CHAPTER 1
INTRODUCTION TO ALUMINUM NITRIDE AND ITS RELATED ALLOYS AND ION IRRADIATION

1.1 INTRODUCTION

Semiconductor materials are the boon to the mankind and they are the soul of almost all the modern technologies. The inevitable usage of semiconductors in a wide range of electronic and optoelectronic devices is due to their capability to form various electrical junctions and heterojunctions (Yacobi 2003). They are classified into elemental (Si, Ge, diamond, etc.,) and compound (AlN, GaN, GaAs, etc.,) semiconductors. Silicon is the prime and the most exploited semiconductor for the electronic devices. However, the indirect band gap of silicon limits the optoelectronic application of the material despite its other unmatchable properties.

1.2 III-V SEMICONDUCTORS

III-V semiconductor materials are the major ingredients for optoelectronics devices and they are also suitable for fast operation devices due to their higher electron mobility (Bolkhovityanov et al 2009). III-V semiconductor materials such as Gallium arsenide (GaAs), Aluminum gallium arsenide (AlGaAs), Gallium phosphide (GaP), Indium phosphide (InP) and Aluminum gallium indium phosphide (AlGaInP) have been utilized to produce infrared, red and yellow light sources. Indeed, the first infrared LED and solid state LASER had been demonstrated using GaAs in the year.
1962. At present, III–V compound semiconductors provide the materials basis for a number of well-established commercial technologies, as well as new cutting-edge classes like high-electron-mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs), laser diodes (LDs), light-emitting diodes (LEDs), photodetectors, electro-optic modulators, and frequency-mixing components (Vurgaftman et al 2001).

However, bright LEDs and laser diodes (LDs) from green to ultraviolet range have become impossible with these conventional narrow band gap III-V materials. In earlier days, weak blue LED had been obtained with SiC. Later, II-VI semiconductor ZnSe showed some potential for blue and green light sources, but structural defects of ZnSe limited the lifetime of light sources. This paved the way for research on wide band gap group III-V/nitride materials comprising of Al – Ga – In – N alloys (Ponce and Bour 1997).

### 1.3 ORIGIN OF ALUMINUM NITRIDE AND ITS RELATED ALLOYS

In fact, Aluminum Nitride (AlN) was the first synthesized material in the III-V compound semiconductor family (Fichter 1907). Then, crystalline structure of Gallium Nitride (GaN) was reported first in 1937. However, growth of crystalline GaN films was achieved in 1969. Consequently, attempt to synthesize Indium Nitride (InN) was made in 1938. Initial synthesis of AlN, GaN and InN was reported in the early twentieth century, although reasonable material quality for device fabrication has only been achieved during the end of nineteen eighties.

AlN, GaN and InN are commonly known as III-nitrides. Figure 1.1 shows the band gap and lattice constant of III-nitrides and other materials
used in the optoelectronic devices with crystal structure. Irrespective of other material properties, III-nitrides are the important candidates for the optoelectronic applications in ultraviolet (UV), visible and infrared region of the electromagnetic spectrum as LEDs and LDs (Ambacher 1998).

![Bandgap of III-nitrides with other semiconductor materials as function of their lattice constant ‘a’ and their crystalline structure](https://example.com/bandgap-chart.png)

**Figure 1.1** Bandgap of III-nitrides with other semiconductor materials as function of their lattice constant ‘a’ and their crystalline structure [Courtesy : Lafont et al 2012]

Due to the direct wide band gap, emission of III-nitride materials can be adjusted between 6.2 eV of AlN to 3.4 eV of GaN and to 0.7 eV of InN by properly varying the ternary and quaternary alloy composition. In addition to that, III-nitrides possess strong bond strength, high thermal conductivity, high melting point, mechanical resistance to high temperature
and aggressive chemical environment. Some of the important physical properties of III-nitrides are listed in Table 1.1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>AI \text{N}</th>
<th>Ga \text{N}</th>
<th>In \text{N}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap energy Eg (eV) at 300 K</td>
<td>6.2</td>
<td>3.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Eg (eV) at 5 K</td>
<td>6.28</td>
<td>3.5</td>
<td>--</td>
</tr>
<tr>
<td>Lattice constants a (Å)</td>
<td>3.112</td>
<td>3.189</td>
<td>3.548</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.982</td>
<td>5.185</td>
<td>5.760</td>
</tr>
<tr>
<td>c/a</td>
<td>1.601</td>
<td>1.626</td>
<td>1.623</td>
</tr>
<tr>
<td>Thermal expansion Δa/a (K\text{^{-1}})</td>
<td>4.2×10^{-6}</td>
<td>3.17×10^{-6}</td>
<td>3.8×10^{-6}</td>
</tr>
<tr>
<td>Δc/c (K\text{^{-1}})</td>
<td>5.3×10^{-6}</td>
<td>5.59×10^{-6}</td>
<td>2.9×10^{-6}</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>3.2</td>
<td>1.3</td>
<td>0.45</td>
</tr>
<tr>
<td>Breakdown field (MV/cm)</td>
<td>12</td>
<td>4</td>
<td>--</td>
</tr>
<tr>
<td>Index of refraction (η)</td>
<td>2.15</td>
<td>2.33–2.67</td>
<td>2.80–3.05</td>
</tr>
<tr>
<td>Dielectric constant (ε_r)</td>
<td>8.5</td>
<td>~9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

These properties emphasize that III-nitrides are the ideal materials for detectors, high-power and high temperature electronic devices. Also, the radiation hardness of the III-nitride materials enables the usage of electronic and opto-electronic devices in space applications.

1.4 BREAKTHROUGH IN III-NITRIDES EPITAXIAL GROWTH

In spite of the unique III-nitrides material properties, epitaxial growth and realization of devices from III-nitrides have been like a mirage until recently due to the non-availability of native substrates and suitable p-type dopant. Amano et al (1986 and 1989) had made the initial breakthrough by achieving device quality GaN layers on sapphire using AlN buffer layers.
and p-type GaN by doping Mg using low-energy electron-beam irradiation (LEEBI). Later, Nakamura et al (1992) had discovered that thermal activation of Mg (p type dopant of GaN) improves p-type conductivity in the GaN layer. These achievements began the new era in solid state lightings, covering the span of wavelength from deep ultraviolet (200 nm) to infrared (1700 nm) region by III-nitrides.

1.5 EVOLUTION OF III-NITRIDE DEVICES

The first blue LED based on the GaN and InGaN layers was commercially available in the year 1994. Continuous improvements in the brightness and fabrication of blue-green LED with increased indium composition in the InGaN active layers had been achieved in the subsequent years. Nakamura et al (1996) demonstrated the first violet laser diode by using InGaN multi-quantum wells (MQW). Shortly, Akasaki et al (1996) had reported the shortest wavelength laser diode in ultraviolet region at 376 nm using AlGaN/GaN/GaInN separate confinement heterostructure (SCH) with a single quantum well (SQW) structure. Advances in the heteroepitaxial growth technologies and an improved understanding of the properties of III-nitride materials have led to the commercial development of violet/blue/green LEDs and blue-violet LDs. In addition to that, entire visible region has been covered with the already available AlInGaP based yellow and red LEDs. On the other hand AlN, GaN and their terenary alloy AlGaN based ultraviolet light sources are found to be less efficient than their visible counterparts. The potential applications of UV LEDs and LDs such as counterfeit currency detection, biomedicine, water-air purification, etc., provide strong impulse to pursuit research in this field.

This chapter briefly describes the crystal structure, growth techniques of AlN, defects in AlN, applications of AlN, overview of characterization techniques and a short note on the effects of ion irradiation.
1.6 CRYSTAL STRUCTURE OF AlN

AlN crystallizes in hexagonal or wurtzite (WZ) and cubic or zinc blende (ZB) crystal structures. Among these, wurtzite structure has been found as the thermodynamical stable phase of AlN. The main difference between these two structures is in the stacking sequence of layered atoms. For the wurtzite structure, the stacking sequence is ABABAB in <0001> direction. For the zincblende structure, the stacking sequence is ABCABC along <111> direction.

