Modeling of gallium nitride molecular beam epitaxy growth

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MODELING OF GaN MOLECULAR BEAM EPITAXY GROWTH

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ABSTRACT

Modeling of GaN Molecular Beam Epitaxy Growth

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III—V nitrides (GaN, InN and AlN) are intensely researched for optoelectronic applications spanning the entire visible spectrum. In spite of realization of commercial devices and advances in processing of materials and devices, the understanding of the processing and epitaxial growth of these materials are incomplete. In this study, a rate equation approach is proposed based on physically sound surface processes to investigate the molecular beam epitaxy growth of GaN using ammonia and ECR plasma source. A surface riding layer of Ga and ammonia or N plasma species are included in the model. The surface riding species are allowed to undergo several physical and chemical processes. Rates of all surface processes are assumed Arrhenius type. The necessary model parameters which are unknown were found by fitting results from simulation to experimental values. In the case of ammonia, the simulated Ga incorporation rate as a function of ammonia pressure and substrate temperature are in excellent agreement with the experimental data. Ga incorporation increases with increasing ammonia overpressure.
and saturates at a maximum rate dictated by temperature. The Ga incorporation rate with temperature exhibits a peak at a temperature for a given set of fluxes due to competition between thermally activated pyrolysis of ammonia and reevaporation of Ga from the surface. The simulated Ga desorption parameter versus time data is also in good qualitative agreement with the experimental data. In the case of ECR plasma, the flux and reactivity of the active nitrogen are modeled based on plasma dynamics and used in our study. As the ECR power increases, the flux of active nitrogen and all other N species, which are by products, increases almost linearly. Thus the Ga to active N flux ratio increases and hence Ga incorporation rate increases and saturates at a maximum rate similar to growth with ammonia. Growth rate versus temperature behavior is also observed to be similar to growth with ammonia. Electron concentration obtained from bulk vacancy concentrations of Ga and N decreases linearly with ECR power unlike the experimental observation of exponential decrease. The discrepancy is due to the fact that the electron concentration is strongly influenced by the incorporation of unintentional impurities from the plasma chamber such as Si, C, and O which are not modeled in our study.
# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................. iii

LIST OF FIGURES ................................................................................................................... vii

ACKNOWLEDGEMENTS ....................................................................................................... ix

CHAPTER 1 INTRODUCTION ............................................................................................ 1  
  1.1 Organization of the Thesis ........................................................................................... 4

CHAPTER 2 LITERATURE OVERVIEW .............................................................................. 5  
  2.1 Molecular Beam Epitaxy ............................................................................................. 5  
      2.1.1 General Description .......................................................................................... 5  
      2.1.2 In-Situ Monitoring Tools ................................................................................ 6  
      2.1.3 Modes of MBE Growth ................................................................................... 8  
      2.1.4 MBE System Preparation ................................................................................. 9  
      2.1.5 Substrate Preparation ..................................................................................... 9  
  2.2 GaN Growth and Devices ......................................................................................... 10  
      2.2.1 III-V Nitride Processing ................................................................................. 10  
      2.2.2 III-V Nitride Devices Applications .............................................................. 14  
      2.2.3 GaN Growth Kinetics with Ammonia as Source ....................................... 16  
      2.2.4 ECR Molecular Beam Epitaxy growth of GaN ........................................... 18  
          2.2.4.1 ECR Plasma Source Characteristics ................................................... 18  
          2.2.4.2 Kinetics of GaN Using ECR Plasma .................................................. 20  
  2.3 Theoretical Modeling of Molecular Beam Epitaxy Growth....................................... 24
LIST OF FIGURES

Figure 1. The Compact 21 is the new RIBER baseline MBE system ..................48
Figure 2. The essential parts of a MBE growth system. The three zones, where the basic processes of MBE take place are also indicated .........................49
Figure 3. Pictorial representations of the three crystal growth models .............50
Figure 4. Structure of GaN M-i-n LED .................................................................51
Figure 5. Emission spectra from GaN M-i-n LEDs using Zn-doped i-layers ....52
Figure 6. Structure of GaN/SiC transistor .........................................................53
Figure 7. A schematic picture of the ECR plasma source .................................54
Figure 8. A schematic magnetic field lines in the emitter zone of a ECR plasma chamber .................................................................55
Figure 9. Emission spectra obtained from a ECR nitrogen plasma .................56
Figure 10. A schematic picture showing the surface processes of the physisorbed material layer .................................................................57
Figure 11. Simulation results of Ga incorporation coefficient versus NH3 pressure along the experimental results of Held et al.[18] ..................58
Figure 12. Simulation results of Ga incorporation coefficient versus substrate temperature along the experimental results of Held et al.[18] ........59
Figure 13. Simulation results of Ga incorporation coefficient versus Ga flux along the experimental results of Held et al.[18] ..................60
Figure 14. Simulation results of floating NH3 and floating Ga versus Ga flux ........61
Figure 15. Simulation results of Ga incorporation coefficient versus substrate temperature for several Ga/NH3 flux ratios along the experimental results of Held et al. .................................62
Figure 16. Simulation results of Ga desorption rate versus time for the growth condition of Jenney et al. [28] .................................................................63
Figure 17. The dependence of atomic N concentration (atoms/cm^3) on ECR power (W) and N2 flow rate (sccm) at a temperature of 1073 K .........64
Figure 18. The dependence of atomic $N$ flux ($\text{atoms/sec}$) on ECR power ($W$) and $N_2$ flow rate (sccm) at a temperature of 1073 K ........................................65

Figure 19. The variation of net electron concentration with the microwave power ($W$) at 973 K for various flow rates along with the experimental data [119] .......66

Figure 20. The variation of net electron concentration with the microwave power ($W$) at 1023 K for various flow rates along with the experimental data [119] .....67

Figure 21. The variation of net electron concentration with the microwave power ($W$) at 1073 K for various flow rates along with the experimental data [119] .....68

Figure 22. 3-D surface plot of $N$ vacancy concentration ($/\text{cm}^3$) versus temperature (K) and ECR power ($W$) for a flow rate of 3 sccm ..........69

Figure 23. 3-D surface plot of $N$ vacancy concentration ($/\text{cm}^3$) versus temperature (K) and ECR power ($W$) for a flow rate of 6 sccm ..........70

Figure 24. 3-D surface plot of $N$ vacancy concentration ($/\text{cm}^3$) versus temperature (K) and ECR power ($W$) for a flow rate of 9 sccm ..........71

Figure 25. Experimental SIMS impurity levels vs. microwave power [119] ..............72

Figure 26. 3-D plot of GaN growth rate versus temperature (K) and ECR power ($W$) for a flow rate 3 sccm ........................................73

Figure 27. 3-D plot of GaN growth rate versus temperature (K) and ECR power ($W$) for a flow rate 6 sccm ........................................74

Figure 28. 3-D plot of GaN growth rate versus temperature (K) and ECR power ($W$) for a flow rate 9 sccm ........................................75

Figure 29. 3-D plot of floating layer of Ga coverage versus temperature (K) and ECR power ($W$) for the case of growth represented in Figure 26 ............76

Figure 30. 3-D plot of floating layer of Ga coverage versus temperature (K) and ECR power ($W$) for the case of growth represented in Figure 27 ............77

Figure 31. 3-D plot of floating layer of Ga coverage versus temperature (K) and ECR power ($W$) for the case of growth represented in Figure 28 ............78
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CHAPTER 1

INTRODUCTION

The technology of crystal growth has advanced significantly during the past three decades. Among the most important of these advances is the development and refinement of molecular beam epitaxy (MBE). Crystals grown by MBE are more precisely controlled in terms of composition, thickness and defects than those grown by any other method. Today MBE grown crystals form the basis for the most advanced device structures in the electronics and optoelectronics industries. Figure 1 shows a schematic of the MBE Research-Compact 21 system with all of the advanced hardware required for operation in a production environment.

MBE is a high vacuum technique (~10^-11 torr) in which crucibles containing a variety of elemental charges are placed in the growth chamber. The ultra-pure elements contained in the crucibles make up the components of the crystal to be grown as well as the dopants to be used. When a crucible is heated, atoms or molecules of the charge are leave the surface by evaporation, and these travel in straight lines to impinge on a heated substrate. The growth chamber walls are usually cooled by liquid N_2 to ensure high vacuum and to prevent atoms /molecules from coming off the chamber walls and incorporating into the growing epilayer as a contaminant.

Crystal growth in a MBE system occurs via the reaction and condensation of
molecules that arrive at the surface via atom, rather than viscous or diffusive flow. In other words, atoms don’t collide with one another en route to the substrate, and atoms that miss or leave the substrate are pumped away nearly immediately. As a result, multilayer structures with extremely abrupt interfaces can be grown. The growth rate in MBE is \( \sim 1.0 \) monolayer/sec. Such a slow growth rate coupled with electronically controlled shutters placed in front of the crucibles allow device engineers to switch the composition of the growing crystal with monolayer control. However, to do so the growth conditions have to be adjusted so that growth occurs in monolayer-by-monolayer mode rather than by 3-dimensional island formation. This requires that the atoms impinging on the substrate have enough kinetic energy supplied by the heated substrate’s thermal energy to reach energetically favorable surface sites, which yields an atomically flat surface profile. Thus the substrate temperature has to be maintained at a point, where it is high enough to provide enough surface migration to the incorporating atoms, but low enough to suppress high temperature defect formation.

In MBE growth, the low background pressure allows the process engineer to use electron beams to monitor the growing crystal. For example, reflection high-energy electron diffraction (RHEED) is routinely used to monitor the crystal structure and microstructure of growing surfaces. Reflection mass spectrometry (REMS) and modulated beam spectrometry (MBMS) can be used to monitor the composition and optical properties of growing surfaces. The in-situ monitoring tools aid in the precise control and hence, excellent reproduction of device structures. Due to the reasons discussed above, MBE is expected to be superior in terms of composition, thickness, doping, and interface control.
Almost every semiconductor has been grown by MBE growth. Even though many materials have been crystallized as epitaxial thin films by MBE [1-3], III-V compound semiconductors in general [4,5], arsenides and nitrides in particular, have received the most attention as prototype materials due to their potential optoelectronic device application [2], in addition to the superior high-frequency and high voltage electronic applications. The group III nitrides have considerable promise for light-emitting materials in the visible/UV part of the spectrum and for high temperature and high field electronics applications [6,7]. (AlGaIn)N-based blue and green LEDs are now commercially available [8,9] and the first results for electrically pumped laser diodes have recently been reported [10].

