBS spectra of as-implanted sample, sample annealed at 700 °C, and sample annealed at 900 °C. During annealing Zn is presumed to have diffused to the surface and been lost to the vapor phase. (b) SIMNRA fit of as-implanted sample. Using SIMNRA, the areal density of Zn in as-implanted sample was found to be $6.56 \times 10^{16}$ atoms/cm$^2$.

Fig. 6.2 (a) shows the measured RBS spectra of the as-implanted sample, a sample annealed at 700 °C, and a sample annealed at 900 °C. The presence of Zn, Si and O can be observed in the RBS spectrum for all three samples. From the RBS results, it was determined that the areal density of Zn in the as-implanted sample was $6.5 \times 10^{16}$ atoms/cm$^2$ (calculated using a surface energy approximation), which is 35% less than the areal density of $1 \times 10^{17}$
atoms/cm² determined by current integration during implantation. This result shows that a significant amount of Zn was lost due to the effects of sputtering during implantation.

For the samples annealed at 700 °C and 900 °C, the areal densities of Zn were $5.9 \times 10^{16}$ atoms/cm² and $3 \times 10^{16}$ atoms/cm², respectively. This indicates that around 10% and 55% of the as-implanted Zn disappeared during sample annealing at 700 °C and 900 °C, respectively. The Zn is presumed to have diffused to the surface and been lost to the vapor phase. From the RBS results the areal densities of O in the as-implanted sample, sample annealed at 700 °C, and sample annealed at 900 °C were $1.9 \times 10^{17}$ atoms/cm², $2.6 \times 10^{17}$ atoms/cm², and $3.3 \times 10^{17}$ atoms/cm², respectively. Similarly to Zn, around 35% of O was lost due to sputtering during implantation. The amount of O is observed to have increased by around 35% and 70% for the samples annealed at 700 °C and 900 °C, respectively, compared to the as-implanted sample. Although heat treatment was performed by flowing a mixture of 96% Ar and 4% H₂ gases, the existence of traces of O₂ or H₂O may be expected in furnace annealing. The increase in O in the annealed samples is due the presence of this O₂ or H₂O during annealing. Finally, in the RBS spectrum of the sample annealed at 900 °C, a shoulder peak around channel number 135 is observed, which is due the dilution of Si in the near surface region due to Zn and especially O.

Fig 6.2 (b) shows the measured RBS spectrum of the as-implanted sample with SIMNRA fit. The areal density of Zn and O was also calculated by using SIMNRA. For SIMNRA simulation 18 different layers were considered and the proportions of Si, Zn and O were changed manually until the best possible fit with the RBS data was achieved. To calculate the areal density a process similar to that explained in section 5.3 was adopted. According to SIMNRA, the areal
density of Zn was $6.56 \times 10^{16}$ atoms/cm$^2$ which is close to the surface energy approximation result, but the areal density of O was $2.47 \times 10^{17}$ atoms/cm$^2$ which is greater than that of surface approximation technique.

Fig. 6.3 X-ray diffraction patterns: (a) as-implanted sample, (b) sample annealed at 700 °C, (c) sample annealed at 800 °C, (d) sample annealed at 900 °C. Zn, ZnO, and Zn$_2$SiO$_4$. Phases are observed in the as-implanted sample and samples annealed at 700 °C and 900 °C.