The wurtzite structure has a hexagonal unit cell. Each unit cell contains 6 atoms of each type. Figure 1.2 shows the wurtzite structure of AlN along with the $a$ and $c$ lattice constants and axis. Figure 1.2 also highlights the $a$ - plane and $c$ - plane. The space group for the wurtzite structure is $P6_3mc$ ($C_{4h}^{6v}$). The wurtzite structure consists of two interpenetrating hexagonal close packed (HCP) sublattices, each with one type of atom, offset along the $c$-axis by 5/8 of the cell height (5/8 $c$). The wurtzite structure is non-centrosymmetric, and thus AlN possesses different properties along different <0001> polar directions. The basal plane <0001> of AlN crystals can be either Al or N polar. The polarity of AlN can be defined with respect to the relative positions of the Al atom and N atom along the {0001} stacking. As the crystal surface is approached from the bulk along the c-direction, if the long bond goes from the nitrogen atom to the Al atom, the crystal is nitrogen polar. Otherwise, if the long bond goes from the Al atom toward the nitrogen atom, the crystal is Al polar.
1.7 GROWTH OF ALUMINUM NITRIDE

1.7.1 Bulk Growth

AlN is the potential substrate material for the ultraviolet (UV) optoelectronic devices. It is having UV transparency below 360 nm and possesses low lattice mismatch with AlGaN layers. For example, the lattice
mismatch between AlN and Al$_{0.5}$Ga$_{0.5}$N is 1.22 %. It necessitates the bulk growth of AlN. Several techniques have been attempted to grow bulk AlN. The Physical Vapor Transport (PVT) or sublimation-recondensation (sublimation) method is so far the most successful bulk crystal growth technique. The typical melt growth method used to grow single crystal boules in the semiconductor industries are not possible for AlN, due to its high melting temperature and large dissociation pressure at the melting point (Grzegory et al 1995). Other growth methods including vaporization (Pastnak et al 1964) and solution routes (Dugger 1974) have also been studied and found impractical.

1.7.1.1 Physical vapor transport growth

Physical vapor transport (PVT) growth of AlN is the significant method for the fabrication of AlN substrates. AlN growth by PVT has been performed for over 35 years. This method was developed by Slack and Nelly (1976, 1977). PVT has also been successfully used to produce several other types of crystals, including SiC which is used as a substrate for III-nitrides. The PVT method is an equilibrium growth process which employs a temperature gradient to evaporate or to dissociate the source material in the hot part of the reactor and condense it on a cooler portion of the reactor, on a seed crystal. For the growth of AlN, the Al source is Al metal or AlN powder. These two sources result in similar growth morphologies, but differ in impurity content, corrosiveness, and evaporation rate. AlN crystals are grown in nitrogen ambient with nitrogen and/or ammonia gas serving as the nitrogen source. Nitrogen ambient is preferred, in order to limit the growth of the AlN crystals by the transport of Al vapor to the growth zone. Growth temperatures are high, typically ranging from 1800 to 2400 °C, and the growth pressure is generally between 76 and 1000 Torr. AlN growth rates are in the order of 10-500 µm/h. PVT is able to produce high-quality AlN crystals with low
dislocation densities. However, it is difficult to control the size and purity of AlN crystals (Schlesser et al 2002, Schowalter et al 2003 and Edgar et al 2002).

The main problem with AlN crystals grown by PVT is the presence of randomly oriented grains within the AlN crystal. These grains possess a microstructure with highly misoriented subgrains. The origin of grain boundaries is due to the difficulty in controlling the nucleation. Moreover, the presence of multiple grains within an AlN substrate is highly undesirable for a substrate to be used in a device manufacturing environment. In addition to that, point defects within the AlN crystal lattice in the form of oxygen impurities, aluminum vacancies, and/or nitrogen vacancies result in poor transparency (Evans et al 2006). These impurities result in a high degree of absorption in the UV region of the spectrum. It becomes a serious problem for UV optoelectronic devices since it prevents UV light from neither entering nor leaving through the substrate.

Increasing the size of a single grain is difficult and the AlN wafers are limited by the size. Major problems with PVT include oxygen contamination, harmful spontaneous nucleation, amber coloring, optical absorption in the UV, crucible material stability and cracking in large diameter boules. On the other hand, epitaxial growth of AlN has become an alternative method to achieve device quality epilayers on the larger size (≥2”).

1.7.2 Epitaxial Growth of AlN

Hydride Vapor Phase Epitaxy (HVPE), Molecular Beam Epitaxy (MBE) and Metal organic chemical vapor deposition (MOCVD) are the most common epitaxial growth techniques for the deposition of AlN epitaxial layers.
HVPE is successful in producing free-standing GaN bulk crystals with high growth rate (10 -100 µm/h). However, the synthesis of freestanding AlN crystals by HVPE is complicated and is only in the nascent stages of development. The impurity incorporation originating from the reactions between AlCl$_3$ and quartz reactor wall, graphite susceptor and homogeneous gas phase reactions have hindered the development of AlN using HVPE. The detailed investigation on the epitaxial growth of AlN by HVPE has been presented in chapter 2.

High quality AlN thin films on foreign substrates (SiC, Sapphire) with high throughput can be grown using MOCVD technique. In addition to a high growth rate (on the order of 1 ~ 10 µm/h) than MBE, MOCVD provides uniform coverage on the substrates and the layer thickness. The growth can be monitored by in-situ reflectometer. The detailed investigation on the AlN growth and detailed information on the MOCVD system, safety measures has been disclosed in chapter 3.

Considering the growth of AlN by MBE, it has the advantage of better control over AlN growth parameters, relatively low growth temperature, no hydrogen carrier gas is involved and in situ characterization. However, it requires ultra high vacuum in the order of $10^{-11}$ torr.

1.8 DEFECTS IN AlN

Most of the interesting properties of matter in the solid state are related to the presence of defects and impurities. The imperfections in solids differentiate the real solids from an ideal crystalline structure. In semiconductors, the defects are introduced due to either thermodynamic considerations or the presence of impurities during the crystal growth process. There is also great scientific interest in III-nitrides class of materials because they appear to form the first semiconductor system in which extended defects
do not severely affect the optical properties of devices. All substrates available for the AlN heteroepitaxy have a high lattice and thermal mismatch. Among the large number of different foreign substrates for the AlN deposition, sapphire and silicon carbide have been considered widely. In particular, sapphire substrate is the choice of AlN, when related to optoelectronic applications and economic reasons. The mismatch in lattice parameters and thermal expansion coefficients between the AlN and these foreign substrates, has led to a generation of high density of defects at the epilayer and substrate interface.

The defects in crystals are typically classified by dimensions. Zero-dimension (0D) or point defects include intrinsic point defects such as vacancies, interstitials, antisite defects and impurity-point defect complexes. Extended defects include linear defects (1D) (dislocations) and planar defects (2D) (grain boundaries, interfaces, stacking faults and micro-cracks). The three dimension (3D) defects include precipitates, holes (including nanopipes) and surface hillocks and pits (so called pinholes). Point defects include mainly substitutional impurities that act as donor and acceptor species in semiconductors. Such shallow defects appear in band theory as states in the forbidden energy gap which lie close to their respective bands with donors close to the conduction band.

Non radiative recombination centres act to kill luminescence due to electron hole recombination across the bandgap of a semiconductor. In the model originally proposed by Schokley, Read, and Hall, these defects form the deep levels in the middle of the bandgap that sequentially capture an electron and a hole. Many intrinsic and impurity related point defects are known to form deep centres. The capture process does not usually result in light with photon energy equal to half the bandgap energy as expected: instead, the electron hole recombination energy dissipates into phonons. In the
case of nitrides such recombinations lead to a long wavelength emission commonly known as yellow luminescence. Nonradiative recombination lowers both the efficiency and the decay time of near band luminescence. Oxygen is the main impurity in the AlN either in the film or crystal. It might be incorporated from the sapphire substrate or the reactor (quartz) components during the growth. In addition to that, the native defects such as nitrogen and aluminum vacancy has also reduce the optical and structural quality of AlN.

