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III-nitride Semiconductors Grown By Plasma Assisted Molecular Beam Epitaxy

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III-nitride Semiconductors Grown by Plasma Assisted Molecular Beam Epitaxy

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

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Abstract

III-NITRIDE SEMICONDUCTORS GROWN
BY PLASMA ASSISTED MOLECULAR BEAM EPITAXY

By Lei He, Ph. D.

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy at Virginia Commonwealth University.

Virginia Commonwealth University, 2004

Major Director: Hadis Morkoç, Ph. D.

III-nitride semiconductors are of great interest owing to their commercial and military applications due to their optoelectronic and mechanical properties. They have been synthesized successfully by many growth methods. Among them, molecular beam epitaxy (MBE) is a promising epitaxial growth method owing to precise control of growth parameters, which significantly affect the film properties, composition, and thickness. However, the understanding of growth mechanism of III-nitride materials grown in this growth regime is far from being complete.

In this dissertation, GaN and AlGaN growth mechanism under metal-rich conditions were investigated. The Ga surface desorption behavior during the growth was investigated systematically using reflection high-energy electron diffraction (RHEED). It
was found that desorption of Ga atoms from the (0001) GaN surfaces under different III-V ratios deviates from the zero\textsuperscript{th}-order kinetics in that the desorption rate is independent of the coverage of adsorbed atoms. The desorption energies of Ga are determined to be 2.76 eV with the Ga coverage closing to 100%, 1.89 eV for a \textasciitilde45\% coverage, and 0.82 eV for a 10\% coverage, as monitored by the change of the RHEED specular beam intensity during growth. In addition, the GaN surface morphology under different III-V ratios on porous templates matches the dependence of Ga desorption energy on the metal coverage, and III/V ratio dominates the growth mode. In a related AlGaN growth mechanism study, a competition between Al and Ga atoms to incorporate into the film was found under metal-rich conditions. Employing this mechanism, Al\textsubscript{x}Ga\textsubscript{1-x}N layers with precisely controlled Al mole fraction, \(x\) in the range 0<\(x\)<1 were obtained under metal-rich conditions. The energy band gap bowing parameter of these Al\textsubscript{x}Ga\textsubscript{1-x}N films was determined to be about 1 eV. The Al\textsubscript{x}Ga\textsubscript{1-x}N layers grown under metal-rich conditions, as compared to that under N-rich conditions, have a better structural and optical quality. Employing Al\textsubscript{x}Ga\textsubscript{1-x}N layers grown under metal-rich conditions, a lateral geometry GaN/AlGaN MQW-based photodetector was fabricated. It exhibited a flat and narrow spectral response in the range of 297~352 nm in the backillumination configuration.
Chapter 1 Introduction

1.1 Motivation

Molecular beam epitaxy (MBE) is a growth method that has enabled the realization of the most advanced semiconductor materials during the last three decades.\textsuperscript{1} Since it allows precise control of beam fluxes and growth conditions, it is widely used to fabricate heterostructure devices where high purity and precise control of layer thickness and composition are required.\textsuperscript{2} The enormous progress in the control of growth parameters afforded by MBE, particularly applied to the growth of III-arsenide semiconductors, has transformed MBE from a sophisticated research tool into a method of commercial production of advanced semiconductor materials. The production of high frequency electronic components (MESFETs, MODFETs, MMICs), as well as optoelectronic devices such as laser diodes, has been realized.\textsuperscript{3,4} Significant progress has also been made to overcome the initial difficulties in the MBE growth of III-phosphides by developing valved phosphorous cracker cells.\textsuperscript{5} The III-nitride semiconductors have recently demonstrated high-power and low-noise microwave performance exceeding that of more mature III-arsenide and III-phosphide technologies. The rapid development of III-nitride materials and devices has attracted the attention of the majority of the compound (III-V or II-VI) semiconductor research community\textsuperscript{6}. 
GaN, AlN, InN, BN and their alloys represent the family of III-nitride semiconductors, where their attractive attributes determine such properties as carrier and light confinement and sheet carrier density at heterointerfaces. A thorough understanding of their growth mechanism is a key issue for further improvement of material quality. So far, extensive studies of material and device properties, in particular for growth by plasma assisted molecular beam epitaxy (PAMBE) on the Ga-polar (0001) surface, have been carried out. However, the large amount of work on epitaxy of GaN or GaN-based alloys for device applications is contrasted by relatively few studies on the physical mechanisms of growth itself. Therefore, a study on the growth mechanism is imperative to obtain high quality III-nitride semiconductor epilayers using PAMBE.

1.2 Objectives

The investigation of surface processes taking place during growth is very important for growth mechanism studies since MBE growth is carried out under conditions that are governed primarily by surface kinetics. Recently, growth studies with MBE indicated that the growth mechanism and the resulting surface structure of III-nitride semiconductor thin films are crucially sensitive to the kinetics, i.e., III-V ratio and growth temperature. Particularly, in PAMBE desirable two-dimensional growth is commonly attained under metal-rich conditions or near metal-rich conditions, suggesting that such growth is stabilized by a metallic adlayer. The diffusion and desorption energies of Ga under these conditions have been studied. However, the reported results are not consistent, and the results suggest that the underlying physics of the III-nitride semiconductors growth diagram is more complex and not yet fully understood. In this
dissertation, the growth mechanism of GaN will be investigated, and the desorption energy of Ga on (0001) surface under Ga-rich conditions during PAMBE growth will be studied using reflection high-energy electron diffraction (RHEED). The growth modes of GaN under different growth conditions will be studied, as well as the growth of Al$_x$Ga$_{1-x}$N epilayers. The method to obtain high quality Al$_x$Ga$_{1-x}$N epilayers with precisely controlled Al mole fractions in a wide range of Al compositions will be presented.

1.3 Literature Review

1.3.1 Introduction to III-nitride semiconductors

III-nitride semiconductors have a wurtzite crystal structure and a direct wide energy band gap. The band gap values are 0.7–1.9 eV for InN (still a subject of sizeable controversy), 3.4 eV for GaN, and 6.1 eV for AlN. Additionally, InN and AlN can be alloyed with GaN to form alloys. These alloys allow tuning of the band gap and emission wavelength. Benefited by these properties, III-nitrides have been widely used for violet, blue and green light emitting devices and for high power/high temperature transistors. Doping of the III-nitrides with both donors and acceptors has been accomplished. The III-nitrides have good thermal conductivity and stability. The fact that III-nitrides can withstand higher temperatures makes device processing easier. Additionally, they have high breakdown fields, which is necessary for high power devices. Owing to these advantages, III-nitride semiconductors are important materials for optical, electronic, and high temperature/high power electronic devices.
1.3.2 History of III-nitride semiconductors

III-nitride semiconductors have been studied for more than a half century. In 1928, Tiede et al.\textsuperscript{17} first reported AlN growth. Following that, Johnson et al.\textsuperscript{18} in 1932 reported the synthesis of GaN by passing ammonia over hot gallium. The synthesis of InN was reported by Juza and Hahn\textsuperscript{19} in 1938. Some three decades later, what appeared to be the harbinger of extensive work began in III-nitride semiconductors.\textsuperscript{20 - 23} However, the lack of p-type conductivity coupled with somewhat poor crystalline quality did not bode well. With the attainment of p-type conductivity in late 1980s, a flurry of activity began in earnest. Since then, nearly every crystal-growth technique has been used in an effort to grow high-quality III-nitride semiconductors. In recent years, various researchers have successfully taken advantage of hydride vapor phase epitaxy (HVPE), Metal Organic Vapor Phase Epitaxy (MOVPE) and MBE techniques, which have yielded greatly improved film quality.

1.3.3 Recent study on Ga desorption energy from GaN surface in MBE

MBE has been widely used for the fabrication of III-nitride based heterostructure devices. So far, light-emitting diodes,\textsuperscript{24, 25} laser diodes,\textsuperscript{26, 27} UV photodetectors\textsuperscript{28} and heterojunction field effect transistors\textsuperscript{29, 30} have been produced using GaN benefited from the capabilities of MBE. Relatively comprehensive studies of material and device properties have been performed concerning surface structures, in particular for growth by plasma assisted MBE.\textsuperscript{7, 8} However, the extensive work on GaN epitaxy for device applications still contrasts relatively few studies concerned with the physics of the growth itself. Only recently, growth studies with MBE indicated that the growth mechanisms and
the resulting surface structures of GaN thin films are crucially sensitive to the kinetics, i.e., Ga/N flux ratio and growth temperature. It is reported that two-dimensional growth, which is desirable for device fabrication, is commonly attained under Ga-rich conditions or near Ga-rich conditions. This result suggests that GaN growth is stabilized by a metallic Ga adlayer.\textsuperscript{10, 11}

Studies on the Ga desorption process have been carried out with mass spectrometry\textsuperscript{31, 16} and Reflection High Energy Electron Diffraction (RHEED)\textsuperscript{12, 14, 15} techniques, however the results are not consistent. A wide range of activation energies is reported for Ga desorption spans values from 0.4 to 5.1 eV\textsuperscript{12 - 16}, while the reported value for GaN decomposition is approximately 3.6 eV.\textsuperscript{32} Ga desorption energies in the absence of an active nitrogen flux have been reported to be 2.05, 3.7, 3.1 and 2.2 eV for Al\textsubscript{2}O\textsubscript{3} (0001)\textsuperscript{33}, 6H-SiC (0001)\textsuperscript{15}, GaAs\textsuperscript{34}, and GaN (0001) surfaces\textsuperscript{31}, respectively. These differences in the Ga desorption energies have been attributed to different Ga bond energies with different substrate atoms. Jones \textit{et al.}\textsuperscript{35} reported that the Ga desorption energy from GaN (0001) surfaces in the presence of NH\textsubscript{3} is 1.4 eV or 0.4 eV, depending on the substrate temperature. This suggests that the growth environment conditions modify the desorption energy, as is confirmed by the dependence of the desorption energy on the III/V ratio.\textsuperscript{14} To our knowledge, however, there has been no systematic study of Ga desorption energy as a function of the Ga surface coverage.

1.3.4 Recent studies of AlGaN growth

Owing to its tunable gap, the Al\textsubscript{x}Ga\textsubscript{1-x}N alloy is of interest for optoelectronic devices.\textsuperscript{36} The direct band gap of this material lies in a typical range of 3.42 (x = 0) to 6.1
eV ($x = 1$) at $T = 300$ K. Devices that employ Al$_x$Ga$_{1-x}$N layers include heterojunction field effect transistors, light-emitting diodes, laser diodes, and photodetectors operating in the UV spectral region between 200 and 365 nm. In all of these devices, the Al$_x$Ga$_{1-x}$N alloy constitutes a pivotal component and determines such properties as the carrier and light confinement, and sheet carrier density at heterointerfaces. With the recent advent of short wavelength sources and detectors, Al$_x$Ga$_{1-x}$N is also being used as an active emission and absorption medium. Though a number of these devices have been reported, there are still serious issues to be addressed. Among them is the control of mole fraction and deteriorating radiative recombination efficiency with increasing Al content. The influence of growth conditions on the Al mole fraction and film quality was studied in the case of MOVPE. There are only a few studies for MBE growth, which include nitrogen sources such as electron cyclotron resonance-microwave plasma and ammonia.

Al$_x$Ga$_{1-x}$N layers grown by PAMBE were traditionally obtained under N-rich conditions. In that case, the Al mole fraction $x$ of Al$_x$Ga$_{1-x}$N films is simply determined by the fluxes of Ga and Al. The mole fraction was controlled by the: 1) Al flux, 2) Ga flux, 3) both Ga and Al fluxes with fixed Al/Ga ratio, and 4) Al/Ga ratio with fixed total flux. As for GaN, Ga-rich growth conditions are preferred to obtain high quality films. However, the growth of Al$_x$Ga$_{1-x}$N under Ga-rich conditions by PAMBE received little attention since the precise control of the Al mole fraction $x$ is difficult. This indicates that the interaction between Ga and Al in nitride growth is complex and more work is needed in this area.
1.4 Organization of the thesis

This dissertation includes the following seven chapters:

Chapter 1: Introduction
Chapter 2: Surface processes
Chapter 3: Growth by MBE
Chapter 4: Characterization methods
Chapter 5: Investigation of growth mechanism of GaN by RHEED
Chapter 6: Investigation of growth mechanism of Al\textsubscript{x}Ga\textsubscript{1-x}N (x=0–1)
Chapter 7: Summary

The current chapter starts with a motivation of the dissertation and is followed by a literature review of III-nitride semiconductors.

A theoretical discussion on how the surface processes in MBE system affect the growth will be given in Chapter 2. The principles of adsorption, desorption, surface diffusion, incorporation, and decomposition processes will be discussed with GaN as the example. In chapter 3, the basics of MBE growth will be introduced and a detailed description of a PAMBE system will be given. This is followed by a discussion of the preparation of sapphire substrates. Subsequently, chapter 4 will present characterization methods used in this dissertation on III-nitride semiconductors. The principles and applications of RHEED, XRD, AFM and PL will be discussed.

Chapter 5 will describe an investigation of the GaN growth mechanism. The desorption energy of Ga on the GaN (0001) surface during growth under Ga-rich conditions will be derived experimentally by monitoring the intensity of the RHEED
specular beam. The results will be discussed based on theoretic calculations. Different growth modes under different growth conditions will also be presented.

The growth mode of Al$_x$Ga$_{1-x}$N epilayers under metal-rich conditions will be discussed in Chapter 6. Al$_x$Ga$_{1-x}$N epilayers with precisely controlled Al mole fraction are achieved in a wide range of Al compositions (0.13 - 0.92). The properties of these epilayers are evaluated by X-ray diffraction (XRD) and photoluminescence (PL).

Finally, Chapter 7 will summarize the key contributions of this dissertation.
Chapter 2 Surface processes

In the MBE technique, thin films are formed on a heated substrate through various reactions between thermal molecular beams of the constituent elements and the surface species on the substrate.\textsuperscript{44} The composition of the epilayer and its doping level depend on the arrival rates of the constituent elements and dopants.\textsuperscript{45} Therefore, MBE growth is carried out under conditions that are governed primarily by kinetics, rather than mass transfer.\textsuperscript{46} A thorough understanding of the growth kinetics, especially the surface processes of growth, is a key issue for further improvement of material quality. A series of surface processes takes place during the growth which are schematically illustrated in Figure 2-1. The most important processes are:

1. **Adsorption**: atomic or molecular species impinge on the substrate surface and “stick” by overcoming the activation barrier.