Fig. 6.3 (a) shows the XRD spectrum of the as-implanted sample. In this spectrum no diffraction peaks attributable to the ZnO phase are observed. A peak at a scattering angle of 43.2° corresponds to reflection from the (101) plane of crystalline Zn [JCPDS No. 40-831], which
confirms the existence of Zn NPs, and a broad peak from 45 to 60° corresponding to amorphous Si is present. Multiple diffraction peaks are observed in the XRD spectrum of the sample annealed at 700 °C (Fig. 6.3(b)). Diffraction peaks at scattering angles of 34.4°, 36.3°, 43.2°, 47.5°, and 62.8° indicate a polycrystalline structure. According to the JCPDS data card no. 40-831, the diffraction peak corresponding to a scattering angle of 43.2° is the reflection from the (101) plane of Zn. Diffraction at the scattering angles of 34.4°, 36.3°, 47.5°, 56.6°, and 62.8° correspond to reflections from the (002), (101), (102), and (103) ZnO planes, respectively (JCPDS No. 36-1451). These sharp diffraction peaks indicate the formation of ZnO NPs with high crystallinity. For the sample annealed at 800 °C for an hour, a diffraction peak at 43.2° corresponding to Zn (101) can be observed in the XRD spectrum [Fig. 6.2(c)]. ZnO diffraction peaks are very small and diffraction peaks at scattering angles of 31.6°, and 34.1° appear. According to the JCPDS data card no. 37-1485, diffraction peaks corresponding to scattering angles of 31.6°, are 34.1° are reflections from the (113) and (410) planes of zinc silicate (Zn$_2$SiO$_4$), respectively. This result shows that at 800 °C the ZnO bonding is breaking down and ZnO is starting to transform to zinc silicate (Zn$_2$SiO$_4$)\(^3\). Fig. 6.2(d) shows the XRD pattern of a sample annealed at 900 °C. It can be observed that sharp diffraction peaks at scattering angles of 31.6°, 34.1°, 38.8°, 49.1°, 56.2°, and 65.6° indicate a polycrystalline structure. According to the JCPDS data card no. 37-1485, diffraction peaks corresponding to scattering angles of 31.6°, 34.1°, 38.8°, 49.1°, 56.2°, and 65.6° are reflections from the (113), (410), (223), (333), (523), and (713) planes of Zn$_2$SiO$_4$, respectively. No diffraction peaks corresponding to Zn are observed for the sample annealed at 900 °C.
The sizes of the crystalline Zn and ZnO NPs were estimated from the diffraction peak widths using the Scherrer equation (Eq. 3.5). The peak position and FWHM of the diffraction peak needed for the Scherrer equation were calculated as explained in section 5.3. In the as-implanted sample, the full width at half maximum (FWHM) of the Zn (101) diffraction peak is 1.92°, and using Eq. 3.5, the minimum average size of the Zn NPs was found to be 4.5 nm. Similarly, for the samples annealed at 700 °C and at 900 °C, using the same equation the average sizes of the ZnO and Zn2SiO4 NPs were found to be 18.2 nm and 16 nm, respectively.

XPS has also been used to study the depth profiles and chemical bonding associated with ZnO structures. Fig. 6.4 (a), (b) and (c) show compositional depth profiles of Zn, O and Si derived from XPS measurements. In Fig. 6.4 (a), the compositional depth profile of the as-implanted sample, Zn can be seen to increase from ~2 atomic % at the surface to a peak concentration of ~19 atomic % at a depth of 10 sputtering cycles (~38 nm). The maximum depth of the Zn distribution is 20 sputtering cycles (~76 nm from surface). The O exhibited a higher mobility during implantation, and appears to have combined with Si to form something approaching SiO2 between the surface and the depth of the maximum Zn concentration.
Fig. 6.4 Atomic concentrations as a function of depth derived from XPS measurements for (a) as-implanted sample, (b) sample annealed at 700 °C, (c) sample annealed at 900 °C. In the as-implanted sample Zn was distributed from the surface to a depth of 20 sputtering cycles. When sample was annealed at 700 °C and 900 °C, Zn diffused in both directions. The sputtering rate was 38 Å/min.