Although active research in material development and device applications has been conducted and significant progress has been made in the past several years in understanding the surface kinetics and the equilibrium surface structures formed during crystal growth by MBE [11-23], the precise growth mechanism and the role of substrate and buffer layers and the process parameters, such as temperature, fluxes, and crystal orientation, are not yet clearly understood. Averyanova et al. [24] and Newman et al. [25] studied the GaN growth from a thermodynamics point of view. Their work focussed on the growth parameter regimes, where GaN could be growth and the GaN decomposition rate can be suppressed. Both researchers assumed the existence of an activation barrier to nitrogen desorption. Averyanova et al. [24] showed that if an activation barrier were included then mass action could quantitatively be applied to control the decomposition rates of GaN. Crawford et al. [26] showed that weakly bound Ga on a Ga terminated GaN surface would inhibit the growth and developed a simple rate equation model to describe

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this. Tarsa et al. [19] examined MBE growth on GaN (0001) and showed that under excess N conditions, the surface morphology evolved according to kinetic roughening. In the MBE growth of GaAlN, Kamp et al. [27] have suggested that there may be a competition between Al and Ga on the group III sublattice, but made no attempt to clarify the situation and stated that more work was needed in this area. Jenney et al. [28] reported their examination of the effect Al has in Ga incorporation and showed that an Al to Ga surface mechanism is in effect due to stronger Al-N than Ga-N bond. Recently, Keleska et al. [29] and Held et al. [30] used a rate equation model, coupling the surface coverages of Ga and N, seeking to describe growth under a very wide range of conditions and techniques.

The aim of this thesis is to modify the theoretical rate equation model employed for LT GaAs growth and InGaAs [31-36] growth to GaN growth with ammonia and ECR plasma source. This will be used for the theoretical investigation the nature of the GaN MBE growth process via computer simulation, and obtain optimum growth conditions.

1.1 Organization of the Thesis

In chapter 2, a brief literature survey covering MBE growth, GaN growth using ammonia and ECR plasma and theoretical studies of MBE growth is presented. The details of the theoretical model, numerical simulation and computational approach are presented in chapter 3. Results and discussion related our study of MBE of GaN using ammonia and ECR plasma, are presented in chapter 4 along with relevant experimental data. Conclusions and recommendations are presented in chapter 5. In the appendix, ECR plasma simulation program and a sample output are presented.
CHAPTER 2

LITERATURE OVERVIEW

2.1 Molecular Beam Epitaxy

2.1.1 General Description

The essential elements of a MBE system are shown schematically in Figure 2. The MBE system may be divided into three zones, where various physical phenomena necessary for crystal growth take place [37]. The first zone is the generation zone in which molecular beams are generated. Next is the transport zone, where the beams travel through from the source to the substrate. The third zone of the MBE system is the area where the crystallization processes take place on a heated substrate.

The molecular beams are generated in the first zone under ultra high vacuum (UHV) conditions in a Knudsen-effusion-cell [37], whose temperature is accurately electronically controlled from outside. Conventional temperature control, based on high performance proportional-integral-derivative (PID) controllers and thermocouple feedback, enables a flux stability of better than ±1% [38]. By choosing appropriate cell and substrate temperature, epitaxial films of the desired chemical composition can be obtained. Accurately selected and subsequently, precisely controlled temperatures of the substrate and of each of the sources of the constituent beams have,
thus, a direct effect on the growth process. The uniformity in thickness as well as the composition of the films grown by MBE depends on the uniformities of the molecular beam fluxes and also on the geometrical relationship between the configurations of the sources and the substrate.

The second zone in the MBE vacuum reactor is the mixing zone, where the molecular beams transport through. As the mean free path of the molecules belonging to the intersecting beams is so long, no collisions or other interactions between the molecules of different species occur in this zone. Thus the molecular beams remain as collimated beams during their transit in this zone.

Epitaxial growth in MBE is realized in the third zone, i.e., on the heated substrate surface. A series of surface processes are involved in MBE growth. The following are the most important ones [39]: 1) adsorption of the constituent atoms or molecules arriving at the substrate surface; 2) surface migration and dissociation of the adsorbed molecules; 3) incorporation of the constituent atoms into the crystal lattice of the substrate or the already growing epilayer; and 4) thermal desorption of the constituent species from the crystal surface.

2.1.2 In-Situ Monitoring Tools

Due to the presence of ultrahigh vacuum environment, MBE growth can be controlled in situ using surface diagnostic tools such as Reflection High-Energy Electron Diffraction (RHEED) [40-53], Auger Electron Spectroscopy (AES) [54-57], ellipsometry [58-62], or optical reflectance-difference technique [63-67] and laser interferometric [68-71] method. These powerful in-situ tools for control and analysis of the growing crystal
eliminate much of the guesswork in MBE, and enable reliable and reproducible fabrication of complex device structures.

RHEED is the one of the most widely used in-situ diagnostic techniques in MBE growth. The physics of RHEED are based on the wavelike nature of electrons. Electrons with energies of 50keV behave as waves with wavelength of the order of 0.1 Å. When a narrow beam of such electrons is incident on the semiconductor surface at a glancing angle, it is diffracted by the crystal lattice within a few monolayers of the surface [72]. The diffraction pattern, thus, observed is characteristic of the arrangement of atoms within a small depth from the surface. Details of the spatial variation of intensities and spot and streak patterns depend upon subtle interactions between the electrons penetrating the bulk, the electrons diffracted from steps at the surface, and electrons diffracted from the surface atomic structure itself.

The use of RHEED and low energy electron diffraction to obtain surface structural information has been discussed in several reviews [73-74]. RHEED diffraction patterns characteristic of various surface structures is distinctly different for various possible surfaces, orientations and stoichiometric conditions of the surface. In addition, the intensities of the diffraction spots and streaks depend upon the smoothness of the growing surface, and the degree to which the surface is contaminated. Transitions from one surface structure to another, and variations in diffracted intensity during epitaxy are used as primary means of growth control in MBE. Two particularly interesting and useful manifestations of RHEED are surface structural transitions observed as a function of the group V coverage of the surface, and intensity oscillations during growth. Cho [75,76] first used MBE to prepare III-V surfaces (GaAs) and study them under a variety of
Neave et al. [77,78] first observed oscillatory behavior in the RHEED streaks in GaAs MBE growth and related it to periodic roughing and smoothing of the surface with a period of one monolayer growth time. The ability to monitor monolayer growth makes RHEED the most powerful tool in MBE growth.

2.1.3 Modes of MBE Growth

There are three well accepted modes of MBE growth which are illustrated schematically in Figure 3. In the island growth model, small clusters are nucleated directly on the substrate surface and then grow into islands of the condensed phase. This type of growth occurs, when the binding energy between the atoms or molecules of deposit is stronger than the binding energy between the atoms of deposit and the substrate atoms. Many metallic systems grown on insulators, alkali halides, graphite and other layer compounds such as mica, exhibit island growth.

The layer-by-layer growth mode displays the opposite characteristics of the island growth model is operating. Since the atoms of deposit are more strongly bound to the substrate than to each other, the first set of atoms condense to form a complete monolayer on the surface, and then a somewhat less tightly bound second layer condenses and so on. Provided the decrease in binding from layer to layer is monotonic toward the value for a bulk crystal of the deposit, the layer-by-layer growth mode is obtained. This growth mode is observed in the case of rare gases on graphite and metals, metal on metal and semiconductor on semiconductor growths.

The third growth mode describes an intermediate mode between the island and layer-by-layer modes. After forming the first monolayer, or a few monolayers,
subsequent layer-by-layer growth is unfavorable and islands are formed on top of this intermediate layer. There are many possible reasons for this mode to occur and almost any factor, which disturbs the monotonic decrease in binding energy required for layer-by-layer growth can cause this mode to operate.

2.1.4 MBE System Preparation

The MBE system must be well-baked, typically, for several days at 473-523 K while under vacuum before its initial use and after every occasion in which air, moisture and other impurities have gained access to the inner chambers. A new MBE system is usually baked under vacuum and without effusion cells. New effusion or cracker cells are separately baked, in a high vacuum system used exclusively for that purpose, to temperatures as high as 1500 K before being placed into the MBE system. The system, with all components in place, is baked again. Every time the system is baked, it must be checked for leaks caused by thermal expansion and contraction. Typical growth chamber pressures under non-growing conditions reaches $10^{-10}$ torr.

2.1.5 Substrate Preparation

The substrate used for MBE growth is of the same material and crystal structure for homoepitaxy and is of either different material and/or different crystal structure for hetero-epitaxy. Typically, nonavailability of quality substrates at low cost leads to used of hetero-epitaxy. The substrate used for III-nitride growth is (0001) sapphire or (100) $\alpha - Al_2O_3$ or InP. For the ease of handling and to reduce breakage, particularly, when complex processing is to be used after growth, it is preferable that the wafer introduced
into the MBE system be 400-500 $\mu m$ thick rather than the 250 $\mu m$ usually used for MOCVD wafers. Commercially available buffers usually have been sliced from a boule with a diamond grit saw, lapped with alumina grit to planarize the wafer and remove some of the saw damaged region and then put through several stages of chemical-mechanical polishing with increasing emphasis on the chemical component for every subsequent stage to completely remove mechanical damage. The details of commercial polishing methods are usually proprietary. The surface quality is generally good enough that extensive further etching is not necessary. However, it is a good practice to degrease the wafers by allowing freshly distilled solvents such as acetone and then methanol to rinse the surfaces.

The substrate is mounted on a molybdenum block. The mounted substrate is introduced into an entry lock that is part of the substrate introduction chamber, often in a cassette with other substrates. The entry lock is isolated from the substrate preparation chamber and evacuated at least to the millitorr range and preferably lower. Then the gate valve between the entry lock and the sample preparation chamber is opened and the sample is transported into the preparation chamber in which a UHV environment is maintained. There it can be stored, heated gently to remove adsorbed $H_2O$, examined by means of several surface analysis methods, such as RHEED and/or Auger spectroscopy.

