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GROWTH, CHARACTERIZATION AND PROCESSING OF GALLIUM NITRIDE FILMS FOR HIGH TEMPERATURE ELECTRONICS AND OPTOELECTRONICS IN BLUE TO UV

A DISSERTATION
SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By
Heon Lee
December 1996
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I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Approved for the University Committee on Graduate Studies:
Abstract

GaN has suddenly become an important optoelectronic material, but the greatest barriers to its application are its high defect density and lack of bulk substrates for epitaxial growth. GaN thin films were grown on (001) GaAs substrates by ECR plasma assisted MBE to study the defect issues. Elemental Ga and physically activated atomic nitrogen are used as group III and group V sources. The growth rate of GaN is only about ~0.2 μm/hr. Due to large lattice and thermal mismatches between GaAs and GaN, the crystalline quality of GaN films is not adequate for electronic or photonic devices. In spite of the cubic symmetry of the substrate, wurtzite structure GaN films grow in a columnar structure and each column is oriented along the c-axis. Several in-plane orientations are observed in the GaN films from X-ray diffraction Φ-scans. While photoluminescence (PL) spectra at 77K show strong band edge related emission at 3.47 eV, they also contain broad defect-impurity related emission around 2.1 eV.

Because bulk GaN can only be grown at extremely high pressures, alternative approaches must be investigated. The much faster growth rate with good crystalline quality of hydride vapor phase epitaxy (HVPE) makes it one of the best approaches to grow pseudo-bulk thick GaN films. These films will be used as the substrates for homoepitaxial growth of subsequent device structures grown by MBE or MOCVD. A new HVPE system, which uses crystalline GaCl₃ and NH₃, as the group III and V sources, respectively, was developed. Thermodynamic calculations were carried out on this growth system in order to understand the growth mechanisms and to optimize reactor design. Growth parameters were optimized in order to obtain high crystalline quality thick GaN films with smooth surfaces. (0001) and (1120) oriented Al₂O₃ wafers are used as substrates. X-ray diffraction and transmission electron microscopy measurements show the GaN films are single crystalline. A high density of crystalline defects, such as dislocations and stacking faults, are observed near the interface and their density decreases drastically with an increase of film thickness. GaN films show very sharp, strong band edge related photoluminescence without any obvious defect related emission. To improve the initial nucleation of GaN crystals on the Al₂O₃ substrates, thin AlN buffer layers were deposited by RF sputtering. The crystalline quality and surface morphology of GaN films grown on AlN buffer layers are greatly improved. The minimum RBS channeling yield and FWHM of X-ray rocking curves of GaN films grown with thin AlN buffer layers are smaller than those of GaN films grown directly on Al₂O₃ substrates.
GaN films were successfully patterned by reactive ion etching (RIE) using Cl (H) containing plasmas. CHF₃/Ar, C₂Cl₂F₃/Ar, C₂Cl₂F₆/Ar/O₂, SiCl₄ and CHCl₃ plasmas were used to etch GaN. Etch rate increases with an increase of RF plasma power and a decrease of chamber pressure for all plasmas used in this study. SiCl₄ and CHCl₃ plasmas etch GaN much faster, up to 4–5 times, than CHF₃ and C₂Cl₂F₆ plasmas under identical etching conditions (plasma power, chamber pressure, gas flow rate, etc.) The GaN etch rate is dependent on the crystalline quality of GaN. Higher crystalline quality GaN films exhibit slower etch rates than defective GaN films. AFM measurements of etched and unetched GaN films, demonstrate that reactive ion etching does not cause any serious surface roughening and the surface becomes smoother after etching due to faster etching of the peaks of the film. XPS analysis reveals that the etched surfaces are slightly contaminated by carbon and oxygen. Serious photoresist mask erosion and hardening are often observed. Therefore, fine pattern transferring to GaN films using photoresist mask and complete removal of remaining photoresist after etching is very difficult. By replacing the etch mask from conventional photoresist to sputtered iron nitride (Fe-8% N) film, GaN films can be finely patterned with vertical etched sidewalls.
Acknowledgments

It was a long journey, not just an easy-going way. I believe it is a very valuable time and there is no regret.

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Chapter 1

Overview of GaN and other Group III nitrides

GaN and other group III nitrides are the most promising semiconductor systems for optoelectronic devices for short wavelength (green, blue, violet and UV) and high power electronic devices operating under high temperatures and high irradiation environments. In group III nitrides, there are a number of unique features which can be utilized for the device possibilities.

(a) a direct bandgap range extending continuously from 1.9 eV for InN to 6.2 eV for AlN
(b) possibility of fabricating quantum well and superlattice devices using lattice matched heterojunctions
(c) low dislocation, surface and interface recombination rates which enable strong radiative recombination in the presence of surfaces and dislocations
(d) high electron mobility and low carrier concentration
The best reported value are 900 cm$^2$/Vsec at room temperature [1] and 25 cm$^2$/Vsec at 950°C [2].
(e) high resistance to degradation due to chemical inertness and low dislocation mobility

Recent improvements in the crystalline quality of epitaxially grown group III nitrides enable the commercial use of these materials. In the first section of this chapter, the materials properties of GaN and other group III nitrides are briefly described to deepen our understanding about these materials. Potential applications of these materials are also described in this chapter.
1-1 Materials Properties of GaN and other Group III nitrides

1-1-1 Crystal Structure and Thermal properties of GaN

GaN can exist in two crystalline structures: wurtzite and zincblende. Figure 1-1 shows the hexagonal (wurtzite) and cubic zincblende structures of GaN. The wurtzite form is the more stable crystalline form of GaN with two chemical formula (GaN) per unit cell. The space group and point group symmetries of this crystal structure are P6₃mc and 6mm, respectively. Even though the lattice parameters can be altered by residual strain, non-stoichiometric N vacancies and impurity atoms, the intrinsic values at room temperature are $a = 3.1892 \pm 0.0009 \, \text{Å}$ and $c = 5.1850 \pm 0.0005 \, \text{Å}$ [3,4].

![Crystal Structure of GaN](image)

Figure 1-1. Crystal Structure of GaN, (a) wurtzite structure (hexagonal), (b) cubic zincblende structure.

The cubic zincblende structure of GaN is meta-stable. This cubic crystalline GaN are obtained when GaN is epitaxially grown on a cubic substrate, such as (100) GaAs [5, 6], (100) Si[7], β-SiC [8] or (100) MgO [9] at relatively lower temperatures. The
calculated lattice constant of cubic GaN, based upon the Ga-N bond distance in wurtzite GaN, is 4.503Å. The measured values range from 4.49 to 4.55Å [8, 10, 11]. The total energy difference between zincblende and wurtzite were was calculated to be approximately 10 ~ 15 meV/atom in favor of the wurtzite structure[12, 13]. The bandgap energy of cubic zincblende GaN is 3.18eV. At high pressure, around 50 GPa, a phase transition occurs in GaN and the wurtzite structure becomes a rocksalt structure [14].

The lattice parameter of GaN single crystal changes linearly with temperature. The reported value of GaN thermal expansion coefficient in the temperature range from 300 to 900K is $+5.59 \times 10^{-6} \text{ K}^{-1}$ in a-axis and $+3.17 \times 10^{-6} \text{ K}^{-1}$ in c-axis [1]. Figure 1-2 shows the values of lattice parameter and thermal expansion coefficient of Group III nitrides and other commonly used substrates. No substrate matches its the thermal expansion coefficient and lattice constant to GaN. Thus any heteroepitaxially grown GaN film contains a high concentration of crystalline imperfections, such as dislocations, and this hampers the performance of GaN based devices. Regardless of large lattice and thermal mismatches to GaN, sapphire (Al$_2$O$_3$) is the most commonly used substrate.

Figure 1-2. Various substrates for Group III nitrides, their thermal and lattice mismatch to Group III nitrides.
1-1-2 Phase Equilibria of GaN

The thermodynamic stability of GaN as a function of growth conditions has been investigated for the case of N₂ and NH₃ as nitrogen sources by Newman et. al. [15]. Figure 1-3, (a) and (b) show the thermodynamically stable regions of GaN growth as a function of substrate temperature and reactant partial pressure.

![Phase Diagrams](image)

Figure 1-3. (a) Phase Diagram for GaN growth from N₂ ambient. (b) Phase Diagram for GaN growth from NH₃ ambient. The regions of thermodynamic stability and each growth process are shown as a function of temperature and gas partial pressure. [15]

While N₂ is used as the nitrogen source, GaN films are grown under thermodynamically unstable regions in most growth techniques, due to the very high equilibrium pressure of N₂ over GaN. Since the thermodynamically favored process is the decomposition of GaN into Ga(l) and N₂ gas rather than deposition, GaN must be grown under thermodynamically unstable regions, GaN actually undergoes congruent sublimation, rather than decomposition, due to the large kinetic barriers to decomposition. Thus, high nitrogen vacancy concentrations with lower growth rates are inevitable. While NH₃ is used as the nitrogen source, the equilibrium pressure of NH₃ over GaN become much lower than that of N₂. Therefore, GaN films can be grown under thermodynamically
stable conditions by hydride vapor phase epitaxy, conventional CVD and plasma enhanced CVD growth techniques and the congruent sublimation of GaN is minimized. GaN films grown with NH$_3$ show lower crystalline defect densities and faster growth rates. One further important issue is the purity of nitrogen sources. High purity nitrogen sources are essential in order to obtain high purity Group III nitrides. The contamination levels for various impurities in ultra pure N$_2$ and NH$_3$, have recently been compared [16]. The overall purity level of ultra high pure N$_2$ is nearly 50 times higher than the best available NH$_3$. Therefore, the N$_2$ process offers the potential for higher purity GaN growth than those using NH$_3$.

1-2 Difficulties in growth of GaN and other Group III nitrides

In spite of the successful fabrication of Group III nitride based light emitting diodes, improvement of crystalline quality of epitaxially grown GaN and other Group III nitrides films is still a very important issue. Due to the absence of bulk single crystals for homoepitaxy and substrates with good lattice and thermal expansion match, any heteroepitaxially grown GaN film contains a high concentration of structural defects. The very high N$_2$ equilibrium pressure at typical growth temperatures also makes GaN films nonstoichiometric and they have a high concentration of nitrogen vacancies which act as the electron donors. As a result, any undoped GaN films exhibits fairly high n-type background conductivity. Because of the lack of a shallow p-type dopant and a self compensation process with native donors, high p-type conductive Group III nitride films are not yet available.

In order to fully utilize the characteristics of Group III nitrides, growth of complicated device structures such as quantum wells and superlattices of alloy nitrides (InGaN, AlGaN, etc.) are very important. Due to a relatively large lattice mismatch between InN and other Group III nitrides and the higher desorption coefficient of In atoms than other Group III atoms at typical growth temperatures, growth of high crystalline quality In content alloy nitrides (InGaN, AlGaN) is very difficult.
1-3 Possible Applications of GaN and other Group III nitrides

There is clearly a great demand from the electronics and optoelectronics industries for the properties while only Group III nitrides can deliver. As the result of success in both the growth of high crystalline quality nitride epitaxial layers (lower dislocation density and background conductivity) and controlled intentional doping, electronic and optoelectronic devices utilizing the characteristics of Group III nitrides are being developed, including: heterojunction field effect transistor, sensors, light emitting diodes, laser diodes and photodetectors. Table 1-1 lists the material characteristics of Group III nitrides and their possible applications. Group III nitride based electronic devices are suitable for high temperature and high power uses and they can be applied in many areas, including: automobile engines, power plants, turbine blades, etc. GaN based blue LEDs can be used in full color displays, full color scanners for FAX and copiers and traffic signal lights. The density of optical data storage, such as CD ROMs and magneto-optic disc, can be increased by a factor of 4 by using InGaN based blue lasers and increased even more by using AlGaN based UV lasers. Development of high resolution laser printer can also be realized by GaN based blue lasers. AlN based materials can also be used for flat panel display and electron multipliers using its negative electron affinity characteristics.
<table>
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<tr>
<th>Characteristics of Group III nitrides</th>
<th>possible applications</th>
<th>final products</th>
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<td>direct band structure</td>
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<td>wide bandgap nature</td>
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<td>• FET and other major carrier devices</td>
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<td>chemical inertness</td>
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<td>negative electron affinity (AlN)</td>
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Table 1-1. The characteristics of Group III nitrides and their possible applications utilizing the characteristics.
Chapter 2

ECR plasma assisted MBE Growth of GaN films on GaAs

As briefly described in Chapter 1-1, Group III nitride semiconductors, especially GaN, are most promising candidates for the development of high power and high temperature electronics and optoelectronics for shorter wavelengths (green, blue to deep UV). The dominant GaN growth technique at present is metalorganic vapor phase epitaxy (MOVPE). Metalorganic group III sources such as TMGa, TEGa, TMAI and TMIn and NH₃ gas are used as the reactants for the III-V nitride compounds. MOVPE has demonstrated the growth of high quality GaN and its alloy nitride epilayers characterized by undoped GaN with background n-type doping level below $4 \times 10^{16} / \text{cm}^3$ and p-type conductivity conversion by intentional Mg doping. These improvements have enabled several device applications in this materials, such as heterojunction field effect transistor using GaInN channel and AlGaIn barrier [1], green, blue and violet LEDs [2-5], p-i-n UV photodetectors [6] blue lasers [7]. Even though group III nitrides have been successfully grown by MOVPE, the as grown GaN films contain a high density of threading dislocations, up to $10^{9} / \text{cm}^3$ [8] and these play a role in the degradation of device performance. Molecular beam epitaxy (MBE) is also used in the growth of GaN and its alloy nitrides. In spite of the poorer results compared to MOCVD to date, MBE has several intrinsic advantages over MOCVD for research and possibly even for production environments. The lower growth temperature in MBE leads to better growth of InN or high In content alloy nitrides and the smaller amount of thermal stress built in the epilayers after cooling allows fabrication of more abrupt and a broader range of heterojunctions. MBE growth also offers utilization of in-situ growth monitoring tools, such as reflection high-energy electron diffraction (RHEED) and mass spectroscopy, which should enable a deeper understanding of growth mechanisms. The ultra high vacuum background of MBE growth
makes it possible to minimize the unintentional doping and to enhance the surface migration of adatoms. More diverse dopants are also available in MBE growth. Group III nitrides can be grown under a hydrogen-free environment in MBE, therefore the passivation of p-type dopants by incorporation of hydrogen atoms can be prevented [9].

2-1 Introduction

2-1-1 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a technique of vacuum evaporation, the earliest and simplest way of depositing thin films. The basic difference between MBE and other vacuum evaporation techniques is that the deposition is accomplished with very precisely controlled molecular or atomic fluxes under an ultra high vacuum (UHV) environment, thus ultra high purity single crystal films can be grown epitaxially by MBE. MBE has been an important technique for the fabrication of novel electronic and photonic devices by bandgap engineering using artificially layered materials[10]. A schematic diagram of a conventional solid source MBE system is shown in Figure 2-1.