Fig. 6.4 (b) is the compositional depth profile of the sample annealed at 700 °C. It is observed that after annealing, Zn has diffused in both directions from the profile peak position, accumulating at the surface and near the interface with the pure Si; O is observed to have diffused into the Si. Thermal diffusion caused the Zn profile to reach a depth of 28 sputtering cycles (~106 nm) after annealing at this temperature. Fig. 6.4(a) shows that in the as-implanted
sample, the Zn profile was everywhere overlapped by O, which is essential for ZnO formation. Fig. 6.4 (c) is the compositional depth profile of the sample annealed at 900 °C. It is observed that after annealing at 900 °C for an hour, Zn has diffused further outside comparing to annealed at 700 °C. The Zn profile can be viewed as having a peak position at a depth of 3 sputtering cycle (~11.4 nm). Thermal diffusion caused the Zn to move towards the surface, here extending only up to a depth of 18 sputtering cycles (~68 nm). It is also observed that O has diffused further inside. The atomic concentration of O also increased as compare to the sample annealed at 700 °C. Its atomic concentration remains constant around 65 atomic % until 19 sputtering cycle (~72 nm) whereas for the sample annealed at 700 °C the atomic concentration was around 62 atomic % until 13 sputtering cycle (~49 nm). For the sample annealed at 900 °C, traces of O can be found up to a depth of 36 sputtering cycles (~137 nm). Also from Fig 6.4, it is observed that the amount of O has increased significantly in the samples that were annealed. This is due the inward diffusion of O present in low concentrations in the furnace during annealing, and is consistent with the RBS results.
Fig. 6.5 shows the comparison of depth profile of Zn and O in as-implanted sample extracted by using two different techniques (XPS and SIMNRA). To find the depth in nm from XPS data, sputtering time is multiplied by sputtering rate (38 Å/min). For SIMNRA the atomic concentration (atoms/cm²) is converted into nm. Densities of 7.14 g cm⁻³, 1.141 g cm⁻³, 2.239 g cm⁻³, and 1.8 g cm⁻³ were used for Zn, O, Si, and C, respectively for the calculation of depth in nm. After using those parameters the depth in nm with corresponding concentrations was plotted. Fig 6.5 (a) shows the depth profile of Zn obtained from two different techniques. It is observed that the concentration increased until 40 nm depth and decreased sharply after that in the XPS profile. In the SIMNRA profile, the concentration increased with depth until 30 nm and then a slow drop is observed. Zn can only be observed up to 80 nm in depth from XPS. On the other hand, the SIMNRA result suggests that Zn can be observed up to 120 nm in depth. The difference could be due to the assumption on densities, changes in sputtering rate during XPS analysis because of non-uniformities in the sample, or uncertainties in fitting parameters.
Fig 6.5 (b) shows the depth profile of O obtained from the two different techniques. Both depth profiles closely matches up to 35 nm and after that XPS suggest a sharp drop in concentration whereas SIMNRA suggest the slow drop in concentration. The region behind this could be due to the same reason as for Zn, or other reasons that are yet to be determined.

Fig. 6.6 XPS spectra showing the BE of Zn 2p1/2 and 2p3/2 signals for (a) as-implanted sample measured after 5 sputtering cycles, (b) sample annealed at 700 °C measured after 5 sputtering cycles, and (c) at different depths for the as-implanted (bottom) and annealed (top) samples. The dotted lines are to suggest the average BE.

In order to monitor the formation of ZnO, the binding energies (BE) of Zn 2p1/2 and Zn 2p3/2 electrons were measured using XPS. Fig. 6.6 (a) shows XPS Zn 2p1/2 and Zn 2p3/2 signals measured after 5 sputtering cycles (~19 nm depth) of an as-implanted sample. It is observed that the peak position of binding energy of the Zn 2p3/2 electrons is 1021.68 ± 0.086 eV. Similarly XPS Zn 2p1/2 and Zn 2p3/2 signals of a sample annealed at 700 °C were also measured after 5 sputtering cycles (~19 nm depth) [Fig. 6.6 (b)]. In the case of the annealed sample, the
peak binding energy position of the Zn $2p_{3/2}$ electrons has increased compared to the as-implanted sample, and is found at $1022.31 \pm 0.058$ eV. Fig. 6.6 (c) shows XPS Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals taken at six different depths for both the as-implanted and annealed samples. The first six curves from the bottom of the figure are the XPS spectra from depths of 2, 5, 7, 10, 12, and 16 sputtering cycles in the as-implanted sample, and, continuing upward, the remaining six curves are the XPS spectra from depths of 2, 5, 7, 10, 12, and 16 cycles in the annealed sample, respectively. It can clearly be observed that the BE for both electrons has increased in the annealed sample. This increase of BE is attributed to a change from Zn-Zn bonding to Zn-O bonding, which supports the XRD results and confirms the presence of a Zn phase in the as-implanted sample that is largely replaced by a ZnO phase in the annealed sample. More quantitative analysis is done in next page.