2.2 GaN Growth and Devices

2.2.1 III-V nitride Processing

GaN films have been grown by many techniques, including chemical vapor deposition[79-82], metal-organic vapor phase epitaxy (MOVPE) [83-90], molecular
beam epitaxy [91-100] and a number of plasma-assisted processes [101-105]. Although all of the commercial nitride devices have been prepared by MOVPE, MBE growth of nitrides has gained ground in recent years. The emergence of MBE as a contender to MOVPE for nitride growth is due to the fact that several technical needs required for successful growth of III-V nitride materials by MBE have been addressed in recent years: the development of effective active nitrogen plasma sources (electron cyclotron resonance (ECR) and radio frequency (RF)) for growth of nitrides by MBE at reasonable growth rates; the identification of suitable substrates for nitride film deposition; the effective control of AlGaN and InGaN alloy compositions in multilayered structures for visible light emitter applications; and the development of doping techniques and identification of dopant sources for AlGaN, GaN and InGaN.

GaN grown by MBE can occur in either the hexagonal (wurtzite, \( \alpha \)-GaN) or the cubic (zincblende, \( \beta \)-GaN) structures. Both polytypes often appear in the same epitaxial layer, leading to stacking faults [106]. The zincblende crystal stacks in an AaBbCc... arrangement which the wurtzite has an AaBbAaBb... configuration with the lower case letters representing the cation and the upper case letter representing the anion. Between these two crystal structures, the nearest-neighbor positions are almost identical, but the relative positions of the second nearest neighbor differ, which explains the observed similarity in the physical properties of these GaN phases. It has been found that the wurtzite structures grow primarily on substrates with hexagonal symmetry, while the zincblende structures grow on substrates with cubic symmetry [107].

Since good quality III-V nitride substrates are unavailable, films must be grown on foreign substrates. The main requirements for an appropriate substrate for GaN
epitaxial growth are: 1) dimensional lattice-matching; 2) thermal expansion coefficient matching; and 3) availability of large diameter wafers in large quantities at low cost. A variety of substrates such as Si, GaAs, NaCl, GaP, InP, SiC, W, ZnO, MgAl₂O₄, TiO₂, MgO [108] and various crystallographic orientations of sapphire have been used as substrates. Table I summarizes the lattice parameters and thermal characteristics of a number of the prospective substrate materials for nitride growth [108]. β-GaN has been epitaxially stabilized on a β-SiC and MgO (100) substrate [93,94], which are closely lattice-matched to β-GaN, and on a GaAs [109,110] and Si substrate [96-100] which have significant mismatch to β-GaN.

For lack of an ideal substrate, nearly all III-V nitride material has been grown on sapphire (Al₂O₃) substrates due to its commercial availability, excellent surface preparation, close thermal match with the nitrides and stability at the high temperatures (∼1273 K). However, sapphire has a very large lattice mismatch with GaN, which inevitably leads to a large defect density in GaN epitaxial layers [111]. To alleviate this problem, it is necessary to grow a thick epilayer to obtain good quality material. Also Amano et al. [112] developed a two-step growth process in which a low temperature AlN—buffer followed by the growth of GaN at higher temperatures which led to significant improvement in the morphology and opto-electronic properties of GaN films. Nakamura et al. [113] and Lei et al. [95-99] reported independently the development of a GaN buffer layer instead of AlN. Lei et al. [95-99] have shown that this two-step growth process of growing a buffer and then, the active epilayer leads to lateral growth approximately 100 times larger than the vertical growth.

For III-V nitride growths, the simplest and cheapest nitrogen source is ammonia.
This compound is quite thermally stable and as a result sets the lower limit of growth temperature significantly high. However, at temperatures as low as 1023 K, Li et al [114] achieved GaN growth rates up to $1 \mu m/h$, substantially greater than those obtained with plasma sources without sacrificing material quality. This increased growth rate is presumably due to the enhanced surface mobility of the nitrogen species when partially bonded to hydrogen, or enhanced efficiency of N incorporation from ammonia into the epilayer.

For low temperature growth, ammonia is an unsuitable source due to its poor decomposition efficiency. Thus ammonia is not a universal nitrogen source for the growth of III-V materials. As a result, a great deal of attention has been focused on the use of in situ plasma generation as a low temperature means of introducing reactive nitrogen to the growth surface. Radio frequency (RF) plasmas are among the most common sources in UHV growth of III-V materials [115-117]. Nitrogen plasmas are generated by inductively coupling RF energy, often at a frequency of 13.56 MHz, into a discharge chamber filled with nitrogen to pressures of $>10^{-6}$ torr. Although RF sources are quite capable of generating useful quantities of atomic nitrogen, they also produce various ionic species with high kinetic energies and neutrals. These undesirable species can result in surface damage and defects.

The most common alternative to RF plasma is the use of electron cyclotron resonance (ECR) plasma [107,110,118-122]. ECR plasma sources rely upon coupling of microwave energy at 2.45 GHz with the resonance frequency of electrons in a static magnetic field. Such coupling allows for ignition of the plasma at low pressures and electric powers, and produces much higher concentrations of radicals compared to RF.
sources. Because these sources operated very efficiently at fairly low powers, air cooling is sufficient. In spite of the low ion energies, it is reported that material quality can be degraded at higher microwave powers [118]. Molnar et al. [119,120] found that by reducing the microwave power, the relative concentration of ions to excited neutrals can be reduced, which improves the material quality dramatically. An alternative to traditional RF and ECR plasma sources is the Kaufman ion source [94,123,124]. This approach produces near mono-energetic species at fairly low ion energies, typically ~28 eV. Further reduction in energy can be attained through the addition of a DC bias to effectively limit the energy of the species which ultimately arrive at the surface. It is reported that decreasing the ion energy by increasing the bias on the substrate decreased the midgap luminescence, but has little or no effect on the structural quality [123].

Most of the GaN films grown are wurtzitic (α- GaN) and have n-type conductivity with high carrier concentration [125], which is believed to result from nitrogen vacancies [125,126] or oxygen impurity incorporation [127]. P-type conductivity has been reported recently in Mg-doped GaN films [113,128]. Zincblende GaN (β- GaN), which is the thermodynamically metastable phase of GaN, is hoped to be more amenable to doping than the wurtzitic GaN, since all other III-V compounds which can be efficiently doped n-type or p-type are cubic [129].

2.2.2 III-V Nitride Devices Applications

In recent years, the III-V nitride semiconductor materials have experienced a tremendous expansion of research and development activity. III-Nitrides are direct band gap semiconductors with energy gaps spanning the spectral region from 1.95eV (InN) to
6.28eV (AlN) with GaN having 3.5eV. The use of these direct band gap semiconductors for optoelectronic applications has facilitated the availability of commercial blue and green light emitting diodes (LEDs) and lasers [130]. Pankove et al. [131] used GaN to produce the first blue LED using an M-i-n type of device (Figure 4), which device can emit either blue, green, yellow or red light depending on the Zn concentration in the light-emitting region (Figure 5)[132]. The light is emitted only from the cathode. If the Zn concentration is different at the two edges of the Zn-compensated region, reversing the polarity of the bias (making the opposite interface of the i-layer the cathode) could cause a change in color, i.e., the device could switch from blue to green or to yellow. Maruska et al. [133] was also the first to use Mg as a luminescent center in a M-i-n diode.

GaN has been used as a heterojunction emitter of a heterobipolar transistor (HBT) comprising a narrower bandgap made of p-type 6H-SiC (Figure 6)[134]. This transistor exhibits a current gain dIc/dIb in the range of $10^3 – 10^7$. It has operated at 808 K with a current gain of 100 and a current density of $1800A/cm^2$. A power density of $30kW/cm^2$ can be sustained. The usual limitation of a power transistor is heating due to various internal losses. A GaN/SiC HBT can operate at elevated temperatures due to internal dissipation without an external cooling means. Hence this new HBT is a good candidate for high power applications.

Other demonstrated GaN based devices are: antistokes LEDs (2.8eV photons emitted with only 1.5V applied) [80], negative electron affinity [135], surface acoustic wave generation devices [90], and solarblind UV photovoltaic detectors [135]. GaN is also predicted to have a high saturated electron drift velocity [136], which results in a
short transit time and therefore, may allow the fabrication of high frequency microwave
type devices (e.g., IMPATT diodes).

2.2.3 GaN Growth Kinetics with Ammonia as Source

The MBE growth kinetics of GaN using ammonia as the source are complicated by the temperature dependence of the dissociation of $NH_3$ and incorporation of active N, and the temperature and compositional dependence of the residence times of the reactants on the GaN surface. This implies that a thorough understanding of the microscopic surface processes and how to intelligently set optimum growth parameters, is of paramount importance. Since the flux and temperature dependencies of the Ga and N surface coverages are not well known, the species that limit the growth cannot be easily identified.

Held et al. [18,30] considered the adsorption of Ga onto an otherwise inert surface in the absence of $NH_3$. They examined two limits: First, at sufficiently high temperature, an incident Ga flux will produce a steady Ga coverage that depends on the incident Ga flux and the Ga residence time. In the steady state, the total amount of adsorbed Ga is constant so that the incident flux must equal the desorbing flux. Second, if the substrate temperature is decreased sufficiently, there will be a temperature below which Ga condenses on the surface forming multilayers and/or droplets. Below this temperature, the system is not in steady state since the incident flux exceeds the desorbing flux, and Ga is adsorbed continuously. The transition from steady state to condensation is sharp and can be determined by measuring the temperature at which the desorbed Ga flux begins to decrease. For a given incident Ga flux, this transition corresponds to a unique
surface temperature described by equilibrium vapor pressure data. Employing DMS and RHEED, the adsorption behavior of Ga terminated GaN was shown to follow the model described above over a significant range of temperatures. Over this range, the flux due to the decomposition of GaN can be neglected compared to the incident and desorbing fluxes of Ga. Further, above the condensation temperature, the difference between the desorbed flux with and without $NH_3$ can be used to measure growth rate. Using RHEED and DMS, they identified the conditions for Ga condensation and presented methods to determine surface composition. They also identified the activation energy for desorption of Ga from the surface to be 2.7eV by analyzing the experimental data using a simple theoretical model.