1.9 APPLICATIONS OF AlN

AlN epitaxial films/crystal serves as an ideal substrate for AlGaN/AlN based deep ultraviolet light emitting devices as well as for III-nitrides (GaN, InN) epitaxial growth. AlN templates or substrates possess closely-matched atomic lattice and thermal properties to the subsequently grown UV light emitters. It has been noted to improve the crystal quality, thermal management, light extraction and overall device performance of UV emitters. It is worth noticing that the lure of ultra-violet solid state light sources has paved way for many applications such as, improving the resolution of photolithography for the fabrication of microelectronic devices, detecting the hazardous gas/particles, high-density optical data storage, biomedical research, sterilization in health care and indeed they are the best alternative for large, toxic, low-efficiency gas lasers and mercury lamps.

In addition to this, AlN has its own applications in surface acoustic wave (SAW) devices and short wavelength LEDs/LDs, where good piezoelectric properties and higher bandgap energies are preferred. Moreover, AlN is a good substrate for certain electronic devices, such as Field Effect Transistors (FET) because its high resistivity ($10^{11} \sim 10^{13} \, \Omega \cdot \text{cm}$) simplifies the device isolation process. The high electrical resistivity of AlN makes it
suitable as an insulating film for metal insulator semiconductor or as passivating layers.

1.10 OVERVIEW OF CHARACTERIZATION TECHNIQUES

1.10.1 X-ray Diffraction

Roentgen in 1895 discovered X-rays and William Coolidge invented the X-ray tube also known as Coolidge tube. These inventions paved the way for numerous applications in medical and scientific fields. X-ray is an invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency) than visible light. The wavelength range for X-rays is from about $10^{-8}$ m to about $10^{-11}$ m and the corresponding frequency range is from about $3 \times 10^{16}$ Hz to about $3 \times 10^{19}$ Hz. The use of X-rays for crystallographic analysis (Connolly 2012) relies on a few basic principals:

1. When an incident beam of X-ray interacts with a target material, one of the primary effects observed is scattering (spherical radiation of the incident x-rays without change in wavelength) of those x-rays from atomic scattering centers within the target material.

2. In materials with some type of regular (i.e., crystalline) structure, X-rays scattered in certain directions will be in-phase (i.e., amplified), while most will be out of phase. This “in-phase” scattering is called diffraction.

3. Measurement of the angular relationships between the incident and the diffracted X-rays can be used to discern the crystal structure and the unit cell dimensions of the target material.

4. The intensities of the amplified X-rays can be used to work out the arrangement of atoms in the unit cell.
The simplest and the most useful description of crystal diffraction have been obtained by Bragg (1913). Strong diffraction occurs when all the wavelets add up in phase. By considering an entire crystal plane as the scattering entity, rather than each individual electron, it is certain to see from Figure 1.3 that strong diffraction results when

\[ n \lambda = 2d \sin \theta \]  \hspace{1cm} (1.1)

where, \( n \) is an integer representing the order of diffraction, \( \lambda \) is the wavelength of X-ray source, \( d \) the interplanar spacing of the reflecting (diffracting) plane and \( \theta \) the angle of incidence and diffraction of the radiation relative to the reflecting plane. The requirement for the angle of incidence to equal that of diffraction is not seen directly from Figure 1.3, but arises from the incorporation of scattering from many planes normal to the surface.

**Figure 1.3**  **Diffraction of a plane wave from successive crystal planes**

Strong diffraction occurs when the angles of incidence and diffraction (\( \theta \)) are equal and the path difference AOB between the two beams is equal to \( n\lambda \).
1.10.2  **High resolution X-ray diffraction instrumentation**

High resolution X-ray diffraction (HRXRD) is the dedicated instrument to probe the structural quality of epitaxial layers, heterostructures and superlattices in detail by maneuvering

- lattice mismatch between layer and substrate
- alloy composition of layer
- layer thickness
- superlattice period
- substrate curvature
- mosaic spread
- layer relaxation

Figure 1.4 shows the photographic image of X’pert PRO MRD (XL) HRXRD system. It comprises of X-ray tube, divergence slit, hybrid monochromator, MRD XL cradle (Sample stage), double axis (PIXcel) detector and triple axis (proportionate) detector. The X-rays are produced using target material of copper. Then, the X-rays travel through the water cooled X-ray tube in to the divergence slit.

1.10.2.1  **Divergence slits**

A divergence slit is used together with an X-ray mirror in order to control the height of the X-ray beam, and therefore the amount (length) of the sample that is irradiated. When the 1/2° divergence slit is used, the X-ray mirror is irradiated over its complete length by the X-ray beam coming from the X-ray tube’s line focus. The height of the X-ray beam emitted by the mirror is then 1.2 mm. The beam height can be reduced by choosing a
divergence slit with a smaller aperture. Smaller divergence slits are used to do measurements in the lower incident angles (<4°).

Figure 1.4 X’pert PRO MRD high resolution X-ray diffraction system

1.10.2.2 Hybrid monochromators

Hybrid (high resolution) monochromators are commonly used for measurements on nearly perfect semiconductor crystals and epitaxial layers. They select a narrow band out of the Kα<sub>1</sub> line. Hybrid monochromator consists of a parabolic shaped graded multilayer (X-ray mirror) and a special channel cut germanium crystals combined in one module. It is a special kind of beam conditioner, which converts the divergent X-ray beam from a line tube focus to a quasi-parallel beam with a pure Kα<sub>1</sub> radiation component. The
X-ray mirror performs a pre-collimation of the divergent beam to a quasi-parallel beam.

Figure 1.5 Schematic of Hybrid Monochromator

The hybrid monochromator delivers a much more intense parallel beam of copper Kα₁ radiation with X-ray wavelength of 1.54 Å. The copper Kα₂ component is suppressed to a level below 0.1%. This makes it suitable for different applications, ranging from high resolution measurements to phase analysis. Figure 1.5 shows the schematic of Hybrid monochromator.

1.10.2.3 MRD XL cradle

The MRD XL 5-axes cradles are used to make scans in three orthogonal directions. The X and Y directions are in the plane of the sample stage while the Z scan direction moves the sample stage forwards. The surface of the sample can be moved to coincide with the diffraction plane (Z movement). In addition X and Y movements are available to alter the measurement position on the sample to map wafer properties or to allow more than one sample to be loaded and measured in sequence. The data collection software can use the X and Y movements to oscillate the sample.
perpendicular to the diffraction plane during measurements. The mounting disk is parallel to the X-Y plane. The Z direction is perpendicular to the mounting disk. Figure 1.6 depicts the five motorized movements of the MRD cradle. The X'Pert PRO and Empyrean diffractometers (MRD cradle and detectors) have four rotation axes which can be used to perform Omega, 2Theta, Phi and Chi scans. Omega (ω) is the angle between the incident beam and the sample surface, 2Theta is the angle between the incident beam and the diffracted beam, Phi (φ) is the rotation angle about the sample normal and Chi (ψ) is the tilt angle about a line in the sample surface normal to the Omega and 2Theta axes. The sample can be rotated (φ movement) and tilted (ψ movement). The cradle is designed for high-resolution measurements, stress, texture, reflectivity, thin-film phase analysis, in-plane diffraction and spot analysis.

Figure 1.6 Five Motorized Movements of the MRD XL cradle
Epitaxy & smoothfit software is used to plot single scan and area scan data. Single scan data consists of a series of intensity values recorded as one of the above axes is scanned. Area scan data consists of a series of single scan made with one axis while a second axis is offset between each scan. In addition to the four scan axes described above, scans can be made with the 2Theta axis moved at twice the rate of the Omega axis. This is referred to as a 2Theta-Omega or an Omega-2Theta scan. The two different ways of naming this scan axis indicate the way the data is displayed. For a 2Theta-Omega, intensity is plotted as a function of 2Theta (the x-axis is in units of \(\theta\)). For an Omega-2Theta scan, intensity is plotted as a function of Omega (the x-axis is in units of \(\omega\)).

1.10.2.4 Proportional detector

Two types of detectors are equipped in the HRXRD system. Rocking curve and compositional analysis have been done by proportional (triple axis) detector whereas reciprocal space mapping has been carried out using PIXcel (double axis) detector. Proportional detector consisting of a cylindrical chamber filled with a xenon/methane gas mixture, is shown in Figure 1.7. The beryllium detector window is 20 mm x 24 mm. The detector is most efficient for Cu K\(\alpha\) radiation and can also be used for radiation with longer wavelengths.

