CHAPTER 1

GROWTH, PROPERTIES AND APPLICATIONS OF GROUP III NITRIDE SEMICONDUCTORS

1.1 WIDE BAND GAP SEMICONDUCTORS

Semiconductors are the foundations of modern technology and the basis for the entire information technology revolution. In particular, semiconductor lasers offer extraordinary capabilities in the development of the information technology. These lasers together with optical fibers are the most important components for high speed communication system.

Despite extensive applications of electronic devices from Si, GaAs, GaP and their alloys are intolerant for operating at high elevated temperatures and caustic environments (Nakayama et al 1993). The wide band gap semiconductors like SiC, ZnO and GaN with their excellent thermal conductivities, large break down voltages and resistance to chemical attacks are the materials of choice for such applications. Wurtzite GaN, AlN and InN have direct band gaps of 3.4, 6.2 and 0.7 eV at room temperature respectively (Jones et al 2006). In view of the available wide range of band gaps, when GaN is alloyed with AlN and InN, the III-nitrides alloy thus form a continuous range of direct band gap energies throughout much of the visible spectrum well into the ultraviolet (UV) wavelengths. This is one of the reasons for the research interest in GaN, AlN, InN and their ternary alloys for short wavelength optoelectronic applications. This leads to major developments in wide-gap III-nitride semiconductors to the commercial
production of high brightness light emitting diodes (LEDs) from green to near UV range. The area of applications of nitride-based LEDs is extremely wide, standard green to violet LEDs are currently used in traffic lights, full colour displays, automotive panel instrument, and other kind of lighting. UV LEDs came recently to the market, the main application being detection of bio particles, those for instance present in bacterial spores with absorption between 260 and 340 nm, air and water purification, medical treatment and diagnosis. UV detectors have a variety of civil and military applications and high temperature sensors are desirable under extreme conditions like jet engines. GaN is able to grow epitaxial layers with crystallographic qualities necessary for device fabrication. This chapter briefs about the crystal structure, growth aspects and applications of gallium nitride.

1.2 GALLIUM NITRIDE (GaN)

Gallium Nitride is the more extensively studied material among group III-nitrides mainly because of its wide band gap nature (3.4 eV) which makes it the best candidate for devices operating in the blue to UV region of the electromagnetic spectrum. GaN based nitride semiconductor devices have several advantages over other wide band gap semiconductors such as SiC and diamond. GaN has high chemical stability even at very high temperature and is suitable for caustic environments. High dielectric breakdown voltage, good thermal stability and electron transport properties make GaN an excellent candidate for electronic devices.

1.2.1 Crystal Structure of GaN

The chemical bond of group III elements with N is predominantly covalent, i.e. the constituents develop four tetrahedral bonds for each atom, because of the large difference in electronegativity of the two constituents, there is a significant ionic contribution to the bond, which determines the
stability of the respective phase, GaN is known to occur in the wurtzite as well as in zincblende crystal structure. Such polytypism is common in wide band gap semiconductors.

1.2.1.1 Wurtzite Structure

III-nitrides crystallize mainly in wurtzite structure, which is the thermodynamically stable structure at ambient conditions. The wurtzite structure has a hexagonal unit cell and thus two lattice constants, ‘a’ and ‘c’. It contains six atoms of each type. The space group for wurtzite structure is \( \text{P6}_3\text{mc} \) (\( \text{C}_{46v}^4 \)). This structure consists of two interpenetrating hexagonal close packed sub lattices, each with one type of atoms, offset along the c axis by \( 5/8 \) of the cell height \( (5/8 \text{ c}) \) and is shown in Figure 1.1 (a).

1.2.1.2 Zincblende Structure

The zincblende structure has a cubic unit cell, containing four group III atoms and four nitrogen atoms as shown in Figure 1.1 (b). The space group for this structure is \( \text{F}-4_3\text{m} \) (\( \text{T}^2_4 \)). The position of the atoms within the unit cell is identical to the diamond crystal structure. Both structures consist of two interpenetrating face centered cubic sublattices, offset by one quarter of the distance along a body diagonal. Each atom in the structure may be viewed as positioned at the center of a tetrahedron, with its four nearest neighbours defining the four corners of the tetrahedron.
1.2.2 Properties of GaN