2. **Desorption**: species not incorporated into the crystal lattice leave the substrate by thermal re-evaporation.

3. **Surface diffusion**: species diffuse on the substrate surface to find low energy crystal sites.

4. **Incorporation**: species bond to the substrate or epilayer by attaching to a dangling bond, vacancy, step edge, \textit{etc.}
5. **Decomposition**: atoms in the crystal lattice leave the surface after breaking their bond.

These surface processes during MBE growth are of principal importance, as they define the primary pathways of composition, point-defect concentration and growth-rate control. They play an important role in optimizing growth parameters so as to obtain high-quality structures with planar or periodically modulated interfaces. In this chapter, the principles of adsorption, desorption, surface diffusion, incorporation and decomposition will be discussed using the GaN system as an example.

2.1 Adsorption

2.1.1 Principle of adsorption

When an adsorbing gas impinges on a uniform solid surface, the gas molecules (atoms) will condense from the vapor phase onto the surface. Depending on the strength of the interaction between an adsorbate and the surface, adsorption is subdivided by convention into 1) physisorption (weak interaction) or 2) chemisorption (strong interaction). Physisorption refers to the weakest adsorbate-surface interaction due to van der Waals forces, where typical binding energies are on the order of 10-100 meV. As the interaction is weak, the physisorbed atoms or molecules do not disturb the structural environment near the adsorption sites to any significant extent. Chemisorption corresponds to the phenomenon in which an adsorbate forms strong chemical bonds with substrate atoms, with typical binding energies of 1-10 eV. The strong interaction changes the adsorbate chemical state. In both physisorption and chemisorption, the adsorbate coverage characterizes the surface concentration of adsorbed species expressed in
monolayer units. The coverage is a relative value associated with a given substrate, but it can be converted to an absolute surface density of atoms.

Considering the kinetic approach for the case of a uniform solid surface exposed to an adsorbing gas, the adsorption rate is defined as

\[ r_a = \sigma f(\Theta) \exp\left(-\frac{E_{\text{act}}}{k_B T_s}\right) \frac{P}{\sqrt{2\pi mk_B T_s}} \]  

(2-1)

In the above equation, \( P \) is the partial pressure of the adsorbing gas. The term \( \sigma \), which is called the condensation coefficient, is responsible for the effects of the orientation and the energy accommodation of the adsorbed molecules. \( f(\Theta) \) is a coverage dependent function which describes the probability of finding an adsorption site. The temperature-dependent Boltzmann term, \( \exp(-E_{\text{act}}/k_B T) \), is associated with the energy of the activated adsorption, where \( k_B \) is the Boltzman constant.

### 2.1.2 Ga adsorption on the surface

The finite equilibrium Ga adlayer coverage has been reported for substrate temperatures and Ga fluxes typically used in molecular-beam epitaxy of GaN.\(^\text{13}\) For large Ga fluxes, up to 2.5 ± 0.2 monolayers of Ga, which is composed by excess Ga adatoms, are adsorbed on the GaN surface. For lower Ga fluxes, a discontinuous transition to the equilibrium coverage is found, followed by a continuous decrease towards zero coverage. For higher Ga fluxes, Ga droplet formation is reported.\(^\text{31}\) Zheng \textit{et al.}\(^\text{15}\) also reported excess Ga adatoms form 2D monolayers first while a transition from 2D to 3D happens with more excess Ga. The adsorption of Ga from excess Ga is 2.4 eV. At the typical growth temperature used in MBE (650 ~ 800 °C), the Ga adlayer does not form a
reconstruction, but rather represents a liquid-like film. Scanning tunneling microscopy (STM) measurements showed that the height of the Ga adlayer is about 3.88 Å (or 1.9 ML) above the GaN surface bilayer. This adlayer is metallic as the tunneling is stable even when the bias voltage is less than 0.2 V.

2.2 Desorption

2.2.1 Principle of desorption

The process in which an adsorbate species gains sufficient energy from thermal vibrations to escape from the adsorption well and leave the surface is called thermal desorption. The desorption probability depends on how strongly the atom is bonded to the substrate surface. The strength of the bond depends on the type of atom and the local geometry of the surface. In the kinetic approach, desorption is described in terms of a desorption rate, $r_{des}$, which is the number of particles desorbing from a unit surface area per unit time. In the most general form, the desorption rate can be written as

$$r_{des} = \sigma^* f^*(\Theta) \exp(-E_{des}/k_B T_s)$$  \hspace{1cm} (2-2)

where $f^*(\Theta)$ describes the coverage dependence and $\sigma^*$ is the desorption coefficient representing steric and surface mobility factors. In order to leave the surface, the adsorption species must overcome the barrier for desorption or the desorption energy $E_{des}$.

The procedure for measuring the lifetime of an adsorbate as a function of the substrate temperature is usually carried out for studying the desorption energy. The lifetime $\tau$ is defined as the average time spent by the adsorbate on the surface from the time of adsorption to the time of desorption, and it obeys the Arrhenius law:
\[ \tau = \tau_0 \exp\left(\frac{E_{des}}{k_B T_s}\right) \]  

(2-3)

where \( \tau_0 \) is a constant. According to Equation 2-2 and 2-3, the desorption process is very sensitive to changes in the substrate temperature. When \( T_s \) is very low, the lifetime of the adsorbate is long enough to allow for the desorption process to be neglected. However, when \( T_s \) is high enough and the desorption rate is larger than the deposition rate, the interface does not grow but rather evaporates.

### 2.2.2 Ga and N desorption from the surface

Ga desorption processes have been carried out previously by mass spectrometry\textsuperscript{31,16} and RHEED\textsuperscript{12,15} techniques, however, the results are not consistent. Activation energies reported for Ga desorption range from 0.4 eV to 5.1 eV\textsuperscript{12,16,31,15} For N, which usually desorbs as a dimer (N\(_2\)), the desorption rate is limited by the surface diffusion of two N atoms. Some reports indicate that N desorption is a 1\(^{st}\) order process.\textsuperscript{50} This indicates that surface diffusion may play less of a role in the desorption mechanism than the surface structure. Another plausible mechanism is that once a N atom diffuses near another N, the N\(_2\) molecule immediately forms, due in part to the large N-N binding energy, and desorbs from the surface because of the highly exothermic nature of the N\(_2\) formation.\textsuperscript{52}

### 2.3 Surface diffusion

#### 2.3.1 Principles of surface diffusion

Surface diffusion describes the motion of adsorbates (atoms or molecules) over the surface of a solid substrate. In most cases, an adsorbate becomes mobile due to thermal activation and its motion is described as a random walk. In the presence of a
concentration gradient, this random walk motion of many particles results in their net diffusion opposite to the gradient direction. From the microscopic point of view, surface diffusion is an activated process, although it is also affected by many factors, such as interaction between diffusing adsorbates, formation of surface phases, presence of defects, etc. For an atom on the surface to diffuse to the next lattice position, it must overcome the lattice potential existing between two neighboring positions. This activation energy required for diffusion, \( E_0 \), is the microscopic origin of the lattice potential.

The average length of diffusion, \( \lambda_s \), in a unit time interval is a very important parameter to characterize the diffusion process and it has an exponential temperature dependence, given by the Einstein equation:\(^{47}\)

\[
\lambda_s = (D_s \tau_s)^{1/2} = (D_{s0} \exp(-\frac{E_D}{k_B T_s}) \tau_s)^{1/2}
\]

(2-4)

where \( D_s \) is the diffusion coefficient, \( \tau_s \) is the lifetime of the diffusion event, \( D_{s0} \) is the temperature independent diffusion coefficient, and \( E_D \) is the diffusion activation energy. At high growth temperatures where the surface diffusion length is larger than the terrace width, atoms move by surface diffusion from the terrace to the step edge to be incorporated into the growing lattice, which is called step flow growth. As the diffusion length decreases, e.g. by reduced temperature, atoms meet and nucleate new islands on the terraces before reaching the edge of an existing island or a step edge. Moreover, islands can nucleate on top of existing islands, a process which leads to rough surface formation and three-dimensional growth.
2.3.2 Ga and N surface diffusion

The diffusivity for Ga and N adatoms on the GaN surface is different. Tosja Zywietz et al.\textsuperscript{50} calculated the potential energy surface for Ga and N adatoms on the GaN (0001) surface, giving immediate insight into stable sites, migration paths, and diffusion barriers. They found that there are two transition sites existing on GaN (0001), as shown in Figure 2-2. For Ga diffusion, the lower energy transition site is the bridge position (0.4 eV), and the higher energy site is the “on-top” position (>3 eV). However, for N adatoms the barrier for bridge diffusion is 1.4 eV, while the barrier for the on-top position is similar to Ga. The significantly lower diffusion barrier for Ga relative to N results in Ga being very mobile at typical growth temperatures, while the diffusion of N is slower by orders of magnitude. It was also reported that the presence of excess N strongly increases the Ga diffusion barrier from 0.4 to 1.8 eV.

The very different mobilities of Ga and N adatoms have important consequences for the growth of GaN. In the Ga-rich regime, the Ga adatoms are highly mobile and a step-flow mode results in 2D growth. Furthermore, if excess Ga adatoms are present on the surface, N adatoms can be efficiently incorporated since the probability that fast moving Ga adatoms capture N atoms is high. However, N-rich growth conditions show roughly a five times higher diffusion barrier for Ga. A rough surface can therefore be expected for N-rich conditions.

2.4 Incorporation

2.4.1 Principles of incorporation

Incorporation is a process where molecules or atoms bond to the crystal through
various reactions between the constituent elements and the surface species on the substrate. This process is controlled by the interplay of thermodynamics and kinetics. The general trends in film growth are understood within the thermodynamic approach in terms of the relative surface and interface energies. However, film growth by MBE is a non-equilibrium kinetic process in which rate-limiting steps affect the growth mode.\textsuperscript{46} Three principal modes of film growth are generally distinguished, as shown in Figure 2-3. These modes are named after their original investigators as follows:\textsuperscript{51}

- Frank-van der Merve (FM) growth mode shown in Figure 2-3(1) is a layer-by-layer growth mode. Each layer is fully completed before the next layer starts to grow, and it is a strictly two-dimensional growth mode.
- Volmer-Weber (VW) growth mode shown in Figure 2-3-(2) is an island growth mode. In this case, three-dimensional islands nucleate and grow directly on the substrate surface which is typically seen in metals unless very low – even below room temperature – deposition conditions are employed.
- Stranski-Krastanov (SK) growth mode shown in Figure 2-3(3) is a layer-plus-island growth mode and represents the intermediate case between the FM and VW growth modes. After the formation of a complete two-dimensional layer of a few monolayer thickness (the exact value of which depends of the local strain), the growth of a three-dimensional layer (islands) takes place.

The occurrence of different growth modes can be understood in terms of the competition between surface desorption and surface diffusion which is discussed in Sec. 2.3.1. Since the desorption and diffusion processes are strongly affected by the deposition rate,
surface condition and temperature, the growth mode and surface of epilayer can be controlled by choosing proper a III/V ratio and a substrate temperature.

2.4.2 Ga and N incorporation

Several studies\textsuperscript{52,53} have revealed that incident Ga atoms are not fully incorporated into the growing GaN at the usual growth temperature in PAMBE (650 ~ 750 °C), even when an excess of N-flux is present (III/V flux ratio < 1). Guha et al.\textsuperscript{31} studied the incorporation ratio of Ga during GaN growth by monitoring the reflected Ga signals detected by the mass spectrometer, and found that the Ga incorporation rate sensitively depended on the growth temperature. At low growth temperatures, the lifetime of Ga adatoms is sufficiently long that almost all Ga atoms encounter N adatoms and are incorporated into the crystal, resulting in a near unity incorporation ratio. As the growth temperature increases, the residence time of a Ga adatom on the surface decreases. Thus, the probability for encountering N adatoms decreases and the incorporation ratio drops.

2.5 Decomposition

2.5.1 Principles of decomposition

In decomposition reactions one compound splits apart into two (or more pieces) by breaking the bond between them. The III-nitrides have chemical bonds with the Ga-N bond strength estimated near 2.2 eV.\textsuperscript{54} In addition, III-nitride bonds are more ionic (31 - 40\%) in nature (excluding BN) than other III-V semiconductors (<8\%).\textsuperscript{55} As in the case of other III-V semiconductors, the heat of formation of GaN is small and similar to InP and AlAs, indicating that GaN easily decomposes.\textsuperscript{2}
2.5.2 Thermal decomposition of GaN

GaN does not melt congruently at pressures typically used in MBE growth, but instead decomposes above 800 °C at atmospheric pressure and at lower temperatures in vacuum. Guha et al.\textsuperscript{31} reported a decomposition rate of 3 ~ 4 monolayer per min at 830 °C. Grandjean et al.\textsuperscript{32} found that the decomposition rate is nearly zero below 750 °C, increases rapidly above 800 °C, and reaches 1 µm/h at 850 °C. This means that it may be impossible to grow GaN at high temperatures and that the growth temperature should be kept below ~800°C. Several different mechanisms have been proposed to explain GaN decomposition. These include decomposition into gaseous Ga and nitrogen, liquid Ga and nitrogen, and sublimation of GaN as a diatomic or polymeric product. The GaN decomposition rate is similar in vacuum and at MOCVD pressures.

2.6 Discussion

The conventional III-V semiconductors are grown under conditions (substrate temperature and system pressure) where the III-V compounds and a vapor are thermodynamically stable. For high quality compound semiconductor growth, the optimum substrate temperatures used are in the range of ~1/2 to 2/3 of the melting temperature of the semiconductor. In the case of III-nitrides, however, synthesis occurs, particularly with MBE, at temperatures significantly below ~1/2 of the theoretically predicted melting temperature. In the case of GaN, the substrate temperature during MBE growth is about ~20 to 35% (600 ~ 900 °C) of the GaN melting temperature (T\textsubscript{m} ~ 2500°C). Thus, GaN growth takes place under kinetic conditions and the surface processes are pivotal toward obtaining high quality III-nitride semiconductors.
The synthesis of GaN involves a metastable growth process which is controlled by a competition between the forward reaction (Ga and N incorporate into the film and GaN epilayer forms) and the reverse reaction (GaN decomposition). The forward reaction depends on the arrival of Ga atoms and activated nitrogen species on the surface, as well as the substrate temperature, while the reverse reaction is strongly affected only by the substrate temperature. In order for net growth to take place, the rate of GaN formation must be larger than the rate of decomposition.