![Proportional Detector of PANalytical X’pert pro MRD system](figure17.png)
**Omega scan**

The detector remains stationary and the sample is rotated about the \( \omega \) axis. The plot of the scattered X-ray intensity as a function of omega is often called rocking curve. Omega scans measure the sample quality by scanning the diffraction spot in an arc and detects broadening by dislocations and wafer curvature.

**Omega-2theta scan**

The sample is rotated by \( \omega \) and the detector is rotated by \( 2\theta \) with an angular ratio of 1 : 2. When there is no offset and \( \omega = 0 \), this is a symmetrical scan (\( \theta \)-\( 2\theta \)) which is vertical in reciprocal space. \( \omega \)-\( 2\theta \) or \( 2\theta \)-\( \omega \) scans probe the diffraction spot along a direction that generally has less broadening. These scans are required for determining the composition of layers, periods of superlattices and thickness of quantum wells and barriers. Both \( \omega \) and \( \omega \)-\( 2\theta \) scans can be called rocking curves, as both involve rocking the sample about the \( \omega \)-axis (this can sometimes cause confusion).

**1.10.2.5 PIXcel detector**

PIXcel is a fast X-ray detection system based on Medipix2 technology. The detector itself is mounted into a rectangular housing with a beryllium entrance window. The PIXcel is optimized for use with Cu K\( \alpha \) radiation with efficiency higher than 94%. This detector is exclusively used for the reciprocal space map (RSM) of the heterostructures. Figure 1.8 reveals the image of PIXcel detector.
Advantages of PIXcel detectors are

- Superior resolution and speed of data collection
- High count rate linearity
- Solid state detector, no cooling or counting gases

![PIXcel detector in the PANalytical X’pert pro MRD system based on Medipix2 technology](image)

**Figure 1.8** PIXcel detector in the PANalytical X’pert pro MRD system based on Medipix2 technology

### 1.10.3 Raman Spectroscopy

#### 1.10.3.1 Introduction

Raman spectroscopy is a contact free and non-destructive analytical technique for material characterization. It has been realized that Raman spectroscopy is a convenient probe of the vibrational energy levels within a molecule, which easily provides molecular fingerprints. On top of that Raman spectroscopy does not require any sample preparation. The intensity of the bands in a Raman spectrum is proportional to the concentration of the corresponding molecules and thus can be used for quantitative analysis. It is
used for the analysis of biological, chemical, and pharmaceutical samples. Additionally, Raman spectroscopy is used for the chemical and physical characterization of semiconductors, gems, catalysts, minerals, polymers, and several other materials.

1.10.3.2 Origin of Raman spectroscopy

Raman spectroscopy is based on the in-elastic scattering of light, which has been discovered by experiments of the Sir Chandrasekhara Venkata Raman in 1928. Sir C. V. Raman received the Nobel Prize for this discovery in 1930. Today, Raman spectroscopy is getting more and more important. It has been used in different areas of life by the recent developments in laser technology, more sensitive detectors, robust spectrometer optics and its easiness in usage. Smekel (1927) theoretically predicted the scattering of monochromatic radiation with change of frequency. The scattering of light by various media had long been studied by Rayleigh in 1871, Einstein in 1910 and others, but no change of wavelength had been observed, with the sole exception of certain types of scattering in the X-ray spectral region observed by Compton (1923). With this background, many scientists have been surrounding the idea of inelastic scattering, which was first reported by Raman et al (1928).

The development of Raman spectroscopy through the years depended largely on the availability of suitable tools and significant advances have invariably followed the invention of new instruments. Developments in Raman spectroscopy occurred slowly during the period from 1930 to 1950, with much of the work immediately following its discovery being devoted to fundamental studies. The rich legacy from the efforts in IR and the Raman spectroscopy during this period resulted in formalizing a sound model of molecular vibration dynamics, setting the foundation for Raman scattering as a predictive and interpretative class of spectroscopy. Unfortunately, the basic
discoveries made during this period were not followed up in chemical measurements until suitable electronic measuring devices were developed much later. When they were available, advances have occurred rapidly in all aspects of Raman spectroscopy from data analysis to instrument miniaturization.

The experimental problems of Raman spectroscopy are the low intensity of the inelastic scattering and the much larger intensity of the Rayleigh scattering. This fact has posed several restrictions to the progress of Raman spectroscopy and had configured instrumentation to a large extent, since the beginning of the experimentation to the present. In the earliest experiments, Raman and his co-worker Krishnan used filtered sunlight as a radiation source and detected the Raman lines of some sixty liquids and gases. They observed the scattering light visually using a set of compensating colored filters to enhance the optical sensitivity. A more definitive spectrum of carbon tetrachloride exhibiting both the Stokes and anti-Stokes lines recorded photographically using 435.83 nm mercury excitation was published by Raman et al (1929). It is interesting to note that at these early times, the Raman spectra could be obtained with relatively simpler apparatus than those required for infrared measurements. As a result, Raman spectra were more extensive and better catalogued than the corresponding infrared spectroscopy (Jones 1987).

1.10.3.3 **Theory of Raman spectroscopy**

The scattering of light by molecules or crystal lattices is a very weak effect. If monochromatic light is scattered by molecules or crystal lattices spectral analysis shows an intense spectral line matching the wavelength of the light source. Additionally, weaker lines are observed at wavelengths which are shifted compared to the wavelength of the light source, these lines are called Raman lines. Although these lines had already
been predicted theoretically, Raman was the first who experimentally confirmed them in 1928. The interaction between matter and light can be interpreted as a collision between a vibrating molecule or lattice and an incident photon. There are three possibilities:

1. If the collision is elastic, the energy of the photon as well as the energy of the molecule do not change after the collision. The elastic scattering of the photon is called Rayleigh scattering. The inelastic collision between a photon and a molecule is known as the Raman effect. The energy difference between the inelastic scattered photons and the incident photons is exactly the difference between two energy levels of a molecular vibration.

2. If the vibrational energy of the molecule is increased after the collision, the energy of the scattered photons is decreased for the same amount and, therefore, can be detected at longer wavelengths. The respective spectral lines are called Stokes-shift.

3. If the vibrational energy of the molecule is decreased after the collision, the energy of the scattered photons is increased for the same amount and, therefore, can be detected at shorter wavelengths. The respective spectral lines are called anti-Stokes-shift. This is only possible if the molecule is in an excited vibrational state before the collision. Figure 1.9 shows the Rayleigh, Stokes and anti-Stokes scattering.
Figure 1.9 Rayleigh, Stokes and anti-Stokes scattering of light by molecules

1.10.3.4 Types of Raman spectra

Raman signal is normally quite weak and people are constantly improving Raman spectroscopy techniques. Many different ways of sample preparation, sample illumination or scattered light detection have been invented to enhance the intensity of Raman signal. There are different types of Raman spectroscopy like

- Stimulated Raman
- Coherent Anti-Stokes Raman Spectroscopy
- Resonance Raman
- Surface-Enhanced Raman Spectroscopy
- Surface-Enhanced Resonance Spectroscopy
- Confocal Raman Spectroscopy
- Micro Raman Spectroscopy
1.10.3.5  Micro-Raman spectroscopy

Micro Raman spectroscopy was used to characterize the AlN layers at different region in this thesis. Figure 1.10 shows the Renishaw RM1000 micro Raman system. The system is equipped with 1800 l/mm grating spectrometer, a Peltier cooled CCD detector, Argon ion laser and Leica optical microscope.

**Important components**

Micro Raman system typically consists of five major components:

1.  Excitation source (Laser).
2.  Optical microscope
3.  Sample illumination system and light collection optics.
4.  Wavelength selector (Filter or Spectrophotometer).
5.  Detector (Photodiode array, CCD or PMT).

Figure 1.10 Renishaw RM-1000 Micro Raman system
Combining a Raman set up with a microscope allows the spectroscopic sampling of very small volumes. The block diagram of micro Raman set up is shown in Figure 1.11. A beam splitter is used to insert the laser into the collection axis. The backscattered light reflects from the sample and then passes through the beam splitter to the detector.