The molecular beams are generated in Knudsen type effusion cells by resistive heating and their temperatures are controlled to an accuracy of ± 1°C in a UHV environment for the precise control of atomic and molecular beams. Mechanical shutters are placed in front of each effusion cell so that the species of molecular beams can be abruptly changed. During the growth, in-situ analysis techniques such as reflection high energy electron diffraction (RHEED) and mass spectroscopy are used to monitor the growth.
2-1-2 Generation of Active Nitrogen Species for nitride growth

Due to the chemical inertness of the nitrogen molecule (N₂) and relatively high values of free energy of formation (ΔG_{formation}) for group III nitrides (GaN, AlN, InN) [11], highly activated nitrogen species such as atomic nitrogen (N) or nitrohydrogen (NH₃) radicals are essential to grow group III nitrides. Figure 2-2 shows the ΔG_{formation} values of various nitrides and oxides as a function of temperature. A lower value of ΔG_{formation} means that there is a stronger tendency for that compound to form. Since InN has a high positive value of ΔG_{formation} at higher temperatures, lower growth temperatures are required to grow InN or high In content group III nitride alloys. For vapor phase growth techniques, including MOCVD and HVPE, a high substrate temperature (1000~1100°C) is generally required to activate the nitrogen containing molecules, typically NH₃, by using thermal energy [1-5, 12]. Growth temperature can be lowered by using more active chemical nitrogen source [13] or by introducing other energy, such as a plasma, to crack the nitrogen containing molecules. For MBE growth of nitrides, more reactive or highly activated
nitrogen species are required due to its much lower growth temperature (600 ~ 750°C) than vapor phase growth techniques.

![Graph showing the Gibbs Free Energy of Formation (kJ/mol) vs. Temperature (K) for various nitrides](image)

**Figure 2-2.** $\Delta G_{\text{formation}}$ (free energy of formation) of various nitrides as a function of temperature.

There are two different ways to generate active nitrogen species. One is the use of a chemically active nitrogen source. Any nitrogen containing gas which can be easily dissociated into either atomic nitrogen or NH$_x$ radical under typical group III nitride growth conditions can be used as the nitrogen source. NH$_3$, N$_2$H$_2$ [14-15], HN$_3$ [13] and DMHy ((CH$_3$)$_2$N$_2$H$_2$) [16] have generally been used for this purpose. In these cases, incorporation of hydrogen atoms into growing nitride film is inevitable and thus, post heat treatment is required to activate p-type dopants. Semiconductors require extreme level of purity. It is thus important that the purity of grown nitride films not be limited by the purity of the above nitrogen source gases since the purity of these gases is not as good as that of nitrogen. The most important advantage of using these chemical nitrogen sources is that
nitride films can be grown without ion damage, which cause rough surfaces and poor crystallinity. The other choice is the use of nitrogen gas which must be dissociated into atomic nitrogen. In order to achieve a reasonable growth rate, a high flux of atomic nitrogen is necessary. Higher plasma power is required to increase the dissociation efficiency and create a high flux of atomic nitrogen however, this results in more severe ion damages from the higher plasma power. The ideal case for the growth of group III nitride using physically activated nitrogen source is the high concentration of atomic nitrogen with low ion energy, in order to maximize the growth rate and to minimize the ion damage in the growing nitride films. RF plasma sources [17-19] and ECR plasma sources [13, 20-23] are most commonly used plasma sources for the growth of group III nitride. Results from both types of sources suggest that RF plasma sources produce a greater flux of atomic nitrogen or excited N₂ radicals and fewer N₂⁺ ions than ECR sources and are thus the source of choice.

2.1.3 Cubic GaN vs. Hexagonal GaN

As briefly described in chapter 1.1.1, the meta-stable cubic zincblende phase of GaN can be epitaxially grown on cubic substrates, such as GaAs, Si, β-SiC and MgO at relatively lower temperatures than typical growth temperatures of hexagonal GaN. The total energy of zincblende GaN is slightly higher than the wurtzite GaN with an difference of about 10 ~ 15 meV/atom. The hexagonal phase of GaN is thus the stable form of GaN. Cubic GaN has some advantages over hexagonal GaN. The substrates for cubic GaN are cheaper, more reliable and have much better crystal quality than those typically used for wurtzite GaN, such as sapphire or α-SiC. Thus, the density of crystalline defects extending from the substrate in to the epitaxial layer, can be reduced in cubic GaN films. High quality cleaved surfaces can be obtained from cubic GaN grown on cubic substrates, unlike wurtzite GaN films on sapphire substrates. Since, the bandgap energy of cubic zincblende GaN is 3.18eV, which is slightly lower value than wurtzite GaN, smaller In content InGaN alloy films can generate longer wavelength photons.

For the ECR-MBE growth, wurtzite GaN films were grown on (0001) oriented sapphire substrates. From the electron diffraction and X-ray diffraction patterns, GaN films were single crystalline, with a high concentration of structural defects [13, 22]. The orientation relationship between GaN films and (0001) sapphire substrates are:

\[ [0001]_{\text{GaN}} // [0001]_{\text{sapphire}}, [1 \overline{1} 0 0]_{\text{GaN}} // [10 \overline{1} 0]_{\text{sapphire}} \]
GaN film is rotated with 30° toward sapphire substrate in order to minimize lattice mismatch. Growth rates determined by profilometry were approximately in the range of 0.1 ~ 0.2 μm/hr. Many of the GaN films grown with ECR plasma displayed rough and uneven surfaces, indicating the presence of significant ion damage. Photoluminescence (PL) measurements were performed at 77K using a 10mW He-Cd laser operating at 325nm. GaN films showed a strong PL peak at 360nm, corresponding to a band to band transition, and a little deep level luminescence originating from crystalline defects.

In this study, (100) GaAs wafers were used as the substrate, in order to obtain the cubic form of GaN films.

2-2 Experimental

In the ECR assisted MBE technique, GaN film is grown by the reaction of elemental Ga with an activated atomic nitrogen species produced by the dissociation of nitrogen gas in an electron cyclotron resonance (ECR) plasma discharge. The plasma energy must be minimized to reduce ion damage in the growing film. Consequently, the activated atomic nitrogen flux limits the growth rate to a very low rate (0.15 ~ 0.25 μm/hr). The plasma also gives rise to a fairly high concentration of silicon and oxygen contamination to the films due to sputtering of the SiO₂ plasma cup in the source during the growth.

Figure 2-3 shows a schematic diagram of the GaN growth system used in this study. A modified Varian GEN II MBE system with a Wavemat™ electron cyclotron resonance (ECR) plasma source is used to grow GaN films. The ECR plasma source is attached to the center of the source flange in order to obtain a uniform flux of activated nitrogen over the whole substrate surface [13, 21-22]. Group III elements are evaporated from standard effusion cells and microwave activated nitrogen gas is supplied by the ECR plasma source. During the growth, pressure is a few times of 10⁻⁴ torr, which is about the maximum value that leaves the fluxes still in the molecular flow regime.
Figure 2-3. Schematic diagram of modified Varian GEN II MBE system with a Wavemat\textsuperscript{TM} ECR plasma source for GaN growth.

2-inch diameter semi-insulating (100) GaAs wafers were used as the substrates. Prior to loading, GaAs wafers were degreased by organic solvents and rinsed by DI water. Wafers were baked at 400°C for an hour in the loading chamber to drive off water and then transferred to the growth chamber. The substrate was exposed to the nitrogen plasma at 740°C for 30 minutes for native oxide removal and surface nitridation. A 300 ~ 500Å thick GaN or AlN buffer layer was grown at 400°C after which the substrate temperature was raised to its final growth temperature. The typical growth conditions for the GaN films grown with the ECR plasma are described in Table 1. The growth rate was about 0.15 - 0.25 μm/hr, which was not changed drastically by the variations in growth parameters. Some of the films showed a ring-type pattern due to ion damage from the toroidal shaped plasma.
<table>
<thead>
<tr>
<th>Substrate Temperature</th>
<th>650 - 740°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Flow Rate</td>
<td>10 - 20 sccm</td>
</tr>
<tr>
<td>Ga Beam Flux</td>
<td>2 - 3 x 10^{-7} torr</td>
</tr>
<tr>
<td>Plasma Power</td>
<td>150 - 200 W</td>
</tr>
<tr>
<td>Chamber Pressure</td>
<td>1.9 x 10^{-4} torr</td>
</tr>
</tbody>
</table>

Table 2-1. Typical growth conditions of GaN films grown by ECR plasma assisted MBE

2-3 Results and Discussion

The properties of GaN films were investigated by various characterization techniques, including X-ray diffraction (XRD), X-ray rocking curve (XRC), Raman spectroscopy, transmission electron micrography (TEM), X-ray photoelectron spectroscopy (XPS), Hall measurements, photoluminescence (PL) and cathodoluminescence (CL). In order to identify the phase of GaN films, XRD and Raman spectroscopy were accomplished. From the position of peaks, information about phase, crystalline orientation and residual stress is obtained. Crystalline quality of GaN films was directly measured from the full width half maximum (FWHM) of XRC. The information about microscopic crystalline quality and orientation is directly visualized from TEM and electron diffraction. Existence of chemical impurities and their distribution in depth are detected by XPS. Electrical properties of GaN films, such as conductivity and mobility, are measured by Hall measurement technique and the optical properties of GaN films are investigated by PL technique. By photoluminescence and cathodoluminescence, bandgap energy and other defect related energy states are measured from the position of luminescence peaks.

2-3-1 Structural Characterization of GaN films

A typical X-ray diffraction pattern, shown in Figure 2-4, indicates that [0001] oriented wurtzitic GaN films were deposited on [001] GaAs substrates. According to the relevant φ-scan, GaN films have several in-plane orientations and thus the GaN films are not single crystalline. An X-ray rocking curve of the (0002) peaks of wurtzite GaN show a FWHM of 720 arcseconds. An example of Raman spectrum obtained in the backscattering...
configuration along z-axis is shown in Figure 2-5. The longitudinal $A_1$ mode at $734 \text{ cm}^{-1}$ and high energy $E_2$ mode at $565 \text{ cm}^{-1}$ are observed in correspondence with selection rules for wurtzite GaN [21, 24]. This means that the GaN film is oriented with the c-axis aligned with surface normal. No variation of peak position is observed in GaN films grown at different temperatures with different thickness thus, the GaN films were fully relaxed by introducing dislocations, stacking faults and other crystalline defects. TO and LO phonon peaks of the GaAs substrate are also observed at 266 and 291 cm$^{-1}$, respectively, which implies that the GaAs substrate lattice is distorted near the interface due to stress caused by the GaN film.

Figure 2-4. Typical high resolution $2\theta / \omega$ X-ray diffraction pattern of GaN film grown on (001) GaAs substrate by ECR plasma assisted MBE.
Figure 2-5. Typical Raman Spectrum of GaN film grown on (001) GaAs substrate by ECR plasma assisted MBE.

Figure 2-6 shows a high resolution cross-sectional TEM photograph of a clearly wurtzite type GaN film grown on a (001) GaAs substrate. Near the interface, the film contained a high density of dislocations and stacking faults. A cluster of zincblende GaN was observed, but the GaN film showed mainly a wurtzite stacking sequence, even though a cubic GaAs (001) wafer is used as the substrate. Figure 2-7, (a) shows the bright field cross-sectional TEM image of a GaN film grown on (001) GaAs at lower magnification. According to Figure 2-7, (a), the GaN film consisted of columnar domains and each domain was not defective. The surface of the GaN films was relatively rough, due to columnar growth mode. An high resolution plane view lattice image of the same GaN film is shown in Figure 2-7, (b). The angle between two adjacent columns is about 30 degrees. Regardless of the large different in-plane orientations of individual columns, their out of plane orientation is parallel to each other.
Figure 2-6. High resolution lattice image of GaN film grown on (001) GaAs substrate at 700°C.
Figure 2-7. (a). Bright field cross-sectional TEM image of GaN film grown on (001) GaAs substrate at 700°C.

Figure 2-7. (b). High resolution plane view lattice image of GaN film grown on (001) GaAs substrate at 700°C.
2-3-2 Chemical and Optical Characterization of GaN films

In order to verify the composition of GaN films, the films were analyzed by X-ray Photoelectron Spectroscopy (XPS). The top 100Å thick surface layer was first etched prior to the analysis to remove surface contaminants. The XPS spectra shown in Figure 2-8 reveals that the GaN films contained fairly high concentration of oxygen (order of $10^{20}$ atoms/cm$^3$) which caused an n-type background conductivity [25-28]. No obvious Si peak was observed, which means the Si content should be less than $10^{19}$ atoms/cm$^3$ (~0.1 atomic %) which is the detection limit of XPS.

![Figure 2-8. X-ray photoelectron spectrum of GaN film grown on (001) GaAs substrate at 740°C.](image)

The optical properties of GaN films were characterized using low temperature (77K) photoluminescence. A 325nm HeCd laser with 10mW power was used to excite electron-hole pairs. The strong bandedge-related emission was observed near the bandgap with broad defect-related emission. It is believed that the origin of broad defect peak is the
complex of crystalline defects and chemical impurities, such as oxygen. Figure 2-9 shows the photoluminescence spectra of GaN grown on a (001) GaAs substrate at 77K.

Figure 2-9. The photoluminescence spectra of GaN film grown on (001) GaAs substrate at 77K.

2-3-3 Effects of Annealing of GaN films

After the growth, GaN films were heat-treated in a quartz tube furnace under N\textsubscript{2} ambient in 600°C to 1000°C for 30 minutes in order to see if this would improve the crystalline quality of the GaN films. Unfortunately, the measurements of full width half maximum (FWHM) of GaN (0002) plane peak in X-ray rocking curves, only shows a slight decrease of FWHM for samples heat treated between 900°C – 1000°C. This may be complicated by contamination of GaN films by As desorbed from the GaAs substrates. Figure 2-10 shows the change of the X-ray FWHM of GaN (0002) peak with respect to annealing temperature.
Figure 2-10. The effect of annealing temperature on X-ray FWHM of GaN (0002) peak.

2-4 Summary

It has been reported that cubic phase GaN films were grown on GaAs substrates[16]. This result is supported by X-ray diffraction, Raman spectroscopy and high resolution cross-sectional TEM. From this work, wurtzite GaN films with (0001) orientation resulted from growth on (001) GaAs substrates by ECR assisted MBE, in spite of the substrate's cubic symmetry. In our GaAs surface nitridation and initial nucleation stages, the wurtzite GaN nuclei dominated the cubic GaN nuclei. Thus, the GaN films were the wurtzite structure however, they contained cubic structure GaN clusters near the interface. Elemental Ga and physically activated atomic N were used as group III and group V sources. The growth rate of GaN was about ~0.2 \( \mu m/hr \). According to the cross-sectional TEM analysis, GaN films consisted of columnar domains. From the relevant \( 2\theta/\omega \) X-ray diffraction results, only (0002) wurtzite peaks were observed with the substrate's (004) plane peak, but a \( \phi \)-scan of X-ray diffraction revealed that several in-plane orientations existed in the GaN films. A considerable amount of oxygen impurities in the film was detected by XPS analysis. Photoluminescence and cathodoluminescence (CL) spectra of GaN films showed both strong bandedge-related emission and broad defect-related emission.
Chapter 3

Hydride Vapor Phase Epitaxy of GaN using GaCl$_3$ and NH$_3$

Recently GaN has attracted immense attention of optoelectronics researchers due to its direct wide bandgap with the capability of bandgap engineering over the green to ultraviolet spectral range. In spite of the successful fabrication of GaN based light emitting diodes [1 – 4], UV photodetectors [5] and laser diodes [6], improvement of crystalline quality of epitaxially grown GaN films is still a very important issue. Because no substrate matches its lattice parameter and the thermal expansion of GaN, any heteroepitaxially grown GaN film contains $10^9 \sim 10^{11}/\text{cm}^2$ of dislocations [7 – 10]. The best way to reduce the crystalline defect density in an epitaxial film is through homoepitaxial growth. Unlike other bulk single crystals such as Si, GaAs, GaP, etc., it is extremely difficult to grow bulk GaN single crystals. Due to the high melting temperature and high N$_2$ equilibrium pressure of GaN (GaN does not melt at a temperature as high as 2573K, at 60kbar), extremely high temperature with high N$_2$ pressure is required to grow GaN single crystal from the melt and these conditions are very difficult to achieve experimentally. In this chapter, growth of thick GaN films using vapor phase epitaxy technique on sapphire substrates with or without sputtered AlN buffer layers was investigated. Due to very high growth rates (up to $50\mu\text{m/hr}$) with moderate GaN crystallinity[11], vapor phase epitaxy is a very suitable technique to grow thick GaN films (pseudo-bulk) which will be used as substrates for homoepitaxial growth of subsequent device structure by MBE or MOCVD.