Group III nitrides possess several remarkable physical properties that make them particularly attractive for reliable solid state device applications. The wide bandgap materials possess low dielectric constants with high thermal conductivity pathways. Group III nitrides exhibit fairly high bond strengths and very high melting temperatures. The large bond strengths could possibly inhibit dislocation motion and improve reliability in comparison to other II-VI and III-V materials. In addition, the nitrides are resistant to chemical etching and should allow GaN-based devices to be operated in harsh environments. These properties may lead to devices with superior reliability. The basic properties of gallium nitride are given in the Table 1.1 (Strite et al 1992)
Table 1.1 Properties of GaN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy bandgap (eV) (300K)</td>
<td>3.44</td>
</tr>
<tr>
<td>Electron mobility (cm² V⁻¹ s⁻¹) (300K)</td>
<td>1350</td>
</tr>
<tr>
<td>Hole mobility (cm² V⁻¹ s⁻¹) (300K)</td>
<td>13</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>&gt; 2573 at (60 kbar)</td>
</tr>
<tr>
<td>Lattice constants (300 K)</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.188</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.185</td>
</tr>
<tr>
<td>Thermal conductivity (W cm⁻¹ K⁻¹) (300 K)</td>
<td>2.1</td>
</tr>
<tr>
<td>Heat capacity (J mol⁻¹ K⁻¹) (300 K)</td>
<td>35.3</td>
</tr>
<tr>
<td>Hardness (Knoop,300K) (GPa)</td>
<td>10.8</td>
</tr>
</tbody>
</table>

1.3 GROWTH OF GROUP III-NITRIDES

1.3.1 Bulk Growth

The requirements for producing GaN thin films or bulk crystals include high growth temperatures, activated nitrogen species or high nitrogen background pressures necessary to overcome the large kinetic barriers of solid phase formation (Newman et al 1993). Figure 1.2 shows the systematic representation for the growth of bulk GaN growth. The high melting temperature of GaN and decomposition pressure at (~ 40 kbar) prevent the growth of bulk crystals from stoichiometric melts by conventional processes such as Czochralski or Bridgman methods. Initially, the growth of bulk GaN single crystals have met with limited success and crystal size in the order of few millimeters. Zetterstrom (1970) was able to increase the crystal size to 1-2 mm platelets by heating pre-synthesized GaN crystals in ammonia ambient at temperatures between 1423-1453 K. Karpinski et al (1984) have grown
bulk GaN single crystals using nitrogen pressure of 20 kbar at the temperature of 1873K which are the suitable conditions for GaN crystallization from the melt. Novel techniques have been used to grow relatively large single crystal of GaN at temperatures below the GaN melting point (Porowski et al 1997). Apart from the unusual high temperatures and pressures for bulk GaN crystal growth, the reason to move the heteroepitaxial thin film approach to obtain high quality single crystals.

![Diagram of nitrogen gas pressure apparatus for high-pressure vapour growth](image)

**Figure 1.2 Nitrogen gas pressure apparatus for the high-pressure vapour growth (synthesis solid diffusion SSD) of GaN**

### 1.3.2 Epitaxial Growth Technique

Epitaxial refers to the method of depositing a monocrystalline film on a monocrystalline substrate. The deposited film is denoted as epitaxial film or epitaxial layer. Epitaxial films may be grown from gaseous or liquid precursors. The substrate acts as a seed crystal and then the deposited film takes on the lattice structure and orientation identical to that of the substrate. This is different from other thin-film deposition methods which normally deposits either polycrystalline or amorphous films, even on single-crystal substrates. If a film is deposited on a substrate of the same composition, the process is called homoepitaxy. In homoepitaxy, a crystalline film is grown on a substrate or film of the same material. This technology is used to grow a film which is more pure than the substrate and to fabricate layers having different doping levels. In heteroepitaxy, a crystalline film grows on a
crystalline substrate or film of a different material. This technology is often used to grow crystalline films of materials for which single crystals cannot be obtained and to fabricate integrated crystalline layers of different materials.

1.3.2.1 Metal Organic Chemical Vapour Deposition (MOCVD)

MOCVD is a process for the deposition of a material that utilizes volatile metalorganic compounds to transport metallic atoms that are relatively nonvolatile at the convenient deposition temperature. Growth of GaN can be performed by introducing trimethyl gallium (TMGa) and ammonia (NH₃) simultaneously into the reaction chamber loaded with a substrate, such as sapphire, heated to elevated temperatures (usually 1073-1273 K).

\[
(CH_3)_3Ga_{(gas)} + NH_3_{(gas)} \rightarrow GaN_{(solid)} + 3CH_4_{(gas)}
\]

(1.1)

Ternary compounds such as AlGaN and InGaN can be obtained by combining TMAl or TMIn simultaneously with TMGa as described in equation (1.1). Adjusting the gas phase composition of the TMAl and TMGa or the TMIn and TMGa controls the solid composition. Schematic representation of MOCVD instrument is shown in Figure 1.3

![Schematic of MOCVD reactor for the growth of GaN](image)

Figure 1.3 Schematic of MOCVD reactor for the growth of GaN
The organometallics transported to the heated substrate by passing the carrier gas, usually H$_2$ or N$_2$, through the organometallic which is kept in a bubbler vessel at a controlled temperature to keep the compound melt. The growth temperature is the important parameter to decide the chemical reaction between the substrate and reaction zone.