Three additional effects determining the final interface morphology of a growing interface include: deposition, desorption and surface diffusion. Their relative importance depends on the microscopic properties of the interface, the bonding energies, and diffusion barriers. The experimentally controllable parameters are the III-V ratio and substrate temperature. By tuning these parameters a variety of morphologies can be achieved, ranging from layer-by-layer growth with an essentially smooth interface to a rough self-affined surface.
Figure 2-1  Surface processes during MBE growth: Adsorption, desorption, surface diffusion, lattice incorporation and decomposition.\textsuperscript{46}
Figure 2-2  Schematic diagram of diffusion paths on the GaN (0001) surface.\textsuperscript{50}
Figure 2-3  Illustration of three distinct growth modes, a) Frank-van der Merwe, b) Volmer-Weber and c) Stranski-Krastanov growth. 47
Chapter 3 Growth by MBE

The experiments in this dissertation were conducted in an SVT molecular beam epitaxy (MBE) system. In this chapter, the salient features of a typical MBE system will be first reviewed in Sec. 3.1, which includes an introduction to the MBE vacuum chamber, the effusion cells, and the radio frequency plasma nitrogen source. A brief description of the preparation of sapphire substrates used for nitride epitaxy in this dissertation will then be given in Sec. 3.2.

3.1 MBE system

MBE is a promising method for synthesizing thin epitaxial materials and heterostructure device structures where high purity and precise control of layer thickness and components are required. This results from the precise control of beam fluxes and growth conditions during MBE. The term “molecular beam” as used in MBE is somewhat of a misnomer since the species in the beams may be either atoms or molecules. During growth in an MBE system, thin films crystallize by means of reactions between thermal-energy molecular or atomic beams of the constituent elements and a substrate surface which is maintained at an elevated temperature in ultrahigh vacuum. The composition of the grown epilayer and its doping level are related to the relative arrival rates of the constituent elements and dopants, which in turn depend on the evaporation rates of the appropriate sources. Since MBE is performed in an ultrahigh
vacuum environment, growth can be controlled in situ by surface sensitive diagnostic methods such as reflection high-energy electron diffraction (RHEED), residual gas analysis (RGA), and/or Auger electron spectroscopy (AES).

3.1.1 MBE vacuum chamber

The essential components necessary in an SVT MBE system for growth of III-nitride semiconductors are schematically illustrated in Figure 3-1. In order to avoid exposing the growth chamber to increased ambient pressure for sample transfer, the SVT MBE system used in this research is equipped with two chambers. The sample is first placed into a small loading or introduction chamber (“load lock”) equipped with a cassette that permits multiple sample loading. A mechanical pump and an ion pump are used to evacuate the load lock chamber and maintain the pressure (low $10^{-8}$ Torr). After evacuation of the loading chamber, the substrate is transferred into a larger growth chamber which is maintained at high vacuum and has provision for growth and analysis.

The vacuum conditions during MBE growth is of paramount importance since residual gas in the growth chamber affects the impurity/contamination levels of the molecular beam and ultimately the film quality. The condition for growing a sufficiently clean epilayer can be simply expressed by the relation between the 1-monolayer deposition times of the beam $t_1 (b)$ and the background vapor $t_1 (v)$: $t_1 (b) = 10^{-5} t_1 (v)$. From this requirement the following condition results for the pressure of the residual gas in the vacuum reactor: $p_i < 2.73 \times 10^{-9}$ Pa. In our SVT MBE system, the residual gas consists mostly of nitrogen, hydrogen and ammonia. Ammonia is very easy to condense.
on the cryopanel walls which are cooled by LN$_2$ since its condensing temperature is –33.5 °C.\textsuperscript{56} The pumping system therefore needs to only pump nitrogen, hydrogen, water vapor, carbon dioxide and oxygen, which may be generated by outgassing of heaters and the system walls. The residual gas pressure routinely achieved in this study is typically on the low 10$^{-9}$ Torr scale. These values increase somewhat during operation due to the increased heat load from the effusion cell furnaces and substrate heater.

A sample manipulator, growth cells, RHEED, cryo-shrouds and pumps comprise the SVT MBE growth chamber. The sample manipulator heats the sample, moves it in and out of the growth position and, rotates it. The manipulator also has provision for temperature measurement with a thermocouple. A radio frequency (RF) activated nitrogen plasma is used as the nitrogen source to provide atomic nitrogen. High-purity group III solid elements (Ga, Al, Si, Mg and In) are used as the metal sources, and the molecular vapor fluxes are generated by heating these metals in conventional effusion cells. The fluxes of metal sources are controlled by changing the temperature of the effusion cells accurately. Simple mechanical shutters in front of the beam sources are used to interrupt the beam fluxes. Therefore, changes in composition and doping can be abrupt on an atomic scale. An \textit{in situ} RHEED operated at 13.9 KeV is used to monitor the growth process and will be discussed further in chapter 4. Two cryo-shrouds are used in the SVT MBE system to improve the background pressure and to prevent thermal interference between the sources. A turbo-molecular pump and a cryo-pump are also used to obtain UHV vacuum in the growth chamber.
3.1.2 Effusion cells

The film quality, thickness uniformity, and composition of compound semiconductors, as well as the reproducibility of growth conditions, critically depend on the uniformity of the impinging molecular beams across the substrate. What is not accomplished by the level of uniformity provided by effusion cells is performed by rotating the substrate. Well-designed effusion cells are the basis of beam sources used in MBE to obtain decent flux transients for growth. In effusion cells, a solid or liquid source material is held in an inert crucible which is heated by radiation from a resistance-heated source. A thermocouple is used to provide temperature control. Conventionally, the heater is a refractory metal wire wound around the crucible and is supported on insulators or inside insulating tubing.

In this research, all metal sources used for epitaxy are conventional effusion cells. Specifically, the Ga cells used in the SVT MBE system are two identical EPI SUMO dual filament effusion cells. They have two independent heater filaments: a tip heater for the crucible lip and the aperture region, and a base heater for the crucible body. The Ga cells are operated in a “hot-lipped” mode, with the tip heater warmer than the base, compensating for increased radiative heat loss in the lip region. Re-condensation of the evaporated Ga is reduced, resulting in more uniform and reproducible beam fluxes. The Al cell used in this research is an ADDON effusion cell with two temperature zones also. Compared to the Ga cells, the bottom zone of the Al cell is a hot zone which is heated by a uniform filament assembly. The top zone (cold zone) is cooled down by a fluid circulation assembly in contact with the crucible open tip. This design prevents creeping
of molten aluminum, which is a serious problem in nitride MBE. The operating temperature for the Ga effusion cells during MBE growth range from 1040°C to 1140°C, while the Al effusion cell is operated at 940°C to 1010°C. The operating temperature for the effusion cells is controlled by a temperature control system (Eurotherm model 818), and the temperature is stabilized within ±1°C.

### 3.1.3 Radio frequency plasma nitrogen source

The SVT MBE system is equipped with an EPI Vacuum Products Unibulb plasma source operating at 13.56 MHz radio frequency to produce active nitrogen with power levels between 90 and 500 W. The system pressure with the RF nitrogen plasma operating is from 2x10⁻⁶ to 1x10⁻⁴ Torr. Well-designed RF sources can have cracking efficiencies as high as 10%, although in most operating conditions the efficiency is about 1%. Owing to N₂ activation by the plasma discharge, the cracking efficiency of the activated nitrogen flux does not depend on the growth temperature $T_s$, but on the power level used for the RF plasma source.

The components in the activated nitrogen flux include nitrogen atoms (N), excited molecules ($N_2^*$), and ionic species ($N_2^+, N^+$). Nitrogen atoms have five valence electrons and bond with all group III elements without any potential barrier. The $N_2^*$ excited molecules interact with a solid state surface through an exothermic dissociative chemisorption mechanism. Therefore, N atoms and excited $N_2^*$ molecules are the species participating in III-N growth by RF assisted PAMBE. In contrast, ionic species of plasma activated nitrogen flux ($N_2^{++}, N^+$) are responsible for ion-surface processes such as adatom-vacancy pair generation, displacement of atoms, embedding of N$_2$-
molecules, and surface atoms sputtering, which are believed to have adverse effects on epitaxial film quality such as polycrystalline growth.66

Optical emission spectra of RF sources are useful in determining the composition of the N flux and which nitrogen species are responsible for growth. Shown in Figure 3-2 is the emission spectrum from our EPI RF-plasma source operating at an input RF power of 350 W and a system pressure of 9x10^{-6} Torr. The RF-source emission is primarily neutral and consists of peaks associated with molecular species (with first-positive but no second-positive molecular series) and atomic species. The first- and second-positive molecular nitrogen emissions occur near orange-red and UV wavelengths, respectively. The atomic nitrogen related emission occurs near red and infrared (IR) wavelengths of 745 nm, 821 nm and 868 nm.

By comparing the peak intensities of different species in the spectra, the relative composition of the radio frequency plasma nitrogen source can be obtained. Figure 3-3 and Figure 3-4 show the relationships between the intensity of atomic nitrogen peaks with RF power and system pressure, respectively. These results suggest that the input power and nitrogen flow may be used to control the composition of the nitrogen plasma beam. From Figure 3-3, the intensity of atomic nitrogen increases linearly with input power. From Figure 3-4, the intensity of atomic nitrogen changes with the system pressure which is controlled by nitrogen gas flow. As depicted, the intensity of atomic nitrogen increases with the nitrogen gas flow when the chamber background pressure is low. When the pressure is higher than 3.0x10^{-5} Torr, however, the intensity of atomic nitrogen peaks starts to decrease. A similar trend has also been reported for the ionic
species. This behavior is explained by enhanced recombination at high nitrogen pressures in the plasma, due to an increased probability of collisions.

3.2 Sapphire substrates for III-nitride epitaxy

3.2.1 Properties of sapphire

Sapphire has been the most widely used substrate for III-nitride epitaxy due to its comparatively low cost, high quality, large diameter, chemical compatibility, and high temperature stability. Furthermore, the optical transparency of sapphire is beneficial in back-illuminated detectors, and LED’s for lack of absorption. In this research, III-nitrides are grown directly on sapphire by SVT MBE or on MOVPE GaN templates.

Sapphire has the space group of $R\bar{3}cR\bar{3}c$ (No. 167, International Tables for Crystallography), and is primarily of ionic bond nature. The unit cell described by Miller-Bravais indices consists of six close packed (0001) planes of O$^{2-}$ ions, sandwiching 12 planes of Al$^{3+}$ ions that occupy two thirds of the available octahedral voids created by the O$^{2-}$ ions. Epitaxial films have been grown on sapphire substrates of several orientations, including $c$ (0001), $a$ (1120), $r$ (1012), and $m$ (1010) planes. The (0001) Al$_2$O$_3$ surface is the most used orientation since it results in $c$-plane oriented GaN epilayers. It is oxygen terminated and incorporates steps along the {1120} and {1100} planes.

3.2.2 Sapphire substrate preparation

There have been no reports indicating that crystal defects present in the sapphire substrate are transferred into the GaN epitaxial film during growth, other than those caused by misfit dislocations. However, the crystal structure of epitaxial GaN is strongly
influenced by the substrate surface preparation. An ideal $c$ plane sapphire surface would have bi-layer steps to obtain uniform surface polarity so that stacking mismatch boundaries and other defects in the epilayer can be reduced. Therefore, in addition to a clean and flat surface, a damage-free and atomically smooth surface is necessary for 2D growth. The sapphire wafers as received from the manufacturer typically have excessive damage and visible scratches since they undergo chemical mechanical polishing. These polished substrates have root-mean square (RMS) roughness values of 3.2 Å over 2×2 µm$^2$ areas.

To prepare an ultra-smooth substrate surface with atomic steps the substrate is degreased followed by chemical etching and a high temperature treatment under a controlled environment. During the degreasing procedure, the substrate is ultrasonically cleaned for 3 minutes each in acetone and methanol, and then rinsed for 3 minutes in deionized (DI) water. The above process is repeated three times to complete the degreasing process. Following degreasing, the substrates undergo a chemical etching process. A number of liquid and gas phase etching techniques have been used to remove residual damage on the sapphire surface. A widely employed chemical treatment is etching in a 3:1 solution of sulfuric-phosphoric acid ($\text{H}_2\text{SO}_4 : \text{H}_3\text{PO}_4$) in the temperature range between 100 to 300°C for 10 to 30 minutes. The solution should not be stirred because stirring leads to inferior surface quality. After etching, the substrate is rinsed in DI water for 3 minutes. Figure 3-5 shows atomic force microscopy (AFM) images of two $c$-plane sapphire surfaces (a) before and (b) after chemical etching. The scratches
become wider and shallower after hot etching and the RMS roughness is reduced from 0.32 nm to 0.21 nm.