Jenny et al. [28] studied the Ga and Al desorption kinetics in the MBE growth of nitrides using ammonia. Their experiment covered the ammonia pressure range of 0 to $20 \times 10^{-6}$ torr. At a temperature of 1023 K and a cation flux rate in the range of 0 to 0.20 ML/sec., they observed that Ga does not incorporate into the film until the ammonia flux exceeds the value needed for stoichiometric AlN due to two reasons. One is that Al cracks ammonia two times better than Ga and the other is the exchange reaction of Al with surface Ga due to stronger Al-N bonds.

Alexeev et al. [137] also studied MBE GaN growth kinetics by using $NH_3$ as source. They found the desorption rate of GaN was almost independent of V/III ratio within the N-rich growth conditions. They observed the activation energy for GaN desorption during the growth was $(3.2 \pm 0.1)$eV, which is nearly equal to the activation energy for free evaporation of GaN. They also studied the Mg-doped GaN under N-rich condition and achieved the p-type conductivity.
Averyanova et al. [24] studied the III-V nitride growth by MBE using a theoretical model which accounts for a physisorption precursor of molecular nitrogen. They found the evaporation was an essential factor influencing the MBE growth process of III-nitride. They explained the reason for the low desorption coefficient is the high thermal stability of nitrides. Using this theory, they obtained values for the evaporation coefficient.

Crawford et al. [26] analysis GaN steady-state growth rate using desorption mass spectroscopy and RHEED, showed that the excess Ga reduces the GaN growth rate. They assumed that $NH_3$ reacts only with the strongly bound Ga, and that the excess Ga in the weakly bound sites reduces the GaN growth rate by blocking the underlying reactive Ga sites. A rate equation giving the steady-state value of the Ga coverage in the weakly bound state was described. Liu et al. [138] found that the coexistence of Ga and GaN enhanced the decomposition of $NH_3$ relative to Ga alone.

2.2.4 ECR Molecular Beam Epitaxy Growth of GaN

2.2.4.1 ECR Plasma Source Characteristics

Gaseous plasmas have been successfully used for some time in thin-film processes, namely, deposition [111,119,120,139] and etching by sputtering [140-143] and by plasma enhanced chemistry [142,144]. Microwave plasma has been used in various thin-film processes, e.g., nitriding, carburizing, oxidation, and polymerization. In particular, electron cyclotron resonance (ECR) microwave plasma is potentially useful for thin-film technology under low gas pressure of $10^{-4}$ to $10^{-6}$ torr. ECR microwave plasma exhibits the following characteristics: 1) generation of dense plasma (electron
density of $10^{10}$ to $10^{12} / cm^3$; 2) generation of highly ionized plasma (10% and higher); 3) generation of fast electrons.

An ECR microwave plasma stream along a moderate gradient field is useful for extracting low-energy ions of approximately several tens of eV. The energy profiles of the extracted ions exhibit minimal energy dispersion. Also, the upper end of the energy profile, which results in damage to the surface of the film and substrate, is somewhat shorter than that of the typical sputtered neutral atoms. Consequently, the ECR plasma stream permits the preparation of several high-quality thin-film materials, such as nitride and oxide, at low substrate temperatures. Electron mobility is much greater than ion mobility, and therefore the electron diffusion coefficient is much greater than the ion diffusion coefficient. Electrons will stream out along the flux with much faster cyclotron motion than ions. Ions in plasma are accelerated to the substrate plate by the electric field, caused by the loss of electrons from the plasma. As a result, the inhomogeneous magnetic field causes the plasma to accelerate along the magnetic flux.

In practice, in order to keep plasma electrically neutral, ions and electrons cannot act independently in the ECR microwave plasma stream. The collective behavior of these charged particles causes them to move with the same diffusion coefficient, i.e., the so-called ambipolar diffusion. The diffusion coefficient depends on the magnetic field gradient. The magnetic field gradient also affects the floating potential on the substrate plate. Consequently, it is considered that the energy of ions extracted following ambipolar diffusion is affected by the field gradient.

A schematic diagram of the ECR source is shown in Figure 7 [145]. The microwave frequency used is 2.45 GHz, corresponding to a magnetic field of 875 G at
the electron cyclotron resonance. The magnetic field is produced by two blocks of Sm-Co permanent magnets opposite one another. The magnetization of each block is 8850 G. By choosing an appropriate distance between the two magnets, it is possible to create an ellipsoidal field zone in the cell where the magnetic field is 875 G. Moreover, the emitter is not situated in the axis of the magnetic structure (see Figure 8)[145]. As a consequence, most ions that move along the magnetic field lines are deflected to the source walls and do not reach the sample in the growth chamber. This would not be the case if the emitter were in the horizontal symmetry plane of the magnetic structure. This simple geometrical arrangement compares advantageously to the use of biased substrates or coils which is reported by some authors[145] in an effort to eliminate the ions species in the plasma.

2.2.4.2 Kinetics of GaN Growth Using ECR Plasma

Electron cyclotron resonance (ECR) plasma sources are currently used to provide plasma activated nitrogen for the growth of III-V nitrides by molecular beam epitaxy [97,98,110,139,146,147]. A major advantage of using a nitrogen plasma instead of other nitrogen sources such as ammonia is the absence of hydrogen during the growth. Nitrogen plasmas produced by ECR plasma sources are composed of neutral atoms and ions. It has been demonstrated that a large number of energetic ions is detrimental as far as the structural and luminescence properties of III-V nitrides are concerned [119,148]. On the other hand, it has been shown that ions may improve the growth to some extent, most likely, by providing surface energy to enhance the annealing of defects [149].
Nitrogen plasmas have been shown to have a variety of excited nitrogen species, including \( N_2^+ \), \( N_2^{+} \), \( N \), and \( N^+ \) [150]. The ECR plasmas used in the work of Molnar et al. [120] were usually characterized both by optical emission spectroscopy and Langmuir probe measurements. An optical emission spectra typical for simulation of ECR nitrogen plasma sources are shown in Figure 9. The measurement was performed using a UV fiber-optic bundle to collect light from a viewport line of sight with the source. The light was dispersed through a 0.25m monochromator.

The highly reactive N species identified by Vaudo et al. [116,151] makes GaN MBE distinctly different from MBE of conventional III-V semiconductors. In the latter case, the group V precursor is supplied as a molecule (\( N_2^+ \), \( N_2^{+} \), \( N^+ \), etc.), which requires further reactions before incorporation. Such reactions may provide sufficient mobility of the V species due to longer surface lifetime and require a group V rich growth regime for best growth conditions. The atomic nitrogen supplied in case of plasma MBE is so reactive that it reacts directly with the surface, a situation quite different from the common MBE growth mode. It obviously implies that different growth modes are operative in these two MBE techniques. Additionally with plasma MBE good results are reported only for Ga-rich growth conditions, unlike in the conventional III-V MBE.

Moustakas et al. [111] used an ECR source for the growth of GaN on sapphire. The base pressure in the MBE system was \( 10^{-11} \) torr before growth. A conventional Knudsen effusion cell was used to evaporate gallium. Passing molecular nitrogen through the ECR source produced various species of atomic and ionic nitrogen. Part of the molecular nitrogen was also introduced downstream of the ECR source. Typically, 10% of the molecular nitrogen gas is converted into atomic nitrogen. Due to this high
decomposition rate, a source pressure of about $10^{-4}$ torr is sufficient for the growth of stoichiometric films. The structure and microstructure of the films were studied by reflection high-energy electron diffraction (RHEED), X-ray diffraction and scanning electron microscopy (SEM). X-ray diffraction studies were performed using a diffractometer. GaN films have been epitaxially grown on a (001) Si by MBE with ECR plasma source. They used a two-step growth process, in which a GaN Buffer is grown at relatively low temperatures and the rest of the film is grown at higher temperatures. This method of film growth was shown to lead to good single crystalline $\beta$-GaN and promote lateral growth resulting in smooth surface morphology.

Meyyappan [152] used a simple method to analyze the characteristics of ECR plasma source for the generation of active nitrogen species in the MBE of III-V nitrides. He studied the effects of reactor geometry, pressure, power, and flow rate on the dissociation efficiency and ion flux. He found that an ECR discharge has a high $N_2$ dissociation efficiency and yields a large flux of atomic nitrogen. He also observed that the operation of ECR plasma with a source pressures of about 1 mtorr and low power levels (~30W) provided ion densities in the mid-$10^{10} cm^{-3}$ range, while providing a high flux of active nitrogen species (atomic and excited $N_2$).

Molnar et al. [119] investigated the role of ionic and nonionic excited species of nitrogen in the growth of GaN by ECR-MBE and found that the kinetics of film growth is significantly affected by the microwave power. They also observed a transition from the island to a layer-by-layer growth and, finally, to a three dimensional growth as ECR power is increased. They found that under the plasma conditions employed, the films contained hydrogen, silicon, carbon, and oxygen impurities, whose concentrations
increased with microwave power. These impurities are likely the result of either sputtering or thermal outgassing of components in the ECR source.

Molnar et al. [120] in a later study also found that in the growth of GaN thin films by ECR plasma source MBE, a flow limiting orifice plays an important role in increasing plasma stability and reducing ion damage and impurities in resultant films. They found that the introduction of an exit aperture affects the ratio of ions to excited neutrals generated in the source, a result attributed to the increased pressure at the discharge area. Additionally, they found that the density of ions arriving at the substrate is reduced by ~30%, when a 1 cm aperture is employed. Correspondingly, GaN films grown with the exit aperture were found to have superior structural, electrical, and luminescent properties.

Sinharoy et al. [153] used ECR plasma-assisted MBE to grow undoped GaN and AlGaN, as well as n-doped GaN, that are comparable in structural and morphological quality to those reported by other researchers using MBE on 6H-SiC substrates. They found the quality of the film was independent of SiC surface type (SI face, C face, on-axis, off-axis). N-type doping levels up to $4.0 \times 10^{20} / cm^3$ were achieved using silicon, and a calibration curve correlating silicon effusion cell temperature to dopant level in the GaN was established for the first time in GaN MBE films.