1.3.2.2 Hydride Vapour Phase Epitaxy (HVPE)

HVPE, one of the techniques used for GaN growth offers high growth rate and produces bulk GaN films. It is a very attractive technique for production of high quality, large diameter and thick GaN layers (>200µm in thickness), which is eventually used as freestanding substrates. In a typical HVPE system designed for deposition, the precursors are gallium chloride (GaCl) and ammonia, while the carrier gas can be either nitrogen or hydrogen. In order to provide GaCl, pure HCl in gaseous mixture with H$_2$ is injected separately into the reactor and put in contact for a sufficiently long period with liquid gallium at temperatures around 1123 K. At this temperature, the acid reacts completely with Ga and gives GaCl along with a negligible amount of GaCl$_3$. At this point, GaCl and ammonia, still separated, are transported in the deposition zone of the reactor where the substrate is kept at temperature between 1273-1473 K. The schematic picture of the HVPE system is shown in the Figure 1.4. The type of chemical reaction which occurs in the HVPE growth is as follows,

$$\text{GaCl} + \text{NH}_3 \rightarrow \text{GaN} + \text{HCl} + \text{H}_2$$ (1.2)
From this reaction it is clear that, since one of the products of the reaction is $\text{H}_2$, the growth rate will be lower when hydrogen is used as carrier gas instead of nitrogen. The high growth rate is indeed one of the most important features of this technique, it is used for preparation of very thick layers, which can be employed as free-standing substrates for subsequent regrowth.

**1.3.2.3 Molecular Beam Epitaxy (MBE)**

Producing high quality layers with very abrupt interfaces and good control thickness, doping and different composition are likely with Molecular beam epitaxy technique. Molecular beam epitaxy takes place in high vacuum or ultra high vacuum ($10^{-8}$ Pa). The most important aspect of MBE is the slow deposition rate (typically less than 1000 nm per hour), which allows the films to grow epitaxially. The slow deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques. During operation, RHEED (Reflection High Energy Electron Diffraction) is often used for monitoring the growth of the crystal layers. A computer controls shutters in front of each furnace, allowing precise control of the thickness of each layer, down to a single layer of atoms.
Conventional MBE cannot be used in growing GaN, because \( \text{N}_2 \) cannot be dissociated by using conventional effusion cells. Plasma source (RF or electron cyclotron resonance plasma) can be used to activate \( \text{N}_2 \), where Ga vapour beam from an effusion cell and the activated nitrogen are directed toward heated substrate forming GaN film. In addition to Ga, MBE chamber can be equipped with Si and Mg cells for n-and p-type doping, In and Al for InGaN and AlGaN growth as well. Ammonia or hydrazine is another source of activated nitrogen that can be cracked into atomic nitrogen in high temperature cracking cell, hydrazine can be decomposed at lower temperature than ammonia but their extreme reactivity makes them dangerous to handle so that it cannot replace ammonia as a source for nitrogen. The schematic picture of the MBE system is shown in the Figure 1.5.

![Figure 1.5 Schematic of MBE reactor for the growth of GaN](image-url)
1.3.3 Novel Growth Techniques

1.3.3.1 Epitaxial Lateral Overgrowth (ELOG)

The epitaxial lateral overgrowth (ELOG) technique has proven to be a relevant process to decrease the dislocation densities from $10^{10}$ to less than $10^7$ cm$^{-2}$ in GaN layers grown on sapphire. Considerable attention has been focused on this technique as the blue laser diode realised using ELOG resulted in a lifetime of more than 10000 hours (Nakamura et al 1998). A typical design of an ELOG substrate consisting of patterned SiO$_2$ mask and window stripes is shown in Figure 1.6. To perform an ELOG, growth of a 0.2 mm GaN layer is performed on a (0001) sapphire wafer. A 0.1 µm thick SiO$_2$ layer mask is patterned to form 4 µm wide stripe windows separated by 7-8 µm wide SiO$_2$ stripes. A thick layer of GaN is grown on the mask. The epilayer first grows on pre-grown GaN through the windows. As the thickness of the epilayer increases, it grows laterally on the SiO$_2$ stripes. At about 10 µm thickness the GaN epilayers, which grow at the two edges of the SiO$_2$ stripes coalesce and a continuous flat GaN layer is formed on the patterned substrate (Jain et al 2000).