The spatial resolution of the system is limited by the laser and objective lens. Using the microscope, any portion of the sample that is of interest can be selected optically through the viewing system of the microscope. With micro-Raman, the vibrational spectra can be measured from micron-sized particles which make it an ideal tool to analyse the semiconductor materials.

Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. More precisely, the major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases, the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect using interference (notch) filters, its cut-off spectral range is ± 80-120 cm$^{-1}$ from the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency Raman modes in the range below 100 cm$^{-1}$. 
Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on the grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure than the ruled once. The magnitude of the stray light produced by holographic gratings is less intense than from ruled gratings of the same groove density. Using multiple dispersion stages is another way of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In such systems, Raman-active modes with frequencies as low as 3-5 cm\(^{-1}\) can be efficiently detected.

In earlier times, single-point detectors such as photon-counting Photomultiplier Tubes (PMT) have been used. However, a single Raman spectrum obtained with a PMT detector in wave number scanning mode had taken substantial period of time. Nowadays, multi-channel detectors like Photodiode Arrays (PDA) or Charge - Coupled Devices (CCD) are used to detect the Raman scattered light. Sensitivity and performance of modern CCD
detectors are rapidly improving. In many cases CCD is becoming the detector of choice for Raman spectroscopy.

### 1.10.4 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a contactless, non-destructive method to study the optical properties of the semiconductors. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material is known as photo-excitation. Photo-excitation causes electrons within a material to move into permissible excited states. When these electrons return to their ground state, the excess energy is released by means of radiative process (emission of light) or a nonradiative process. The energy of the emitted light or photoluminescence relates to the difference in energy levels between the excited state and the ground state. The quantity of the emitted light is related to the contribution of the radiative recombination process. The radiative emission intensity is proportional to the impurity density (Gfroerer 2000).

The luminescence experiment in semiconductors can be divided into three stages, as indicated in below Figure 1.12. In the first stage, the sample is excited out of the ground state which is described by a completely filled valence band and an empty conduction band. The laser excitation source creates electron-hole pairs due to a transfer of electrons from the valence into the conduction band (Figure 1.12a). In the second stage, the non-equilibrium electron and hole distributions tend to relax back into the ground state. The initial intraband relaxation is caused by energy transfer to the crystal lattice, i.e., a step-by-step excitation of lattice vibrations (Figure 1.12b). Finally, the electron-hole pairs recombine under emission of light which is the photoluminescence process (Figure 1.12c). Due to the attractive Coulomb interaction between the charge carriers, the emission spectrum contain contributions from states at or above the fundamental energy gap $E_g$ and also
from sharp discrete lines just below $E_g$ which originate from bound excitonic states (Iakoubovskii et al 1999).

![Diagram of luminescence processes](image)

**Figure 1.12** Basic processes involved in a luminescence experiment in optically excited semiconductors

1.10.4.1 Recombination mechanism

Any electron which exists in the conduction band will eventually fall back to a lower energy position in the valance band. It must move back into an empty valence band state and consequently, when the electron falls back down into the valence band, it also effectively removes a hole. This process is called recombination. There are three basic types of recombination in the semiconductor material (Roshko et al 2003). It is classified into band to band recombination, defect level recombination and auger recombination.

Radiative (band to band) recombination dominates in direct bandgap semiconductors. Radiative recombination occurs when an electron in the conduction band recombines with a hole in the valance band and the
excess energy is emitted in the form of photon. The emitted photon has energy similar to the band gap.

Recombination through defects, also called as Shockley-Read-Hall (SRH) recombination. An electron (or hole) is trapped by an energy state in the forbidden region which is introduced through defects in the crystal lattice. These defects can either be unintentionally introduced or deliberately added to the material, for example in doping the material. If a hole (or an electron) moves up to the same energy state before the electron is thermally re-emitted into the conduction band, then it recombines.

An Auger Recombination involves three carriers. An electron and a hole recombine, but rather than emitting the energy as heat or as a photon, the energy is given to a third carrier, an electron in the conduction band. This electron then thermalizes back down to the conduction band edge. Auger recombination is most important in heavily doped or heavily excited material.

1.10.4.2 PL Instrumentation setup

PL setup consists of Ar\(^+\) Ion laser, wave train, sample holder, Spectrometer and Photomultiplier tube (PMT) detector. Figure 1.13 shows the PL setup used for the optical characteristics of nitrides.

1.10.4.3 Ar\(^+\) ion laser

The properties of argon are the best understood of all the ionized gas laser media. The wavelength of the photon depends upon the specific energy levels and in turn the wavelength of the Ar\(^+\) ion laser can be tunable to 488 nm and 514 nm by using the appropriate wavelength selective mirrors. To attain the population inversion for lasing, four-level transition model is utilized instead of conventional three-level model.
A model four-level laser transition scheme is depicted in Figure 1.14. A photon of frequency $\nu_1$ excites or pumps an atom from $E_1$ to $E_4$. If the $E_4$ to $E_3$ transition probability is greater than that of $E_4$ to $E_1$, and if $E_4$ is unstable, the atom will decay almost immediately to $E_3$. If atoms that occupy $E_3$ have a relatively long lifetime, the population will grow rapidly as excited atoms cascade from above. The $E_3$ atom will eventually decay to $E_2$, emitting a photon of frequency $\nu_2$. Finally, if $E_2$ is unstable, its atoms will rapidly return to the ground state, $E_1$, keeping the population of $E_2$ small and reducing the rate of absorption of $\nu_2$. In this way the population of $E_3$ is kept large and that of $E_2$ remains low, thus establishing a population inversion between $E_3$ and $E_2$. Under these conditions, the absorption coefficient at $\nu_2$ becomes negative. Light is amplified as it passes through the material, the greater the population inversion, the greater the gain.
A typical four-level laser transition scheme utilized to attain population inversion

![Diagram of a four-level laser transition scheme](image)

A four-level scheme described above, has a distinct advantage over three-level systems, in which E1 is both the origin of the pumping transition and the terminus of the lasing transition. In the four-level arrangement, the first atom that is pumped contributes to the population inversion, while over half of the atoms must be pumped from E1 before an inversion is established in the three-level system.

### 1.10.4.5 Wave Train

The Wave train is an external ring cavity frequency doubler for single frequency continuous wave pump laser. It is no active laser itself.

**Frequency Doubling**

A strong light wave traversing a solid, transparent material can affect the electron distribution in the material. This result in a non-liner
relationship between the strength of the electric field of the injected light wave (fundamental wave) and the polarization of the material causing the generation of a light wave with doubled frequency (Second Harmonic Generation, SHG). In order to get a high portion of the second harmonic wave, materials with exceptionally high non-linearity, the nonlinear optical crystals are preferably used for frequency doubling.

For given material the conversion efficiency, i.e. the ratio of the harmonic power to the injected fundamental power, reaches its maximum value if the phase matching condition is fulfilled. The β-Barium Borate (BBO) crystal has been used in the wave train for the frequency doubling crystal.

**Closed Loop Purge Unit**

The shorter the SHG wavelength (244 nm), contamination and outgassing becomes higher. Especially inside the Resonator block (RB) wherein the BBO crystal was placed. The power densities for the SHG wavelength are extremely high in the RB. Due to the flexibility and modularity of the wavetrain doubling cavity it is not vacuum tight but sealed against dust. The cavity gets contaminated each time when the resonator cover is removed.

The closed loop purge (CLPU) is a stand-alone unit that adapts a special filtering technology. It incorporates a cartridge, containing desiccant and a molecular sieve, a coarse and a fine filter unit. All this is to remove particles and outgassed vapours and supply clean and dry air inside the doubling cavity. This CLPU will enlarge the lifetime of the BBO crystal. After the frequency doubling the laser with 244 nm wavelength has been led into the sample holder. The sample holder has the provision to load thin films
of various sizes (10 mm to 50 mm diameter) and it has a special holder to load the powder samples.

1.10.4.6 Automated Imaging Spectrometer

Spectrometers are automated, triple grating spectrometer with 320mm focal length and 550nm focal length. Designed for multi-channel PMT detector. These spectrometers are ideal for a variety of research applications. Spectrometers feature a 150nm to 15µm wavelength range (depending on the grating and detector used) and excellent wavelength resolution (better than 0.06nm using a 1200 gr/mm grating). Other features include high-precision automated slits, a high precision stepper drive and a USB 2.0 computer interface. The drive mechanism of the spectrometers allows for rapid and precise scanning, offering selectable step size. The on-axis triple grating turret, mounted on the drive, supports three grating which are rotated automatically via software.