Fig. 6.7 Quantitative analysis of Zn and ZnO phases in a sample annealed at 700 °C at the 2$^{nd}$ sputtering cycle (1 sputtering cycle ~ 3.8 nm). It is observed that at this depth of ~ 7.6 nm, the ZnO phase is more abundant than the Zn phase.
Fig. 6.7 represents the quantitative analysis of the Zn and ZnO phases in the annealed sample at the 2\textsuperscript{nd} sputtering cycle or \(\sim 7.6\) nm (1 sputtering cycle \(\sim 3.8\) nm) with fitting parameters. The peak position was kept at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE. The FWHM was kept at 2.94 eV for both the peaks. The areas under the corresponding curves (for Zn phase 31730 \(\pm 1261\) and for ZnO phase 64758 \(\pm 1260\) in arbitrary units) show that in this sputtering cycle, the ZnO phase was more prevalent than the Zn phase.

Fig. 6.8 Quantitative analysis of Zn and ZnO phases in sample annealed at 700 °C at different sputtering cycles. Up to 15\textsuperscript{th} sputtering cycle the amount of ZnO phase is greater than Zn Phase. After 16\textsuperscript{th} sputtering cycle Zn phase is dominate the ZnO phase and from 18\textsuperscript{th} sputtering cycle no trace of ZnO phase is observed till 23\textsuperscript{rd} sputtering cycle.
To study quantitatively the abundances of the two phases as a function of depth in the sample, Zn 2p₃/₂ peaks at different depths were fitted by keeping parameters constant (the peak positions were kept at 1021.8 eV for Zn-Zn BE and 1022.4 eV for Zn-O BE and FWHM for both the peaks same). The areas under the peaks for both Zn-Zn bonding and Zn-O bonding are plotted for different depth cycles to study the Zn and ZnO phases as shown in Fig 6.8. It is observed that from the surface the ZnO phase is greater than the Zn phase until the 15th sputtering cycle. After the 16th sputtering cycle the amount of Zn phase is greater than the ZnO phase and from the 18th sputtering cycle to 22nd no trace of ZnO phase is observed. A small amount of ZnO phase is observed after the 23rd sputtering cycle. Also, from the 9th to 15th sputtering cycle no trace of Zn phase is found. This indicates that all the Zn in that region converted to ZnO. As compare to the previous result in Chapter 5, we have successfully optimized the experiment to increase the ZnO NPs.

Fig. 6.9 HRTEM image of as-implanted sample. Few Zn Particles can be observed near the surface. Maximum concentration of the Zn particles can be observed in between 35 to 40 nm depth. The sizes of NPs are not uniform and here can be found as small as 4 nm and as big as 6 nm.
A cross-sectional view of HRTEM image taken from the as-implanted sample is shown in Fig 6.9. The distribution of Zn in the Si can be observed in Fig 6.9 (a). Few Zn Particles can be observed near the surface and the concentration of Zn particles increases as the depth increases. This supports XPS depth profile result. Maximum concentration of the Zn particles can be observed in between 35 to 40 nm depth. Also, this result is very close to the XPS depth profile result (maximum concentration at ~ 38 nm depth). Fig 6.9 (b) shows the different sizes of Zn NPs. The sizes of NPs are not uniform and here can be found as small as 4 nm and as big as 6 nm. From an XRD spectrum of the as-implanted sample, application of the Scherrer equation indicates a lower limit on the average NP size of ~4.5 nm. This result is close to the HRTEM result.