3-1 Introduction
3-1-1 Chemical Vapor Deposition Basics

Hydride Vapor Phase Epitaxy (HVPE) is a type of Chemical Vapor Deposition (CVD). As the part of an introduction for chapter 3, a brief summary describing this chemical vapor deposition process is provided. CVD is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit. Since CVD enables one to produce thin films of almost any metallic element, as well as compounds such as carbides, nitrides, oxides, arsenide, phosphide, intermetallics and many others, the CVD process is now an essential technology in the manufacture of semiconductors and other electronic components. The main advantage of the CVD technique is the production of uniform, reproducible and adherent layers of various materials with high crystallinity and purity at relatively high deposition rates in simple and cheap commercially available non-vacuum equipment. However, there are some disadvantages, among which are the use of high deposition temperatures, chemical hazards caused by toxic, explosive, flammable or corrosive gases, a strong tendency for deposition on furnace sidewalls and reactor geometry influences on the deposition.

3-1-1 (a) Typical Chemical Reactions in CVD Process

Chemical reactions used in CVD to obtain solid deposition are very diverse and include thermal decomposition (pyrolysis), reduction, hydrolysis, oxidation, carbidization and nitridation. They can be used either singly or in combination.

(a) thermal decomposition (pyrolysis)

Pyrolysis is defined as a reaction in which a vapor phase substance decomposes into its component elements, or into more stable compounds at a sufficiently higher temperature. The solid reaction products are deposited on the substrates. CVD processes using this reaction have simplicity in equipment due to the utilization of only one precursor and high reaction efficiency. This kind of reaction, which has a positive enthalpy of reaction (ΔH), is typically performed in cold-wall reactors to minimize the wall deposition. Halides, hydrides, halohydrides and metallo-organic sources of metallic elements are commonly used reactants for this process. For the pyrolysis reaction of hydrides or metallo-organic sources, the reaction can occur at lower temperature.

\[ \text{XH}_2(g) = \text{X}(s) + 2\text{H}_2(g) \]
\[ \text{XF}_6(g) = \text{X}(s) + 3\text{F}_2(g) \]
(b) hydrogen reduction

Reduction is a chemical reaction process in which an element gains an electron. The reduction process can be considered as a decomposition process favored by the presence of another reactant (hydrogen in this case) which helps to remove the decomposition products, thus leading to a decrease of temperature. Reduction reactions are very important in CVD, particularly for the hydrogen reduction of the metal halides. The major advantage of hydrogen reduction is that reaction generally takes place at a lower temperature than the equivalent decomposition reaction. These reactions are reversible, thus permitting in-situ vapor phase etching of substrates. Since this reaction commonly has a positive enthalpy of reaction, cold-wall reactors are used to minimize wall deposition. Halides, halohydrides and oxo(halogenides of metals are the typical reactants for this process.

\[
\begin{align*}
XF_6(g) + 3H_2(g) &= X(s) + 6HF(g) \\
XCl_4(g) + 2H_2(g) &= X(s) + 4HCl(g) \\
XCl_4(g) + 2YCl_3(g) + 5H_2(g) &= XY_2(s) + 10HCl(g)
\end{align*}
\]

(c) metal reduction (reduction with substrate)

Although hydrogen is the most common reductant, there are other elements which are even more powerful reductants, such as Zn, Cd, Mg, Na and K. These metals can be used to reduce the halides of Ti, Zr and Hf, whereas H₂ cannot be used so readily. In order to be useful in CVD, the by-product chloride must be volatile at the growth temperature. In some cases, the substrate itself can take part in the CVD reactions. The substrate can serve as a reductant for the reactant (typically metal halide vapor), being converted into a volatile halide and the process leads to metal deposition. In this case, self limitation of deposited film thickness is achieved.

\[
\begin{align*}
XCl_4(g) + 2Y(s) &= X(s) + 2YCl_2(g) \\
WF_6(g) + 3Si(substrate) &= W(s) + 3SiF_4(g)
\end{align*}
\]

(d) oxidation and hydrolysis

Hydrolysis is a chemical process by which a vapor phase compound reacts with water vapor and leads to the formation of a solid reaction product, usually an oxide. A CO₂ + H₂ mixture can substitute for water vapor. Both oxidation and hydrolysis reactions are two of the most important methods to obtain the oxide deposits.

\[
\begin{align*}
XH_4(g) + O_2(g) &= X(s) + 2H_2O(g) \\
YH_6(g) + 2O_2(g) &= YO(s) + 3H_2O(g) \\
2XCl_3(g) + 3H_2O(g) &= X_2O_3(s) + 6HCl(g)
\end{align*}
\]
\[2 \text{XCl}_3 (g) + 3 \text{H}_2 + 3 \text{CO}_2 (g) = \text{X}_2 \text{O}_3 (s) + 6 \text{HCl} (g) + 3 \text{CO}(g)\]

(e) carbidization and nitridation

Carbidization is a CVD process resulting in the formation of a carbide thin film. Hydrocarbons are commonly used reactants. In the nitridation process, ammonia and hydrazine (N\(_2\)H\(_4\)) are used as the nitrogen-containing reactants for the deposition of nitride films. Nitrogen gases can be used to grow nitride films. Due to the chemical inertness of nitrogen, nitrogen must be activated by a plasma. Both carbidization reactions with methane and nitridation reactions with ammonia can occur at normal or low pressures and can be activated either thermally or by RF glow discharge.

\[\text{XCl}_4 (g) + \text{CH}_4 (g) = \text{XC(s)} + 4 \text{HCl}(g)\]

\[\text{XCl}_3 (g) + \text{NH}_3 (g) = \text{XN(s)} + 3 \text{HCl}(g)\]

3-1-1 (b) Sources of Activation for Chemical Reactions in CVD

CVD process can be classified according to their method of overcoming the activation energy of chemical reactions. These reactions can be activated by several methods, such as thermal activation, plasma activation and photon energy activation.

(i) thermal activation

This typically takes place at high temperature ( > 900°C), in order to overcome the energy barrier of chemical reactions by thermal energy. The chemical reactions occur in both atmospheric pressure and low pressure environments. If metallo-organic precursors are used (MOCVD), the temperature can be lowered considerably.

(ii) plasma activation

A glow discharge is produced in the gaseous reactant mixture which is maintained at a pressure of 0.1 ~ 1 torr. The reactions between different species in the plasma lead to the formation of thin films on various substrates over a wide temperature range. Typically, deposition takes place at much lower temperature ( 300 ~ 500°C) than the case of thermal activation. Microwave or RF power is introduced to excite the plasma and low pressure is required to maintain the plasma. Activation energy for the reaction is overcome by energy supplied by the plasma. The advantages of this method are the capability of producing high quality films at lower temperature and of obtaining amorphous structured films. The main disadvantages are low deposition rate and efficiency, difficulty of controlling the film
composition and thickness uniformity, irradiation damages in growing films and the relative complexity of deposition system.

(iii) photo-enhanced activation

Electromagnetic radiation, usually short-wave ultraviolet is the source of energy to promote the dissociation of reactant gases and to enhance the chemical reactions for deposition. Either UV lamps or lasers are commonly used to irradiate the substrate surface. The deposition takes place at low temperature (200 ~ 400°C) and low pressure (~1 mTorr).

3-1-1 (c) CVD Growth Mechanisms and Rate Determining Step

A CVD deposition reaction is almost always considered to be a heterogenous reaction, since it occurs as a catalytic reaction in an adsorbed layer on the surface of the substrate and growing film. The CVD reaction is an usual heterogeneous process and can be summarized in four steps, which are shown graphically in Figure 3-1.

(i) The reactant gases enter the reactor by forced flow.
(ii) They diffuse through the boundary layer.
(iii) They are adsorbed on the surface of the substrate where the chemical reaction takes place at the interface and other events, such as lattice incorporation and surface migration may also take place at this stage.
(iv) The gaseous by-products of the reaction desorb and diffuse away from the surface through the boundary layer.

Among all of steps above, the slowest step will be the rate determining step and will determine the deposition rate, whereas in steady state conditions, all steps will proceed at the same rate.
Figure 3-1. Sequence of steps occurring in the gas phase and on the substrate surface during a CVD process.

3-1-1 (d) Factors Effecting CVD Film Growth Rate

In a CVD process, the film deposition rate is influenced by total gas flow rate, gas flow velocity, substrate temperature, reactant partial pressure, crystallographic orientation of the substrate and reactor geometry.

(i) the effects of total gas flow rate and gas flow velocity
In the case of type I mass transportation controlled processes, the deposition rate increases linearly with an increase of total gas flow rate, but is independent of the change of gas flow velocity. For type II diffusion controlled processes, the deposition rate increases with an increase of both total gas flow rate and gas flow velocity. Unlike the cases of mass transport controlled processes, the deposition rate is independent on both total gas flow rate and gas flow velocity in the surface kinetics controlled processes.

(ii) the effects of substrate temperature
In the case of type I mass transportation controlled processes, the deposition rate increases with an increase of temperature for an exothermic process and decreases with temperature for an endothermic process. The growth rate always increases moderately with increasing temperature for both exothermic and endothermic processes in diffusion controlled cases. For surface kinetic controlled cases, growth rate increases exponentially with an increase of temperature in either process (both exothermic and endothermic processes).

(iii) the effects of reactant partial pressure
In both diffusion and surface kinetics controlled processes, the deposition rate is proportional to the concentration of reactant (reactant partial pressure), whereas for the case of type I mass transportation controlled processes, the effect of reactant partial pressure on deposition rate can be predicted from thermodynamic reaction.

3-1-2 Conventional Hydride Vapor Phase Epitaxy

The terminology "Hydride Vapor Phase Epitaxy" refers to a process which uses the group V hydride. Group III source is the metal mono-chloride formed by reacting HCl gas with liquid group III metals. Both the source reaction and the deposition reactions are done inside a hot walled quartz reactor. The reactions occur under near-equilibrium conditions and since they are reversible, controlled in-situ etching to remove the wall deposition is possible by flowing only HCl gas. Because group III and group V species can be controlled independently, hydride VPE is generally considered to be a more flexible growth technique.

The advantages of the hydride VPE method are that epitaxial growth on large wafers with multiple wafer operation is possible and high growth rate is achieved, simultaneously. Unlike liquid phase epitaxy, smooth surfaces are attainable and quaternary alloy semiconductors, such as Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$, can be grown with accurate composition. Due to its high throughput, the process is well suited for commercial use.

The hydride VPE method has however, some problems. Wall deposits often occur in the growth zone and these can significantly alter the partial pressures of important reactants in the deposition zone[12]. Thus, predicting alloy composition from vapor flows is complicated. The purity of grown material is often limited by the purity of HCl gas. Since HCl is highly corrosive unless the environment is anhydrous and since is stored in cylinders which must be made of high-pressure steel, the HCl gas is a likely source of metal impurities in grown films. Using the hydride VPE technique, Al compounds are very
difficult to grow [13], because there is the high reactivity of Al metal and AlCl vapor with fused quartz and very high temperature is required to grow Al compounds.

A basic design of a typical hydride VPE reactor is shown in Figure 3-2. The reactor is divided by three functional parts: a source zone which contains the liquid metals, a mixing zone in which the hydrides and metal chlorides are mixed and a deposition zone where crystal growth takes place. Good mixing of metal chlorides with the hydrides is very crucial for high quality epitaxial layer growth, and thus baffles[14, 15] or nozzles[16] are added for proper mixing. Horizontal reactors have historically been more popular than vertical reactors even though substrate rotation for improved uniformity is more easily implemented using a vertical design. In the horizontal geometry with the substrate held in the horizontal plane or at a slightly tilted plane, the gas flow is often modeled using a boundary layer model. The thickness uniformity of this boundary layer can influence the thickness uniformity of the grown layer if diffusion across the boundary layer is the rate determining step.

![Diagram of conventional hydride VPE reactor](image)

Figure 3-2. The schematic diagram of conventional hydride VPE reactor.

For the case that growth rate is not a function of temperature or is weakly dependent on temperature, crystal growth is limited by mass transport of the chemical species toward the growth zone or by the rate of diffusion across the boundary layer or by the rate of mass transport of the exhausted reaction products. For cases which the crystal growth rate is strongly dependent on temperature, growth is limited by the chemical reaction rate or by the absorption or desorption rates. Mass transport limited growth usually has only a weak substrate orientation dependence and a high flow rate dependence, whereas kinetically limited growth has a strong substrate orientation dependence and a low flow rate dependence.
3-1-3 Modified Hydride Vapor Phase Epitaxy for GaN Growth

The growth of GaN using hydride vapor phase epitaxy (HVPE) has a long history and has been widely used because of its high growth rates (up to 100 μm/hr) and lack of carbon incorporation into the film. In conventional chloride transport VPE of GaN, the Ga source is gallium mono-chloride (GaCl), which is stable only at temperatures above 600°C and is produced by the reaction of liquid gallium with HCl gas [17-21]. The supply of GaCl is controlled by the Ga cell temperature and the flow rates of the HCl gas and H₂ carrier gas. To produce GaCl from the reaction of HCl gas with the molten gallium metal, two temperature zone furnace is required and it is very difficult to control both Ga cell temperature and substrate temperature independently.

Gallium tri-chloride (GaCl₃) can also be used as the Ga source. Due to its high vapor pressure [22], GaCl₃ can easily be heated by circulating a hot fluid around the GaCl₃, which is then transported into reactor by a carrier gas. GaCl₃ is a crystalline solid at room temperature with a melting temperature of 78°C and high purity crystals are commercially available. GaCl₃ vapor is stable, even at high temperature, but very reactive with H₂ or liquid gallium and reduces to gallium mono-chloride. The vapor pressure of GaCl₃ at various temperatures is shown in Figure 3-3. Other researchers have reported VPE growth of GaAs using GaCl₃. Rubinstein and Myers [23] used GaCl₃ as a Ga source, but before being supplied to the deposition zone of the reactor, it was reduced to a mono-chloride by reacting with metallic Gallium. Hasegawa [24,25] and others have also used GaCl₃. In these cases, GaCl₃ was reacted with hydrogen and reduced to GaCl before crystal synthesis. In this study, the Ga source was GaCl₃ and NH₃, and N₂ gases were used as the nitrogen source and carrier gas, respectively. H₂ and HCl gases were not used to develop the much safer and simpler process.
Figure 3-3. The vapor pressure of GaCl₃ at various temperatures.

3-2 GaN Growth system

An open flow horizontal quartz tube with a single zone hot wall furnace was used as the reactor. The crystalline GaCl₃ was melted and heated to 100°C in a separated quartz cell by an electric heater. At that temperature, the vapor pressure of GaCl₃ is about 20 mm Hg. The GaCl₃ vapor was transported to the reactor by nitrogen carrier gas. Nitrogen gas was also used in order to dilute the ammonia and to increase the total gas flow rate. The supply of GaCl₃ was controlled by the combination of GaCl₃ cell temperature and flow rate of the N₂ carrier gas. The typical N₂ flow rate for GaCl₃ transport was 0.1 slm (standard liter per minute). The actual GaCl₃ vapor supply was about 0.003 slm under the above conditions. During the process, 1.0 - 2.5 slm of NH₃ and 1.0 - 2.0 slm of N₂ were introduced into the reactor. The resulting V/III ratio was about 500 to 700. The growth temperature was varied over the range of 930 ~ 1050°C. Atmospheric pressure was
maintained during the growth. Figure 3-4 shows a schematic diagram of the VPE system used to grow GaN using GaCl₃/N₂ and NH₃/N₂.