1.10.4.7 Operations of spectrometer

Spectrometer unit equipped to operate as spectrographs have at least one entrance slit and a PMT flange. Options for side entrance and side exit are also available. When taking measurements with a spectrograph, the light to be analysed is diffracted by the grating and dispersed across the exit focal plane. An array detector such as a PMT array mounted at the exit is used to measure, or take a snapshot of a range of wavelengths. The grating position for a particular wavelength range is identified by the center wavelength position. Data for a PMT detector may be recorded for each individual pixel, as an image or with the vertical pixels in each pixel column summed as a spectrum.
Spectrometer unit can also be equipped to operate as monochromator with an entrance and an exit slit. As the name suggests, a monochromator is used to select a single wavelength of light. There are four typical applications for the spectrometer when configured as a monochromator. Scanning monochromator – the instrument can be used to measure the spectral output of emitted light. The light can come from the sun, a laser diode, a glow discharge, etc. Tunable light source – with a broadband light source directly coupled to the entrance slit, the spectrometer can provide a specific band pass (range of wavelengths) at the exit. Changing the slit width will vary the spectral bandpass. Spectral filter – the spectrometer can be used to select a particular bandpass of light, at different selected wavelengths. Fixed wavelength measurement – the spectrometer, when set to a fixed wavelength and bandpass with a single channel detector coupled to the exit slit, can monitor the variations in an incoming light signal, such as laser power.

1.10.4.8 Photomultiplier tube detector

Photomultiplier tube (PMT) detectors typically offer much higher sensitivity than solid state detectors and operate effectively in the UV/VIS and near infrared (NIR). A conventional PMT is a vacuum tube which contains a photocathode, a number of dynodes (amplifying stages) and an anode which delivers the output signal. Figure 1.15 depicts the important components of the PL setup.
1.10.5 Scanning electron microscopy

1.10.5.1 Introduction

Electron Microscopes use a beam of highly energetic electrons to examine objects on a very fine scale. Electron Microscopes are developed due to the limitations of light Microscopes. The wavelength of light source in the conventional microscopes restricts the magnification and resolution in micrometers level. In the early 1930's, this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures (Voutou et al 2008). This required 10,000x plus magnification which was just not possible using optical microscopes due to aberrations and limit in the wavelength of Light. Conventional light microscopes use a series of glass
lenses to bend light waves and create a magnified image, while the scanning electron microscope creates the magnified images by using electrons instead of light waves.

Hence the imaging techniques such as scanning electron microscopy (SEM), Transmission Electron microscopy (TEM/HRTEM), Scanning Tunneling microscopy (STM), Atomic force Microscopy (AFM), etc., have been developed to observe the sub-micron size materials. Though the principles of all the techniques are different, the one common thing is that they produce a highly magnified image of the surface or the bulk sample (Joshi et al 2008). This examination can yield information about the topography (surface features of the sample), morphology (shape and size of the particles making up the sample), composition (the elements and compounds that the sample is composed of and the relative amounts of them) and crystallographic information (how the atoms are arranged in the sample). Figure 1.16 shows the cross sectional view of optical microscope and scanning electron microscope.
1.10.5.2 Development of scanning electron microscopy

Max Knoll and Ernst Ruska began work on the development of electron lenses at the Technical University of Berlin, Germany, in 1928 (Stadtländer 2007). Knoll built a first “scanning microscope” in 1935. However, as he was not using demagnifying lenses to produce a fine probe, the resolution limit was around 100 µm because of the diameter of the focused beam on the specimen. In 1938, Von Ardenne clearly expressed the theoretical principles underlying the scanning microscope that it was difficult to compete with TEM in resolution achieved for thin samples. Thus, the scanning electron microscopy development was oriented more toward observing the surface of samples. The first SEM was described and developed in 1942 by Zworykin, who showed that secondary electrons provided topographic contrast by biasing the collector positively relative to the sample. One of his main improvements was using an electron multiplier tube as a preamplifier of the secondary electrons emission current. He reached a resolution of 50 nm. Many scientists and technologists quickly recognized the SEM ability to obtain information from the surfaces of bulk samples over a large range of length-scales.

In 1948, Oatley began to build a SEM based on Zworykin’s microscope. Following this development, in 1956, Smith disclosed that signal processing could be used to improve micrographs. He introduced nonlinear signal amplification, and improved the scanning system. Besides, he was also the first to insert a stigmator in the SEM to correct the cylindrical imperfections in the lens. In 1960, Everhart and Thornley improved the secondary electron detection. A new detector was created with a positively biased grid to collect electrons, a scintillator to convert them to light, and a light-pipe to transfer the light directly to a photomultiplier tube. In 1963, Pease and Nixon combined all of these improvements in one instrument with
three magnetic lenses and an Everhart–Thornley detector (ETD). This was the prototype for the first commercial SEM, developed in 1965 by the Cambridge Scientific Instruments Mark I “Stereoscan”. The SEM, that are being used today are not very different from this first instrument (Bogner et al 2007).

1.10.5.3 Interaction between electron beam and sample

When the beam of electrons strikes the surface of the sample and interacts with the atoms of the sample, signals in the form of secondary electrons, backscattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc. Figure 1.17 reveals the electron beam interactions with sample. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for a SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as Energy Dispersive X-ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample (Joshi et al 2008).

The SEM has a considerably better depth of field (DOF) than an optical microscope i.e. the ability to maintain sharp focus of detail as the specimen surface height changes. This facilitates the examination of the specimens that have a very irregular topography. If the DOF of an optical microscope is said to be 1, the DOF of the SEM is typically 300 times better. In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lenses, which deflect the beam horizontally and vertically. So that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect
and amplify the signals and display them as an image on a monitor in which the raster scanning is synchronized with that of the microscope.

Figure 1.17  Schematic diagrams of electron beam interactions with sample

The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the sample. SEM requires that the sample should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non conducting specimen may also be imaged uncoated using specialized SEM instrumentation such as the “Environmental SEM” (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage. FE-SEM produces clear, less electrostatically distorted images with spatial resolution down to 1.5 nm. This is 3 to 6 times better than conventional SEM due to reduced penetration of
low kinetic energy electrons probes closer to the immediate material surface. High quality, low voltage images are obtained with negligible electrical charging of samples using FE-SEM.

1.10.5.4 Field emission scanning electron microscopy (FE-SEM) instrumentation

Electrons are liberated from a field emission source and accelerated in a high electrical field gradient in FE-SEM. Within the high vacuum column, the primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object/sample. As a result, secondary electrons are emitted from each spot on the sample. The angle and velocity of these secondary electrons relate to the surface structure of the sample. A detector catches the secondary electrons and produces an electronic signal and then it is converted as an image. Figure 1.18 shows the schematic of FE-SEM.

Vacuum

The FESEM can be classified as a high vacuum instrument (less than 1x10^-7 Pa in the ions pumps). This vacuum allows electron movement along the column without scattering and helps to prevent discharges inside the instrument. The vacuum design is a function of the electron source due to its influence on the cathode emitter lifetime in FESEM.

Source of electrons

In standard electron microscopes, electrons are mostly generated by heating a tungsten filament by means of a current to a temperature of about 2800 °C. Sometimes, electrons are produced by a crystal of lanthanum hexaboride (LaB6) that is mounted on a tungsten filament. This modification
results in a higher electron density in the beam and a better resolution than the conventional device. In a field emission (FE) scanning electron microscope "cold" source is employed. An extremely thin and sharp tungsten needle (tip diameter $10^{-7}$-$10^{-8}$ m) functions as a cathode in front of a primary and secondary anode (Yao et al 2007).

The voltage between cathode and anode is in the order of a magnitude of 0.5 to 30 KV. As the electron beam produced by the FE source is about 1000 times smaller than in a standard SEM, the image quality is markedly better (Bogner et al 2007). As field emission necessitates an extreme vacuum ($10^{-8}$Torr) in the column of the microscope, a device is located inside the column to regularly decontaminate the electron source by a current flash.