Fig. 6.10 HRTEM image of sample annealed at 700 °C. ZnO NPs are located near the surface of the substrate and some are clustered deeper in the substrate. In the region in between, very few to no ZnO NPs are observed.
Fig 6.10 shows the cross-sectional view of HRTEM image taken from the sample annealed at 700 °C. From Fig 6.10 (a), it is observed that most of the ZnO NPs are located near the surface of the substrate and some are clustered deeper in the substrate. In the region in between, very few to no ZnO NPs are observed. This result coincides with the XPS depth profile result for the sample annealed at 700 °C. Fig 6.10 (b) show the ZnO NPs of different sizes. As was the case for the as-implanted sample, the sizes of NPs are not uniform, and here most have diameters in between 15 and 20 nm. This supports the result calculated using the Scherrer equation with the XRD spectrum for the sample annealed at 700 °C, which yielded a lower limit on the average size of ZnO NPs of ~18.2 nm.

![Normalized PL intensity vs. Energy (eV)](image)

**Fig. 6.11** Room temperature PL measurement of sample annealed at 700 °C. Sharp near-band-edge UV emission is observed at 3.302 eV (375.5 nm).
To investigate the optical properties of the implanted samples, PL measurements were performed on both as-implanted and annealed samples. No PL signal was observed from the as-implanted sample. Fig. 6.11 shows the RT-PL spectrum of the sample annealed at 700 °C. Sharp near-band-edge UV emission is observed at 3.302 eV (375.5 nm). This is slightly blue shifted compared to the UV emission of bulk ZnO (Fig. 4.12(b)). Stress effects in the ZnO NPs or self-absorption effects in the ZnO single crystals could be the cause of the blue shift because the NPs here are too large to induce significant quantum size effects in the excitons. The full width at half maximum (FWHM) of the PL emission band is observed to be 88 meV at RT, which is smaller than the FWHM (113 meV) reported by other workers for high purity ZnO nanoparticles grown by ion beam synthesis.

Fig. 6.12 PL measurements of sample annealed at 700 °C: (a) low temperature PL measurements, (b) peak energy vs. temperature for annealed sample. At 15 K, donor-bound excitonic emission \((D,X)\) [about \(3.366 \pm 1.31 \times 10^{-4}\) eV], and acceptor-bound excitonic emission \((A,X)\) [at about \(3.316 \pm 5.56 \times 10^{-4}\) eV] are observed.
Low-temperature PL spectra of the annealed sample are presented in Fig. 6.12 (a). Donor-bound excitonic emission \((D, X)\) [about \(3.366 \pm 1.31 \times 10^{-4}\) eV], and acceptor-bound excitonic emission \((A, X)\) [at about \(3.316 \pm 5.56 \times 10^{-4}\) eV] are observed at 15 K temperatures. The donor-bound excitonic energy and acceptor-bound excitonic energy both decrease with increasing temperature \(T\) (Fig. 6.12 (b)) according to the Varshni law\(^9\) (Eq. 4.3). By keeping the value of \(\theta_D = 920\) K\(^9\), the value of \(E(0)\) is calculated by the same method describe in chapter 4.3 and in acceptor-bound excitonic emission \((A, X)\) it was found to be 3.316 eV. For donor-bound excitonic emission \((D,X)\), the value of \(E(0)\) is 3.3678 eV.