Though hot etching removes some material from the surface, it cannot produce a smooth surface free of damage and scratches. To eliminate nearly all surface damage, a high temperature annealing process must be used. Cui et al.\textsuperscript{73} annealed sapphire substrates at 1000, 1100, 1200, 1300, and 1380 °C for 30 and 60 min periods and examined them using AFM. An atomically flat $c$ plane sapphire surface can be obtained through an annealing process in air at 1380 °C for 1 hour. The resulting uniform terrace structure becomes clearly visible as shown in Figure 3-6 (RMS = 0.07 nm) Terrace-like features appear with ~0.2 µm long terraces that are 1.5 Å in height. When the annealing time is extended to 3 hours at 1380 °C, the surface roughness increases to 0.14 nm.
Figure 3-1  The essential components necessary in a SVT MBE system for growth of III-nitride semiconductors.
Figure 3-2  The emission spectra from our EPI RF-plasma sources operating at an input RF power of 350 W and a system pressure of $9 \times 10^{-6}$ Torr.
Figure 3-3  Intensity of nitrogen RF spectrum peaks versus RF power. The system pressure is $9 \times 10^{-6}$ Torr.
Figure 3-4  Intensity of nitrogen RF spectrum peaks versus system pressure. The RF power is 350 W.
Figure 3-5  AFM image of (a) an as-received sapphire substrate. The scratches are caused by mechanical chemical polish. (b) AFM image of a sapphire substrate after a 180 °C etch in sulfuric/phosphoric acid. Some improvements are apparent, but scratches remain. Image size is 2 µm x 2 µm.
Figure 3-6 AFM image of sapphire following a 1 hr anneal at 1380 °C in atmosphere. An atomically flat surface is clearly visible, with atomic step heights of 0.15 nm. Image size is 2 µm x 2 µm.
Chapter 4 Characterization methods

Four major characterization methods were used in this study to investigate the growth mechanism and sample quality of III-nitride semiconductors. In-situ reflection high energy electron diffraction (RHEED) was employed to monitor the evolution of the surface during growth. The surface morphology of the grown samples was evaluated ex-situ by atomic force microscopy (AFM) after growth. The crystalline quality and lattice-mismatch were measured by single crystal x-ray diffraction (XRD). Finally, optical properties were measured by using photoluminescence (PL) at temperatures from 15 K to 300K.

4.1 RHEED

4.1.1 Introduction

RHEED is a technique for probing the surface structure of solids in ultrahigh vacuum (UHV). This surface information comes from the diffraction of high-energy electrons from a clean, well-ordered single crystal. Electrons with high energy and a grazing angle of incidence scatter elastically from only the first few atomic layers of such a crystal. Compared to other diffraction methods, this glancing-incidence-angle geometry allows RHEED to be the ideal in situ technique for studying real-time surface changes during growth.74
4.1.2 Fundamentals

The underlying principle of RHEED is the diffraction of electrons by a periodic lattice. For non-relativistic electrons, the wavelength $\lambda$ (in Å) can be written in Equation 4-1, where $E$ is the energy of the electron (in electron volts). For a primary beam energy of 5-50 KeV this relationship gives $\lambda$ ranging from 0.17 to 0.055 Å.\(^{75}\)

$$\lambda = \sqrt{\frac{150.4}{E}}$$  \hspace{1cm} (4-1)

These high energy electrons are scattered by surface atoms as they impinge on the sample surface. In kinematical scattering theory,\(^{76}\) the maximum value for scattering amplitude is obtained when the wave vectors $k_0$ and $k'$ of the incident and diffracted beams differ by the reciprocal-lattice vector $G$ of the surface atoms:

$$\Delta k = G$$  \hspace{1cm} (4-2)

The beam intensity can be shown to fall off rapidly for $\Delta k \neq G$, so the diffraction condition, $\Delta k=G$, is responsible for the bright spots that appear on the phosphor screen in the diffraction experiment. This result can be understood with the 3-D Ewald sphere (Figure 4-1 a),\(^{77}\) which is a sphere of radius $k$. Only when the sphere passes through a reciprocal lattice point, the difference between incident and diffracted beam vector is a reciprocal lattice vector $G$, and the intensity of diffraction is the highest at these directions. The diffraction image forms by projecting the pattern of these intersections to a phosphor screen. Ultimately, this constructive interference results in the bright patterns on the phosphor screen. Considering the distances in reciprocal space are inversely proportional to distances in real space, a 2-dimensional (2D) plane in real space should be
a 1-dimensional (1D) line in reciprocal space. As a result, a real and smooth 2D surface should be a set of infinitely long rods in the reciprocal space (Figure 4-1 b), which results in a RHEED pattern with streaky lines. For a 3D rough surface, the RHEED pattern should be a set of spots (Figure 4-1 c).

A typical RHEED system consists of an electron gun, a phosphor screen and an image-processing system. Figure 4-2 shows the typical design for a RHEED system in an MBE system. Typical acceleration voltages range from 10 KeV to 30 KeV. This high energy is necessary to image a reciprocal space into the relatively small solid angle of the phosphor screen. It has the additional advantage of reducing the influence of stray fields. The electron beam interacts with the sample at an angle that is typically in the range of 0.5~2.5°. The diffracted electron intensity pattern is converted to visible light by a phosphor screen. A charge-coupled device (CCD) camera outside the UHV system is used to record the RHEED pattern.

4.1.3 Applications

The RHEED technique provides a great deal of useful information about a surface, since the diffraction pattern spot intensities describe the scattering processes within the topmost atomic layers of a crystal. Typically, there are two applications of RHEED: static detection and dynamic detection. The former depends on features of the diffraction pattern itself, and the latter is based on the intensity change of a diffraction spot as a function of time.

**Static detection mode** The RHEED pattern of a clean single crystal surface reveals information about the surface quality. For a semiconductor epilayer, the RHEED
pattern exhibits streaky lines or spots with high contrast and low background intensity. A RHEED pattern with streaky lines represents a flat and smooth surface, however, the spotty pattern represents a rough surface. A smaller full-width half maximum (FWHM) value of the lines also indicates a higher quality surface. Random defects in the 2-dimensional periodicity of the surface will broaden the lines and increase the background intensity. In contrast, a RHEED pattern consisting of spots represents a rough surface of epilayer.\textsuperscript{74} Because RHEED is sensitive only to the first few atomic layers, it provides information about any surface reconstructions. In addition, changes in separation between RHEED streaks, which are related to changes in the surface lattice constant, can be used to study strain relaxation or superlattice structure.\textsuperscript{78}

**Dynamic detection mode**  Another use of RHEED is to monitor the evolution of the surface structure during growth. “Intensity oscillation” is one of the most important dynamic detection techniques to monitor thin film growth. It was experimentally found that if epitaxial growth follows a layer-by-layer mode, then regular oscillations in the specular beam intensity occur.\textsuperscript{79} This oscillation can be understood qualitatively in terms of the surface roughness. As material is deposited, 2D islands nucleate and increase the step density. This causes the diffraction features to become “smeared out,” reducing their intensity at the detector. When these 2D islands coalesce and the surface becomes flatter again, the intensity recovers. This process is repeated with continued deposition and causes the intensity to oscillate. The period of an oscillation therefore corresponds to the time it takes to deposit a monolayer. In practice, oscillations can be used to calibrate the deposition rate.\textsuperscript{80, 81}
In this research, the RHEED static detection mode is used to evaluate the surface quality of III-nitride semiconductors. With regard to the dynamic mode, the intensity of the RHEED specular beam under different growth conditions is used to investigate the Ga desorption behavior on GaN.

4.2 AFM

4.2.1 Introduction

Atomic Force Microscopy (AFM) is a robust technique used to study the surface topography of a variety of materials on the nanometer to micrometer scale. It was invented by G. Binnig et al.\textsuperscript{82} in 1986, and he\textsuperscript{83} reportedly obtained atomic resolution of a graphite surface utilizing AFM. In the recent decade AFM has become a universal tool in material research, especially in nanotechnology.\textsuperscript{84} AFM primarily measures surface topography, but has other variants that measure electrical, magnetic, and physical properties.\textsuperscript{85}

4.2.2 Fundamentals

When a tip moves toward a sample, it may interact with the sample surface when the two are sufficiently close. The tip-surface interactions depend on the separation between the tip and sample. AFM measures changes in the tip-sample forces to obtain surface characteristics of the sample. Due to different measurement modes, these forces may vary and may be due to physical features on the sample, or arise from magnetic or electric forces between the tip and the sample.

The principle of AFM operation is illustrated in Figure 4-3. A sharp tip a few microns long is located at the free end of a cantilever (\textasciitilde 100 to 200 microns long). The
interatomic forces between the tip and sample surface atoms cause the cantilever to deflect. The cantilever displacement is then measured by a deflection sensor. An optical reflection scheme is most commonly used due to its high signal-to-noise ratio. Typically, sensors can detect deflections as small as $10^{-2}$ Å. As shown in Figure 4-3, a laser beam is reflected off the backside of the cantilever and hits a position-sensitive photodetector. Any tip motion causes a detectable change in the laser’s path. The electronic system of the AFM operates a feedback and control circuit that can adjust and record the motion of the tip. The surface topography can then be mapped while the tip is scanned over the sample.

4.2.3 Applications

There are two primary modes of operation for AFM under ambient conditions: contact mode and tapping mode. In contact mode, the AFM tip is in physical contact with the sample and is subjected to repulsive forces. The tip-sample interaction causes the cantilever to bend as its encounters changes in surface topography. This method is preferred for atomically flat surfaces that are not easily damaged. A more commonly used mode is tapping mode, where the tip is in intermittent contact with the surface. In this case, the cantilever is oscillated at its resonance frequency and the tip ‘taps’ the surface during scanning. The resolution of this mode may be slightly lower than for contact mode, but it causes significantly less sample damage. During tapping mode operation, the amplitude of oscillation is used as the feedback signal (vs. the DC cantilever deflection in contact mode). In this mode, the tip-sample forces are reduced and minimize sample
damage. In this research, the AFM tapping mode will be used to investigate the surface morphology of III-nitride semiconductors grown under different growth conditions.

4.3 XRD

4.3.1 Introduction

X-ray diffraction (XRD) is a powerful tool for investigating the crystalline structure of materials. The first XRD patterns of rock salt were obtained in 1911. Single-crystal diffraction and powder diffraction were the two dominant methods used during the first sixty or seventy years. Single-crystal diffraction for structural analysis revealed the crystal and molecular structure of inorganic, organic and more recently biological compounds. The powder diffraction method is used to determine the crystal orientation and the scattered intensity when more than one phase is present in the specimen. For III-nitride semiconductor epilayers, XRD is mainly used to evaluate the quality of the film, determine the mole fraction of alloys, and investigate the thickness and fine structure of materials with superlattice structures.

4.3.2 Fundamentals

X-rays are electromagnetic radiation of exactly the same nature as light but with much shorter wavelength. The unit of wavelength measurement in the x-ray region is the angstrom (Å), equal to $10^{-8}$ cm, and x-rays used in diffraction have wavelengths of 0.5–2.5 Å, which is close to the spacing of atoms in crystals. Since atoms are arranged periodically in a lattice, diffraction occurs when x-rays are coherently scattered by them and reveals the crystal structure. Bragg’s Law is the simplest and most useful description of crystal diffraction:
where \( n \) is an integer representing the order of diffraction, \( \lambda \) is the x-ray wavelength, \( d \) is the interplanar spacing of the diffracting planes, and \( \theta \) is the angle of incidence. Details about the crystal structure can be obtained from the maxima in an XRD pattern using Bragg’s law.

In this research, a Philips X’pert XRD system is used to study III-nitride semiconductors. Figure 4-4 shows the typical schematic diagram of an XRD system. An x-ray source, beam conditioner, and detector are the necessary elements of an X-ray system. X-rays are produced in an x-ray tube by accelerating a high-energy electron beam towards a metal anode, resulting in characteristic x-ray transitions in the anode. The beam conditioners are used to collimate and monochromate the x-rays. The specimen is mounted on a sample holder which can rotate along 3 axes: Phi(\( \Phi \)), Psi(\( \Psi \)) and Omega(\( \Omega \)). A detector is used to collect the diffracting x-rays, where the detector can move through the Bragg angle while scanning.

### 4.3.3 Applications

For III-nitride semiconductor materials, XRD is mainly used to evaluate the quality of the film, determine the mole fraction of alloys, and investigate the thickness and fine structure of materials with superlattice structures. There are two basic types of XRD scan modes: \( \theta-\omega \) (rocking curve) scan and \( \theta/2\theta \) scan.

**\( \theta-\omega \) scan (or Rocking Curve)** In this case, the orientation of \( \Delta k \) (the difference of the incident wave vector \( k_0 \) and diffracted vector \( k' \)) varies relative to the sample normal while maintaining its magnitude, as shown in Figure 4-5 (a). Resulting data of intensity
vs. \( \omega \) (sample angle) show detailed structure of materials being investigated. The width of the rocking curve is a direct measure of the range of orientations present in the irradiated area of the crystal, as each sub-grain of the crystal is probed as the crystal is rotated. For a film that is not truly epitaxial, the width of a rocking curve indicates the quality of the epilayer.

\( \theta-2\theta \) scan In this case, the magnitude of \( \Delta k \) varies while maintaining its orientation relative to sample normal, shown in Figure 4-5 (b). Resulting data of intensity vs. \( 2\theta \) shows peaks for \( \Delta k \) values satisfying the diffraction condition. This scan mode is used to identify the lattice constant, and ultimately determine the mole fraction of alloys. It is also used to investigate the thickness and fine structure of materials with superlattice structures.

In this research, the XRD \( \theta-\omega \) scan mode will be used to characterize the structure quality of III-nitride semiconductors. The \( \theta-2\theta \) scan mode will be used to determine the Al mole fraction \( x \) in \( Al_xGa_{1-x}N \) films.

4.4 PL

4.4.1 Introduction

Depending on the excitation source, there are a few types of luminescence. In the case of photo-excitation, this luminescence is called photoluminescence (PL). Electroluminescence (EL) requires excitation by an electric current and cathodoluminescence (CL) requires electron bombardment. PL is the most widely used experimental method for the optical characterization and investigation of semiconductors,
since it is a contactless and nondestructive method. The intensity and spectral content of PL spectra can be used to characterize various important material properties.

4.4.2 Fundamentals

Photo-excitation causes electrons within the material to move into allowed excited states. When these electrons return to equilibrium, their excess energy is released and may cause the emission of light (a radiative process) or not (a nonradiative process). The energy of the emitted light is related to the difference in energy levels between the excited state and equilibrium state. The intensity of the emitted light is related to the relative contribution of the radiative process to nonradiative process.