In ELOG GaN layer, alternate stripes have high and low dislocation density. Since the device is fabricated on the GaN stripes with low density of defects, the size of the device is limited by the width of these stripes. Also, the device fabrication requires careful alignment of the device structure with the underlying mask stripe. Therefore it is desirable to have a continuous large area layer with low density of defects.
Figure 1.6 Design of an ELOG substrate consisting of patterned SiO2 mask and window stripes.

1.4 SUBSTRATES

Single crystalline III-nitride films are being grown heteroepitaxially on a number of closely lattice-matched substrates. The lattice constant and thermal expansion coefficient of widely used substrate materials for III-nitride epitaxy is given in Table 1.2 (Liu et al 2002).

Table 1.2 Properties of prospective substrates for growth of III-nitrides

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>Symmetry</th>
<th>Lattice parameters (Å)</th>
<th>Coefficient of thermal expansion(10⁻⁶/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>Wurtzite GaN</td>
<td>Hexagonal</td>
<td>3.189</td>
<td>5.185</td>
</tr>
<tr>
<td>GaN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wurtzite AlN</td>
<td>Hexagonal</td>
<td>3.112</td>
<td>4.982</td>
</tr>
<tr>
<td>Hexagonal Al₂O₃</td>
<td>Hexagonal</td>
<td>4.758</td>
<td>12.991</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>5.4301</td>
<td>-</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>5.4533</td>
<td>-</td>
</tr>
<tr>
<td>6C-SiC</td>
<td>Hexagonal</td>
<td>3.08</td>
<td>15.12</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>Cubic</td>
<td>4.36</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>3.252</td>
<td>5.213</td>
</tr>
</tbody>
</table>
1.4.1 Sapphire (Al₂O₃)

Sapphire (0001) is the universally used substrate material for GaN growth and the first growth of GaN was established on sapphire substrate. The reasons behind the frequent use of sapphire substrate are: (a) low price, (b) availability of large area crystals of good quality, (c) high transparency, (d) high thermal stability and fairly matured growth technology. The lattice mismatch between sapphire and GaN is ~ 13%. Nitridation of the sapphire substrate prior to buffer layer growth provides the best quality GaN layer (Grandjean et al 1996, Keller et al 1996).

1.4.2 Silicon Carbide (SiC)

SiC is excellent substrate for GaN growth. It has a hexagonal structure (4H and 6H polytypes) with a low lattice mismatch (about 3%) and low thermal expansion coefficient mismatch to GaN. SiC is extremely stable even at high temperatures and has an excellent thermal conductivity, which is a very important property for high-power applications (Lin et al 1993, Kisielowski et al 1996). The main drawbacks are that SiC is very expensive compared to sapphire and obtaining clean surfaces of SiC prior to growth appears to be a major obstacle.

1.4.3 Zinc Oxide (ZnO)

ZnO is considered as a promising substrate for III-nitrides, since it has a close match for GaN c- and a-planes and close stacking order (Hamdani et al 1997, Detchprohm et al 1992). The lattice mismatch between ZnO and GaN is only about 2%. It is also necessary to chemically etch ZnO in order to obtain a smooth surface ready for the growth, but it is rather difficult. The etchant reported are not fully satisfying and the etched surface is not mirror-like. Also ZnO surface is not stable in a hydrogen or ammonia ambient.
1.4.4 Silicon (Si)

Si substrates are very attractive, not only because of the high quality, availability and low price, but also for the possibility of integration of Si based electronics with wide bandgap semiconductor devices. Si (100) and Si (111) substrates are employed for wurtzite GaN growth (Lei et al 1992, Kung et al 1995). Both wurtzite and zincblende phases are usually observed to be accompanied with a large number of dislocations, stacking faults and twins. Good quality epilayers are obtained upon the growth of AlN buffer layer on Si (111) substrate prior to GaN epitaxy.

1.4.5 Gallium Arsenide (GaAs)

GaAs (001) substrates are extensively used for both wurtzite and cubic GaN growth (Kuwano et al 1994, Menninger et al 1996, Yang et al 1996). GaAs substrate is not very stable at elevated temperatures. It has a lattice mismatch of about 20 % with cubic GaN. GaAs may be a good candidate for the growth of cubic GaN. Like sapphire, a low temperature GaN buffer layer growth (Kuznia et al 1994) and substrate surface nitridation process also improve the layer quality (Fujieda and Matsumoto 1991).