Tafermer et al. [154] used mass spectroscopy of recoiled ions (MSRI) and RHEED to monitor the surface structure and the near surface layer composition during the pre-growth preparation step and the deposition of GaN thin films on Si(001), $Al_2O_3(0001)$ and GaAs (001) substrates by MBE using ECR plasma source. They found that the crystallinity of the GaN films initiated on Si, $Al_2O_3$, and GaAs were strongly

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affected by the initial treatment of the substrate. Their results demonstrate that MRSI and RHEED are powerful real-time surface composition probes for nitride thin film synthesis.

Sung et al. [155] studied epitaxial growth of GaN on sapphire (0001) substrate by ECR MBE and found that the formation of Ga droplets at the growth surface depends strongly on the growth temperature and the Ga cell temperature. Flat and smooth surfaces were obtained at the growth temperature of 1023 K with a growth rate of $0.5 \mu m/h$.

2.3 Theoretical modeling of MBE growth

In the past thirty years, a variety of theoretical models have been developed to study the crystal growth processes of MBE, such as Monte Carlo (MC) simulations [156-160], molecular dynamics (MD) simulations [161-163], stochastic models [164-168], and kinetic rate equations [33,169].

The Monte Carlo (MC) [156-160] simulation model is widely used to study the MBE growth kinetic of compound semiconductors. A variety of surface kinetic processes are considered in the MC simulation. The processes are in corporation of the atoms on the surface from flux. Intra-layer migration, inter-layer migration and evaporation of atoms from the surface. Migration and back evaporation processes are assumed to be thermally activated and their rates are typically calculated using Arrhenius type rate equation. The advantage of this model is the relative simplicity of the representation of the substrate and of the kinetics. The disadvantage is that it is computation intensive and size limited. Therefore studies requiring to parts per million (ppm) concentration of constituents such as doping kinetics can not be studied.

In a molecular dynamics (MD) [161-163] simulation, the surface kinetics are
described by a set of equations of various motions of the surface molecules or atoms. These equations are based on Newton's second law of motion and the potential energy functions of semiconductors such as Leonard-Jones [161], Stillinger et al. [170] and Marmorkos et al. [171]. The macroscopic growth kinetics of the atoms occur in microsecond to millisecond time scales whereas the atomistic processes occur and are simulated in the order of picosecond time scales. The advantages of the MD simulation is that it is very useful for the study the atomistic details of surface kinetic processes. The disadvantage are computation-intensive and size limited similar to the MC simulations.

Venkatasubramanian [164,165] developed a stochastic model for the growth of compound semiconductors. The model is based on the master equation approach with modified solid-on-solid condition which means that the atoms do not absorb exactly on the top of atoms (like in simple cubic structure) but in vacant site whose projection falls in between a pair of nearest neighbor atoms in the layer beneath. In the modeling, the diamond cubic structure and the two-sublattice nature of the zincblende structure were taken into account. The developed model was then extended to accommodate to alloying of the two sublattices up to four elements with two elements in each sublattice can be accommodated.

The stochastic model was used to study the MBE growth kinetics of a hypothetical compound semiconductor and diamond cubic alloy in which the effect of the surface diffusion process on the growth kinetics. The stochastic model has also been successfully employed to study the surface roughening kinetics in Ge [167]. One of the important features of the model is that it is not limited by the crystal size and can be employed to study the doping kinetics in the crystals. Muthuvenkaturaman et al. [31,32]
studied the antisite arsenic incorporation in the low temperature MBE of GaAs using stochastic model and simulated the surface growth processes in the low temperature molecular beam epitaxy of GaAs. The results of the model, i.e., temperature, growth rate and flux ratio dependencies of antisite As incorporation rate agree well with the data of Luysberg et al. [172]

In the rate equation (RE) model, the time evolution of a epilayer is described by a set of first order differential equations in coverage of each species in each layer. The surface kinetic processes such as incorporation, inter-layer and intra-layer migration and evaporation account for the change in concentration of each layer as the epilayer evolves. Useful growth data can be obtained from the concentration of the layer versus time. This model employs fewer variables, but the result are less activate.

Natarajan et al. [34,35] used a rate equation model to study the low temperature MBE of GaAs. Their results of antisite concentration as a function of temperature and As/Ga beam equivalent pressure were in good agreement with the experiments. Colayni et al. [36] investigated growth dynamics of InGaAs using a rate equation model. Their In incorporation coefficient versus substrate temperature is in excellent agreement with experimental data for various As overpressures. They explained their results based on competing surface processes such as segregation and incorporation.

Recently, Koleske et al. [29] used a kinetic model to explain the metal organic vapor phase epitaxy (MOVPE) growth of GaN. The model based on measured desorption rates and assumptions on the precursor dissociation and sticking probabilities, showed the growth temperature and V/III ratio greatly influenced the growth of high quality GaN films. They explained the relationship between the growth temperature, V/III ratio and
GaN quality in terms of how the growth parameters influence the incorporation of Ga and N atoms into the growing film. Held et al. [30] used a rate equation model to investigate the growth kinetics of GaN (0001) as a function of growth parameters by using desorption mass spectroscopy. The transition was modeled by rate equations based on the following main assumptions: 1) Ga could adsorb into either of two weakly adsorbed states; 2) Ga from these weakly adsorbed states could, in turn, either chemisorb or desorb; 3) $NH_3$ only incorporated N at step edges; 4) Ga was more mobile on a Ga covered surface than on a nitrided surface. With these assumptions, they found an abrupt growth mode transition between excess Ga and excess nitrogen as a function of growth parameters. In the models of Koleske et al. [29] and Held et al. [30] they used only the time evolution of the surface coverage of the constant species, but not the coverage of all layers.
CHAPTER 3

RATE EQUATION MODEL FOR GROWTH OF GaN USING AMMONIA

3.1 Kinetic Rate Equation Model

Nitride MBE growth involves the presence and dynamics of a physisorbed material (PM) state riding on the surface for the constituent elements, especially for the $NH_3$ molecule. Typically, these molecules/atoms form a weakly bound precursor state with Van der Waal type binding. This layer of material undergoes two dynamic processes, chemisorption into regular lattice sites and desorption out of the layer into vacuum. The $NH_3$ molecules in the PM layer undergo the following chemical reaction by pyrolysis:

$$NH_3 + Ga \text{ (crystal surface)} \leftrightarrow GaN \text{ (crystal surface)} + \frac{3}{2} H_2 \quad (3.1)$$

The growing surface acts as a catalyst for the reaction. A schematic diagram illustrating the surface dynamic processes of the PM layer is shown in Figure 10. The surface processes including the chemical reaction given by Equation 3.1 are thermally activated. The time constants associated with these processes (which are inverse of the rates) are described in the Arrhenius rate form as:

$$\tau_i = \tau_{0i} \exp\left(\frac{E_i}{k_B T}\right) \quad (3.2)$$

28
where $\tau_{0,i}$ are time factor constants and $E_i$ refers to activation energy for the $i^{th}$ surface process. $k_B$ is the Boltzmann constant and $T$ is the temperature in K.

MBE growth typically involves several kinetic processes on the crystal surface such as adsorption, reevaporation and surface migration processes, such as intralayer and interlayer migration. The rate of adsorption depends on the flux rate, $J$, and the availability of proper sites on the surface for adsorption. The reevaporation and migration processes are assumed to be thermally activated and are modeled as Arrhenius type with frequency factor and activation energy given by:

$$R_i = R_{0,i} \exp \left( \frac{-E_i}{k_B T} \right)$$

(3.3)

where $R_{0,i}$ is the frequency prefactor, and $E_i$ is the activation energy for the $i^{th}$ process. $k_B$ is the Boltzmann constant and $T$ is the temperature in K. $R_{0,i}$ is given by:

$$R_{0,i} = 2.08 \times 10^{10} T$$

(3.4)

based on the phonon frequency obtained using the equipartition energy principle. The atomic interactions are assumed pairwise and only up to the second nearest neighbor interactions are considered.

The time evolution of the growing epilayer is described through the change of macrovariables resulting from the surface processes. The macrovariables of growth are normalized with respect to the maximum number of possible atoms in the layer. The macrovariables considered are the layer coverage of Ga and N in the layers given as:

$C_{Ga} (2n):$ layer coverage of Ga in the $2n^{th}$ layer

$C_N (2n + 1):$ layer coverage of N in the $(2n + 1)^{th}$ layer

$C_{Ga,phy}$: layer coverage of Ga in the PM layer
where n is the layer index, with the regular Ga belonging to even numbered layers, and the regular N belonging to the odd numbered layers. The layer coverage of atoms is 1 when the layer is completely full and 0 when the layer is completely empty. Additionally, the coverage in the PM layer satisfies:

\[ C_{\text{Ga,phy}} + C_{\text{NH}_3,\text{phy}} \leq 1.0 \quad (3.6) \]

The time evolution of the layer coverage of Ga in the \( 2n^{th} \) layer due to the various surface processes is given by:

\[
\frac{dC_{\text{Ga}}(2n)}{dt} = \left[ C_N(2n+1) - C_{\text{Ga}}(2n) \right] J_{\text{Ga}} + \left[ \frac{C_{\text{Ga,phy}}}{\tau_{\text{in}}} \right] - R_0 e^{-\frac{E_{\text{d, Ga}}(2n+2)}{kT}} \left[ C_{\text{Ga}}(2n+2) - C_N(2n+3) \right] + R_0 e^{-\frac{E_{\text{d, Ga}}(2n-2)}{kT}} \left[ C_{\text{Ga}}(2n-2) - C_N(2n-1) \right] - R_0 e^{\frac{E_{\text{d, Ga}}(2n)}{kT}} \left[ C_{\text{Ga}}(2n) - C_N(2n+1) \right] - R_0 e^{\frac{E_{\text{d, Ga}}(2n)}{kT}} \left[ C_{\text{Ga}}(2n) - C_N(2n+1) \right] \]

\[ \times \left[ \left[ C_N(2n+1) - C_{\text{Ga}}(2n+2) \right] + \left[ C_N(2n-3) - C_{\text{Ga}}(2n-2) \right] \right] \quad (3.7) \]

where the term \( (A1) \) denotes the increase in \( C_{\text{Ga}}(2n) \), due to adsorption of Ga from the incoming molecular beam and the PM layer. The rate of adsorption is the product of the available sites for In incorporation on the surface, \( \left[ C_N(2n-1) - C_{\text{Ga}}(2n) \right] \) and the fluxes of Ga, \( J_{\text{Ga}} \) from the molecular beam and \( C_{\text{Ga,phy}} / \tau_{\text{in}}^{\text{Ga}} \) from the PM layer. The sticking coefficient of Ga is taken as unity. The term \( (B1) \) describes the increase in \( C_{\text{Ga}}(2n) \) due to migration of Ga into the \( 2n^{th} \) layer from adjacent layers, \( (2n+2) \) and \( (2n-2) \).
\[ C_{Ga}(2n+2) - C_N(2n+3) \] and \[ C_{Ga}(2n-2) - C_N(2n-1) \] are the fraction of available sites for Ga in the \(2n^{th}\) layer. The rate of migration and reevaporation are described by Arrhenius type rate equations given by Equation (3.3). Similar equations and arguments hold for all other layers.