A typical PL system is shown in Figure 4-6, and includes a light source for excitation, filters and collecting optics, a sample holder, a dispersive element such as a monochromator, and an optical detector. Samples are usually mounted in an optical cryostat in order to achieve low temperatures. A lamp with a monochromator or a laser with tunable wavelength is used for the PL excitation. In this research, a He-Cd laser with emission wavelength of 325 nm is used as the excitation source for the GaN study, and a Ti-sapphire laser in combination with the optical parametric oscillator for the AlGaN study. The laser beam passes through filters which select the main laser emission line and cut off undesirable lines, and is then focused to a small spot on the sample. The luminescence from the sample is collected by condenser optics and converted to a collimated beam. The beams that pass through the spectrometer are detected by a photomultiplier and are converted to an electrical signal. The ac signal is then fed to a
lock-in amplifier, and the amplified signal is inputted into a computer to be collected and analyzed.

4.4.3 Applications

PL has been widely applied to the study of III-nitride semiconductors. The properties of semiconductors can be studied by analyzing the steady-state PL (SS-PL) spectra, time-resolved PL (TR-PL) spectra and transient dependences, or by measuring the PL excitation (PLE) spectra. In particular, SS-PL spectroscopy is widely used to qualitatively characterize the band gap, quality, and band structure of GaN epilayers and alloys.

**Band gap determination**  The most common radiative transition in semiconductors occurs between states in the conduction and valence bands, with the energy difference equal to the band gap. Band gap determination is particularly useful when working with new compound semiconductors. However, caution must be exercised as the transitions observed may involve excitons and/or impurity related transitions, in which case their binding energies must be known before a bandgap determination can be made. This implicitly assumes that the particular transition used for bandgap determination is identified, which in the early stages of materials development is difficult. Reflection, which is sensitive to the density of states in the energy bands, is a more dependable technique for bandgap determination. It is this technique that was applied in this research to determine the optical gap of the AlGaN alloys grown by MBE.

**Impurity levels and defect detection**  Radiative transitions in semiconductors involve localized defect levels. The PL energy associated with these levels can be used to
identify specific defects, and the PL intensity can be used to determine their concentration. Quantitative studies of point defects in GaN by PL are rarely undertaken. Often, a qualitative estimate of the donor concentration in \( n \)-type GaN is made by comparing the ratios between the defect and near-band-edge emission intensities.\(^95,96\)

Temperature dependence of the defect-related PL intensity in GaN is often used to determine the nature of an optical transition. For example, the donor-acceptor pair (DAP) transitions were distinguished from the conduction band-acceptor (eA) transitions by the temperature behavior of PL.\(^97,98\) The yellow (YL) band is used to estimate the impurity levels in GaN since it is related to transitions from the shallow donors (at low temperature) or conduction band (at elevated temperatures) to a deep acceptor. The origin of the deep acceptor is not well established, but usually it is attributed to a Ga-vacancy-related defect.\(^99\) The ionization energy of this acceptor is about 0.9 eV, therefore no quenching of the YL band is typically observed up to room temperature.\(^100,101\)

**Material quality**  Quantum efficiency (QE) is usually used to evaluate semiconductor quality, although there have been very few attempts to estimate the absolute value of the PL intensity, and the direct measurement of the QE is not straightforward.\(^91\) Göldner et al.\(^102\), performed the simultaneous detection of the calorimetric absorption (measure of nonradiative recombination), transmission, reflection, and excitation power, and reported a QE below 20% for thin GaN layers grown by MOCVD on sapphire and up to 75% for bulk GaN crystal grown by HVPE. An indirect method based on quantitative analysis of the competition of radiative and nonradiative recombination channels was suggested by
Reshchikov and Korotkov. In this research, PL will be used to characterize the optical quality of III-nitride films grown under different growth conditions.
Figure 4-1  a) The 3D Ewald sphere configuration; b) A real 2D smooth surface in the reciprocal space; c) A 3D rough surface in the reciprocal space.
Figure 4-2  Schematic diagram of the RHEED technique in an MBE system.
Figure 4-3  Schematic diagram of the AFM technique.
Figure 4-4  Schematic diagram of the XRD technique.
Figure 4-5  Schematic configuration of XRD a) $\theta/\omega$ scan: the orientation of $\Delta k$ varies relative to the sample normal while maintaining its magnitude; and b) $\theta/2\theta$ scan: the magnitude of $\Delta k$ varies while maintaining its orientation relative to the sample normal.
Figure 4-6  Schematic diagram of the PL technique.
Chapter 5 Investigation of the desorption energy of Ga by RHEED

In this chapter, the growth mechanism of GaN by plasma assisted molecular beam epitaxy (PAMBE) will be investigated. First, the general issues related to growth of GaN will be introduced in Sec. 5.1, followed by a discussion of the growth rate and the GaN surface morphology phase diagram under different growth conditions in Sec. 5.2 and Sec 5.3, respectively. In Sec. 5.4, a study of the desorption energies of Ga from the GaN (0001) surface using RHEED during growth will be discussed in detail.

5.1 GaN Growth by PAMBE

5.1.1 Introduction

These studies of GaN growth were carried out in a plasma-assisted MBE system equipped with two conventional Ga effusion cells and a radio frequency (RF) plasma source for the nitrogen. The growth system was discussed in detail in Chapter 3. GaN templates grown by metalorganic chemical vapor deposition (MOCVD) were used as substrates, because they have smooth surfaces with atomically flat terraces. Figure 5-1 shows an AFM image of a typical MOCVD GaN template, which has an RMS roughness of ~0.17 Å. The GaN epilayers studied here were grown on these substrates using temperatures in the range of 650 °C to 775 °C. To obtain sufficient Ga flux, two EPI Ga effusion cells were installed in the PAMBE system and were operated in the range of...
1050 °C to 1140 °C. The system background pressure during the growth was varied from 2.6x10^{-6} Torr to 3x10^{-5} Torr by changing the nitrogen flux of the RF nitrogen plasma source.

### 5.1.2 Substrate preparation

The preparation of an atomically clean and smooth substrate surface is very important for semiconductor epitaxial growth. *Ex-situ* substrate cleaning methods aim to remove any metallic and organic contamination from the substrate surface and typically form of a thin passivating oxide. Substrate preparation within the MBE UHV system (*in-situ*) usually includes a preliminary heating step to outgas adsorbed gases in the preparation chamber, and a final heating for oxide removal and preparation of an atomically clean surface in the growth chamber.

In this work, we use the following steps for ex-situ preparation of the ~1.5 µm GaN/Al₂O₃ (0001) MOCVE GaN templates:

1. Degreasing in hot acetone and methanol.
2. Rinse in de-ionized water (DI).
3. Etch in 1:3 HCl:H₂O.
4. Rinse in DI and N2 blow drying.

The templates are loaded onto holders and introduced into the MBE system, where they are:

1. Outgassed in UHV up to temperatures of 600 °C~ 650 °C.
2. Outgassed up to 750 °C in fluxes of N to maintain the stoichiometry of the surface, since GaN decomposition occurs above 800 °C.
In-situ RHEED observation of MOCVD GaN templates provides a method to monitor the real-time surface changes during the outgassing processes. The typical RHEED pattern of an MOCVD GaN template before growth is streaky and long, with 2x2 reconstruction, indicating a very smooth and planar GaN surface with (0001) polarity.

5.2 Growth rate as a function of III and N fluxes

There are two growth regimes that influence the GaN growth rate and depend on the III and N element fluxes ($J_{Ga}$ and $J_N$, respectively): the N-rich growth regime and Ga-rich growth regime.103

In the N-rich regime, the GaN growth rate is limited by the amount of available Ga atoms. The growth rate increases monotonically with the flux of Ga atoms ($J_{Ga}$). This regime corresponds to the so-called N-stable growth condition and occurs for any substrate temperature when $J_{Ga}/J_N<1$. In this case, an increase of the substrate temperature contributes to the N-stabilization of the surface since it increases the Ga desorption rate.

In the Ga-rich regime, the GaN growth rate is limited by the amount of available reactive nitrogen since excess Ga is present on the surface. The growth rate increases monotonically with increasing flux of reactive nitrogen species ($J_N$). This growth regime corresponds to the so-called Ga-stable growth condition, which for sufficiently low substrate temperature (where Ga desorption is not significant), the fluxes of Ga and N satisfy $J_{Ga}/J_N>1$. The excess Ga can be thermally adsorbed on the surface to form 2-D Ga adlayers, and 3-D Ga droplets will form when the Ga adlayers are more than 3 monolayers thick.104
Figure 5-2 shows the growth rate of GaN under different III/V ratios with the substrate temperature at 700 °C. When the Ga cell temperature is low, the growth rate increases linearly with the Ga cell temperature (determines the Ga flux J_{Ga}) for the same system pressure (determines the N flux J_N). This behavior indicates N-rich growth conditions. The growth rate saturates when the Ga cell temperature is higher than a certain value. Above that temperature the growth rate remains constant, although the Ga cell temperature increases, and the growth is under Ga-rich conditions. The Ga cell transition temperature from the N to Ga rich regimes varies with the system pressure, and is shown in Figure 5-2 as the solid line, which indicates a stoichiometric condition with J_{Ga}/J_N~1. On the left side of the solid line (J_{Ga}/J_N<1) growth is in the N-rich regime, whereas on the right side (J_{Ga}/J_N>1) growth is in the Ga-rich regime. Although the desorption rate of Ga will increase with substrate temperature, the growth rate does not change much in the growth temperature range of 650 ~ 750 °C.8

5.3 Surface morphology diagram for GaN

Growth conditions such as growth temperature and III/V ratio significantly affect the growth mechanism of GaN and the resulting surface morphology.104, 7 As a function of Ga coverage on the surface, four growth regimes can be discriminated in a GaN growth diagram (Figure 5-3):

(a) N-rich growth regime: excess N covers the GaN surface (J_{Ga}/J_N<1)

(b) Transition growth regime: presumably stoichiometric condition. The surface coverage of Ga or N can be neglected (J_{Ga}/J_N~1)

(c) Ga-rich growth regime: Ga adlayer covers the GaN surface (J_{Ga}/J_N>1)
(d) Ga droplet growth regime: Ga droplet formation on top of the Ga adlayer ($J_{Ga}/J_N>>1$).

**Figure 5-4 (a) and (b)** shows typical AFM and RHEED results, respectively, for GaN grown in the N-rich regime. Bragg spots always appear in the RHEED pattern during growth, and the surface morphology is characterized by small islands in AFM images. These results indicate that the surface is very rough with an RMS roughness of $\sim 5.0$ nm. The theoretical considerations of Zywietz *et al.*\(^{50}\) show a low Ga adatom mobility on N-rich GaN (0001) surfaces and a significantly shorter Ga diffusion length than under Ga-rich conditions. Low adatom mobility would lead to a high island nucleation rate and to multilayer growth, consistent with the rough GaN surface observed by RHEED and AFM.

In the transition regime, Bragg spots appear with weak streaky lines between them in the RHEED pattern (**Figure 5-5b**). The surface morphology is characterized by inverted pyramids in AFM (**Figure 5-5a**). The origin of these inverted pyramids is still unclear, but they appear similar to the “V-shaped” defects observed for GaN growth which are defined by \{10-11\} facets. It is worth noting that the surface morphology of GaN layers grown in this regime strongly depends on the substrate temperature. At higher growth temperatures, the pyramids start to merge together. When the substrate temperature is higher than 750 °C, the surface becomes flat with deep pits.

During growth under Ga-rich conditions, the RHEED pattern remains streaky (**Figure 5-6b**). The surface morphology is characterized by atomically flat terraces (**Figure 5-6a**), which is much smoother than that obtained in the N-rich and transition regimes. The RMS roughness in the Ga rich case is less than 1.0 nm. Under this growth
condition, the Ga adatoms are abundant and highly mobile at the substrate temperatures employed, which results in a 2D growth mode and smooth surface. There are some small hexagonal pits on the surface, with a density of $10^8 \sim 10^9$ cm$^{-2}$, when the temperature is higher than 750 °C. A higher desorption rate of Ga at this temperature may cause this phenomenon since higher substrate temperatures shift the growth toward the lower III/V regime.\textsuperscript{103}

Under the Ga-droplet regime, the surface morphology is smooth (Fig. 5-7a). In contrast to the sample grown in the Ga-rich regime, no hexagonal pits are observed in large-area images. However, some spiral hillock features are visible on the surface, which may be interpreted as small excess Ga clusters that act as precursors for Ga droplets. The typical size of the “macroscopic” Ga droplets observed on the sample is 3-5 µm at a density of $10^5$ cm$^{-2}$, as determined by optical microscopy. A streaky RHEED pattern during the growth is shown in Figure 5-7 (b).

5.4 Study of the desorption energies of Ga on the GaN (0001) surface

From the GaN surface morphology diagram, it is clear that the surface of GaN grown under Ga-rich condition is desirable for device fabrication since it is atomically smooth. Some groups also report that the better electrical and optical properties of GaN grown in this regime are believed to be as a result of the competition between diffusion and desorption of Ga species on the GaN surface during growth.\textsuperscript{104 - 106} RGA, RHEED, and AFM methods have been used to determine the desorption and diffusion energies of various species involved in growth with RF nitrogen or ammonia, and Ga.\textsuperscript{31,12} However,
the results are not consistent. In this work, the desorption energy dependence on the
growth conditions in the Ga-rich regime will be investigated by RHEED.

5.4.1 Principles of RHEED measurement of the Ga desorption energy

During GaN growth in MBE, a certain fraction of active nitrogen flux $J_N$ to Ga flux $J_{Ga}$ arriving at the surface must be maintained. When Ga atoms impinge on the GaN surface, they are either incorporated into the epilayer with active nitrogen, adsorbed on the surface to form a Ga adlayer, or re-evaporated. The desorption process becomes significant when the substrate temperature is higher than 650 °C. When the incorporation, adsorption and desorption processes reach equilibrium and the GaN growth proceeds under steady state conditions, the desorption rate can be expressed as\(^{52}\)

$$k = \nu_0 \exp\left(-\frac{E_{des}}{k_B T}\right)$$  \hspace{1cm} (5-1)

where $\nu_0$ is the attempt frequency. At GaN growth temperatures used during MBE of 650 °C ~ 780°C, the Ga adatoms do not condense into a reconstruction, but rather represent a liquid like film.\(^{107}\) This disordered film causes an attenuation of the RHEED specular beam intensity.\(^{48}\) As a result, the dependence of the RHEED intensity (or desorption rate) versus substrate temperature indicates the desorption kinetics of Ga in real time. We interpret the relationship between the RHEED intensity and desorption energy as follows:

$$I \sim \exp\left(-\frac{E_{des}}{k_B T_s}\right)$$ \hspace{1cm} (5-2)

The Ga atoms desorb from the surface at a substrate temperature $T_s$ with the desorption energy $E_{des}$. 
5.4.2 The desorption energy of Ga determined by RHEED during growth

Figure 5-8 shows the variation of RHEED specular beam intensity during GaN growth at different substrate temperatures under stoichiometric conditions. In this case, the Ga flux is slightly higher than that of nitrogen. Only one Ga cell was used and the temperature was kept constant at 1140 °C. The system pressure was 8x10⁻⁶ Torr. The substrate temperature was varied from 648 °C to 680 °C. Since this temperature range is small, it can be assumed that the coverage change of the Ga adlayer on the GaN surface caused by increasing substrate temperature is negligible. Therefore, the desorption energy can be treated as a constant and calculated by zero\textsuperscript{th}-order desorption kinetics. The exponential relationship in Figure 5-8 supports this assumption, and the desorption energy $E_{\text{des}} = 0.82 \pm 0.02$ eV is determined using Equation (5-2).