Fig. 6.13 PL intensity vs. temperature with error bars for both donor-bound excitonic emission \((D,X)\) and acceptor-bound excitonic emission \((A, X)\) peaks of the sample annealed at 700 \(^\circ\)C. Intensities decrease with temperature.
**Fig 6.13** shows the peaks intensity of both donor-bound excitonic emission (D,X) and acceptor-bound excitonic emission (A, X) with respect to the temperature of the sample annealed at 700 °C. The intensity of The PL intensity of donor-bound and acceptor-bound excitonic emission is found to be a function of temperature. PL intensity decreases with increasing temperature. No negative thermal quenching effect on donor-bound excitonic emission is observed here, although it has been reported elsewhere\textsuperscript{10} for ZnO NCs. The intensity of donor-bound excitonic emission (D, X) is higher than that for acceptor-bound excitonic emission (A, X) except in the temperature range from 48 K to 75 K. The IQE of the sample annealed at 700 °C was determined using the method explained in Section 3.2. The IQE for ZnO at 200K is estimated to be 10%.

PL life time measurements were done on the sample annealed at 700 °C. Fig. 6.14 (a) shows a PL lifetime measurement for donor-bound excitonic emission (D, X) from the sample at 4 K. The ZnO NPs exhibit a single exponential decay. A lifetime of 320 ps was measured at 4 K, which is close to the excitonic radiative lifetime of bulk ZnO (322 ps).\textsuperscript{11} PL lifetime measurement of acceptor-bound excitonic emission (A, X) from the annealed sample at 4K is shown in Fig 6.14 (b). The decay of the acceptor-bound excitonic emission (A, X) is found to be biexponential with time constants of $\tau_s = 133$ ps and the $\tau_f = 872$ ps. The fast decay constant is most probably due to the non-radiative recombination and the slow decaying component is attributed to the radiative lifetime.\textsuperscript{12}
Fig. 6.14 PL lifetime measurements of the annealed sample at 4 K: (a) donor-bound excitonic emission (D, X), (b) acceptor-bound excitonic emission (A, X). (D, X) exhibits a single exponential decay, and a lifetime of 320 ps was measured at 4 K. The decay of (A, X) is found to be biexponential with time constants of $\tau_s = 133$ ps and the $\tau_f = 872$ ps.

6.3 Summary and Conclusions

ZnO- and Zn$_2$SiO$_4$-phase NPs have been successfully synthesized by dual beam implantation of 45 keV ZnO$^-$ molecular ions at a fluence of $1 \times 10^{17}$ ions/cm$^2$ and 15 keV of O$^-$ ion at a fluence of $2 \times 10^{17}$ ions/cm$^2$ into Si at room temperature, followed by thermal annealing at different temperatures in a mixture of 96% Ar and 4% H$_2$ for 1 h. RBS measurements confirmed the fluence of Zn and O ions in the as-implanted material. Also, RBS results show a significant amount of Zn was depleted due to the sputtering effect during implantation and also
during thermal annealing. XRD patterns show that crystalline ZnO NPs were present after thermal annealing at 700 °C and had an average size of ~17.5 nm, and when annealed at 900 °C, Zn$_2$SiO$_4$ NPS formed and their average size was ~19 nm. In the as-implanted sample, only Zn NPs with an average size of at least ~4.5 nm were observed. From XPS, it was found that Zn was distributed from the Si surface to a depth of ~76 nm in the as-implanted sample, and electron binding energies indicate that Zn-Zn bonding was dominant at all depths. This leads to the conclusion that a Zn phase was present, and, coupled with the XRD results, that Zn nanoparticles were distributed over the ~76 nm depths in the as-implanted sample. The highest concentration of Zn in the as-implanted sample was 38 nm beneath the Si surface, and the measured Zn distribution closely matches SRIM simulation results. After annealing at 700 °C, a broader spatial distribution of Zn was observed, with Zn distributed to maximum depth of ~106 nm. A shift in Zn electron binding energies indicates that Zn-O bonding was present at all depths. A quantitative study of the formation of Zn and ZnO phases showed that up to a depth of 15 sputtering cycles ZnO phase dominated the Zn phase and after that Zn dominated the ZnO phase. When annealed at 900 °C, Zn migrated more towards the surface and binding energies increased further, indicating the formation of Zn-Si bonding. This leads to the conclusion that a ZnO and Zn$_2$SiO$_4$ phase were present, and, coupled with the XRD results, that ZnO and Zn$_2$SiO$_4$ NPs had formed. HRTEM showed the formation of Zn NPs having variable diameters from 4 nm to 6 nm in the as-implanted sample. In the annealed sample, nanoparticles were in the range of 16 nm to 20 nm in diameter. Structural characterization results show majority of Zn transfer to ZnO and Zn$_2$SiO$_4$ phase. No PL emission was observed from as-implanted and sample annealed at 900 °C. For the sample annealed at 700 °C, RT-PL measurement showed band-edge
emission in the UV region with a FWHM of 88 meV. Low temperature PL showed that the intensity of both donor-bound excitonic emission and acceptor-bound excitonic emission are function of temperature. TR-PL measurements performed at 4K revealed an excitonic lifetime for donor-bound excitonic emission (D, X) of 320 ps, and that acceptor-bound excitonic emission (A, X) had two characteristic lifetimes, of 133 ps and 872 ps.