![Schematic diagram of the modified VPE system for GaN growth using GaCl₃/N₂ and NH₃/N₂.]

Figure 3-4. Schematic diagram of the modified VPE system for GaN growth using GaCl₃/N₂ and NH₃/N₂.

3-3 Thermodynamic Analysis

A theoretical analysis is an essential step to design a CVD process. This should predict what will happen to the various reactions and what the resulting composition of the deposit and reaction mechanisms are likely to be. This analysis provides only a guideline for an experimental program because of the complexity of the CVD phenomena, a complete and accurate model of the CVD reactions is still beyond reach. Many parts of analyzing CVD processes are accomplished empirically. A CVD reaction is governed by both thermodynamics and kinetics. Thermodynamic analysis deals with the driving force which indicates the direction the reaction is going to proceed while kinetics defines the transport processes and determines the rate control mechanism. From the calculation of thermodynamic equilibrium, the following information is obtained:

(i) the composition and amount of deposited material that is theoretically possible under any given deposition conditions, such as temperature, pressure and input concentrations of reactant.
(ii) the existence of various gaseous species and their equilibrium partial pressures.
(iii) the possibility of multiple reactions and the number and composition of possible solid phases.
(iv) the possibility of reaction between the substrate and the gaseous or solid species.

These calculations are based on chemical equilibrium, which is rarely attained in CVD reactions. While the thermodynamic possibility of a CVD reaction is a necessary condition, it is not sufficient to guarantee the deposition. It must also be established whether the process is kinetically favorable. Indeed, there are many thermodynamically favorable reactions that are kinetically unfavorable because of their extremely low deposition rates or kinetic barriers.

To analyze the GaN growth process using GaCl₃ and NH₃, GaCl₃, GaCl, NH₃, N₂, H₂, HCl and Cl₂ are chosen to describe the growth system. The chemical reactions related to those species in the reactor can be listed as follows.

reaction 1 \[ \text{NH}_3(g) = 0.5 \text{ N}_2(g) + 1.5 \text{ H}_2(g) \]
reaction 2 \[ \text{GaCl}_3(g) + \text{H}_2(g) = \text{GaCl}(g) + 2 \text{ HCl}(g) \]
reaction 3 \[ \text{GaCl}(g) + \text{NH}_3(g) = \text{GaN}(s) + \text{HCl}(g) + \text{H}_2(g) \]
reaction 4 \[ \text{GaCl}_3(g) + \text{NH}_3(g) = \text{GaN}(s) + 3 \text{ HCl}(g) \]
reaction 5 \[ \text{GaCl}_3(g) = \text{GaCl}(g) + \text{Cl}_2(g) \]
reaction 6 \[ \text{GaCl}_3(g) + 0.5 \text{ N}_2(g) = \text{GaN}(s) + 1.5 \text{ Cl}_2(g) \]
reaction 7 \[ \text{GaCl}(g) + 0.5 \text{ N}_2(g) = \text{GaN}(s) + 0.5 \text{ Cl}_2(g) \]
reaction 8 \[ \text{GaN}(s) + 1.5 \text{ H}_2(g) = \text{Ga}(l) + \text{NH}_3(g) \]
reaction 9 \[ \text{GaN}(s) = \text{Ga}(l) + 0.5 \text{ N}_2(g) \]
reaction 10 \[ \text{GaN}(s) + \text{HCl}(g) = \text{GaCl}(g) + 0.5 \text{ N}_2(g) + 0.5 \text{ H}_2(g) \]

Reactions 1 to 4, which are directly related to the GaN formation and 9 to 10, which represent the gas phase etching of GaN, have very negative values for the change of Gibbs free energy at standard state (\(\Delta G^\circ\)) at typical GaN growth temperatures. Thus, these reactions are thermodynamically preferable. If they have enough energy to overcome the energy barrier, the reaction will spontaneously proceed to thermodynamic equilibrium. On the other hand, reactions 5 through 8 have very positive values of \(\Delta G^\circ\) at our growth temperature. These reactions are not thermodynamically preferred and thus do not occur spontaneously. Because they cannot affect the thermodynamic equilibrium of our growth
system, these reactions can be ignored. Figure 3-5 shows the $\Delta G^\circ$ values of the above reactions with respect to the temperature.

![Graph showing $\Delta G^\circ$ vs Temperature for reactions 1 to 10.](image)

Figure 3-5. The change of Gibbs Free energy ($\Delta G^\circ$) values as a function of temperature for reactions 1 to 10.

The equilibrium partial pressures of all gaseous species and thermodynamic driving forces for GaN deposition reaction are calculated, in order to clarify whether the growth of GaN from GaCl$_3$/N$_2$ and NH$_3$/N$_2$ is predicted from the thermodynamic equilibria reactions. In all cases, the standard state is taken as the pure substance at one atmosphere. All thermodynamic data used in this paper is from ‘Thermochemical data of pure substance’ tabulated by Ihsan Barin[26].

The nitrogen source, NH$_3$, is not stable at high temperature, and will thermally decompose to nitrogen and hydrogen gases by reaction [1].

\[
\text{NH}_3(g) = (1-\xi) \text{NH}_3(g) + \frac{\xi}{2} \text{N}_2(g) + \frac{3\xi}{2} \text{H}_2(g) \quad \text{reaction [1]}
\]

where $\xi$ is the extent of reaction. The terminology ‘extent of reaction’ is defined as the fraction of reactants consumed by the reaction under the specified conditions. The unity
value of extent of reaction means that all reactants are converted to product and the reaction is complete. A zero value of extent of reaction means that all reactants are reserved and no reaction occurs. The equilibrium value for the extent of reaction [1], (ξ_{eq}), at 1300 K (a typical growth temperature) is about 0.9995. Hence most of the ammonia decomposes to nitrogen and hydrogen at that temperature in thermodynamic equilibrium. However, it is not easy to reach thermodynamic equilibrium in such an open flow system with a high flow rate. The experimentally measured value of ξ is about 0.1 or less under typical growth parameters. The actual value of ξ is dependent on the NH₃ partial pressure, residence time, and surface condition. Both NH₃ partial pressure and residence time can be changed by varying the NH₃ and N₂ flow rates.

Some portion (typically less than 10%) of the ammonia has to be turned into nitrogen and hydrogen by thermal decomposition. The H₂ gas, produced from the thermal decomposition of ammonia, will promote the reduction of GaCl₃ to GaCl. Even though the direct reduction of GaCl₃ to GaCl is not thermodynamically favorable, the hydrogen reduction of GaCl₃ to GaCl can occur, spontaneously. η is defined as the extent of the reaction for hydrogen reduction of GaCl₃ to GaCl. The reaction can be written as:

\[ \text{GaCl}_3(g) + \text{H}_2(g) \rightarrow \text{GaCl}(g) + 2 \text{HCl}(g) \]  \text{reaction [2]}

Thus, at a given temperature and knowing the extent of reaction for ammonia decomposition (ξ), the equilibrium extent of the reaction [2] (η_{eq}) can be calculated. For typical flow rates (NH₃=1.0 slm, N₂=2.1 slm, GaCl₃=0.003 slm) and growth temperatures (1100 K, 1200 K and 1300 K), the relationship between ξ and η_{eq} is shown in Figure 3-6.

At these temperatures, η_{eq} is almost unity (complete reaction) for all values of ξ larger than 0.02. This implies that most of the GaCl₃ is converted to GaCl at these temperatures under thermodynamic equilibrium, since the measured ξ is always larger than 0.02. Thus the majority of gallium chloride vapor inside the deposition zone is the mono-chloride.
Figure 3-6. The relationship between the extent of reaction for ammonia decomposition ($\xi$) and the equilibrium extent of the reaction [2] ($\eta_{eq}$) at typical growth temperatures ($T = 1100K, 1200K$ and $1300K$).

GaCl vapor, produced by reaction [2] will react with the remaining NH$_3$ to form GaN. This reaction can be written as:

$$\text{GaCl}(g) + \text{NH}_3(g) = \text{GaN}(s) + \text{HCl}(g) + \text{H}_2(g) \quad \text{reaction [3]}$$

at $t = t_o$, $c\eta - a(1 - \xi) = 2c\eta - (1.5a\xi - c\eta)$

where $a$ and $c$ are the incoming flow rates of NH$_3$ and GaCl$_3$. The reaction constant $J$ for reaction [3] at $t = t_o$ (not in thermodynamic equilibrium) can be expressed as:

$$J = \frac{a_{\text{GaN}} \cdot (3a\xi - 2c\eta)}{a(1 - \xi)}$$

The reaction constant, $J$, is the parameter which determines the direction of the reaction. If $J$ is smaller than the equilibrium constant ($K_{eq}$) the forward reaction is thermodynamically favorable. Because a GaN film is a pure solid substance, its activity ($a_{\text{GaN}}$) is unity. In this case, the thermodynamic driving force ($\Delta G$) for the reaction [3] is as follows:
\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{3\xi - 0.006\eta}{1 - \xi} \right) \]

In the typical growth temperature region, the change of Gibbs free energy for reaction [3] in the standard state (\(\Delta G^\circ\)) is positive. This reaction is thus not thermodynamically favorable in the standard state. Thus gas phase etching rather than GaN deposition is predicted under these conditions. As the value of \(\xi\) becomes smaller, the thermal decomposition of ammonia is impeded, and the thermodynamic driving force (\(\Delta G_3\)) for reaction [3] becomes negative (reaction [3] can occur). By adding nitrogen gas into the reactor, the total flow rate becomes high and the partial pressure of ammonia decreases, hence \(\xi\) becomes small enough to produce a negative value for \(\Delta G\). The effects of \(\xi\) on \(\Delta G_3\) (the thermodynamic driving force for reaction [3]) at fixed value of \(\eta\) (\(\eta = 0.99, 0.5\) and 0.01) are shown in Figure 3-7.
Figure 3-7. The effects of $\xi$ on $\Delta G$ (the thermodynamic driving force for reaction [3]) at fixed value of $\eta$ ($\eta = 0.99$, 0.5 and 0.01), where $\xi$ and $\eta$ are the extent of the reaction for thermal decomposition of ammonia and hydrogen reduction of GaCl$_3$, respectively.

According to Figure 3-7, $\Delta G$ changes only very slightly with respect to the changes of $\eta$. Hence any GaCl produced from the hydrogen reduction of GaCl$_3$ will react with ammonia to make GaN if $\xi$ is low enough to make $\Delta G$ negative. If the hydrogen reduction of GaCl$_3$ is not completed, the remaining GaCl$_3$ can react with ammonia via reaction [4].

$$\text{GaCl}_3(g) + \text{NH}_3(g) = \text{GaN}(s) + 3\text{HCl}(g) \quad \text{reaction [4]}$$
Under typical GaN growth conditions, reaction [4] is thermodynamically favorable. Even though GaCl₃ is known to be much less reactive than GaCl₂[23, 24, 27], the driving force for reaction [4] is much higher (more negative value) than that of reaction [3]. According to the calculated value of equilibrium partial pressure of GaCl and GaCl₃, the dominant Ga species in the reactor is GaCl₂[24]. Therefore, the growth of GaN is governed by GaCl₂ (reaction [3]), rather than GaCl₃ (reaction [4]). A thick deposition of GaCl₃ is always observed on the exhaust side of the reactor, which implies that unreacted GaCl combines with HCl at a lower temperature and forms GaCl₂, which is the more stable form of gallium chloride at temperatures lower than 600°C.

Figure 3-8 shows the equilibrium pressure of all gaseous species inside the reactor. The calculation is based on thermodynamic equilibrium of reactions from [1] to [4] and reaction [10], maintenance of total pressure and materials conservation inside the reactor.

\[
\text{GaN(s) + HCl(g) = GaCl(g) + 0.5 H}_2\text{(g) + 0.5 N}_2\text{(g)} \quad \text{reaction [10]}
\]

The reaction [10] is the reverse reaction of reaction [3] and has the physical meaning of high temperature gas phase etching of GaN by HCl. Since an open flow type reactor is used, the total pressure inside the reactor is maintained at one atmosphere, regardless of the chemical reactions occurring.

\[
P_{\text{total}} = 1 \text{ atm} = P_{\text{NH}_3} + P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{GaCl}_3} + P_{\text{GaCl}} + P_{\text{HCl}}
\]

GaN is the only condensed phase product, thus the number of chlorine and hydrogen atoms inside the reactor must be conserved during the growth. It is assumed that a negligible number of chlorine and hydrogen atoms are incorporated into the growing GaN crystal.

\[
3N^0_{\text{GaCl}} = 3N_{\text{GaCl}_3} + N_{\text{GaCl}} + N_{\text{HCl}} \quad \text{[Cl]}
\]
\[
3N^0_{\text{NH}_3} = 3N_{\text{NH}_3} + 2N_{\text{N}_2} + N_{\text{HCl}} \quad \text{[H]}
\]

where \(N^0\) and \(N\) stand for the initial number of molecules per unit time and the number of molecules per unit time at \(t = t_o\), respectively. According to Figure 3-8, almost all the NH₃, GaCl₃ and HCl gases are consumed by reaction [1], [2] and [10], respectively under thermodynamic equilibrium at temperatures greater than 600°C. The partial pressure of GaCl is saturated at higher temperature and this means GaCl is not consumed by reaction [3].
Figure 3-8. The equilibrium pressure of any gaseous species inside the reactor as the function of temperature.

In order to describe the driving force of either GaN deposition or gas phase etching of GaN, a new parameter is introduced. The driving force for GaN deposition, $\Delta Ga$ is defined as:

$$\Delta Ga = N_{GaCl_3} + N_{GaCl} - N^0_{GaCl_3}$$

where $N$ and $N^0$ stand for the number of Ga containing molecules at time $t=t_0$ and $t=0$. A positive value of $\Delta Ga$ means that at time $t_0$ more Ga atoms exist in the reactor than were initially present. These excess Ga atoms must be supplied by gas phase etching of GaN (reaction [10]), thus gas phase etching of GaN is thermodynamically favored. A negative value of $\Delta Ga$ means GaN deposition is thermodynamically favored. Figure 3-9 shows the effect of $\xi$ and growth temperature on $\Delta Ga$. The lower the extent of the ammonia decomposition reaction ($\xi$) and the lower the growth temperature, the more negative is the value of $\Delta Ga$, i.e. GaN deposition is enhanced.
Figure 3-9. The effect of the extent of the ammonia decomposition reaction and growth temperature on $\Delta G_a$.

3-4 Results and Discussion

3-4-1 GaN VPE Growth

Growth of GaN using the above GaCl$_3$ precursor and reactions was investigated under a variety of growth conditions. GaN films were grown under the different sapphire surface nitridation conditions, substrate temperatures, V/III ratios ($[\text{NH}_3]/[\text{GaCl}_3]$) and total gas flow rates. Their effects on the structural, chemical and optical properties, film growth rate and surface morphology of GaN films were investigated in order to optimize the GaN growth conditions.

In these experiments, (0001) and (11$ar{2}0$) oriented sapphire wafers were used as substrates. Prior to the growth, they were degreased by organic solvents and chemically etched with a hot HCl + H$_2$PO$_4$ (3:1) solution in order to remove polishing damage and smooth the surface. After loading the substrates, the reactor was pumped and purged five
times with high purity nitrogen. The substrates were heated to the growth temperature and held for 10 ~ 30 minutes under a NH$_3$ / N$_2$ ambient in order to nitridate the substrate surface. From XPS analysis, both strong oxygen and nitrogen peaks were observed. This implies that the sapphire surface was nitridated during this heating phase [28]. After surface nitridation, GaCl$_3$ was supplied to the reactor using nitrogen carrier gas. Because chemical reactions are not occurred at low temperature (~500°C), low temperature buffer layer was not used in these experiments. GaN films were deposited either directly on the bare sapphire substrates or on the AlN buffer layer which were RF-sputtered, instead of low temperature buffer layers.