Interestingly, it was found that the desorption energy changes for different growth conditions. Higher Ga desorption energies resulted for higher III/V ratios. In the transition regime, the desorption energies are in the range of 0.82 to 0.94 eV, slightly increasing with the number of Ga atoms on the surface. Under Ga-rich conditions, the desorption energies are found to be 1.24 to 1.89 eV for substrate temperatures of 667 °C to 773 °C. Finally, the desorption energy is 2.76 ± 0.02 eV in the Ga-droplet regime, where there is an absence of any active nitrogen flux. In this case, Ga atoms accumulate on the GaN surface without forming a GaN epilayer, and the coverage of the Ga adlayer is approximately 100%.
### 5.4.3 The relationship between Ga desorption energy and Ga adlayer coverage

Table 5-1 lists the results of Ga desorption energies for different III/V ratios on the GaN surface at different substrate temperatures. It is clear that the growth environment affects the Ga desorption energy. This phenomenon can be explained by the dependence of desorption energy on the local bond strength, which is determined by the separation between atoms. A simple approach based on the Madelung Model\(^\text{77}\) allows a first degree understanding of the relationship between the cohesive energy and the separation between atoms:

\[
U(r_0) = -\frac{N\alpha q^2}{r_0}(1 - \frac{\rho}{r_0})
\]

Equation (5-3) shows the total cohesive energy of a crystal of 2N ions at their equilibrium separation \(r_0\). \(\alpha\) is the Madelung constant and the parameter \(\rho\) is of the order of 0.1\(r_0\). In this treatment, it is clear that the cohesive energy has a reciprocal relationship to the separation \(r_0\). Under the steady state condition of GaN growth, the equilibrium separation \(r_0\) between Ga-Ga atoms can be related to the Ga coverage \(C\) as follows:

\[
C(r) \propto \frac{1}{r^2}
\]

Ultimately, the relationship between the Ga desorption energies and surface coverage can be deduced.

In this work, the Ga desorption energy was determined to be 2.76 eV under very Ga rich conditions with a coverage of about 100%. This result is very close to the cohesive energy of Ga (2.81 eV)\(^\text{77}\), defined as that energy required to remove a Ga atom from a Ga reservoir. Since this condition corresponds to a Ga-Ga separation of 2.7 Å\(^\text{108, 109}\), the
coverage of Ga under different growth conditions can be calculated based on these values as follows:

\[ C(r) = C_{100\%} \left( \frac{r_{100\%}}{r} \right)^2 \]

with \( r_{100\%} = 2.7 \text{ Å} \). The results of this calculation are listed in Table 5-2. The coverage is determined to be 45% under Ga-rich conditions when the desorption energy is 1.89 eV. Under stoichiometric conditions most Ga atoms are incorporated into the GaN epilayer, with only a few Ga atoms remaining on the surface to produce a low Ga monolayer coverage. The desorption energy is about 0.82 eV when the coverage decreases to about 10%.

Note that in Ref. 16, much higher desorption energies for Ga desorption from Ga droplets, top of Ga adlayer and bottom of Ga adlayer were reported. In their experiments, Ga atoms were deposited without nitrogen being impinging on the surface and the amount of Ga adlayer was controlled by varying the length of time that the Ga effusion cell shutter remained open. After deposition, the shutter was closed and a quantitative in situ method, line-of-sight quadrupole mass spectrometry, was used to monitor the of Ga atoms. Desorption energies were determined by the dependence of the decay time of the desorption process on substrate temperature. A desorption energy of 3.1 eV was reported for Ga evaporating from Ga droplets which is comparable with our result (about 2.8 eV). However, their desorption energies for desorption from the top of Ga adlayer with 3.7 eV and 4.9 eV from the bottom of Ga adlayer are much larger than our value (0.82 ~ 1.89 eV). It should be mentioned that in our experiments, the desorption of Ga adatoms was
monitored by RHEED under steady state during the growth. Under this condition, the Ga adlayer in its entirety is kept in dynamical equilibrium and the in-plane distance between Ga adatoms is at the equilibrium separation. While the process monitored Ref. 16 represents the transient state, and the in-plane separation between Ga adatoms is very likely not fully relaxed before evaporating. As mentioned in this dissertation, the separation between Ga adatoms strongly affects the desorption energy. Therefore, the desorption energy determined under transient state may be larger than that under equilibrium separation.

5.4.4 GaN grown on etched GaN templates

A comparison between the desorption and diffusion energies can be used to predict growth regimes where layer-by-layer or lateral epitaxy may be possible. Varying the GaN surface morphology under different III-V ratios on porous templates at a temperature of 700°C is consistent with the Ga desorption energy being dependent on the coverage. Figure 5-9 (a) shows a typical AFM image of GaN epilayers etched in molten KOH for 1 min, which are later used as templates for further growth. The pores on the template have a hexagonal shape of about 200 nm in width and 50 nm in depth. After a 2-hour regrowth of GaN by MBE on these templates, the surface morphologies vary under different growth conditions. Typical AFM images of GaN re-grown under stoichiometric conditions and Ga-rich condition are shown in Figure 5-9 (b) and (c), respectively. Under stoichiometric conditions, hexagonal pits still appear on the surface with a depth of 50 nm, which is similar to that of the substrate. However, under Ga-rich conditions, the surface is atomically smooth without pits.
This behavior indicates that the III/V ratio strongly affects the surface morphology. As we have found, the desorption energy increases from 0.82 to 2.76 eV for increasing III/V ratio, whereas the diffusion energy decreases with III/V ratio (0.4 eV (Ga-rich), to 1.8eV (N-rich) conditions)\(^{50,110}\). For stoichiometric conditions, we take the average value of these limiting cases, and consider the diffusion energy to be 1.1 eV. Therefore, under stoichiometric conditions the diffusion energy is larger or comparable to the desorption energy. Consequently, a Ga atom is preferentially desorbed or incorporated into the GaN film at the arrival site, instead of diffusing to a new site. In contrast, when the diffusion energy is smaller than the desorption energy under Ga-rich conditions, Ga adatoms are very mobile and move about on the surface to find new sites with lower potential energy, such as the edge of a step or the bottom of a pit.\(^{67}\) As a result, GaN growth follows the layer-by-layer growth mode with the pores being filled and the surface becoming smooth as growth proceeds.

### 5.5 Conclusions

The growth of GaN was investigated and the dependence of growth rate and surface morphology on growth conditions was studied. It was found that the growth mode of GaN is determined by a competition between Ga surface diffusion and desorption, which is significantly affected by Ga coverage on the GaN surface.

In the N-rich regime, the surface is covered with an abundance of N and the coverage of excess Ga is zero. Under this condition, the diffusion energy of Ga (1.8 eV) is much greater than the desorption energy (<0.82 eV), resulting in a significantly shorter Ga diffusion length. Reduction of the diffusion length to less than the mean distance
between the available bonding sites leads to roughening of the surface. Under very Ga-rich conditions (Ga-droplets regime), the surface is covered with Ga and the coverage is close to 100%. In this regime, the Ga desorption energy (2.76 eV) is very large, resulting in the formation of Ga droplets. Between these two extremes, the coverage of excess Ga is in the range of 0 to 100% for Ga-rich and stoichiometric conditions. In these two growth regimes, the diffusion and desorption energies of Ga are comparable, resulting in a smooth surface morphology with some pits that depend on the III/V ratio.

Under stoichiometric conditions the diffusion energy is slightly larger or comparable to the desorption energy. Consequently, a Ga atom prefers either to incorporate into the GaN film or desorb from the surface, instead of diffusing to a new site. In contrast, the diffusion energy is smaller than the desorption energy under Ga-rich conditions. Ga atoms are very mobile in this case and prefer to diffuse on the surface to find new sites with lower potential energy. As a result, GaN growth follows the layer-by-layer growth mode and produces a smoother surface.
Figure 5-1  AFM image of an MOCVD GaN template. The RMS roughness of the template surface is 0.17 Å.
Figure 5-2  The growth rate of GaN at 700 °C vs. Ga cell temperature with the system pressure at $0.7 \times 10^{-5}$ Torr (diamond); $1.0 \times 10^{-5}$ Torr (circle); $1.5 \times 10^{-5}$ Torr (triangle) and $3.0 \times 10^{-5}$ Torr (square). The solid line indicates the stoichiometric condition ($J_{Ga}/J_N \approx 1$). The N-rich regime ($J_{Ga}/J_N < 1$) is situated to the left side of the solid line; while the Ga-rich regime ($J_{Ga}/J_N > 1$) is on the right side.
Figure 5-3 Surface morphology diagram of GaN grown by PAMBE on MOCVD GaN templates.
Figure 5-4  Typical (a) AFM results and (b) RHEED results for GaN grown in the N-rich regime.
Figure 5-5  Typical (a) AFM results and (b) RHEED results for GaN grown in the transition regime.
Figure 5-6  Typical (a) AFM results and (b) RHEED results of GaN grown in the Ga-rich regime.
Figure 5-7  Typical (a) AFM results and (b) RHEED results for GaN grown in the Ga droplet regime.
Figure 5-8  Variation of the RHEED specular beam intensity during GaN growth at a substrate temperature ranging from 648 °C to 680 °C under stoichiometric conditions. The Ga cell temperature is kept constant at 1140 °C, and the pressure is $8 \times 10^{-6}$ Torr.
Figure 5-9 The dependence of GaN surface morphology under different III-V ratios at 700 °C on KOH etched GaN templates. (1) Etched GaN template; (2) Following a 2-hour growth of GaN under stoichiometric conditions; and (3) The same as in (2) but under Ga-rich conditions.
Table 5-1  Summary of Ga desorption energies for different Ga III/V ratios on the GaN surface at different substrate temperatures indicated in the “Ts range” row.

<table>
<thead>
<tr>
<th>Ga density in Ga monolayers</th>
<th>Growth condition</th>
<th>Transition regime</th>
<th>Ga-rich regime</th>
<th>Ga-droplet regime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_{des} (±0.02 eV)</td>
<td>0.82</td>
<td>0.94</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>Ts range (°C)</td>
<td>648~680</td>
<td>659~696</td>
<td>667~727</td>
</tr>
</tbody>
</table>

Table 5-2  The desorption energies with different Ga-Ga separation and Ga coverage.

<table>
<thead>
<tr>
<th>III/N ratio</th>
<th>1.0</th>
<th>1.2</th>
<th>1.5</th>
<th>2.2</th>
<th>2.4</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{des} (±0.02 eV)</td>
<td>0.82</td>
<td>0.94</td>
<td>1.24</td>
<td>1.59</td>
<td>1.89</td>
<td>2.76</td>
</tr>
<tr>
<td>Ga-Ga Separation (Å)</td>
<td>9.2</td>
<td>8</td>
<td>6.1</td>
<td>4.8</td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td>Coverage (%)</td>
<td>8.6</td>
<td>11.4</td>
<td>19.6</td>
<td>31.6</td>
<td>45.6</td>
<td>100</td>
</tr>
</tbody>
</table>
Similar to GaN, there are two regimes for Al\(_x\)Ga\(_{1-x}\)N growth: the metal-rich growth regime and N-rich growth regime. As mentioned in Chapter 1, the growth of Al\(_x\)Ga\(_{1-x}\)N under metal-rich conditions by PAMBE with precise control of the Al mole fraction \(x\) is difficult, since the interaction between Ga and Al in nitride growth is complex. However, in these studies, precise control of the Al mole fraction \(x\) in the entire range (0<\(x<1\)) for Al\(_x\)Ga\(_{1-x}\)N alloys grown under metal-rich conditions was obtained. The growth mechanism will be investigated in Sec. 6.1, and the Al\(_x\)Ga\(_{1-x}\)N epilayer properties, such as energy gap bowing parameter, crystal structure and optical properties, will be discussed in Sec. 6.2. In Sec. 6.3, an application of a high quality Al\(_x\)Ga\(_{1-x}\)N epilayer grown under metal-rich conditions, a backilluminated ultraviolet (UV) photodetector, will be introduced.

### 6.1 Growth mechanism of Al\(_x\)Ga\(_{1-x}\)N under metal-rich conditions

Al\(_x\)Ga\(_{1-x}\)N epilayers were grown on (0001) sapphire substrates by PAMBE using effusion cells for the metallic species and an RF plasma source for the active nitrogen. In all samples, the sapphire substrate was nitridated by RF N\(_2\) plasma first. This process, which the nitrogen diffused into sapphire and substitutes for oxygen to bond with aluminum, is important for GaN epi-growth. After that, an initial AlN buffer layer (~50
nm) was first grown at 850 °C on the nitridated sapphire substrate. The substrate temperature was then reduced to ~700 °C for the growth of Al$_x$Ga$_{1-x}$N layers, which is in a medium temperature range for nitride MBE. The Al mole fraction $x$ of the Al$_x$Ga$_{1-x}$N epilayers was evaluated using the peak separation between GaN and AlGaN peaks in XRD curves. It was assumed that the variation of the lattice parameter $c$ between GaN and AlN is proportional to the aluminum mole fraction (Vegard’s law). Representative samples were cross-checked with secondary ion mass spectroscopy (SIMS) and Rutherford back scattering (RBS) results, which were in good agreement with the XRD data.