6.5 References


CHAPTER 7

CONCLUSION AND OUTLOOK

In this dissertation, the structural and optical properties of ZnO nanostructures embedded in silicon based substrate synthesized by ion implantation have been investigated in detail. The main results of the experiments are summarized as follows.

In the first experiment (Chapter 4), ZnO nanostructures were synthesized successfully by the implantation of low energy (35 keV) ZnO molecular ions into thermally grown SiO₂ to a fluence of \(5 \times 10^{16}\) ions/cm² followed by thermal annealing. This is one of two reported experiments on ZnO molecular ions into SiO₂. We did the low energy implantation to compare to the other reported experiment. Also for the first time, we did extensive structural and optical characterization of the nanostructures synthesized by molecular ion implantation, which will help in the development of the technique for future device applications. In the as-implanted sample, Zn nanoparticles up to 5 nm in diameter were observed up to a depth of 50 nm with the highest concentration at 25 nm. After annealing, Zn atoms had diffused in both directions from the depth of peak concentration, combined with O, and formed ZnO nanoparticles having diameters up to 8 nm. The UV emission peak was blue shifted as compare with bulk ZnO, due to the quantum-confinement effect. The excitonic lifetime of (D, X) emission was found to be 160 ps and (A, X) emission had lifetimes of 43 ps and 620 ps. It was observed that below 20 K the recombination process was due to radiative recombination, and above 20 K the recombination was dominated by non-radiative processes. To the best our knowledge, these are the first reported low temperature lifetime measurements for ZnO synthesized by this ion implantation technique. From structural characterization, it was observed that ZnO
nanoparticles were small in diameter and formed from the surface to ~ 55 nm. Comparing the FWHM of PL band-edge UV emission with the other high quality ZnO nanoparticles, it was found that our ZnO nanoparticles synthesized by this method were of high quality. Due to these properties of the sample, the fabrication technique described here can be used to prepare ZnO nanoparticles in a Si/SiO₂ matrix, which could be used to integrate optoelectronic applications into semiconductor devices.