3-4-2 Structural Characterization of GaN films

Structural quality of GaN films grown by HVPE, was characterized by various techniques. X-ray diffraction 2θ/ω-scan, X-ray rocking curve, reciprocal space mapping, X-ray diffraction ϕ-scan, cross-sectional TEM, cross-sectional HRTEM, electron diffraction and Raman spectroscopy techniques were used, in order to figure out the phase identification, in-plane and out of plane orientation and to measure structural defect density of GaN films.

X-ray diffraction was used to determine the crystallinity and the orientation of the GaN films. Figure 3-10 shows the 2θ/ω X-ray diffraction pattern for thick GaN films on (0001) Al$_2$O$_3$. Only c-type plane peaks of GaN and Al$_2$O$_3$ are observed. This implies that the GaN film and sapphire substrate basal planes are parallel to each other, i.e. GaN [0001] // sapphire [0001].
Figure 3-10. The 2θ/ω X-ray diffraction pattern for thick GaN films on sapphire.

For GaN films grown on α-Al₂O₃ substrates, only (000l) type plane GaN peak and (1120) substrate peaks are observed. From the Figure 3-11, which shows the reciprocal space mapping of GaN film grown on the (1120) plane Al₂O₃ substrate, the GaN [0001] direction is parallel to Al₂O₃ [1120] direction. Al₂O₃ substrate peak is much stronger and sharper than epitaxial GaN film peak due to the better crystallinity of the substrate.
Figure 3-11. Reciprocal space mapping of (0001) GaN films grown on (11\bar{2}0) Al\textsubscript{2}O\textsubscript{3} substrate.

X-ray diffraction φ-scan technique was used to determine the in-plane orientation relation between the film and the substrate [29]. To obtain a X-ray diffraction φ-scan pattern, the sample is tilted along χ-angle to the specific angle at which the diffraction vector q is normal to the specific crystallographic plane. 2θ and ω angles are set for the specific crystallographic plane and then the sample is rotated along its surface normal (φ-angle). When the Bragg law is satisfied, a diffraction peak is observed. Figure 3-12 shows a schematic diagram for X-ray diffraction φ-scan.
Figure 3-12. Schematic illustration of X-ray diffraction \( \phi \)-scan.

Figure 3-13 shows the \( \phi \)-scan of GaN films grown on (0001) \( \text{Al}_2\text{O}_3 \) in order to determine the in-plane orientation. GaN (10\( \bar{1} \)2) plane peaks and \( \text{Al}_2\text{O}_3 \) (1\( \bar{1} \)23) plane peaks are observed. Only one set of reflection peaks from both GaN (10\( \bar{1} \)2) planes and \( \text{Al}_2\text{O}_3 \) (1\( \bar{1} \)23) planes is observed with 60° spacing. This indicates that both the GaN films and sapphire substrate are single crystals. The angular position of the GaN (10\( \bar{1} \)2) peaks are well matched to the sapphire (1\( \bar{1} \)23) peaks. This means the hexagonal basal plane of the GaN crystal is rotated 90°(30°) around the c-axis with respect to the sapphire’s basal plane to minimize the lattice mismatch strain, i.e. GaN [10\( \bar{1} \)0] // sapphire [1\( \bar{1} \)20].
Figure 3-13. The φ-scan of GaN film grown on (0001) Al₂O₃ substrate. The GaN [\(\{10\overline{1}0\}\)] direction is parallel to sapphire [\(\{1\overline{1}20\}\)] direction.

Figure 3-14 shows the φ-scan of the GaN films grown on (11\(\overline{2}0\)) Al₂O₃ substrates. Both GaN (10\(\overline{1}2\)) plane peaks and Al₂O₃ (11\(\overline{2}3\)) plane peaks are observed. Only one set of reflection peaks from GaN (10\(\overline{1}2\)) planes is observed with 60° spacing. For substrates, one set of (11\(\overline{2}3\)) plane peaks are observed with 180° spacing. This indicates that both GaN films and sapphire substrate are single crystals. The angular position of the GaN (10\(\overline{1}2\)) peaks are well matched to the sapphire (11\(\overline{2}3\)) peaks. This means GaN [\(\{10\overline{1}0\}\)] direction is parallel to sapphire [0001] direction.
Figure 3-14. The $\phi$-scan of GaN films grown on (11\(\bar{2}0\)) Al\(_2\)O\(_3\) substrates. The GaN [10\(\bar{1}0\)] direction is parallel to the sapphire [0001] direction.

Table 3-1 shows the relationship of crystallographic orientations between GaN films and Al\(_2\)O\(_3\) substrates from the $\phi$-scans of the GaN (1,0,-1,2) plane and Al\(_2\)O\(_3\) (1,1,-2,3) planes.

<table>
<thead>
<tr>
<th>GaN on a-Al(_2)O(_3)</th>
<th>GaN on c-Al(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN [0001] // Al(_2)O(_3) [11(\bar{2}0)]</td>
<td>GaN [0001] // Al(_2)O(_3) [0001]</td>
</tr>
<tr>
<td>GaN [10(\bar{1}0)] // Al(_2)O(_3) [0001]</td>
<td>GaN [10(\bar{1}0)] // Al(_2)O(_3) [11(\bar{2}0)]</td>
</tr>
</tbody>
</table>

Table 3-1. The relationship of crystallographic orientations between GaN and Al\(_2\)O\(_3\).

The atomic configuration of a (11\(\bar{2}0\)) plane of Al\(_2\)O\(_3\) substrate is shown in Figure 3-15. An a-Al\(_2\)O\(_3\)'s [0001] direction has two fold symmetry thus, only two reflection peaks
are observed in the $\phi$ -scans of $\text{Al}_2\text{O}_3\ (1,1,-2,3)$ plane. Since the surface atomic configuration has a pseudo-hexagonal symmetry, [0001] oriented GaN films are grown on $\text{a-Al}_2\text{O}_3$ substrates. This crystallographic orientation relationship between GaN films and $\text{a-Al}_2\text{O}_3$ substrates is commonly observed in MOCVD grown films [30].

![Surface atomic configuration of (1120) Al$_2$O$_3$ substrate.

A bright field cross-sectional transmission electron microscopy (TEM) image of a GaN film grown on c - $\text{Al}_2\text{O}_3$ substrate at 1000°C is shown in Figure 3-16. The [0001] direction of the GaN film is parallel to the surface normal. A high density of threading dislocations parallel to the c-axis with the burgers vector of 1/3 $[1120]$ is observed. Some of them are bent, but most of these dislocations cross the film from interface to surface, due to their zero resolved force on the glide plane. The observed dislocation density is a few times $10^{10}/\text{cm}^2$. The relevant high resolution lattice image with electron diffraction is shown in Figure 3-17. GaN lattice image with hexagonal stacking sequence is clearly observed.
and also spotty electron diffraction (ED) pattern, which is very typical ED pattern for single crystal, is observed for GaN films.

Figure 3-16. Bright Field cross-sectional TEM image of GaN film grown on c-Al₂O₃ substrate at 1000°C.
Figure 3-17. High resolution lattice image and electron diffraction pattern of GaN film grown on c-Al$_2$O$_3$ substrate at 1000°C.

Raman spectra of GaN films grown on c-Al$_2$O$_3$ substrate by HVPE using GaCl$_3$ and NH$_3$ at various temperatures are shown in Figure 3-18. The solid line represents a GaN film with n-type background conductivity of 8x10$^{19}$/cm$^3$ and mobility of 3 cm$^2$/Vs. The dotted line is the spectra of a GaN film with n-type background conductivity of 4x10$^{19}$/cm$^3$ and mobility of 40 cm$^2$/Vs. The conductivity and mobility are confirmed by Hall measurements. The growth temperatures for GaN films shown in Figure 3-18, are 960°C for solid line and 995°C for dotted line. All other growth conditions are identical. From the Raman spectroscopy, information about crystalline quality, residual stress and
background conductivity of GaN films can be obtained. In our scattering configuration with incident and scattered light propagating along the z-axis, \( A_1 \) (LO), \( E_1 \) (TO) and \( 2E_2 \) phonons are allowed to participate in the scattering. According to Figure 3-18, the low energy \( E_2 \) phonon (142 cm\(^{-1}\)) and the high energy \( E_2 \) phonon (566 cm\(^{-1}\)) of GaN are observed. Observation of low energy \( E_2 \) phonon (142 cm\(^{-1}\)) indicates that GaN films grown by HVPE are of good crystalline quality. The peak at 530 cm\(^{-1}\), which is forbidden by selection rule, is close in frequency to the \( A_1 \) TO phonon of GaN. This peak is originated by plasmon-phonon coupling. Due to screening by free carriers (up to a few times of \( 10^{19}$/cm\(^3\) of background conductivity for both samples), GaN \( A_1 \) LO phonon at 734 cm\(^{-1}\) is disappeared.

The frequencies and attribution of GaN phonons shown in Figure 3-18 are in general agreement with other Raman data for epitaxial films and bulk single crystals [31–35]. The spectra of both samples have the continuous background spectrum larger than 2000 cm\(^{-1}\). This is caused by electronic scattering or weak photoluminescence. The positions of phonon peaks are identical over GaN films grown under different conditions with different film thickness. This implies that stress due to lattice mismatch and thermal mismatch is mostly relaxed in GaN films grown by HVPE [36].
3-4-3 Chemical and Optical Characterization of GaN films

X-ray Photoelectron Spectroscopy (XPS) was used to characterize impurities in the GaN epilayers. Carbon, hydrogen, chlorine and oxygen are major possible impurities of GaN films grown by hydride vapor phase epitaxy. Chlorine and oxygen peaks were observed in GaN films grown at lower temperature (~850°C). These films have a dark yellowish color, because GaCl₄ was incorporated into the grown films at lower growth temperatures and subsequently oxidized to form Ga(OH)₄ after the growth. By contrast, GaN films grown at higher temperatures (950 ~ 1050°C) showed no presence of oxygen and chlorine peaks. These films were transparent and specular. XPS spectra for GaN films grown at 850°C and 1000°C are shown in Figure 3-19.
Figure 3-19. XPS spectra for GaN films grown at 850°C and 1000°C.

In order to characterize the optical properties of GaN films, photoluminescence (PL) measurements were done at both room temperature and 77 K. A 10 mW He-Cd laser operating at 3.82 eV was used as the excitation source. At room temperature, only band edge emission near 3.40eV was observed. At 77 K, the spectrum consisted of several peaks including an exciton bound to a neutral donor (I₂), an exciton bound to a neutral acceptor (I₁) and donor-acceptor pairs. The spectrum is dominated by I₂ emission near 3.47 eV [37, 38]. Figure 3-20 shows typical PL spectra at both temperatures. The band edge emission peak had a FWHM of 60 meV at room temperature and the exciton bound to donor emission peak had a FWHM of 25 meV at 77 K. A very weak deep level luminescence band near 2.1 eV was also observed at both room temperature and 77 K. The FWHM of PL peaks of GaN films grown by HVPE are very comparable to that of GaN films grown by MOCVD. According to the PL spectra, the thick GaN films grown by VPE using GaCl₃/N₂ and NH₃/N₂ have good crystalline quality.
Figure 3-20. Typical Photoluminescence spectra of GaN films at 77K and room temperatures.

3-4-4 Surface Morphology of GaN films

Scanning Electron Microscopy (SEM) was used to characterize the surface morphology of GaN films grown on c-sapphire substrates. Commonly, it is very difficult to achieve a very smooth surface over a large area in chloride VPE growth of GaN films due to the high deposition and gas phase etching rates. The localized flux uniformity and growth temperature play key roles in determining the surface morphologies of GaN films. In this experiment, we fixed the V/III ratio at approximately 500. The position of the sapphire substrate (1 inch distant from the NH$_3$/N$_2$ nozzle) and the configuration of the GaCl$_3$/N$_2$ and NH$_3$/N$_2$ nozzles were also fixed to optimal positions. The effect of the growth temperature on surface morphology of GaN films was investigated. For GaN films grown below 950°C, shown in Figure 3-21 (a), the surface was covered by GaN crystallites (islands) with an approximate size of a few microns. These islands did not coalesce and there are holes all the way to the substrate. The 2θ/θ X-ray diffraction scan shows only (0001) type plane peaks with broad FWHM. The PL spectra shows only band
edge emission at room temperature which implies that each GaN crystallite has good crystalline quality. According to the X-ray diffraction φ-scan, several different in-plane orientations were observed. This means each crystallite has a different in-plane orientation and they are rotated relative to each other.

As the growth temperature was increased to 975°C, as shown in Figure 3-21 (b), the crystallites coalesce to one another and the surface become smoother, however, grooves and micro-holes which have about 50 ~ 60° inclined sidewalls were observed. The films grown in this temperature regime have narrower X-ray diffraction and photoluminescence lineweights. The surface morphology of films grown at similar temperatures (965°C) but a 3 times longer growth time are shown in Figure 3-21 (c). A terrace structure with micro-holes at the edge of the terraces is observed, although no individual GaN islands are observed. This confirms that the film has grown laterally, rather than three dimensionally. From the φ-scan of the GaN (10Ω2) peak, the film is single crystal. Figure 3-21 (d) shows the surface morphology of a GaN film grown at 995°C, which has the smoothest and the flattest surface. At the boundary of two laterally grown islands, thin shallow grooves are observed. Higher growth temperature and longer growth time appear to give better surface morphologies because of coalescence of the islands.
Figure 3-21. Scanning Electron Micrographs (SEM) of GaN films grown on c-Al₂O₃ substrates at various growth temperatures. Surface morphologies are changed with respect to the growth temperature and time. (a) $T = 950^\circ$C, $t = 1$ hour, (b) $T = 975^\circ$C, $t = 1$ hour, (c) $T = 975^\circ$C, $t = 3$ hours, (d) $T = 995^\circ$C, $t = 1$ hour.

The origin of the grooves shown in the Figure 3-21 (d), of GaN grown at 995°C for 1 hour, is explained in Figure 3-22. In the initial nucleation stage, GaN crystals are nucleated on the Al₂O₃ surface with one or two degrees of misorientation to each other. After the lateral growth of GaN nuclei, grooves form at the boundary of the GaN nuclei with an inter-angle of about 120 degrees. Thus, these grooves are evidence of lateral growth and they can be minimized by precise control of epitaxial layer nucleation.
3-4-5 Improvements of Structural and Optical Properties of GaN films using RF Sputtered AlN Buffer Layer

In order to grow high crystalline quality GaN films on foreign substrates with large lattice and thermal mismatches, a so-called two step growth technique is commonly used [39~42]. In this technique, a thin layer is first formed at low temperature and then growth temperature increases to the more normal growth regime. A thin and smooth-surface buffer layer is necessary to achieve uniformly distributed nucleation. For MBE or MOCVD growth of GaN, low temperature (400~700°C) grown GaN [39] or AlN [40~42] buffer layers have been used. GaN nuclei with proper orientation are chosen and grow preferentially. Finally, laterally growing GaN nuclei coalescence and the entire GaN film grows uniformly. Thin grooves are sometimes formed at the boundary of laterally growing GaN crystals. Figure 3-23 shows the growth process of single crystalline GaN films on the thin AlN or GaN low temperature grown buffer layers [42].
Figure 3-23. Two-Step growth of single crystalline GaN film on sapphire substrate [42].