6.1.1 Al$_x$Ga$_{1-x}$N growth under metal-rich conditions

To produce metal-rich conditions, an overabundant Ga flux (two Ga sources) at 1125 °C and an Al cell at 1005 °C were used to maintain a high metal flux rate. A moderate N pressure in the range of $2.7 \times 10^{-6}$ to $9 \times 10^{-6}$ Torr was used during growth, and the growth temperature was about 700 °C. In this case, the N flux determined the total growth rate. The dependence of the growth rate on the system pressure, which is proportional to the N flux from the RF plasma source, is shown in Figure 6-1. The growth rate increases linearly with increasing flux of the reactive nitrogen species, as it is expected for growth under metal-rich conditions. Variation of the nitrogen partial pressure (determined by N flow) with fixed Al and Ga cell temperatures produced Al$_x$Ga$_{1-x}$N epilayers with mole fractions spanning nearly the entire compositional range ($0 < x < 1$). In Figure 6-2, the dependence of Al mole fraction in Al$_x$Ga$_{1-x}$N epilayers grown under metal-rich conditions at a constant substrate temperature is shown versus the
system pressure. The Al mole fraction is about inversely proportional to the N flow, and the Al concentration increases rapidly when the pressure is lower than $4 \times 10^{-6}$ Torr.

6.1.2 $\text{Al}_x\text{Ga}_{1-x}\text{N}$ growth under N-rich conditions

For a comparative analysis, albeit limited to a few mole fractions, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers grown under nitrogen-rich conditions were studied as well. Under this condition, an overabundant N flux was used to maintain metal-limited growth conditions. Only one Ga source was used, and the Ga flux was fixed with cell temperature being at 970 °C. The Al mole fraction in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film was controlled by varying the Al cell temperature from 970 to 1010 °C. The growth temperature was about 700 °C, or the same as that for the metal-rich condition. The dependence of the Al mole fraction at a constant substrate temperature versus Al cell temperature is shown in Figure 6-3. As expected, the Al mole fraction increases linearly with increasing Al flux. The highest $x$ obtained under these conditions is about 0.35, which is limited by the highest operation temperature of the Al cell (1010 °C).

In this regime the Al mole fraction remained the same with increasing N pressure, since it is determined by the Al and Ga fluxes at a given substrate temperature. The N flow rate beyond a certain point, which is determined by what is sufficient to satisfy bonds with the available Al and Ga species, does not have a notable effect on the surface kinetics to cause a change in the mole fraction.

6.1.3 Energy band bowing parameter in $\text{Al}_x\text{Ga}_{1-x}\text{N}$

$\text{Al}_x\text{Ga}_{1-x}\text{N}$ is widely used in electronic and optical devices, such as light emitting diodes (LED’s)\textsuperscript{114}, laser diodes (LD’s)\textsuperscript{28}, and UV photodetectors\textsuperscript{38}. In all of these devices,
precise knowledge of the band gap as a function of $x$ is a prerequisite for band gap engineering in order to fulfill device applications. So far, intense work has been carried out to determine the bowing parameter for the bandgap dependence of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys.\textsuperscript{115 - 117} The dispersion of bowing parameters reported by various researchers extends from $-0.8$ eV (upward bowing) to $+2.6$ eV (downward bowing). The differences in the bowing parameter can be attributed to the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ being prepared by different techniques with various qualities and, in some cases, to the range of alloy compositions being narrow. In this research, a systematic study of the dependence of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ band gap on Al mole fraction over the entire range of Al composition ($0<x<1$) was carried out.

The Al mole fraction $x$ was obtained from the out-of-plane lattice constant ($c$) measured by a set of high resolution x-ray rocking curves using a measurement technique described by e.g. Fatemi.\textsuperscript{118} The method is based on the linear relationship between lattice constant and the Al mole fraction. Since the position of AlGaN alloy can be determined by this method precisely, the main error is caused by the un-uniformity of the Al mole fraction cross the sample. The deviation of composition value cross the sample is about 2%. To verify the composition, SIMS and RBS data were also obtained. The results for the Al mole fraction determined by XRD, SIMS, and RBS methods are summarized in Table 6-1. While the Al mole fraction obtained from SIMS and RBS are in general close to those from XRD, they are somewhat higher with a maximum deviation of $\sim3\%$.

Reflectance and PL spectra were also measured at 15 K for the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples. For reflectance measurements, a 30 W deuterium lamp was used as a light source,
whereas for PL measurements a 60 mW He-Cd laser (325 nm) was used. The reflected light and the luminescence signal were dispersed by a 0.5 m focal length spectrometer with 1200 grooves/mm grating blazed at 250 nm. Signals were detected by a photomultiplier tube using the photon counting mode. The Al$_x$Ga$_{1-x}$N band gap was determined from the low-temperature reflectance spectra as the critical photon energy where the reflectance oscillations faded due to above-band absorption. The accuracy was estimated as ±0.1eV for this method with fluctuations of the bandgap energy among different points of the sample. The results are included in Table 6-1. Reflectance measurements are more appropriate for determination of the band gap than PL measurements because a redshift in PL commonly occurs from carrier localization caused by potential fluctuations, as depicted in the inset of Figure 6-4. In addition, it is not always possible to determine whether the observed transitions in the emission measurements, such as in PL, are band-to-band or related to excitons bound to various defects and impurities and what their binding energies are. This, at least in part, accounts for the Al$_x$Ga$_{1-x}$N band gap obtained from PL always being lower than the actual value, as clearly shown in Figure 6-4 for an Al$_x$Ga$_{1-x}$N ($x = 0.13$) sample measured at 15 K.

Assuming a parabolic distribution of deviation, a second-order approximation was used. The bowing parameter $b$ is defined as the coefficient of the parabolic term in the phenomenological expression for the alloy energy band gap:

$$E_{g(x)} = E_{g}^0 x + E_{g}^1 (1 - x) - bx(1 - x)$$  (6-1)

where $E_{g}^0$ and $E_{g}^1$ are the energy band gaps of the GaN and AlN binary end points, respectively. Note that a positive value of $b$ represents a downward bowing, and a
negative $b$ represents an upward bowing. The band gaps of GaN ($E_g^0 = 3.505$ eV at 4 K)\textsuperscript{2} and AlN ($E_g^1 = 6.20$ eV at 2K)\textsuperscript{119} were used to plot the energy band gaps of Al$_x$Ga$_{1-x}$N alloys versus the calibrated Al mole fractions, as depicted in Figure 6-5. A least-squares fit to the data yields a bowing parameter of $b = 1.0$ eV for the entire range of alloy compositions.

6.1.4 Growth mechanism of Al$_x$Ga$_{1-x}$N under metal-rich conditions

Figure 6-6 shows the growth rate as a function of Al mole fraction in Al$_x$Ga$_{1-x}$N alloys. The growth rate decreases markedly with increasing $x$, approaching typical growth rates of GaN and AlN in metal-rich conditions when $x$ approaches 0 and 1, respectively. This phenomenon indicates that the incorporation of Al and Ga atoms is not constant for different N fluxes. Figure 6-7 describes the incorporation of Al and Ga in the films versus the system pressure (or N flux). The Al incorporation rate, expressed as the growth rate of AlN in $\mu$m/hr, is calculated from the product of the measured growth rate and AlN mole fraction of the Al$_x$Ga$_{1-x}$N films. The Al incorporation rate remains constant with increasing N flux, maintaining a value close to the AlN film grown rate under the same conditions. In contrast, the Ga incorporation rate increases linearly with N flux. It is reasonable to assume that the available N is preferentially used to form AlN. As a result, all Al atoms are incorporated and bond with N first. The remaining N is then available for GaN bonds in the alloy. Consequently, the N arrival rate determines the mole fraction in the presence of an abundant amount of Ga in some range of substrate temperatures. As expected, under these conditions, the Al mole fraction in Al$_x$Ga$_{1-x}$N remains constant even with increasing temperature of the Ga sources.
This phenomenon can be explained by preferential formation of the AlN component in the Al\textsubscript{x}Ga\textsubscript{1-x}N alloy under metal-rich growth conditions. It reflects a competition in the incorporation of the Al and Ga atoms. Indeed, the Al-N bond is stronger than the Ga-N bond, since the cohesive energy per bond for Al-N is $E_{\text{AlN}} = 2.88$ eV, while for Ga-N bond is $E_{\text{GaN}} = 2.20$ eV.\textsuperscript{54} The preferential incorporation of Al atoms is energetically favored due to the stronger Al-N bond. The difference of 680 meV is significantly higher than the value of $k_B T \sim 90$ meV at the growth temperature. Thus, the exchange reaction:\textsuperscript{53}

$$\text{GaN} + \text{Al} \Rightarrow \text{AlN} + \text{Ga}$$

is expected, resulting in complete incorporation of all arriving Al atoms. Therefore, Ga atoms behave as a surfactant during the growth of AlGaN alloys by PAMBE under metal-rich growth conditions. They may participate in the growth process but not all the Ga atoms incorporate in the film. A similar surfactant behavior has been reported for Ga on MBE GaN films\textsuperscript{108, 120} and for In during MBE growth of InGaN alloys\textsuperscript{121}.

\section*{6.2 Properties of Al\textsubscript{x}Ga\textsubscript{1-x}N grown under metal-rich conditions}

\subsection*{6.2.1 Optical properties of Al\textsubscript{x}Ga\textsubscript{1-x}N films\textsuperscript{111}}

An example of temperature-dependent PL spectra of an Al\textsubscript{x}Ga\textsubscript{1-x}N layer grown under metal-rich conditions with Al mole fraction $x = 0.13$ is shown in \textbf{Figure 6-8}. PL spectra of all the Al\textsubscript{x}Ga\textsubscript{1-x}N layers grown under metal-rich conditions indicated relatively broad near-band-edge emission peaks and defect-related bands in the green and blue regions at low temperatures. Interestingly, the width of the main peak decreased with increasing temperature due to fast quenching of its high-energy side: the full width at half maximum (FWHM) decreased from 93 to 63 meV in the temperature range between 15
and 100 K for the sample depicted in Figure 6-8. This phenomenon can be explained by
the existence of compositional fluctuations in the Al$_x$Ga$_{1-x}$N. Indeed, the narrowing of the
emission peak with temperature due to quenching of its high-energy side can be
attributed to thermal release of free carriers from the shallower short-range wells and
their percolation into the deeper ones caused by local compositional fluctuations.$^{122}$

The PL intensity for the samples grown under metal-rich conditions generally
quenched at higher sample temperatures, as compared to the N-rich samples. The
quenching behavior of Ga- and N-rich Al$_x$Ga$_{1-x}$N for two samples with similar Al
composition is compared in Figure 6-9. At 15 K the quantum efficiency of PL (the ratio
of the PL power to the incident power, accounting for the geometry of the optical
experiment) was markedly higher for the Al$_x$Ga$_{1-x}$N layers grown under Ga-rich
conditions (3 – 48 %) compared to the layers grown under N rich conditions (1 – 10 %).
These values in turn are much higher than radiative efficiencies obtained for a large set of
GaN layers (Ga polarity) grown under similar conditions: 0.01 – 0.3 % for Ga-rich and
0.1 – 2 % for N-rich GaN. Such an improvement of radiative efficiency in Al$_x$Ga$_{1-x}$N,
especially under Ga-rich conditions, points to a reduced density of dislocations, although
carrier confinement cannot be excluded. With increasing temperature, the PL intensity
quenched above approximately 100 K with the activation energy of about 80 meV for
both the AlGaN layers grown under Ga- and N-rich conditions. The quenching of the
near-band-edge luminescence can be attributed to the activation of electrons from the
bottom of the conduction band in local potential minima caused by composition
fluctuations to the regions where the free electrons are captured by some nonradiative
centers. Very roughly, the energy of 80 meV reflects in such a case the amplitude of potential fluctuations caused by the alloy and or other sources of inhomogeneities. This assumption can be supported by the following experimental observation. With increasing temperature from 15 to 100 K the near-band-edge luminescence line narrowed. This phenomenon has been explained by thermal activation of electrons from local minima and their condensation in particular potential minima with the lowest energy.

6.2.2 Crystalline structure of Al\textsubscript{x}Ga\textsubscript{1-x}N films

The Al\textsubscript{x}Ga\textsubscript{1-x}N films grown by PAMBE under metal-rich and N-rich conditions were characterized by x-ray rocking curves (\(\omega\)-scan). The structural quality of the Al\textsubscript{x}Ga\textsubscript{1-x}N films was evaluated by the full width at half maximum (FWHM) of the (0002) peak. The best Al\textsubscript{x}Ga\textsubscript{1-x}N sample grown under metal-rich conditions with Al composition up to \(x = 0.26\) exhibited a remarkably narrow FWHM of 1.9 arcmin for (0002) diffraction, while the higher Al sample (\(x = 0.71\)) still exhibited a FWHM of \(\sim 5.5\) arcmin. Even for a mole fraction of \(x = 0.92\), the FWHM of (0002) was 8.8 arcmin. However, for N-rich conditions, the FWHM of Al\textsubscript{x}Ga\textsubscript{1-x}N films were typically in the range of 9–12 arcmin even with small \(x\) value. The surfactant-like behavior of Ga atoms may explain the good x-ray diffraction (XRD) results for metal-rich conditions versus those for N-rich conditions.

6.2.3 Defects of Al\textsubscript{x}Ga\textsubscript{1-x}N films\textsuperscript{123}

The defects and microstructure of Al\textsubscript{x}Ga\textsubscript{1-x}N layers (\(x = 0.10–0.25\)) grown by PAMBE under metal- and N-rich conditions were studied by transmission electron microscopy (TEM) in Lawrence Berkley National Laboratories. Using the two beam
conditions for g-vectors parallel to the [0002] and [1120] directions, where the former is out of contrast for edge dislocation while the latter is out of contrast for screw dislocations, the concentrations of each type of dislocation (edge, screw and mixed) was determined for both types of films.