The migrational activation energy for a particular layer is a function of the layer coverage of that layer, the activation energies of isolated atoms, \(E_{d,iso}\), and the second neighbor atom-atom pair interaction energy, \(E_{Ga,Ga}\), with a factor of four for the maximum possible neighboring atoms. In the mathematical form, the activation energy for Ga migration in the \((2n-2)^{th}\) layer is given as:

\[
E_{d,Ga}(2n-2) = E_{d,Ga,iso} + 4E_{Ga,Ga}C_{Ga}(2n-2)
\] (3.8)

The term \((C1)\) denotes the decrease in \(C_{Ga}(2n)\) due to migration of Ga out of the \(2n^{th}\) layer into the adjacent layers, \((2n+1)\) and \((2n-3)\). The description of the rate of this process is similar to term \((Bl)\), with \(E_{y}(2n)\) being the activation energy for migration from \(2n^{th}\) layer, \([C_{N}(2n+1) - C_{Ga}(2n+2)]\) and \([C_{N}(2n-3) - C_{Ga}(2n-2)]\) being the fractions available for Ga atoms to migrate in the adjacent layers \((2n+1)\) and \((2n-3)\), respectively. The term \((D1)\) describes the decrease in \(C_{Ga}(2n)\) due to the reevaporation of Ga atoms from the \(2n^{th}\) layer with activation energy for reevaporation, \(E_{e,Ga}(2n)\). The description of the activation energy for reevaporation, \(E_{e,Ga}\) is similar to that of \(E_{d,Ga}\) and is given as:

\[
E_{e,Ga}(2n) = E_{e,Ga,iso} + 4E_{Ga,Ga}C_{Ga}(2n)
\] (3.9)
with \( E_{r,Ga,iso} \), is the reevaporation energy for the isolated Ga atom. Equations similar to Equations 3.7-3.9 are written for N in the \((2n+1)^{th}\) layer.

The time evolution of the layer coverage of \( i^{th} \) species in the PM layer, \( \frac{dC_{i,phy}}{dt} \), is given by:

\[
\frac{dC_{i,phy}}{dt} = (J_i (1 - S_i)) - \frac{C_{i,phy}}{\tau_{ev}^i} - \frac{C_{i,phy} S_i}{\tau_{in}^i}
\] (3.10)

where \( i \) represents either Ga or \( NH_3 \) in case of \( NH_3 \) as source and active \( N \) in case of ECR plasma as source. In the above equation, the first term denotes the increase in PM coverage due to arrival of \( i^{th} \) species flux into the PM layer. The next two terms denote the net loss of PM layer coverage due to reevaporation and chemisorption into the appropriate site, respectively. \( S_i \) in Eq. (3.10) represents the sum of all the available sites for the \( i^{th} \) species. For example, in the case of Ga incorporation, i.e., \( i \) is represented by Ga, \( S_{Ga} \) is given by

\[
S_{Ga} = \sum_n [C_{N}(2n-1) - C_{Ga}(2n)]
\] (3.11)

A similar equation is written for N. It is noted that \( S_i \) is not a constant and it varies with time as the coverage evolves. \( \tau_{ev}^i \) and \( \tau_{in}^i \) represent the time constants for incorporation and reevaporation of the \( i^{th} \) species from the PM layer, respectively.

3.2 Computational Details

The description of the evolution of each bilayer of GaN requires two first order nonlinear differential equations (Equation 3.7), one describing the time evolution of each
of the normalized macrovariables. The time evolution of the PM layer requires two additional equations (Equation 3.10). In this work simultaneous growth of 80 bilayers (two variables Ga and N) and the PM layer (two variables Ga and NH₃) are considered requiring a total of 162 (= 80 \times 2 + 2) coupled nonlinear first order differential equations. The system of equations was integrated using a Fourth-order Runge Kutta method with time steps of less than 10⁻⁶ sec. to get the values of each of the macrovariables as a function of time for a growth time of 20 sec. The growths were simulated on the Silicon Graphics ORIGIN-2000 supercomputer. The average coverages of Ga and N in individual layers at the end of growth are obtained from the solution of the differential equations by considering the coverage of a few layers in the bulk, viz., the layers far from the substrate and the surface. Model parameters for the program were obtained by fitting our results with that of the Held et al. [18] for two data points of Ga incorporation versus temperature plot. A list of the model parameters and their values are obtained by fitting to experimental results that is used for comparison and presented in Table II.
CHAPTER 4

RESULT AND DISCUSSION

4.1 Ammonia as Source

4.1.1 GaN Incorporation and Desorption Studies

Two sets of growth conditions, one following the experiments of Held et al. [18] and the other following Jenny et al. [28] were employed. The growth direction was [100] for both the sets. In the case of Held et al. [18], the temperature was in the range of 1013-1113 K; \( NH_3 \) pressure, \( P_{NH_3} \), was in the range of \( 0 - 4.0 \times 10^{-5} \) torr and Ga flux rate, \( J_{Ga} \), was in the range of \( 0 - 2.8 \) ML/sec. In the case of Jenny et al, the temperature was 1023 K; \( NH_3 \) pressure, \( P_{NH_3} \), was in the range of \( 0 - 15.0 \times 10^{-7} \) torr and Ga flux rate, \( J_{Ga} \), was 0.14 ML/sec. \( P_{NH_3} \) was converted to a flux rate, \( J_{NH_3} \), using the following equation:

\[
J_{NH_3} = \frac{P_{NH_3}}{\sqrt{2\pi nk_B T}}
\]

(4.1)

where \( m \) is the molecular weight of the \( NH_3 \) molecule, \( k_B \) is the Boltzmann constant and \( T \) is the source temperature.

Ga incorporation rate was obtained by time averaging Ga layer coverage for the entire growth period. A plots of Ga incorporation rate (ML/sec.) versus
$P_{NH_3}$ (torr) at constant Ga fluxes of 0.5 ML/sec. and 1.0 ML/sec. at the temperature of 1058 K is shown in Figure 11 for the growth conditions of Held et al. [18] along with their experimental data. The agreement between the results is excellent for the experimental values of Ga flux 1.0 ML/sec. case. In Figure 11, the vertical line clearly separate the pressures into two regimes with $P_{NH_3}$, less than $2.5 \times 10^{-5}$ torr (left of the line) representing the $NH_3$-limited regime and $P_{NH_3}$, more than $2.5 \times 10^{-5}$ torr (right of the line) representing the Ga-limited regime. It is found that the Ga incorporation rate is linear in the $NH_3$ reaction limited regime. In this regime, the excess Ga rides on the surface and reevaporates from the PM layer with an activation energy of approximately 0.2eV.

A plot of Ga incorporation rate (ML/sec.) versus temperature is shown in Figure 12 for the growth conditions of Held et al. [18] along with their experimental data. The agreement between the results are excellent for most temperature values for a growth rate of 1.0 ML/sec. The incorporation rate increases with temperature till 1093 K and then decreases. This behavior is due to competition between two thermally activated processes, the $NH_3$ reaction given by Equation 3.1 and the reevaporation of Ga from the surface through the PM layer. The plots Ga incorporation rate versus temperature for Ga fluxs of 0.5 ML/sec., 1.5ML/sec., and 2.0 ML/sec. from simulation are also shown in Figure 12. It is noted that the temperature at which the growth rate peaks increases with the growth rate due to unavailability of surface Ga for evaporation and less residence time.

Growth rate verses Ga flux rate from our simulation is shown in Figure 13 along
with experimental results of Held et al. [18]. The growth rate is Ga-limited with nearly unity incorporation up to a certain Ga flux, then the growth rate is \( NH_3 \)-limited for higher Ga fluxes. In the \( NH_3 \)-limited range, the growth rate reduces with Ga flux. The agreement between the results is excellent at low and high Ga flux rate. The simulation results deviate from experiments in the intermediate flux rate. The reason for this discrepancy is not clear. The reason for our observation is as follows. As the Ga flux rate increases, the proportion of Ga in the PM layer increases as shown in Figure 14. At the same time, the \( NH_3 \) proportion decreases as \( C^- + C^+ \leq 1.0 \). As the \( C^+ \) decreases, the incorporation rate of N decreases and hence the growth rate decreases.

The Ga incorporation rate (ML/sec.) as a function of temperature for several Ga / \( NH_3 \) flux ratios is shown in Figure 15. For this set of data, the ratio was fixed and the temperature was varied. Even though the experimental [30] and simulation results are in the same approximate range, they do not agree either qualitatively or quantitatively. The trend seems similar. The reason for the discrepancy is not clear.