In contrast to a conventional tungsten filament, a FE tip has large lifetime, provided the vacuum is maintained stable. Comparison of electrons sources at 20 kV by Goldstein et al (2003) is given in Table 1.2.

Table 1.2 Comparison of electron sources used in SEM/FE-SEM

<table>
<thead>
<tr>
<th>Source</th>
<th>Brightness(A/cm²)</th>
<th>Lifetime (h)</th>
<th>Virtual source size</th>
<th>Energy spread (eV)</th>
<th>Beam Current stability (%h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten Hairpin</td>
<td>$10^5$</td>
<td>40-100</td>
<td>30-100 µm</td>
<td>1-3</td>
<td>1</td>
</tr>
<tr>
<td>LaB₆</td>
<td>$10^6$</td>
<td>200-1000</td>
<td>5-50 µm</td>
<td>1-2</td>
<td>1</td>
</tr>
<tr>
<td>Cold field emission</td>
<td>$10^9$</td>
<td>&gt;1000</td>
<td>&lt;5nm</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>Thermal Field Emission</td>
<td>$10^8$</td>
<td>&gt;1000</td>
<td>&lt;5nm</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Schottky Field Emission</td>
<td>$10^8$</td>
<td>&gt;1000</td>
<td>15-30nm</td>
<td>0.3-1.0</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 1.18  Schematic diagram of Field Emission - Scanning Electron Microscope (FE-SEM)
Column with lenses and apertures

The electron beam is focused by the electro-magnetic lenses (condenser lens, scan coils, objective lens and stigmator coils) and the apertures in the column to a tiny sharp spot. The current in the condenser lens determines the diameter of the beam. A low current results in a small diameter whereas a higher current results in a larger beam. A narrow beam has the advantage of better resolution, but the disadvantage is that, the signal to noise ratio is worse. The situation is reversed when the beam has a large diameter.

The scan coils deflect the electron beam over the object according to a zig-zag pattern. The scan velocity determines the refreshing rate on the screen and the amount of noise in the image. Scan coils consist of upper and lower coils, which prevent the formation of a circular shadow at low magnification.

The objective lens is the lowest lens in the sample column. The objective lens focuses the electron beam on the object. At a short working distance, the objective lens needs to apply a greater force to deflect the electron beam. The shortest working distance produces the smallest beam diameter, the best resolution, but also the poorest depth of field.

The stigmator coils are utilized to correct irregularities in the x and y deflection of the beam and thus to obtain a perfectly round-shaped beam. When the beam is not circular, but ellipsoidal, the image looks blurred and stretched.

Sample chamber

The sample is mounted on a holder, and then it is inserted through an exchange chamber into the high vacuum part of the microscope and
anchored on a moveable stage. In the FESEM, the sample can be moved in horizontal and vertical directions on the screen by operating the arrows in the Position box. In the real microscope, the sample can be repositioned in the chamber by means of a joy stick that steers in left right axis, or forward and backward. In addition, the object can be tilted (e.g. for stereo views), rotated and moved in Z direction (closer or further away to the objective lens).

**Image formation**

When the primary electrons bombard the sample object, secondary electrons (SE) are excited from the top surface layer of the specimen (0 to 10 nm). They are defined as having an energy range from 0 to 50 eV, the majority of SEs having energy from 3 to 5 eV. The secondary electrons emitted at the point of impact of the beam and these electrons are dependent on the shape of the sample. These secondary electrons strike the scintillator (fluorescing mirror) that produces photons. The signal produced by the scintillator is amplified and transduced as a video signal that is in synchrony with the scan movement of the electron beam.

1.10.6 **Atomic Force Microscope**

The atomic force microscopy (AFM) is one of a family of scanning probe microscopes (SPMs) which has grown steadily since the invention of the scanning tunneling microscope by Binning and Rohrer in the early nineteen eighties. Among SPMs, the first to be invented was the Scanning Tunneling Microscope (STM). The STM measures the tunneling current between a sharp, conducting tip and a conducting sample. The STM can image the sample’s topography and also measure the electrical properties of the sample by the “tunneling current” between them. The STM technique, however, has a major disadvantage in that it cannot measure non-conducting material. This problem has been solved by the invention of the Atomic Force
Microscope (AFM) which may be used to measure almost any sample, regardless of its electrical properties. The AFM can easily take a measurement of conductive, non-conductive, and even some liquid samples without delicate sample preparation. This is a significant advantage over the extensive preparation techniques required for TEM or SEM. As a result, the AFM has greatly extended the SPM’s applicability to all branches of scientific research.

1.10.6.1 Principle of AFM

Instead of a conducting needle, the AFM uses a micro-machined cantilever with a sharp tip to measure the sample’s surface. Depending on the distance between the atoms at the tip of the cantilever and those at the sample’s surface, there exists either an attractive or repulsive force/interaction that may be utilized to measure the sample surface. AFM is typically used to measure a wide variety of samples, which have relatively small roughness. The force between the atoms at the sample’s surface and those at the cantilever’s tip can be detected by monitoring the cantilever deflection. This deflection of the cantilever can be quantified by the measurement of a laser beam that is reflected off the backside of the cantilever and onto the Position Sensitive Photo Detector (PSPD). The tube-shaped scanner located under the sample moves a sample in the horizontal direction (X-Y) and in the vertical direction (Z). It repetitively scans the sample line by line, while the PSPD signal is used to establish a feedback loop which controls the vertical movement of the scanner as the cantilever moves across the sample surface.

1.10.6.2 Primary components of atomic force microscopy instrument

The XE-100 AFM system consists of the sample stage with PSPD, cantilever, control electronics, microscope for locating the sample surface, XEP user interface Software, computer & monitor and an illuminator.
1.10.6.3 Cantilever

Cantilevers are generally made up of Silicon (Si) or Silicon Nitride (Si$_3$N$_4$) and are manufactured using macro-machining techniques. The cantilever is the part sensing the surface properties (for example, the topographic distribution, the physical solidity, electrical properties, magnetic properties, chemical properties, etc.) by detecting the degree of deflection due to the interaction with the sample surface, and it is very important component determining the sample resolution. Figure 1.19 shows the SEM image of the Silicon Cantilever.

![Figure 1.19 Scanning Electron Microscope image of the Silicon cantilever](image)

Compared to the Silicon Nitride cantilever, the Silicon cantilever has a curvature of the tip of less than 10nm, and is more commonly used. Moreover, in noncontact mode, which has a high resonant frequency, the rectangular shaped cantilever with a bigger Q-factor is used more than the V shape. The cantilever used in the XE-100 AFM system is rectangular shaped silicon cantilever, for use in both contact mode and non-contact mode. In addition, the upper surface of the cantilever (the opposite side of the tip) is coated very thinly with a metal such as gold (Au) or aluminum (Al) to enhance the high reflectivity of the laser beam. However, for Electrostatic
Force Microscopy (EFM) or Magnetic Force Microscopy (MFM), the whole cantilever and tip is coated to measure the electric or magnetic properties, there is no extra coating on the cantilever to enhance the high reflectivity. In AFM there are two important modes for analysing the semiconductor’s sample surface that are contact and non-contact modes.

1.10.6.4 Contact Mode AFM

As the distance between the atoms at the cantilever tip and the atoms on the surface of the sample becomes shorter, these two sets of atoms will interact with each other. When the distance between the tip and the surface atoms becomes very short, the interaction force is repulsive due to electrostatic repulsion, and when the distance gets relatively longer, the inter-atomic force becomes attractive due to the long-range van der Waals forces. This inter-atomic force between atoms can bend or deflect the cantilever, and the amount of the deflection will cause a change in the reflection angle of the beam that is bounced off the upper surface of the cantilever. This change in beam path will in turn be detected by the PSPD (Position Sensitive Photo Detector), thus enabling the computer to generate a map of the surface topography. Atomic force microscopy instrument used in the present study has been depicted in the Figure 1.20.