In this work, we deposited a thin layer of AlN (200 ~ 1000Å) using a RF sputtering system (Perkin-Elmer 4400). Target material was AlN, and Ar with 5 ~ 10% of N₂ was used as a working gas. The plasma power was in the range of 300 to 700W and typical chamber pressure was about 5 mTorr. The surface morphologies of sputtered AlN layers was very smooth. From AFM measurements shown in Figure 3-24 (a) ~ (d), the minimum RMS roughness was just 0.395 nm for AlN films grown on a-plane Al₂O₃ substrates and was as low as 1.326 nm, in the case of AlN grown on c-plane Al₂O₃ substrates. The roughness was not changed by the thickness of sputtered AlN layer. It is believed that as-
sputtered AlN films were amorphous or micro-crystalline from the results of X-ray diffraction and electron beam diffractions, however the post heat treatment before growth is initiated at typical GaN growth temperatures, caused the AlN thin films to crystallize and the surfaces became rough and faceted and hexagonal-shaped grains are observed. The RMS roughness increases up to 15.173 nm.

Figure 3-24. Atomic force microscopy of AlN buffer layer deposited by RF sputtering. (a) 300Å thick AlN on c-AI₂O₃, RMS roughness = 1.454 nm, (b) 1000Å thick AlN on c-Al₂O₃, RMS roughness = 1.326 nm, (c) 300Å thick AlN on a-Al₂O₃, RMS roughness = 0.395 nm, (d) 1000Å thick AlN on c-Al₂O₃, heated at 1000°C for 5 minutes, RMS roughness = 15.173 nm. Scale bar represents 1µm for all figures.
At lower growth temperature (< 960°C), lateral growth mode is not dominant and several different in-plane orientations are observed, even in the case of GaN films grown on the sputtered AlN buffer layer. At higher growth temperatures (980°C ~ 1020°C), GaN nuclei coalesce with each other by 2-D lateral growth, and the resulting GaN epilayers became single crystalline. The surfaces of GaN films grown at higher temperature become smooth. The surface morphologies of GaN films grown with and without AlN buffer layer under identical growth conditions are shown in Figure 3-25 (a) ~ (c). The surface morphologies of GaN films grown on the AlN buffer layers were much smoother than those of GaN films grown directly on Al₂O₃ substrates without AlN buffer layer. GaN films grown on AlN buffer layer at high growth temperature (980°C ~ 1020°C) exhibit hexagon-shaped marks on the surface and thin grooves with a 120° angle caused from a degree or two of misorientation between GaN nuclei, and which are evidence of strong lateral growth of GaN.
Figure 3-25. Surface morphology of GaN films grown at 1020°C on various substrates (a) GaN grown directly on the c-Al₂O₃, (b) GaN grown on c-Al₂O₃ with 500Å thick AlN buffer layer, (c) GaN grown on a-Al₂O₃ with 500Å thick AlN buffer layer.
Photoluminescence spectra at 77K of GaN films grown under identical growth conditions with and without an AlN buffer layer are shown in Figure 3-26. The spectra are dominated by exciton bound neutral donor excitation (Iₐ) at 3.47 eV and no yellow band luminescence is present. GaN films grown on an AlN buffer layer show a much sharper and clearer luminescence peak with a FWHM of 29 meV compared to GaN grown directly on sapphire.

![Figure 3-26. 77K Photoluminescence spectra of GaN films grown under identical growth conditions with and without AlN buffer layer.](image)

Another measure to quantify the crystalline perfection of GaN films is Rutherford Backscattering spectroscopy (RBS) and channeling. Because the film thickness is much thicker than the penetration of He⁺ particle with an energy of 2.2 MeV, all backscattered He⁺ ions result from the top part of the GaN films. GaN films grown on a-Al₂O₃ with 500Å thick AlN buffer layers show RBS minimum channeling yields as low as 3.3%. This can be compared to the RBS yields for SiGe on Si (4 – 6%) [43] and GaAs on Si (5 – 7%) [44] which are similar heteroepitaxial systems with sizable, but not as large lattice mismatch as GaN/ Al₂O₃. The 3.3% minimum RBS channeling yield is very low and indicates that GaN films grown by VPE on the sputtered AlN buffer layer are of very high crystalline
quality. The lowest RBS minimum channeling yields for GaN films grown on c- Al₂O₃ are higher than those of GaN grown on a-Al₂O₃, both directly and with an AlN buffer layer. The lowest RBS minimum channeling yields for GaN films grown on c- Al₂O₃ with AlN buffer layer is about 8.4% and without AlN buffer layer is about 10.3%, respectively. Figure 3-27 shows the RBS channeling spectra of a GaN film grown on 500Å AlN/ a-Al₂O₃ at 1020°C and a GaN film grown on 500Å AlN/ c-Al₂O₃ substrate.
Figure 3-27. (a) RBS channeling spectra of GaN film grown on 500Å AlN/ a-Al₂O₃ substrate at 1020°C with a minimum RBS yield of 3.3%. (b) RBS channeling spectra of GaN film grown on 500Å AlN/ c-Al₂O₃ substrate at 1020°C with the minimum RBS yield of 8.4%.
RBS tilting scans are particularly useful to examine c-axis oriented materials where there may be some misorientation or tilting between crystallites. The tilting scan RBS signal provides a quantitative measure of the relation between tilting angle of sample. The full width half minimum of the valley in RBS tilting scan is directly related to the crystalline quality of the samples. For better quality crystals, the valley of the RBS signal is deeper and narrower. Figure 3-28 shows the RBS tilting scan of three different GaN samples. Sample (a) and (b) are the GaN films grown with 500Å thick AlN sputtered buffer layer on a-Al₂O₃ and c-Al₂O₃ substrates, respectively. Sample (c) is a GaN film grown directly on c-Al₂O₃ substrate. All other growth parameters among these three samples are identical to each other. Three different curves in Figure 3-28 are intentionally aligned along x-axis with identical x and y axis scale. As consistent to the result of minimum channeling of RBS, Sample (a) shows the deepest and narrowest valley and sample (c) shows the shallowest and widest valley. This leads an conclusion that GaN films grown with thin sputtered AlN buffer layer on a-Al₂O₃ exhibit the best crystalline quality, by improving the initial nucleation of GaN.

![Graph showing RBS tilting scans](image)

Figure 3-28. RBS tilting scans of GaN films grown with and without AlN buffer layer.
3-5 Summary

Thermal decomposition reactions of ammonia and hydrogen reduction of GaCl₃ to GaCl are the thermodynamically favored under our growth temperature and gas flow conditions and they play essential role in GaN growth. If thermodynamic equilibrium is achieved, gas phase etching of GaN by HCl is predicted over GaN deposition from GaCl and ammonia. From experimental measurements in our system, thermal decomposition of ammonia is far from equilibrium and less than 10% of ammonia decomposes. Under this condition, GaN deposition is thermodynamically favored in agreement with experiments.

The GaN films grown under optimized conditions are single crystalline with a smooth surface morphology and show very sharp and strong band edge related photoluminescence without any obvious defect related emission. GaN films grown on both c-plane and a-plane Al₂O₃ substrates show (0001) orientation. No obvious impurity peak such as chlorine and oxygen is observed in XPS analysis. Higher growth temperatures (>970°C) and longer growth times are very important to obtain smoother surface morphologies of GaN films. By depositing a thin AlN buffer layer on the Al₂O₃ substrates by RF sputtering, the crystalline quality and surface morphology of GaN films are greatly improved. The minimum RBS channeling yield of GaN films grown with thin AlN buffer layer is smaller than that of GaN films grown directly on Al₂O₃ substrates.
Chapter 4

Reactive Ion Etching of GaN Films by Chlorine (Hydrogen) Based Plasmas

GaN and its alloy nitrides (InGaN and AlGaN) are leading candidates for the development of optoelectronic devices operating in the green to UV, as well as electronic devices for high power and high temperature environments, due to their direct wide band structure and chemical inertness. This has generated an intensive effort in the growth, processing and characterization of these materials. In order to realize device applications of these materials, a reliable etching technology for the fabrication of small geometry electronic and photonic devices must be established. Although hot phosphoric acid [1,2] and sodium hydroxide solution [3] slightly etch GaN, it is almost impossible to transfer fine patterns to GaN films by any wet chemical etch due to the extreme chemical stability of GaN. GaN films are commonly grown on electrically insulating substrates such as sapphire. Thus, backside contact can not be used to fabricate devices and multiple electrical contacts must always be made from the topside, necessitating a good dry etching process. Therefore, it is necessary to investigate various dry etching processes of GaN and its alloy nitrides to produce a useful etching technology.

As an introduction, the means of transferring fine patterns onto a film by photolithography and etching, basic physical properties of the plasma, the plasma etching mechanisms and the methods of evaluating the plasma etching process are briefly described in this chapter. followed by discussion of the experimental investigation.
4-1 Introduction

4-1-1 Basic Properties of the Plasma

The simplest plasma reactors consist of opposed parallel plate electrodes in a chamber with a low pressure, typically ranging from 10 mTorr to 1 Torr. When a high frequency voltage is applied between the electrodes, current flow generates a plasma which emits a characteristic glow. Reactive radicals and charged species are generated by this electrical discharge process. The plasma is an ionized and dissociated gas mixture with equal numbers of free positive and negative charges. The extent of ionization is typically very small, only one charged particle per million neutral atoms and molecules. The positive charge is mostly in the form of singly ionized species, (i.e. atoms, radicals or molecule fragments). The majority of negatively charged particles are usually free electrons. Due to an electron's much lighter mass, energy transfer from electrons to gas molecules is very inefficient when they collide. Therefore, electrons often attain much higher average kinetic energy ($T_{\text{electron}} >> T_{\text{gas}}$). These energetic electrons can excite high temperature type reactions, such as formation of free radicals, in a low thermal temperature plasma. Without a plasma, generating the same reactive species would require temperatures in $10^3$ to $10^4$ °K.

In any case, free electrons are the main current carriers because of their much higher velocity, compared to ions. Although there are equal number of positive and negative charged particles in a plasma, diffusion and recombination processes tend to deplete charge in the adjacent gas phase, forming a thin boundary layer, called a “sheath”. Since charged particles are much more abundant in the central glow of the plasma than in the sheath, the plasma itself is a good conductor and while the plasma sheath is not. Thus, most of the potential drop appears across the sheath and the voltage across the sheath ranges from a few volts to hundreds of volts.

Because of the electron's much higher velocity, they diffuse faster and escape to the electrode surfaces more easily than ions. Therefore, electrode surfaces get charged negatively and plasma itself becomes positively charged with respect to electrodes. Due to the electric field built across the sheath, the positive ions are accelerated through it and bombard the electrode surface with appreciable kinetic energy and thus participate in directional etching. A schematic diagram of a typical plasma etching system is shown in Figure 4-1. Because the chamber walls are electrically conductive, they contribute to the grounded electrode area. The RF powered electrode thus has a smaller area than the grounded electrode. The RF current density at the RF powered electrode is much higher.
than that at the grounded electrode and this results in a thicker sheath with larger sheath voltage at the RF powered electrode. Etch substrates are placed on the RF powered electrode to utilize the ion bombardment effect.

![Diagram of RF glow discharge and its potential distribution](image)

Figure 4-1. Schematic illustration of RF glow discharge and its potential distribution.

**4-1-2 Plasma Etching Mechanism**

Plasma assisted etching can be described as follows: A specific molecular gas is chosen such that when it is activated in a glow discharge, the ions and radicals that are formed by excitation, dissociation and ionization will react with the solid substrate, forming a volatile reaction product. This plasma assisted etching process can be divided into seven steps as shown in Figure 4-2. First, reactive species, either ions or radicals, must be generated in the plasma. Second, these particles have to reach the solid surface, either by diffusion or driven by the electrical field. These particles must be adsorbed on the surface. Adsorbed particles can react with surface atoms and form volatile reaction products. Finally, reaction products have to be removed from the surface by either desorption or ion bombardment.
Figure 4-2. Schematic representation of basic steps in plasma etching.

Plasma etching mechanisms can be grouped into three functional categories. These three basic plasma etching mechanisms are shown schematically in Figure 4-3 and are briefly explained.

Figure 4-3. Basic mechanisms of plasma etching with schematic sideview. (a) physical etching (b) simple chemical etching (c) ion enhanced chemical etching.
(a) Physical sputtering mechanism

The ballistic ejection of materials from the surface occurs when positive ions are propelled into surfaces by the negative going potentials at the edge of the plasma. An ion transfers its kinetic energy to a small region of the substrate at the point of impact, and some substrate atoms receive enough of this energy to be ejected from the surface. A low pressure and long mean free path are required for atoms to leave from the surface without being backscattered and redeposited. This process is distinguished from the other mechanisms in that the interaction is purely mechanical. The etch rate of this mechanism is only determined by the bonding forces between surface atoms and usually much lower than chemical or ion assisted etching. Sputtering is inherently unselective because the ion energy required to eject materials is large compared to differences in surface bond energies and chemical reactivity. For many applications, sputter etching cannot be used because of its lack of selectivity. When chemical reactive etching is not available, sputter etching is always a possible solution.

(b) Simple chemical etching

Active neutral species, commonly Cl, F or H atoms, from the plasma can adsorb to the surface and react to form volatile products. The etch rate of this mechanism is often determined by the reaction product volatility. Without product volatility, the reaction product will accumulate and coat the whole surface. Etchant supply is impeded by the coating of the reaction product and this cuts off further etching reaction. In this etching process, the only function of the plasma is to maintain a supply of gaseous etchant species. Consequently, it is also possible to etch by this mechanism without a plasma when the feed gas is inherently reactive. Because ion bombardment plays no roll, etching is non-directional (i.e. isotropic). Masked areas are undercut with an isotropic circular profile. Chemical etching is the most selective mechanism. Unwanted reactions will not take place at all when thermodynamics are unfavorable due to large difference in an etchant’s chemical affinity for various materials. By proper choice of reactant gases, one can often find reactions that will etch one material, but not another.

(c) Ion enhanced chemical etching

A directional negative-going electric field always forms along the plasma boundaries. This intense sheath field propels positive ions into the boundary surfaces at normal incidence. Hence, there is an anisotropic ion flux at plasma solid boundaries. This ion bombardment enhances reactions between the substrate and neutral species from the gas phase and stimulates directional etching. The ability of an ion to stimulate the etching
reaction depends more on its energy and mass than on its chemical identity. The effect of neutral species and ions can be synergetic with the resulting material removal rate exceeding the sum of separate pure chemical etching and pure sputtering. In this mechanism, neutral species cause little or no etching without ion bombardment. Ions accelerated across the plasma sheath damage the substrate atoms, making them more reactive toward incident neutral radicals. By the collisions of ions into the substrate surface, highly reactive dangling bonds are formed and the surface lattice structure is broken. Thus surface atoms become loosely bound to each other. Since the ions are accelerated and strike the surface vertically, the etching induced is quite directional and anisotropic.

4-1-3 Plasma Etching Characteristics

Plasma etching processes can be characterized by (i) etch rate, (ii) etch selectivity, (iii) etch uniformity and (iv) etched surface quality. Overall production rate and cost are determined by these factors. While a faster etch rate is desirable for economical process throughput, this does not necessarily result in lower cost, as yield and etching equipment cost are often much more important factors than etch rate. Etch selectivity defines the relative material etching rate in a plasma. The selectivity must be high enough to insure that the etch mask is not removed or seriously eroded and the sublayer beneath a patterned mask layer will not be attacked during the etching. Etch uniformity means the evenness of etching across the whole wafer. Etch rate variation can be caused by both plasma composition non-uniformity and reactor geometry. Finally, the etched surface must have good morphology and be free of physical and electrical damage. Surface quality is mainly influenced by temperature, ion bombardment, etchant and crystallographic orientation of the surface. Under some conditions, etched surfaces may be unacceptably rough, pitted and contaminated. The etched surface can be degraded by contamination from sputtering and etch residue. The etched surface also can be electrically damaged by contamination, radiation and charging.