Desorption rate of Ga, \( D_{Ga} \), was found as the difference between the arriving atoms and the change in the total atom concentration in the crystal and the PM layer in a preset short period of time. Mathematically, it can be written as:

\[
D_{Ga} = J_{Ga} \Delta t - \sum_{all-layer} [C_{Ga}(2n)(t + \Delta t) - C_{Ga}(2n)(t)] - [C_{Ga,phy}(t + \Delta t) - C_{Ga,phy}(t)] \quad (3.13)
\]

where \( \Delta t \) was arbitrarily chosen as 0.1 sec. A Plot of Ga desorption rate computed using Equation 3.13, \( D_{Ga} \) versus time for a \( NH_3 \) pressure of \( 2.95 \times 10^{-7} \) torr is shown in Figure 16. The Ga flux was on from 10 to 20 seconds and at 20 seconds, the Ga flux was terminated. The Ga desorption rate initially increases rapidly and reaches a steady state.
within 3 sec. After the Ga flux is terminated, the Ga desorption flux decreases exponentially to zero in 3 sec. There are two components to the desorption process, one from the surface riding Ga and the other from the crystal with activation energies of 0.2 eV and 2.54 eV (isolated adatom), respectively. This behavior is in qualitative agreement with the results of Jenny et al. [28] and Held et al. [18]. Quantitative comparison is not possible due to the arbitrary units of the experimental data.

4.1.2 General Observations and Implications

GaN growth using $NH_3$ involves competition between $NH_3$ pyrolysis and Ga reevaporation which are both thermally activated. For every set of Ga flux and $P_{NH_3}$, there is an optimum temperature for maximum Ga incorporation. This value of maximum incorporation rate can be less than either the Ga flux rate for Ga limited case or the N incorporation rate for ammonia reaction limited case, depending on the growth conditions. For a given growth temperature and Ga flux, the Ga incorporation rate saturates beyond a particular $NH_3$ pressure. Ga reevaporation has two components, one from the PM layer and the other from the surface of the crystal.

Additionally, it is clear from the discussion related Figure 13 there is an additional competition between the species occupying the PM layer, i.e. Ga and $NH_3$. Thus competition decides the proportion of each species in the layer which, in turn, decides the dynamics of growth and growth rate.

For the growth conditions studied, the practical lower limit for ammonia decomposition appears to be 973 K. In general, the ammonia reaction rate increases with temperature as it is thermally activated. The ammonia decomposition can change with
substrate, polarity, and growth condition, even though in this study, the influence of substrate type, orientation and polarity are not studied. The surface polarity will influence the growth kinetics, but in our model, this influence gets embedded indirectly in the fitted model parameters.

4.2 Modified Rate Equation Model for Growth of GaN

Using ECR Plasma

The operation of an ECR source is extremely complex and characterized by a strong coupling of various physical and chemical phenomena: power coupling, magnetic field-microwave interaction, plasma generation, plasma heating, rarefied gas flow, generation and transport of active species, and interaction of various species with walls and wafers. Thus, kinetic models such as particle in cell techniques to study the physics of plasma sources are extremely complex. Recently, simple zero-dimensional models have been used to analyze high density plasma used in processing applications [173,174]. In this chapter, a brief discussion of the zero-dimensional model of Meyyappan et al.[173,174] for ECR plasma simulation is presented. The parameters required for the model and results of the ECR simulation program, SAMPR [173,174] are also discussed. Finally, the results from the SAMPR are used in our MBE growth model.

4.2.1 ECR plasma zero-dimensional model

A zero-dimensional model simply consists of balance equations for total mass, mass of various neutral and ionic species, and gas energy along with a plasma power (energy) balance equation. A Mass balance is considered for each of the neutral and ionic
species in the plasma and accounts for changes due to flow balance due to flow, creation, and annihilation reactions. In addition to mass balance, power balance is also considered.

The possible nitrogen species considered are $N_2^+, N_2^+, N \ldots$ etc. The simplicity of the approach does not permit investigation of microwave magnetic field interaction and related details; rather, the ECR power is just a lumped input parameter. The model provides volume averaged densities of all species, gas, and electron temperatures. Obviously, no information on plasma uniformity or spatial profiles can be obtained from such a global model.

Electron impact, rotational, vibrational, and electronic excitation of $N_2$, ionization, dissociative ionization, and dissociation are included in this model. Neutral-neutral collisions have been ignored since the operating pressure in ECR devices is in the millitorr range. The wall collision of ions is assumed to liberate the corresponding neutral with a sticking probability of unity. The sticking coefficient for N atom recombination with stainless steel walls is taken to be 0.1.

4.2.1.1 The ECR Model Parameters and Their Influence

ECR parameters similar to the ones used for experimental ECR-MBE growth [119] are employed for this study. ECR plasma results from a systematic parametric study are presented to illustrate the effects of varying pressure, power, flow rate, and reactor dimensions. The operation range of ECR plasma parameters is summarized in Table III. The reactor dimensions correspond to a compact ECR source appropriate to fit onto a flange leading to the MBE growth chamber. It is assumed that the pressure and flow rate can be independently fixed at desirable values by adjusting the pumping speed.
Note that the pressure is likely to vary along the length of the reactor under low pressure conditions ($< 5\text{mTorr}$), since the pressure drop required to push the required mass flow through the system may be large. Such a variation cannot be accounted for in the present analysis. In the appendix, an ECR plasma simulation output file sample is presented. This output file provides details of about ECR plasma output.

The active N volume density versus ECR power (W) and $N_2$ flow rate (sccm) is shown in Figure 17. The active nitrogen N density increases with both power and $N_2$ flow rate as expected. The flux of nitrogen atoms $J_N$ is obtained by using the following equation:

$$J_N = \frac{f_{\text{total-mass-flow}} \times F_{\text{nitrogen-mass-fraction}} \times N_0 \times S_{\text{source-cross-section}} \times M_{\text{molecular-weight}}}{N_0}$$

where $f_{\text{total-mass-flow}}$ is the total mass flow, $F_{\text{nitrogen-mass-fraction}}$ is the nitrogen atom mass, $N_0$ is the Avagodro number, $S_{\text{source-cross-section}}$ is the source cross-sectional area and $M_{\text{molecular-weight}}$ is the molecular weight.

A plot of flux of active N verses ECR power (W) and flow rate of $N_2$ (sccm) is shown in Figure 18. The active N flux increases with both ECR power (W) and $N_2$ flow rate (sccm). Since the flux is directly proportional to the density which increases with both ECR power and $N_2$ flow rate as shown in Figure 17.

4.2.2 Modified Rate Equation Model

The Rate Equation Model for growth of GaN using Ammonia is adopted directly for growth with ECR plasma. All of concepts, definitions, equations and parameters, physics and mathematics are the same. But the flux of N in the simulation program
should replace that of \( \text{NH}_3 \). For ECR plasma, the fluxes of active nitrogen N can be obtained from ECR plasma source computer program SAMPR. Additionally, the PM layer equation, i.e., equation 3.6 should be replaced with a similar equation for active N.

### 4.2.3 Results and Discussion

The net electron concentration can be calculated using the following equation 4.2:

\[
n_{\text{electron-concentration}} = 3n_{\text{GaN}} \sum [C_N(n) - C_{Ga}(n + 1)] / n
\]

(4.2)

where \( n_{\text{GaN}} (~10^{23} \text{ cm}^{-3}) \) is a concentration of GaN at room temperature, \( C_N(n) \) and \( C_{Ga}(n + 1) \) are the \( n^{th} \) layer coverage of N and \( (n + 1)^{th} \) layer of Ga, respectively, where \( n \) is constant. The reason for the 3 in equation 4.2 is that every Ga vacancy provides 3 electrons in crystal.

Plots of net electron concentration versus microwave power (W) for various flow rates are shown in Figures 19-21, respectively, for 973K, 1023K and 1073K along with the experimental results of Molnar et al. [119]. The experimental results of Molnar et al. [119] agree qualitatively with our results, but not quantitatively. With increasing ECR power, the active N flux increases and hence a decrease in the bulk N vacancies and the electron concentration. The dependence on the \( N_2 \) flow rate is very weak with higher flow rate resulting in higher concentration. This is due to higher growth rate and hence less time for migration of both Ga and N at higher flow rate, which results in a greater Ga vacancy concentration. Figures 22-24 represents the N vacancy concentration versus temperature (K) and ECR power (W) for a different flow rate in a 3-D surface plot. The reason for poor quantitative agreement between the experiments with our results is as follows. Secondary ion mss spectrometry (SIMS) analysis of GaN films show that the
concentration of Si, C, and O exhibit an experimental dependence as shown in Figure 25. [119]. Unfortunately, our ECR plasma model (SAMPR) does not capture this effect and our model does not allow for impurity incorporation. Films grown at high microwave power may have compensating centers due to impurities such as C, O, Si etc. Thus, our results can not quantitatively agree with the experimental results of Molnar et al. [119].

Three-dimensions surface plots of growth rate ($\mu m/hr$) versus temperature (K) and ECR power (W) are shown in Figures 27-29, respectively, for flow rates of 3, 6, and 9 sccm. The general trend is the same in all three cases. The growth rate (below 1073 K) increases with temperature due to faster incorporation of active N which is thermally activated. Beyond a critical temperature (large 1073 K), the growth rate decreases slightly due to evaporation of Ga directly from the crystal surface and from the floating Ga layer. This observation is confirmed by the therr-dimensions surface plots of floating Ga (PM layer) against temperature and ECR power as shown in Figures 29-31, respectively, for flow rates 3 sccm, 6 sccm and 9 sccm. The growth rate is constant with ECR power as the growth condition already into N rich condition even with the lowest ECR power 18 W.
A rate equation approach is employed to investigate the MBE growth of GaN using ammonia. A surface riding material layer of Ga and \( NH_3 \) along with the associated dynamics, incorporation of Ga and N into the crystal and desorption are included in the model. Rates of all surface processes are assumed Arrhenius type. The simulated Ga incorporation rate as a function of ammonia pressure and substrate temperature are in excellent agreement with the experimental data [18]. Ga incorporation rate increases with increasing \( NH_3 \) overpressure and saturates at a maximum value at a large \( NH_3 \) overpressure. It clearly shows that the \( P_{NH_3} \) separates the growth regime into two areas: the Ga-limited and the \( NH_3 \)-limited. It is found that the Ga incorporation rate is linear in the \( NH_3 \)-limited and the excess Ga rides on the surface and reevaporates from the PM layer and the crystal surface. The Ga incorporation rate exhibits a peak at 1093 K due to competition between thermally activated pyrolysis of \( NH_3 \) and reevaporation of Ga from the surface. The growth regime is split into two parts in the Ga incorporation rate versus Ga flux rate behavior separated by at the peak incorporation rate:
Ga-limited and $NH_3$-limited. There are some differences between the simulation results and the experimental results. The reason for our observation is that the $NH_3$ proportion in the PM layer decreases and results in the GaN growth rate decreases. The simulated Ga desorption parameter versus time is also in good agreement with the experimental data of Jenny et al [28].