In the second experiment (Chapter 5), we tested a new procedure designed to create ZnO and Zn or Zn₂SiO₄ and Zn NPs at a depth of few nanometers from the surface of the substrate, and studied the structural and optical properties of the NPs so produced. Zn, ZnO and Zn₂SiO₄ NPs were synthesized successfully by the implantation of low energy (35 keV) ZnO⁻ molecular ions into Si (rather than SiO₂ as has been done previously) to a fluence of 1 × 10¹⁷ ions/cm² at room temperature, followed by thermal annealing in a mixture of 96% Ar and 4% H₂ for 1 h. When a sample was annealed at 700 °C, Zn and ZnO NPs having an average size of ~20 nm and ~17 nm, respectively, were observed. But when a sample was annealed at 900 °C, Zn₂SiO₄ and Zn NPs having average sizes of 21 nm and 18.5 nm, respectively, were formed. RT-PL measurement of the sample annealed at 700 °C showed band-edge emission in the UV region with a FWHM of 111 meV. No emission was observed from Zn₂SiO₄ and Zn NPs. For LT-PL, both (D, X) and (A, X) emission were present and both followed the Varshni law. Optical characterization results suggested that there was no surface plasmon resonance (SPR) absorption effect for the Zn particles. It could be either that the particle size was big or this fabrication technique is not suitable for this application. For ZnO nanoparticles, UV emission was observed. Since the ZnO nanoparticles were fewer in number than Zn nanoparticles in the
sample after annealing, new techniques have to be developed to increase the concentration of ZnO nanoparticles for future device application of ZnO nanoparticles.

The third experiment (Chapter 6) was an extension of the work reported in Chapter 5. Here, we modified the procedure by implanting O\(^-\) to increase the ZnO and Zn\(_2\)SiO\(_4\) NP concentrations. We carried out this new technique to create Zn, ZnO and Zn\(_2\)SiO\(_4\) NPs at a depth of few nanometers from the surface of the substrate, and studied in detail the structural and optical properties of the NPs produced. This is the first experiment of its kind. ZnO- and Zn\(_2\)SiO\(_4\)-phase NPs were successfully synthesized by dual beam implantation of 45 keV ZnO\(^-\) molecular ions at a fluence of \(1 \times 10^{17}\) ions/cm\(^2\) and 15 keV of O\(^-\) ion at a fluence of \(2 \times 10^{17}\) ions/cm\(^2\) into Si at room temperature, followed by thermal annealing at different temperatures in a mixture of 96% Ar and 4% H\(_2\) for 1 h. It was observed that a significant amount of Zn was depleted due to sputtering during implantation and also during thermal annealing. The average sizes of Zn NPs in an as-implanted sample, ZnO NPs in a sample annealed at 700 °C, and Zn\(_2\)SiO\(_4\) NPs in a sample annealed at 900 °C had average sizes of ~4.5 nm, 17.5 nm, and 19 nm, respectively. No PL emission was observed from the as-implanted sample and the sample annealed at 900 °C. For the sample annealed at 700 °C, RT-PL measurement showed band-edge emission in the UV region, and that both (D, X) and (A, X) emission were functions of temperature. TR-PL measurements performed at 4K revealed a picosecond life time. From the XPS and TEM results it was observed that annealing caused Zn to migrate in both directions. This migration increased the thickness of the ZnO layer and reduced the concentration of ZnO. Due to the continuous demand for smaller and smaller device fabrication, it is necessary to implant with low energy and short annealing time. This technique will be useful if rapid thermal
annealing (RTA) is adopted with the as-implanted samples. Also to avoid the contamination on
the sample due to the other gases or air annealing, vacuum annealing can be done. So from our
experimental result it is clear that this technique is one of the best techniques to synthesize
ZnO in an Si/SiO₂ matrix by using ion implantation technology.

In the future, this research can be extended in various directions. The work of Chapter 4
can be extended to study the sizes of ZnO nanoparticles and corresponding optical properties
by changing the implantation energies and/or fluence. The work of Chapter 6 can be extended
to understand the effect of different gases on the optical and magnetic properties of the ZnO
nanoparticles by changing the annealing gases and/or annealing temperature and/or annealing
time. Similarly detailed study on the sizes of ZnO nanoparticles and corresponding optical
properties can be done by changing the implantation energies and/or fluence and then
thermally annealing in a rapid thermal annealing system (RTA). Also, the work of Chapters 4
and 6 can be extended by focusing on integrating optoelectronic applications into
semiconductor devices.