4-2 Experiments

4-2-1 Sample Preparation

GaN films used in this experiment were mainly grown by electron cyclotron resonance (ECR) plasma assisted MBE on semi-insulating (100) GaAs and (0001) sapphire
substrates. Elemental Ga and a nitrogen plasma were used as source materials. The growth conditions for the GaN film are described in Table 4-1. Characterization of the GaN films by X-ray diffraction, Raman spectroscopy and cross-sectional transmission electron microscopy showed that the GaN films had the wurtzite structure. The films grown on (100) GaAs consisted of columnar crystalline domains, oriented with the c-axis normal to the surface [4] whereas the films grown on (0001) sapphire were found to be single crystal with the c-axis normal to the substrate surface [5]. GaN films grown on (0001) sapphire substrates by metalorganic vapor phase epitaxy (MOCVD) were also used in order to investigate the effect of crystalline quality on etch rate. Trimethylgallium (TMG) and ammonia were used as the group III and V precursors, respectively and growth temperature was in the range of 1050°C ~ 1160°C. The GaN films grown by MOCVD method were also single crystal and showed much narrower full width half maximum (FWHM) X-ray rocking curves. They are believed to have better crystalline quality than those grown by ECR plasma MBE.

<table>
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<th>on sapphire</th>
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</tr>
<tr>
<td>plasma pressure</td>
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Table 4-1. The growth conditions for GaN films grown by ECR plasma assisted MBE.

GaN films with a thickness between 0.9 and 2.1 μm were patterned with positive photoresist, and etched using a Drytek model DRIE-184 reactive ion etching system. CHF₃ and C₂ClF₃ gases were introduced into the RIE chamber and Ar gas was added in order to stabilize the plasma discharge and enhance the etching anisotropy by increasing the non-reactive ion bombardment. The RF plasma power was varied between 100W and 700W and the pressure varied between 60 and 300 mTorr. CHF₃ and C₂ClF₃ flow rates were varied between 20 and 50 sccm. After etching, the remaining photoresist was removed by exposing the samples to an oxygen plasma and dipping them into H₂SO₄ : H₂O₂ (1:3) solution. Sometimes, due to photoresist hardening during the etching, it was very difficult
to remove the photoresist mask layer completely and it was often observed that the etched edges were not sharp, due to serious mask erosion during the process. To prevent photoresist mask erosion during etching, 0.5 ~ 1µm thick sputtered iron nitride (Fe - 8% N) films were used as an alternative mask layer. After sputtering the iron nitride film, a photoresist mask was formed by conventional photolithography techniques and then patterned with H₂SO₄ : H₂O₂ : H₂O (1:1:10) solution to etch the iron nitride. Since the resist has not been exposed to a plasma, the remaining resist was easily removed by acetone after patterning the iron nitride layer. To investigate the etching behavior of SiCl₄ and CHCl₃ plasmas, a triple chamber Zylin™ reactive ion etching system was used. The RF plasma power was varied from 100W to 500W and the chamber pressure was varied between 70 mTorr and 150 mTorr. The flow rates for SiCl₄ and CHCl₃ were set to 21 sccm and 30 sccm, respectively. No other gas additives were used. The etched surface morphology was checked by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) was used to detect the presence of the etched surface contamination and micro Raman spectroscopy and photoluminescence was used to investigate the degradation of crystal quality by etching. Etch rates were measured by a Tencor alphastep™ profilometry after mask removal.

### 4-2-2 Selection of GaN etching plasmas

Chlorine-containing plasmas are the most promising etchants for GaN. Several research groups have reported reactive ion etching or ECR plasma etching of GaN and its alloy nitrides using SiCl₄ [6, 7], BCl₃ [8, 9], C₂ClF₅ [10, 11], and Cl₂ [12 ~17]. Hydrogen-containing gases, such as CH₄ [13 ~16, 18, 19], CHF₃ [10, 11], HBr [20, 21] and HCl [17, 18, 22] have also been used to etch GaN. Possible reaction products of GaN with various radicals are shown in Table 4-2.

<table>
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<td>no</td>
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</tbody>
</table>

Table 4-2. Possible etching products of GaN
In this experiment, CHF<sub>3</sub>/Ar, C<sub>2</sub>ClF<sub>3</sub>/Ar, C<sub>2</sub>ClF<sub>4</sub>/Ar/O<sub>2</sub>, SiCl<sub>4</sub> and CHCl<sub>3</sub> plasmas were used for the reactive ion etching of GaN films. The active etching neutrals of these plasmas are either Cl or H atoms, because only Ga chloride and hydride are volatile. F atoms can not play any role as an active etching species because of very high sublimation temperature of Ga fluoride, up to 800°C. The possible etch reaction products of these plasmas are Ga chloride or Ga hydride. Both CHF<sub>3</sub> and C<sub>2</sub>ClF<sub>3</sub> gases are non-flammable and less toxic and corrosive than other candidate gases used for etching GaN, such as SiCl<sub>4</sub>, BCl<sub>3</sub> and Cl<sub>2</sub>, but they have only one active etching atoms per molecule. Figure 4-4 shows the binding energies and active radicals of the plasma gases used in this experiment.

![Chemical structures](image)

**Figure 4-4.** Interatomic binding energies of plasma gases used for reactive ion etching of GaN.
4-3 Results and Discussion

4-3-1 Effects of RF plasma power, chamber pressure, gas flow rate and GaN crystal quality on etch rate

Figure 4-5 shows the results of etch rate experiments of GaN in CHF$_3$/Ar, C$_2$ClF$_5$/Ar, C$_2$ClF$_5$/Ar/O$_2$ plasmas as a function of RF plasma power. The chamber pressure was kept at 100 mTorr and the flow rate of CHF$_3$ and C$_2$ClF$_5$ was 50 sccm. The flow rates of Ar and O$_2$ gas were 20 sccm and 10 sccm, respectively. The etch rate increased linearly with increasing RF plasma power for all three plasmas.

![Figure 4-5. The effect of RF plasma power on GaN etch rate.](image)

Under higher RF plasma power conditions, more reactive radicals were generated due to a higher dissociation efficiency. The plasma sheath thickness becomes thicker and the voltage across the plasma sheath increases with the increase of RF plasma power. Therefore, the rates of both chemical etching by neutral species and physical etching by energetic positive ions are increased at higher RF plasma power. The etch rate of
$\text{C}_2\text{Cl}_2\text{F}_2/\text{Ar}/\text{O}_2$ (50/20/10 sccm) plasma was larger, up to 90%, compared to $\text{C}_2\text{Cl}_2\text{F}_2/\text{Ar}$ (50/20 sccm) plasma. The added oxygen atoms can combine with surface nitrogen atoms to form volatile NO$_x$ complexes and this increases the etch rate, slightly. An undesirable serious surface degradation and contamination were often observed in samples etched by $\text{C}_2\text{Cl}_2\text{F}_2/\text{Ar}/\text{O}_2$ plasma.

The effects of chamber pressure on etch rate are shown in Figure 4-6. The RF plasma power was set to 200W and the flow rate of CHF$_3$ and $\text{C}_2\text{Cl}_2\text{F}_3$ was 50 sccm plus 20 sccm of Ar. For both CHF$_3$/Ar and $\text{C}_2\text{Cl}_2\text{F}_3$/Ar plasmas, the etch rate increases with decreasing chamber pressure. As the pressure is reduced, the self bias dc voltage across the sheath increases. The energy of ions bombarding the substrate surface thus increases with a decrease of chamber pressure. When the ion bombardment energy exceeds the threshold energy for sputtering at very low pressures, the physical sputtering etch rate increases very rapidly and dominates the material etch rate. Therefore, the etch rate increases with decreasing pressure. Chemical etching by neutral species plays less of a role due to its decrease in concentration near the substrate surface. In an intermediate pressure regime, where the ion bombardment energy does not exceed the threshold of sputtering, etching by an ion induced chemical etching mechanism is promoted and the etch rate thus increases with lowering pressure. At higher pressures, ion bombardment energy decreases and chemical etching by reactive neutral species dominates. This causes a decrease of etch rate, regardless of the increased concentration of reactive neutral species at higher pressures. From an observation of the etched surface morphologies by scanning electron microscopy, etch pits are observed only in samples etched at high pressures. The concentration of these etch pits is in the range of $10^8$ / cm$^2$. The higher etch rate at lower pressure implies that the physical etching process dominates the reactive ion etching of GaN using either CHF$_3$/Ar or $\text{C}_2\text{Cl}_2\text{F}_3$/Ar plasma.
Figure 4-6. The effects of chamber pressure on GaN etch rate by CHF₃/Ar and C₂ClF₅/Ar plasmas.

The effect of gas flow rate on etch rate is shown in Figure 4-7. The etch rate is not strongly dependent on the gas flow rate of CHF₃ or C₂ClF₅, indicating that the etch rate is dominated by either the rate of etch product removal from the surface or the surface reaction rate. The etch rate was enhanced by adding Ar gas up to 20%, but it was not changed by a further increase in the Ar flow rate. Ar gas added in conventional halocarbon plasmas stabilizes the plasma discharge and stimulates the gasification of the etching products [23, 24]. Thus, etch rate is increased by adding Ar gas into plasma. Further increases in Ar gas reduces the concentration of reactive etchant species due to dilution.
Figure 4-7. The effect of gas flow rate on GaN etch rate.

The effect of the crystal quality of GaN films on their etch rate is shown in Figure 4-8. Three different kinds of GaN films were used. The first group is the GaN films grown on (100) semi-insulating GaAs substrate by ECR plasma assisted MBE. These GaN films have wurtzite crystal structure with a strong (0001) texture. The second group of GaN films were grown on c-sapphire single crystal by ECR plasma assisted MBE. From the result of X-ray diffraction and electron diffraction characterization, these films are also wurtzitic single crystals with c-axis normal to the substrate surface, but showing fairly broad X-ray rocking curve and photoluminescence emission. The last group of GaN films were grown on the same substrate as the second group, but by MOCVD. These samples were grown at much higher temperature, up to 1160°C, and showed better crystallinity than second group of samples from comparison of FWHM of X-ray rocking curve and photoluminescence spectra. The conditions for etching were identical for all three groups of samples. A C2ClF/Ar plasma was used with flow rates of 30/10 sccm. Chamber pressure was kept as 60 mTorr. RF plasma power was varied from 100W to 500W. For all three groups, the etch rate increased with an increase of RF plasma power. The etch rate of first group samples, for which crystalline quality was poorest, was the highest. The best crystalline quality samples, the MOCVD grown samples, had the lowest etch rate over the
entire range of RF plasma power. The maximum ratio of etching rate between the best and the worst sample is smaller than a factor of two. The GaN atoms around the crystalline defects are loosely bound to each other and can be easily removed from the surface during etching. Thus, more defective crystals exhibit a faster etch rate under identical etching conditions.

Figure 4-8. The effect of the crystal quality of GaN films on their etch rate.

SiCl₄ and CHCl₃ gases were also used to etch GaN. Although these gases are relatively toxic and multiple chamber equipment is required for safe etching operations, they have more active species for etching (Cl and H atoms) per molecule and thus showed much faster etch rates under the same chamber pressure and RF plasma power and the same kind of GaN films compared to the CHF₃ or C₂ClF₅ plasmas. The basic etching behavior effects of RF plasma power and chamber pressure on the etch rate, of SiCl₄ and CHCl₃ plasmas showed the same manner as those of CHF₃ and C₂ClF₅ plasmas. The etch rates of both SiCl₄ and CHCl₃ plasmas increased linearly with the increase of RF plasma power and decrease of chamber pressure. Figure 4-9 show the relationship between plasma power and GaN etch rate for SiCl₄ and CHCl₃ plasmas under constant chamber pressure.

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and gas flow rate. The chamber pressure was kept at 110 mTorr and the flow rates were 21 sccm for SiCl₄ and 30 sccm for CHCl₃. The etch rate was about 1500Å/min with 500W of input RF power for both plasmas. The etch rates were approximately 4 times faster than those of CHF₃ and C₂ClF₃ plasmas.

![Graph showing etch rate vs. plasma power](image)

Figure 4-9. The relationship between plasma power and GaN etch rate for SiCl₄ and CHCl₃ plasmas.

Figure 4-10 shows the relationships among chamber pressure, GaN etch rate and the measured dc self bias voltage, for the case of reactive ion etching of GaN by CHCl₃ plasma under a fixed RF plasma power of 150W and CHCl₃ flow rate of 30 sccm. Both GaN etch rate and self bias voltage increase with a decrease of chamber pressure. The etch rate varies also linearly with the measured dc self bias. This implies that the etch process is dominated by physical or an ion-induced etching mechanism rather than a chemical etching mechanism. The etch rate changes drastically from 220Å/min to 25Å/min with the change of chamber pressure from 70 mTorr to 150 mTorr.
4-3-2 Characterization of crystal quality, surface contamination and surface morphology of reactive ion etched GaN surfaces

In reactive ion etching, the surfaces being etched are subject to bombardment by energetic ions and electrons. These incident species can produce various forms of radiation damage in the materials being etched including electron traps, displaced atoms and implanted atoms. In order to investigate degradation of crystal quality by etching, micro-Raman spectroscopy was used. Micro Raman spectra of the etched and unetched parts of the film, obtained in the backscattering configuration along the z-axis, are shown in Figure 4-11. The E\textsubscript{1} (TO) mode at 565 cm\textsuperscript{-1} and the A\textsubscript{1} (LO) mode at 730 cm\textsuperscript{-1} are both observed, in correspondence with the selection rule for wurtzite GaN [4, 11,25, 26]. No shift or broadening of the peak in the etched part was observed, implying that any degradation of GaN crystal quality is not caused by reactive ion etching process. The decrease in the peak intensity is due to the reduction of the film thickness from 9000Å to 5000Å by etching.

Figure 4-10. The relationships among chamber pressure, GaN etch rate and the measured dc self bias voltage.
Figure 4-11. Micro Raman spectra of the etched and unetched parts of GaN film grown on (100) GaAs by ECR plasma assisted MBE

The effect of reactive ion etching under harsher etching conditions (higher plasma power with lower pressure) on the photoluminescence (PL) spectra of doped GaN films was investigated. Mg doped p-GaN films were chosen and patterned by reactive ion etching by C<sub>2</sub>ClF<sub>5</sub>/Ar plasma (50/20 sccm) with the plasma power set at 500W and chamber pressure of 80 mTorr for 30 min. One half of the GaN surface was exposed to the plasma and the other half protected by a mask. Photoluminescence was done with the smallest sized laser beam and PL spectra were taken from both etched surface and unetched surface. The PL spectra shown in Figure 4-12 are almost identical to each other. No shift, generation or alternation of PL peaks is observed. The PL spectrum of the etched surface exhibited a stronger and narrower Mg dopant related emission than that of unetched surface.
Figure 4-12. Photoluminescence spectra of reactive ion etched and unetched Mg doped p-GaN films at 77K. The etching is carried out by C₃ClF₅/Ar plasma with the plasma power of 500W and chamber pressure of 80 mTorr for 30 min.

Surface contamination is an inevitable event in reactive ion etching. There are a number of surface contamination sources, including polymeric residues, deposition of nonvolatile solids sputtered from the chamber surface and implanted atoms. In this experiment, surface contamination issue is checked by X-ray photoelectron spectroscopy. By irradiating X-ray photons into the surface, the electrons of surface atoms are excited and ejected from the atoms with a characteristic energy. The emission of photoelectrons can only occur very near the surface. From measuring the number of photoelectrons and their characteristic energies, the chemical species and composition of the surface can be identified. X-ray photoelectron spectroscopy of GaN film etched by C₃ClF₅/Ar plasma with a plasma power of 400W and pressure of 100 mTorr for 10 min are shown in Figure 4-13. The oxygen 1s peak intensity of the etched film increased slightly, and a carbon 1s peak was observed, which was not observed in the unetched film. No other peaks for Cl or F were observed. This indicates that the GaN surface was contaminated by carbon and oxygen during the reactive ion etching process.
Figure 4-13. X-ray photoelectron spectroscopy of GaN film etched by C\textsubscript{2}ClF\textsubscript{5}/Ar plasma.