1.4.6 Effect of Buffer Layer

The large difference in lattice parameter and in thermal expansion rates between III-nitrides and substrate gives serious difficulties in the growth of high quality films for optoelectronic applications. The initial stages of growth are very important for obtaining a good quality heteroepitaxial film. The mode of growth is determined by several experimental parameters including the interfacial energy of solid and vapour phase and the growth temperature. The roughness of the nucleation layer is larger at higher growth temperatures (Hwang et al 1995). Therefore, a smooth thin buffer layer is
grown at a low temperature followed by the main layer growth at higher temperatures. The buffer layer grown at low temperature is amorphous in nature and is recrystallised at a higher temperature over a short duration.

The present GaN technology uses a very thin (in nm scale) GaN or AlN buffer layer grown at low temperature between the substrate and the main epitaxial layer (Yoshida et al 1983).

1.5 APPLICATIONS OF GALLIUM NITRIDE (GaN)

1.5.1 Light Emitting Diodes (LEDs)

The GaN based LEDs evolved from simple p-n junction devices comprising only GaN, to single quantum well (SQW) InGaN structures. The GaN p-n junction LED emission wavelengths were in the range of 370-390 nm, together with deep level emission at 550 nm. The great achievement as a result of high-brightness blue and green LEDs is the fabrication of white LEDs. There are two basic options. The first method would be colour mixing through integration of red, blue and green LEDs in the same package. The second is colour conversion through the use of a phosphor or organic dye inside the package to convert the blue light from a GaN LED into white light (Park et al 2003). The efficiency of this approach is less than that of the colour-mixing technique since the phosphor efficiency is less than 100%, but it has substantial savings in terms of cost.

Traffic lights using InGaN/AlGaN blue-green LEDs promise to save vast amounts of energy, since their electrical power consumption is only 12% of that of the present incandescent bulb traffic lights and have extremely long lifetime (>10^6 h). By combining high-power and high-brightness blue, green and red LEDs, many kinds of applications such as LED full-colour displays and LED white lamps are now possible with the benefits of high reliability and low energy consumption (Wierer et al 2004).
1.5.2 Laser Diodes (LDs)

Blue lasers with their shorter wavelength will permit higher recording densities of all media based on laser technology, including CD-ROM and magneto-optical (MO) disk drives (Yang et al 1999). There is also a large potential market in projection disk displays, where LDs with the three primary colours would replace the existing liquid crystal modulation system. The laser-based system would have advantages in terms of greater design simplicity, lower cost and broader colour coverage. The high output power of GaN based LDs and fast off/on times should also have advantages for improved printer technology with higher resolution than existing systems based on infrared lasers. In underwater military systems, GaN lasers may have applications for communications because of a transmission pass band in water between 450 and 550 nm.

1.5.3 Ultraviolet (UV) Detectors

The AlGaN system, spanning band gaps of 3.4 - 6.2 eV, is ideal for fabrication of solar-blind UV detectors (Munoz et al 2001). UV detectors have a variety of military and civil applications and high temperature sensors are desirable under extreme conditions like inside jet engines.

1.5.4 High-Power and High-Temperature Applications

There is an increasing interest in the use of compound semiconductors for several high power/high temperature solid state devices for applications in power electronics, control and distribution circuits. While silicon and to a much lesser extent GaAs have been used for power devices, emerging GaN and SiC have significant advantages because of wider bandgaps (higher operating temperature), larger breakdown voltages (higher operating voltage), higher electron saturated drift velocity (higher operating
current) and better thermal conductivity (higher power density). The basic building blocks of SiC and GaN power technology are gate-turn off thyristors (GTOs), insulated gate bipolar transistors (IGBTs) and metal oxide semiconductor controlled thyristors (MTOs) (Pearton et al 2002). Common high power electronic devices are also used in uninterruptible power supplies, advanced motors, adjustable speed drives and motor controls, switching power supplies, solid state circuit breakers and power conditioning equipment.

1.6 SCOPE OF THE PRESENT INVESTIGATION

In the last few years, GaN and related compounds have emerged as the key material for the applications in LEDs, LDs, UV detectors and high temperature high power electronic devices. There has been interest in the development of GaN based low noise circuit elements, particularly transistors with superior characteristics. The aim of the present investigation is to study some of the important issues associated with III nitrides processing such as material growth and characterization, effect of ammonia flow rate on (Cl-VPE) grown gallium nitride (GaN). High energy light ion (Lithium), high energy intermediate and heavy (Nickel and Gold) ions irradiation induced effects have been analyzed. Both ohmic and Schottky contacts on GaN have been realized and characterized.