In contact mode AFM the probe makes “soft contact” with the sample surface, and the study of the sample’s topography is then conducted by utilizing the repulsive force that is exerted vertically between the sample and the probe tip. Even though the interatomic repulsive force in this case is very small, on the order of 1~10 nN, the spring constant of the cantilever is also sufficiently small (less than 1 N/m), thus allowing the cantilever to react very sensitively to very minute forces.
The AFM is able to detect even the slightest amount of a cantilever’s deflection as it moves across a sample surface. Therefore, when the cantilever scans a convex area of a sample, it will deflect upward, and when it scans a concave area, it will deflect downward. This probe deflection will be used as a feedback loop input that is sent to an actuator (Z-piezo). In order to produce an image of the surface topography, the Z-piezo will maintain the same cantilever deflection by keeping a constant distance between the probe and the sample – if the cantilever tip reaches a lower area, the Z actuator will move the cantilever down by that distance, or back up if the cantilever’s tip begins rising.

1.10.6.5 Non-contact Mode AFM

There are two major forces, the static electric repulsive force and attractive force, existing between atoms a short distance apart: The static
electric repulsive forces \( (F_{\text{ion}}) \) between ion cores and the static electric attractive forces \( (F_{el}) \) between valence electrons and ion cores. When the distance between the atoms at the end of the probe tip and the atoms on the sample surface becomes much shorter, the repulsive forces between them become dominant, and the force change due to the distance change becomes greater and greater. Therefore, contact AFM measures surface topography by utilizing the system’s sensitive response to the Repulsive Coulomb Interactions that exist between the ion cores when the distance between the probe tip and the sample surface atoms is very small. However, when the distance between the probe tip and the sample atoms is relatively large, the attractive force \( F_{el} \) becomes dominant. Ion cores become electric dipoles due to the valence electrons in the other atoms, and the force induced by the dipole-dipole interaction is the van der Waals Force. Non-contact AFM (NC-AFM) measures surface topography by utilizing this attractive atomic force in the relatively larger distance between the tip and a sample surface.

In Non-Contact mode, the force between the tip and the sample is very weak so that there is no unexpected change in the sample during the measurement. The tip will also have an extended lifetime because it is not abraded during the scanning process. On the other hand, the force between the tip and the sample in the non-contact regime is very low, and it is not possible to measure the deflection of the cantilever directly. So, Non-Contact AFM detects the changes in the phase or the vibration amplitude of the cantilever that are induced by the attractive force between the probe tip and the sample while the cantilever is mechanically oscillated near its resonant frequency. A cantilever used in Non-Contact AFM typically has a resonant frequency between 100 kHz and 400 kHz with vibration amplitude of a few nanometers. Non-Contact mode in the AFM is very useful for probing the epitaxial films, without damaging the surface. In this thesis the non-Contact mode of the
AFM has been used to access the surface morphology of the AlN films and the AlGaN/GaN-HS.

1.11 ION IRRADIATION EFFECTS

The study of ion irradiation effects in the semiconductors is mandatory for understanding the materials or devices characteristics, when it comes for utilization in the space application. The space radiation environment consists of different kinds of particles with energies ranging from keV to GeV and beyond. As they pass the solar system, most of them are trapped in the magnetic fields of the planetary system. Such trapped radiation fields around the earth are known as Van Allen belts.

The main sources of energetic particles radiation in the earth space that are of concern to spacecraft industries are: (i) Trapped radiation – charged particles as they pass through earth’s magnetic field and constitute the radiation belts with the protons, electrons and heavy ions. (ii) Cosmic radiation; they are the low flux, energetic and heavy ions from outer space with energies beyond TeV and include protons, nitrogen, oxygen, iron, etc. (iii) Solar flares – during the sudden bursts of the sun, huge quantities of energetic particles like protons, electrons, with small fluxes of alpha particles and heavy ions are ejected. Energies range to hundreds of MeV.

Infact, ion beam irradiation can play an important role in the study of defects related to semiconductors, as controlled amount of defects can be introduced by selecting suitable irradiation parameters. Defects like point or extended defects can also be selectively introduced by the proper choice of ion mass and energy of the irradiation ions.
When these particles impinge on the semiconductor, they enter into it, transfer energy to the semiconductor lattice and introduce defects. These defects can have a profound influence on the semiconductor properties and on the characteristics of devices fabricated on it, which may be either beneficial or deleterious, depending on the application. In order to avoid the deleterious effects of some of these particle-induced defects and utilize the beneficial effects of others, depending on the application, it is imperative to understand the effect of irradiation on electronic materials and devices fabricated on them. To achieve this, the structure, introduction rate, introduction mechanism and thermal stability of the defects could be determined, so that they can be reproducibly introduced, avoided or eliminated, depending on the application.

Ion beams after penetrating inside materials lose their kinetic energy through collisions with (1) nuclei, (2) bound electrons of the target atoms and (3) free electrons inside the target material. Ions penetrate some distance inside the material until they stop. In case of high energy ions, the ions slow down mainly by the electronic energy loss. In the beginning of the slowing down process, they move atoms in a straight path. When the ions are slowed down sufficiently, the collision with nuclei (the nuclear stopping) become more and more probable, and eventually ions are stopped by nuclear scattering. When atoms of the solid receive significant recoil energies, they are removed from their lattice positions and produce a cascade of further collisions in the material.

The calculation of penetration range requires the knowledge of the rate of energy loss of ions. According to the classical scattering theory, the interaction of the moving ions with the target atoms is described assuming two separate processes, collisions with nuclei and collision with electrons. The former is due to the coulomb repulsion between the ion and the target
nuclei. The nuclear stopping component is usually considered separately because the heavy recoiling target nucleus can be assumed to be unconnected from its lattice during the passage of the ion. The elastic recoil energy transferred to it can be treated simply as the elastic scattering to two heavily screened particles. Excitations or ionization of electrons are only a source of energy loss and do not influence the collision geometry. This is justified if the energy transferred to the electrons is small compared to the exchange of kinetic energy between the atoms, a condition usually fulfilled in ion implantation. The ion is thus deflected by nuclear encounters and continuously loses energy to the electrons.

1.11.1 Irradiation with Swift Heavy Ions (SHI)

High energy light ions are most suitable for defect engineering, because the point defects produced by these ions are almost uniformly distributed within deep inside the sample and the ions get implanted at a depth of more than 100 µm. This excludes the possibility of any interference from implanted ions in modifying the material properties. In some cases, the samples can be made thinner than the range of ions where the ions pass through the samples or samples may be grown on substrates such that the range of the ions is more than the film thickness. In contrary to the interaction of swift heavy ion (SHI) where electronic energy loss above threshold causes track formation, the damage accumulation by high energy light ions (HELI) is largely due to the nuclear energy loss (Kamarou et al 2005). The HELI irradiation produces point defects due to nuclear energy loss in the samples and can be estimated using Stopping Range of Ions in Matter (SRIM) calculation. Moreover, the electronic energy loss of HELI is very high compared to the nuclear energy loss but much less than the threshold energy for track formation, which can be uniquely utilized for defect engineering and material modification through ionization of native defects. During the slowing
down process, low energy ions lose energy through the nuclear energy loss process.

In the case of high energy ions, the electronic energy loss dominates over the nuclear energy loss. Heavy ions lead to extremely strong electronic excitations inside a narrow cylinder around each ion path. The initial interaction processes of the energy transfer from a high energy heavy ion to electrons bound to inner shells take only $10^{-19}$ to $10^{-17}$ s and slightly longer for collective electronic excitations like formation of plasmons (Schiwietz 2004). Hence, just after the passage of the SHI, the narrow cylindrical target zone coaxial with the ion path consists of two component plasma of cold lattice atom and hot electrons. Such a narrow region is often called ionization spike.

1.12 SCOPE OF THE THESIS

The present thesis deals with the epitaxial growth of AlN layer on sapphire substrate using Hydride Vapor Phase Epitaxy (HVPE) and Metal Organic Chemical Vapor Deposition (MOCVD) system. Detailed investigation of low temperature AlN nucleation layers and its effect on the quality of high temperature AlN layers grown by HVPE has been presented. The role of nucleation islands coalescence in determining the structural quality and surface morphology of MOCVD grown AlN layers has been studied. In addition to this, swift heavy ion (SHI) irradiation on the AlGaN/GaN heterostructures grown by MOCVD has been performed to study the modifications in structural and optical properties.