The surface morphologies of etched and unetched GaN films grown under identical conditions were examined by atomic force microscopy (AFM). The GaN films were grown on (100) GaAs substrate by ECR-MBE. The reactive ion etching was done by C\textsubscript{2}ClF\textsubscript{5}/Ar plasma with the plasma power of 400W and chamber pressure of 100 mTorr for 20 min. Measured etch rate was 100Å/min. 3µm x 3µm areas of the film surface were scanned. Figures 4-14, (a) and (b) show a perspective view of the surfaces of etched and unetched films. The unetched film has a root mean square (RMS) roughness of 17.548 nm, while the RMS roughness of the reactive ion etched film is only 12.607 nm. This implies that the surface is certainly not roughened by the etching process and may actually be smoother with more rapid etching of the peaks of the film. This result is consistent with GaN films etched by other plasmas.
Figure 4-14. Atomic force microscopy (AFM) image of GaN surface. (a) etched GaN surface with 12.607nm of RMS roughness. (b) unetched GaN surface with 17.548nm of RMS roughness.
4-3-3 Patterning of GaN thin films

GaN thin films were successfully etched by various gas mixtures, including CHF$_3$/Ar, C$_2$ClF$_5$/Ar, C$_2$ClF$_5$/Ar/O$_2$, SiCl$_4$ and CHCl$_3$ plasmas. To transfer fine quality patterns into GaN films by reactive ion etching, both optimization of each etching parameter and development of suitable etch mask are very important. Figure 4-15 shows a scanning electron micrograph of GaN films etched in a C$_2$ClF$_5$/Ar (50/20 sccm) plasma with a plasma power of 500W and chamber pressure of 100 mTorr. Conventional Shipley 1813 positive photoresist was used as the etch mask. No obvious surface roughening is observed in the etched surface, but etched side wall has inclined severely and boundary between etched and unetched parts is not very clear. Due to the extreme chemical inertness of GaN, GaN films must be etched under very severe conditions and photoresist can be easily eroded and hardened. Another disadvantage of a photoresist etch mask is its difficulty of removal after etching. To remove the remaining photoresist, the entire substrate is exposed to an O$_2$ plasma and then dipped into H$_2$SO$_4$ + H$_2$O$_3$ (3:1) solution. The GaN surface is possibly contaminated and oxidized during this process, thus a better etch mask which has to be very durable during etching, easy to remove after etching and also easy to be finely patterned, is required to obtain fine-patterned GaN films.

Figure 4-15. The scanning electron micrography of patterned GaN films with photoresist mask.
Figure 4-16, (a) and (b) show scanning electron micrographs of patterned GaN films. The etching was done by C$_2$ClF$_7$/Ar (30/10 sccm) plasma with a plasma power of 500W and chamber pressure of 70 mTorr. The etch rate was about 230Å/min. The etched side walls are very distinctive and almost vertical. No mask erosion was observed. Instead of a photoresist mask, an iron nitride (Fe-8% N) film was used as the mask. Iron nitride was very resistive to etching under typical GaN etching condition (Cl basis etching), because no iron halide is volatile, whereas it was very soluble to H$_2$SO$_4$ + H$_2$O$_2$ + H$_2$O (1:2:10) solution. Therefore, iron nitride films can be finely patterned by a wet etching process with conventional photoresist mask. 1μm thick iron nitride films were deposited on GaN by RF sputtering. Because sputtering is done at room temperature, no obvious interfacial reaction or degradation of the GaN films was observed. A photoreist mask layer was formed on the iron nitride surface by conventional photolithography processes.
Figure 4-16. (a) The scanning electron micrography of patterned GaN films with iron nitride mask. (b) The scanning electron micrography of etched sidewall of patterned GaN films with iron nitride mask.

4-4 Summary

Reactive ion etching of GaN films was successfully performed using Cl (H) containing plasmas such as CHF$_3$/Ar, C$_2$ClF$_5$/Ar, C$_2$ClF$_5$/Ar/O$_2$, SiCl$_4$ and CHCl$_3$. Under higher RF plasma power and lower chamber pressure, self bias dc voltage increases and the etching species are accelerated more energetically and thus faster etch rates are obtained for all plasmas used in this study. It is proved that Cl and H radicals are much more active etching species than F radical, because SiCl$_4$ and CHCl$_3$ plasmas etch GaN much faster, up
to 4–5 times, than CHF₃ and C₂ClF₅ plasmas under the identical etching conditions (plasma power, chamber pressure, gas flow rate, etc.) GaN films with better crystalline quality exhibit slower etch rates than those of defective GaN films. AFM measurements of etched and unetched GaN films reveal that reactive ion etching process does not cause any serious surface roughening. According to XPS analysis, the etched surfaces are slightly contaminated by carbon and oxygen. Since GaN films must be etched under rather harsh environments, serious photoresist mask erosion is often observed. By replacing the etch mask from a conventional photoresist to sputtered iron nitride film, GaN films can be finely patterned with vertical etched sidewalls.
Chapter 5

Conclusions and Future Work

5-1 Conclusions

GaN thin films were grown on (001) GaAs and (0001) sapphire substrates from the elemental Ga vapor and physically activated atomic nitrogen by plasma assisted MBE. Due to the large lattice and thermal mismatches to GaAs and sapphire substrates, the crystalline quality of GaN films was not good enough to be used as electronic or photonic devices. For both substrates, the GaN films were the wurtzite structure. While single crystalline GaN films were grown on sapphire substrates, GaN films grew in a columnar structure on (100) GaAs substrates and each column was c-axis oriented. Relevant PL spectra at 77K showed broad defect related emissions around 2.1 eV with strong band edge related emission at 3.47 eV.

In order to obtain better crystalline quality GaN films which can be used for electronic or photonic devices, good substrates which have much closer lattice parameter and thermal expansion coefficient to GaN are necessary. The best substrate for GaN growth is single crystal GaN. Unlike other bulk single crystals, such as Si, GaAs, GaP, etc., it is extremely difficult to grow bulk GaN single crystals, due to the high melting temperature and high N₂ equilibrium pressure. Thus, thick pseudo-bulk GaN films might be used as substrates for homoepitaxial growth of subsequent device structures by MBE or MOCVD.

Due to much faster growth rate than any other growth techniques with good crystalline quality, hydride vapor phase epitaxy is one of the best ways to grow pseudo-bulk thick GaN films. A new hydride VPE technique for the growth of thick GaN films was developed. Crystalline GaCl₃, was used as the group III source and NH₃ as the group
V precursor. N₂ gas was used as the carrier gas. In order to understand the growth mechanisms and to optimize reactor design and growth parameters, such as growth temperature, partial pressures and flow rates of reactants, thermodynamic calculations were carried out for our growth system. According to the results of thermodynamic calculations under typical growth conditions, GaN films can not grow under thermodynamic equilibrium conditions. Most of the NH₃ decomposes to N₂ and H₂ due to its thermal instability at typical GaN growth temperatures and N₂ is too stable to grow GaN. Etching of GaN by HCl gas, produced from the reaction between GaCl₃ and H₂, dominates over GaN deposition from the reaction between GaCl and NH₃, under thermodynamic equilibrium. From the experimental measurements, less than 10% of the NH₃ gas decomposes under typical growth conditions because the total gas flow rate is quite high and thus, the resident time of each gas species is too short to reach thermodynamic equilibrium. In this condition, GaN formation overcomes the etching process by HCl. Therefore, GaN growth is thermodynamically favored.

We demonstrated that the hydride VPE technique using GaCl₃ and NH₃ is very suitable for growth of thick GaN films due to its much faster growth rate compared to other GaN growth techniques. Growth parameters were optimized in order to obtain high crystalline quality thick GaN films with smooth surfaces. (0001) and (1120) oriented Al₂O₃ wafers were used as substrates. From characterization by X-ray diffraction and transmission electron microscopy, the GaN films were single crystalline. A high density of crystalline imperfections, such as dislocations and stacking faults, were observed near the interface and their density decreases drastically with an increase of film thickness. Photoluminescence reveals that GaN films show very sharp and strong band edge related photoluminescence without any obvious defect related emission. Chlorine and oxygen impurities are not detected in XPS analysis. In order to improve the initial nucleation of GaN crystals on the Al₂O₃ substrates, thin AlN buffer layers were deposited by RF sputtering. The crystalline quality and surface morphology of GaN films were greatly improved by the AlN buffer layers. The minimum RBS channeling yield and FWHM of X-ray rocking curves of GaN films grown with thin AlN buffer layers is smaller than those of GaN films grown directly on Al₂O₃ substrates.

Reactive ion etching is one of the key technologies required to make electronic and photonic devices. Cl (H) containing plasmas, such as CHF₃/Ar, C₂ClF₃/Ar, C₂ClF₆/Ar/O₂, SiCl₄ and CHCl₃, can be successfully used to etch GaN films. Under higher RF plasma power and lower chamber pressure, self bias dc voltage increase and the etching species are accelerated more energetically. Therefore, faster etch rates are obtained with higher RF plasma power and lower chamber pressure for all plasmas used in this study. GaN films
with better crystalline quality exhibit slower etch rates than those of defective GaN films. AFM measurements of etched and unetched GaN films reveal that the surface is certainly not roughened by the reactive ion etching process and may actually be smoother with more rapid etching of the peaks of the film. According to XPS analysis, the etched surfaces are slightly contaminated by carbon and oxygen. Since GaN films must be etched under rather harsh environments due to its chemical inertness, serious photoresist mask erosion is often observed. By replacing the etch mask from a conventional photoresist with a sputtered iron nitride film (Fe-8% N), GaN films can be finely patterned with vertical etched sidewalls.

5-2 Future Work

In order to fabricate real electronic and photonic devices based upon GaN and other Group III nitrides, many technical problems remain to be solved. For example, Figure 5-1 shows typical technical difficulties to be overcome for the fabrication of a GaN based laser diode.

Figure 5-1. The typical technical difficulties to fabricate the GaN based laser diode.
These difficulties include growth of high crystalline quality Group III nitride films, high conductivity doping for both p and n type, fabrication of low resistance ohmic metal contacts, dry etching processes, alloy nitride growth for bandgap engineering and facet cleaving and high reflectivity mirror coating.

We grew thin GaN layers as potential device structures. Low defect density GaN films with precise control of doping and alloy composition are required. Due to large lattice and thermal mismatch between GaN films and substrates, the quality of GaN films grown directly on sapphire and GaAs substrates was not good enough to be used as devices. Thus, hydride vapor phase epitaxial (HVPE) growth of thick GaN films, was investigated for use as a substrate for homoepitaxial growth of subsequent device structures. High crystalline quality thick GaN films with smooth surface morphology were successfully grown by HVPE. Reactive ion etching processes for the fine patterning of GaN films were successfully developed using Cl (H) containing plasmas.

As a future work, homoepitaxial growth of thin GaN and other Group III nitrides films must be studied. Either MBE or MOCVD techniques can be used to grow GaN and other Group III nitrides layers on GaN substrates (pseudo-bulk thick GaN films), with precise control of alloy composition and dopant concentration. In order to prevent the nucleation of crystalline defects, such as dislocations from the interface between GaN substrates and over layers, the surface of the GaN substrates should be atomistically smooth. It is extremely difficult to achieve such a smooth GaN surface from HVPE technique, due to very fast growth and gas phase etching rates during the growth. Therefore, surface planarization techniques such as chemical-mechanical polishing (CMP) [1,2] and etch back [3-5] must be developed for the planarization of HVPE grown GaN films and surface cleaning techniques must be developed to prevent any contamination caused by the planarization process. Figure 5-2 shows a schematic illustration of the etch back process.
Figure 5-2. The schematic illustration of etch back process.
References

Chapter 1


Chapter 2


Chapter 3

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Chapter 4


Chapter 5

Appendix

(1) Sample Preparation for RIE

(i) Clean the GaN film with TCE -> acetone -> methanol -> D.I. water.
(ii) Deposit FeN (Fe-8% N) film by RF sputtering.
    thickness: 2000Å ~ 1μm
    power: 300 ~ 500 W
    pressure: 5 mTorr
(iii) prebake at 80°C for 10 minutes.
(iv) Deposit ~1μm thick positive photoresist (Shirply 1813).
(v) Expose to UV with mask.
(vi) Develop and rinse with D.I. water.
(vii) postbake at 120°C for 20 minutes.
(viii) Pattern FeN layer.
    Dip into H₂SO₄ : H₂O₂ : H₂O (1:1:10) solution for 5 minutes.
    rinse with D.I. water.
(ix) Remove remaining photoresist by acetone.
(x) Rinse with D.I. water and blow dry by N₂.
(xi) Etch GaN film under Cl(H) containing plasmas.
(xii) Remove FeN mask by H₂SO₄ : H₂O₂ : H₂O (1:1:10) solution.
(xiii) Characterize the sample.
(2) VPE growth procedure

(1) Substrate preparation

(i) Clean the sapphire substrate with TCE -> acetone -> methanol -> D.I. water.
(ii) Etch the sapphire substrate with boiling HCl+H₂SO₄ (3:1) solution.
(iii) Rinse with D.I. water and blow dry by N₂.
(iv) Deposit AlN buffer layer by RF sputtering.
    thickness: 300Å - 500Å
    power: 300 ~ 700 W
    pressure: 5 mTorr

(2) Loading and Unloading the substrate

(i) Loading the substrate in reaction tube.
(ii) Pump and purge with high purity N₂ for 5 times.
(iii) Keep N₂ flow through the reaction tube with 300 ~ 500 sccm.
(iv) Heat up the furnace to growth temperature (furnace in position A).
(v) Begin to flow NH₃ (1~2 slm) and N₂ (1~2 slm).
(vi) Place the furnace in position B and hold for 10 ~ 20 minutes for surface nitridation.
(vii) Begin to flow GaCl₃ / N₂.
(viii) GaN growth in progress.
(ix) Stop flowing GaCl₃ / N₂ and hold for 10 minutes.
(x) Stop flowing NH₃ (1~2 slm).
(xi) Place furnace in position B.
(xii) Unload the substrate after cooling.
(3) Routine Characterization Procedure of GaN films

(i) X-ray Diffraction : $2\theta/\omega$-scan (nondestructive)
    for phase identification, measurement of out of plane orientation and residual stress.

(ii) X-ray Rocking curve : $\omega$-scan (nondestructive)
    for measurement of crystallinity of films from the FWHM of X-ray rocking curve.

(iii) X-ray Diffraction : $\Phi$-scan (nondestructive)
    for measurement of in plane orientation of film and single-crystallinity.

(iv) Photoluminescence (nondestructive)
    for measurement of optical property of GaN films; position and linewidth of PL peaks from band edge emission and from defect - impurity complex, etc.

(v) Raman spectroscopy (nondestructive)
    for phase identification and measurement of crystallinity of GaN films.

(vi) Scanning Electron Microscopy (slightly contaminated by thin Au film)
    observation of surface morphology of GaN film and film thickness measurement from cross-sectional view.

(vii) Hall Measurement (slightly contaminated by In electrode)
    for measurement of electrical properties; type of carrier, carrier concentration and mobility.

(viii) X-ray Photoelectron Spectroscopy (nondestructive, but destructive for depth profiling)
    for chemical impurity characterization.