TEM bright-field images are shown in Figure 6-10 for a pair of samples grown under N- and metal-rich conditions. These data show that the density of dislocations under N-rich conditions in the vicinity of the substrate decreases from \(\sim 5 \times 10^{10} \text{ cm}^{-2}\) at the substrate interface to \(\sim 2 \times 10^{10} \text{ cm}^{-2}\) at the surface. The majority (\(\sim 95\%\)) of all dislocations were out of contrast in images recorded for a g-vector parallel to [0002], indicating that they were pure edge dislocations.

The microstructure and defect distribution in layers grown under metal-rich conditions differed significantly. Despite similar densities of dislocations in layers grown under metal-rich conditions (\(7 \sim 8 \times 10^{10} \text{ cm}^{-2}\) near the substrate and \(\sim 5 \times 10^{10} \text{ cm}^{-2}\) at the layer surface) to those grown under N-rich conditions, there was a significant difference in their type distribution. In layers grown under metal-rich conditions, all three types of dislocations (edge, screw and mixed) were present with comparable densities. The differences of the microstructure for these two Al\(_{x}\)Ga\(_{1-x}\)N films may cause the film grown under metal-rich conditions to have a higher radiative efficiency, which is discussed in Sec. 6.2.4.
6.3 Backilluminated ultraviolet (UV) photodetector structure with AlGaN/GaN multi-quantum wells

High quality GaN and AlGaN films are the key to successful fabrication of optical and electrical devices. In Chapter 5, the growth behavior of GaN was investigated under different growth conditions. It was shown that GaN with an atomically smooth surface could be obtained under Ga-rich conditions. Additionally, high quality AlGaN layers with Al mole fraction $x$ being controlled precisely in the entire compositional range (0<$x$<1) were obtained with a high radiative efficiency under metal-rich conditions. These results provide the basis to realize a high quality UV photodetector. In this work, a backilluminated UV photodetector based on a multiple quantum well (MQW) structure was obtained with GaN and AlGaN layers grown under metal-rich conditions.

6.3.1 Structure preparation

MQW-based detectors have several advantages over bulk devices. Higher quantum efficiency and faster response are expected due to their high absorption coefficient and lateral carrier mobility. Moreover, the cutoff wavelength of photodetectors can be adjusted by designing different well widths and barrier heights. A schematic structure of the GaN/AlGaN MQW photodetector used is shown in Figure 6-11. The sample was grown by PAMBE on sapphire. An initial AlN buffer layer (~50 nm) was first grown on the nitridated sapphire substrate at 850°C. The substrate temperature was then lowered to about 700°C for the growth of a 1 µm Al$_{0.35}$Ga$_{0.65}$N layer under metal-rich conditions. This Al$_{0.35}$Ga$_{0.65}$N layer is used to produce a short-wavelength cutoff. Next, films of 7 nm Al$_{0.2}$Ga$_{0.8}$N and 4 nm GaN were alternatively grown to form MQWs with 21 periods to
create a long-wavelength cutoff. A lateral geometry is used in order to take advantage of high carrier mobility. A control sample with a 0.9 \, \mu\text{m} GaN epilayer on a 40 nm AlN buffer layer was also grown on a sapphire substrate. Coplanar Ohmic contacts were fabricated by directly evaporating gold onto the top surfaces of the samples. The width of the metal stripes is 1 mm and the spacing between them is 0.8 mm. The resistances between two neighboring electrodes were determined to be around 50 k\,\Omega for the MQW sample and 10 k\,\Omega for the control sample, as measured directly using a multimeter in dark. The MQWs below the metal stripes form the active region for the photoresponse. Photocurrent is produced by lateral diffusion of photogenerated carriers from one electrode to the other, as indicated by the dark arrow in the active region in Figure 6-11.

6.3.2 Device performance

The spectral responsivity of the detector was measured using a UV-enhanced xenon lamp and a lock-in amplifier at the Institute for Ultrafast Spectroscopy and Lasers and New York State Center for Advanced Technology. The spectral response for backillumination is shown by the solid line in Figure 6-12, which is normalized to the peak responsivity of 0.03 A/W at 330 nm. A flat and narrow band response in the wavelength range of 297 ~ 352 nm is obtained and the signal-to-noise ratio is up to 10^3. The photocurrent was found to increase linearly with optical power as measured at 330 nm. The sharp long-wavelength cutoff at 352 nm is produced by the electron-heavy hole (e-hh) absorption in the MQW region, while the sharp short-wavelength cutoff at 297 nm is introduced by the band-to-band absorption of the Al_{0.35}Ga_{0.65}N layer.
The spectral response curve of the GaN bulk sample for topside illumination is also shown in **Figure 6-12** by the dotted line. Comparing with its 365 nm long-wavelength cutoff, the corresponding cutoff of the MQW-based detector shows a 13 nm blueshift because of quantum effect. The spectral response measured by illuminating the metal surface of the MQW sample is plotted as the dashed line in **Figure 6-12**. Without involving the contribution of the AlGaN layer, only a 352 nm long-wavelength cutoff is observed and the photo response curve extends to deep UV wavelengths by keeping an almost constant responsivity. The photoresponse is much flatter than that for the GaN bulk detector in the active wavelength range.

### 6.4 Conclusions

In this chapter, the growth mechanisms of Al\_xGa\_{1-x}N layers were investigated. A competition occurs between the Al and Ga atoms with regard to film incorporation since the Al-N bond is stronger than the Ga-N bond. It results in a preferential formation of the AlN component in the Al\_xGa\_{1-x}N alloy under metal-rich growth conditions. Thus, all Al atoms are incorporated first. The remaining N is then available for the formation of GaN bonds for the alloy. Consequently, next to the Al flux, the mole fraction $x$ is determined by the N arrival rate in the presence of an abundant amount of Ga on the surface. Under this condition, the Al mole fraction $x$ for Al\_xGa\_{1-x}N layers can be precisely controlled in the entire compositional range (0<$x$<1). The energy band gap bowing parameter of these Al\_xGa\_{1-x}N films was determined to be 1 eV. The Al\_xGa\_{1-x}N layers grown under metal-rich conditions, compared to that under N-rich conditions, have better structural and optical quality. With Al\_xGa\_{1-x}N layers grown under metal-rich conditions, a lateral
geometry GaN/AlGaN MQW-based photodetector was realized. A flat and narrow spectral response in the range of 297–352 nm was achieved using a backillumination geometry.
Figure 6-1  Growth rate of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys as a function of system pressure under Ga-rich conditions. [$T_{\text{Al cell}} = 1005$ °C, $T_{\text{Ga cells}} = 1005$ °C, $T_{\text{substrate}} = 700$ °C]
Figure 6-2  Aluminum mole fraction $x$ in Al$_x$Ga$_{1-x}$N alloys as a function of system pressure under metal-rich conditions. [$T_{\text{Al cell}} = 1005 \, ^\circ\text{C}$, $T_{\text{Ga cells}} = 1125 \, ^\circ\text{C}$, $T_{\text{substrate}} = 700 \, ^\circ\text{C}$]
Figure 6-3  Aluminum mole fraction $x$ in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys as a function of Al cell temperature under N-rich conditions. [$T_{\text{Ga cells}} = 970 \degree \text{C}, T_{\text{substrate}} = 700 \degree \text{C}$]
Figure 6-4  Low-temperature (15 K) reflectance and PL spectra of an Al$_x$Ga$_{1-x}$N ($x \sim 0.13$) sample. The inset is a schematic energy band diagram showing the effects of any local Al$_x$Ga$_{1-x}$N fluctuations.
Figure 6-5  Experimental data of energy band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0<x<1$) plotted as a function of Al composition (solid circle), and the least squares fit (solid line) giving a bowing parameter of $b = 1.0$ eV. The dashed line shows the case of zero bowing.
Figure 6-6 Growth rate of Al$_x$Ga$_{1-x}$N alloys as a function of Al mole fraction $x$ under Ga-rich conditions.
Figure 6-7  Incorporation rate of Al (solid square) and Ga (open circle) as a function of system pressure under Ga-rich conditions. [T_{Al\ cell} = 1005 °C, T_{Ga\ cells} = 1125 °C]
Figure 6-8  PL spectra of a representative Al$_x$Ga$_{1-x}$N layer with $x = 0.13$ grown under Ga-rich conditions.
Figure 6-9  Temperature dependence of the PL quantum efficiency for Al$_x$Ga$_{1-x}$N layers grown under metal-rich (empty square) and N-rich conditions with $x\sim$0.15 (solid circle).

$E_A = 80$ meV
Figure 6-10  TEM bright-field images of layers grown under N-rich/Ga-rich conditions recorded under: (a)/(d) multi-beam condition, (b)/(e) two-beam condition with g-vector parallel to [0002] and (c)/(f) g-vector parallel to [1120].
Figure 6-11  Schematic diagram of the backilluminated UV detector based on the GaN/AlGaN multiple quantum wells.
Figure 6-12  Spectral responsivity curves of the MQW-based sample for backside (solid line) and top side (dashed line) illumination, and the control GaN sample for top side illumination (dotted line). All curves are normalized to the peak responsivity of the backilluminated MQW detectors.
Chapter 7  Summary

III-nitride semiconductors (AlN, GaN, InN, and their alloys.) have attracted a great deal of attention among many semiconductor research communities, since they have direct wide band gaps in the range of possibly from 0.8 eV (depending on the accurate determination of the InN bandgap) to 6 eV at room temperature. This property alone extends the optoelectronics applications beyond the conventional compound semiconductors, such as GaAs and ternaries and quaternaries based on it. Furthermore, the nitride semiconductors are chemically inert with high thermal conductivity, and can operate at higher temperatures due to their large band gaps. In the past several years, GaN and its alloys with InN and AlN have been commercialized for light-emitting diodes, laser diodes, UV photodetectors and heterojunction field effect transistors. GaN-based nitride semiconductors have several advantages over other wide band gap semiconductors such as SiC and diamond in that they can be doped as both n- and p-type, have direct band gaps and form heterostructures suitable for device applications.

Remarkable progress in the growth of high quality epitaxial III-nitride films has recently been achieved with the assistance of a variety of methods. Among all growth methods, MBE is a highly accurate growth method with in-situ monitoring features that provide excellent composition and quality control. A significant advantage of PAMBE is
the capability of growth at relatively low substrate temperatures. This becomes important for InN containing III-nitride semiconductors, which decompose at relatively low temperatures. The growth at low growth temperatures is not under equilibrium condition, however. As mentioned in Chapter 2, the growth process relies on a balance between adsorption and desorption processes with conditions chosen so that the adsorption rate is greater than the desorption rate. The film quality is determined by a competition between diffusion and desorption processes occurring on the surface of the growing film. There have been some published studies on modeling of III-nitride growth in an MBE environment, however, it is difficult to quantitatively estimate the diffusion energy on and desorption energy. A thorough study of the growth mechanisms is still needed.

In this research, the Ga surface desorption behavior was investigated using reflection high-energy electron diffraction (RHEED) during the GaN growth by plasma assisted molecular beam epitaxy (PAMBE). It was found that the desorption of Ga atoms from the GaN (0001) surface under different III-V ratios depends on the coverage of adsorbed Ga atoms, which is determined by the III/V ratio. Although applicable within a small temperature range for the same III/V ratio, zeroth-order kinetics can be applied to determine the approximate desorption energy. The desorption energies are determined to be 2.76 eV for a Ga coverage of about 100%, 1.89 eV for 45% coverage, and 0.82 eV for 10% coverage, all determined by monitoring the intensity change of the RHEED specular beam when the growth is stable. Moreover, GaN layers were grown on etched GaN surfaces featuring a porous like network. The GaN surface morphology varying under different III-V ratios on porous templates is consistent with this result that the
dependence of Ga desorption energy on the coverage, and that the III/V ratio dominates the growth mode.

In the N-rich regime, the surface is covered with an abundance of N and the coverage of excess Ga is zero. Under this condition, the diffusion energy of Ga is much greater than the desorption energy. The surface morphology in this regime is very rough. Under very Ga rich conditions (Ga-droplets regime), the surface is covered with Ga and the coverage is close to 100%. Too many excess amounts of Ga atoms accumulate on the surface which led to the formation of Ga droplets.

Between these two extremes, the Ga coverage is in the range of 0% to 100% for stoichiometric and Ga-rich conditions, respectively. Under stoichiometric conditions, the Ga coverage is low, and the diffusion energy is comparable to the desorption energy. Consequently, Ga atoms prefer to incorporate into the GaN film or desorb from the surface instead of diffusing to a new site. In contrast, the diffusion energy is smaller than the desorption energy under Ga-rich conditions. The Ga atoms are very mobile in this case and prefer diffuse on the surface to find lower energy sites. As a result, the GaN growth mechanism follows a layer-by-layer growth mode, resulting in a smooth surface.

The growth mechanism of AlGaN was also studied as part of this dissertation. A competition between Al and Ga atoms for incorporated into the AlGaN film was found under metal-rich conditions, which led to preferential formation of the AlN component in the Al$_x$Ga$_{1-x}$N alloy. Thus, all Al atoms are incorporated first consuming the needed N atoms. The remaining N then form bonds with Ga for the GaN component of the alloy. Taking advantage of this mechanism, Al$_x$Ga$_{1-x}$N layers with precisely controlled Al mole
fraction, $x$, in the entire range (0<x<1) were obtained under metal-rich conditions. The energy band gap bowing parameter of these $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films was determined to be 1 eV. The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers grown under metal-rich conditions have much better structure compared to those grown under N-rich conditions, and the XRD results are about 2 arcmin for small $x$ values. The PL quantum efficiency of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ grown under metal-rich conditions is also higher than that under N-rich conditions. The highly mobile nature and surfactant effect of Ga during $\text{Al}_x\text{Ga}_{1-x}\text{N}$ growth in the metal-rich regime are believed to improve the film’s structural and optical property. With $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers grown under metal-rich conditions, a lateral geometry $\text{GaN/AlGaN MQW-based photodetector}$ was realized. A flat and narrow spectral response in the range of 297~352 nm was achieved in the backillumination configuration.
Table 6-1  Energy band gap data measured by reflectance spectra on Al\(_x\)Ga\(_{1-x}\)N alloys. The Al mole fraction was measured by XRD, and corroborated by SIMS, and RBS. A correction was made based on second-order calibration factors obtained from SIMS and RBS.

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