The rate equation model was extended to ECR plasma MBE growth with necessary modifications. The growth conditions were kept identical to that used in the experiments of Ref [119]. The effect of the microwave power of the ECR plasma on the electron concentration was studied. The plots of the net electron concentration versus power (W) for various flow rates show that with increasing ECR power, the active N flux increases and hence the bulk N vacancies and the electron concentration decreases. It was found that the dependence of the electron concentration on the $N_2$ flow rate is very weak that is due to the fact that the simulation growth conditions are in a high nitrogen regime. We investigated the influence of impurities in the GaN film growth at high microwave power. Plots of growth rate versus temperature and ECR power for various flow rates show the same general trend. The growth rate below 1073 K increases with temperature due to evaporation of Ga directly from the floating Ga layer and from the crystal surface. Under the N-rich condition, the growth rate is constant with ECR power.

The following issues are recommended for future investigations: (1) Include Al and In into cation sublattice to study other nitrides; (2) Include impurity incorporation from the ECR chamber with its known dependencies; (3) Investigate to see if a simple analytical model can be developed which can be used easily without much computation.
Table I. Properties of prospective nitride substrates*

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>Symmetry</th>
<th>Lattice parameters</th>
<th>Coefficient of thermal expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wurtzite GaN</td>
<td>Hexagonal</td>
<td>(a = 3.189 \ \text{Å})</td>
<td>(5.59 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 5.185 \ \text{Å})</td>
<td>(3.17 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>Wurtzite AlN</td>
<td>Hexagonal</td>
<td>(a = 3.112 \ \text{Å})</td>
<td>(4.20 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 4.982 \ \text{Å})</td>
<td>(5.30 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>(\alpha - Al_{2}O_{3})</td>
<td>Hexagonal</td>
<td>(a = 4.758 \ \text{Å})</td>
<td>(7.50 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 12.991 \ \text{Å})</td>
<td>(8.50 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>(a = 5.4301 \ \text{Å})</td>
<td>(3.59 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>(a = 5.6533 \ \text{Å})</td>
<td>(6.00 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>Hexagonal</td>
<td>(a = 3.08 \ \text{Å})</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 15.12 \ \text{Å})</td>
<td>...</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>Cubic</td>
<td>(a = 4.360 \ \text{Å})</td>
<td>...</td>
</tr>
<tr>
<td>InP</td>
<td>Cubic</td>
<td>(a = 5.8693 \ \text{Å})</td>
<td>(4.50 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>GaP</td>
<td>Cubic</td>
<td>(a = 5.4512 \ \text{Å})</td>
<td>(4.65 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>MgO</td>
<td>Cubic</td>
<td>(a = 4.216 \ \text{Å})</td>
<td>(10.5 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>(a = 3.252 \ \text{Å})</td>
<td>(2.9 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 5.213 \ \text{Å})</td>
<td>(4.75 \times 10^{-6} / \text{K})</td>
</tr>
<tr>
<td>(MgAl_{2}O_{4})</td>
<td>Cubic</td>
<td>(a = 8.083 \ \text{Å})</td>
<td>(7.45 \times 10^{-6} / \text{K})</td>
</tr>
</tbody>
</table>

### Table II. Fitted model parameters such as energies, time constants and frequency factors and their dependences.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Model Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{\text{phy},\text{Ga}}$</td>
<td>prefactor for physisorbed Ga incorporation</td>
<td>$1.6 \times 10^{-4}$ s</td>
</tr>
<tr>
<td>$\tau_{\text{Phy},N}$</td>
<td>prefactor for physisorbed N incorporation</td>
<td>$2.8 \times 10^{-12}$ s</td>
</tr>
<tr>
<td>$\tau_{\text{Phy},\text{Ga}}$</td>
<td>prefactor for physisorbed Ga evaporation</td>
<td>$1000.0$ s</td>
</tr>
<tr>
<td>$\tau_{\text{Phy},N}$</td>
<td>prefactor for physisorbed N evaporation</td>
<td>$3.5 \times 10^{-1}$ s</td>
</tr>
<tr>
<td>$R_{\text{d},\text{Ga}}$</td>
<td>frequency factor for Ga for diffusion</td>
<td>$2.4 \times 10^8$ / s</td>
</tr>
<tr>
<td>$R_{\text{d},N}$</td>
<td>frequency factor for N for diffusion</td>
<td>$4.38 \times 10^7$ / s</td>
</tr>
<tr>
<td>$E_{\text{Ga}}$</td>
<td>activation energy for incorporation of Ga</td>
<td>$0.0$ eV</td>
</tr>
<tr>
<td>$E_{\text{N}}$</td>
<td>activation energy for incorporation of N</td>
<td>$2.5$ eV</td>
</tr>
<tr>
<td>$E_{\text{Ga-N}}$</td>
<td>2nd neighbor atom-atom pair interaction energy for Ga</td>
<td>$0.174$ eV</td>
</tr>
<tr>
<td>$E_{\text{N-N}}$</td>
<td>2 neighbor atom-atom pair interaction energy for N</td>
<td>$0.190$ eV</td>
</tr>
<tr>
<td>$E_{\text{Ga}^{-}\text{N}}$</td>
<td>neighbor atom-atom pair interaction energy for Ga-N</td>
<td>$0.92$ eV</td>
</tr>
<tr>
<td>$E_{\text{d,iso}}$</td>
<td>activation energy for diffusion for isolated Ga, atom</td>
<td>$1.2$ eV</td>
</tr>
<tr>
<td>$E_{\text{d,iso}}$</td>
<td>activation energy for diffusion for isolated N atom</td>
<td>$1.2$ eV</td>
</tr>
<tr>
<td>$E_{\text{ev}}$</td>
<td>activation energy for the Ga evaporation</td>
<td>$0.18 + 0.06C_{\text{Ga}}^{\text{phy}}$ eV</td>
</tr>
<tr>
<td>$E_{\text{ev}}$</td>
<td>activation energy for the N evaporation</td>
<td>$0.18 + 0.06C_{\text{N}}^{\text{phy}}$ eV</td>
</tr>
</tbody>
</table>

* $C_{\text{Ga}}^{\text{phy}}$ — Ga coverage in the physisorbed layer
* * $C_{\text{N}}^{\text{phy}}$ — N coverage in the physisorbed layer

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Table III. Operation range of ECR plasma parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source radius ( r )</td>
<td>1.27 cm</td>
</tr>
<tr>
<td>Source length ( L )</td>
<td>10.00 cm</td>
</tr>
<tr>
<td>Nitrogen pressure</td>
<td>4.00 mtorr</td>
</tr>
<tr>
<td>ECR plasma power</td>
<td>18-25 W</td>
</tr>
<tr>
<td>( N_2 ) flow rate</td>
<td>3-9 sccm</td>
</tr>
</tbody>
</table>
Figure 1. The Compact 21 is the new RIBER baseline MBE system. (courtesy of Riber, USA/EAST coast)
Figure 2. The essential parts of a MBE growth system. The three zones, where the basic processes of MBE take place are also indicated.
Figure 3. Pictorial representations of the three crystal growth models: a) island growth; b) layer plus island growth; and c) layer-by-layer growth.
Figure 4. Structure of GaN M-i-n LED [131].
Figure 5. Emission spectra from GaN M-i-n LEDs using Zn-doped i-layers [132].
Figure 6. Structure of GaN/SiC transistor [136].
Figure 7. A schematic picture of the ECR plasma source [145].
1) Microwave emitter;
2) Power feedthrough;
3) Impedance adapter;
4) Microwave generator;
5) Gas supply;
6) Permanent magnets;
7) Water cooling.
Figure 8. A schematic magnetic field lines in the emitter zone of a ECR plasma chamber (in the xz plane at y=0) [145].
Figure 9. Emission spectra obtained from a ECR nitrogen plasma [120].
Figure 10. A schematic picture showing the surface processes of the physisorbed material layer.
Figure 11. Simulation results of Ga incorporation coefficient versus \( NH_3 \) pressure along the experimental results of Held et al. [18].
Figure 12. Simulation results of Ga incorporation coefficient versus substrate temperature along the experimental results of Held et al. [18].
Figure 13. Simulation results of Ga incorporation coefficient versus Ga flux along the experimental results of Held et al. [18].

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Figure 14. Simulation results of floating $NH_3$ and floating $Ga$ versus $Ga$ flux.
Figure 15. Simulation results of Ga incorporation coefficient versus substrate temperature for several Ga/NH$_3$ flux ratios along the experimental results of Held et al. [18].

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Figure 16. Simulation results of Ga desorption rate versus time for the growth conditions of Jenny et al. [28].
Figure 17. The dependence of atomic N concentration (atoms/cm³) on ECR microwave power (W) and N₂ flow rate (cc/min) at a temperature of 573 K.
Figure 18. The dependence of atomic $N$ flux (atoms/sec) on ECR power ($W$) and $N_2$ flow rate (sccm) at a temperature of 573 K.
Figure 19. The variation of net electron concentration with the microwave power ($W$) at 973 K for various flow rates along with the experimental data [119].
Figure 20. The variation of net electron concentration with the microwave power (W) at 1023 K for various flow rates along with the experimental data [119].
Figure 21. The variation of net electron concentration with the microwave power \((W)\) at 1073 K for various flow rates along with the experimental data [119].
Figure 22. 3-D surface plot of $N$ vacancy concentration ($/cm^3$) versus temperature ($K$) and ECR power ($W$) for a flow rate of 3 $sccm$. 

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Figure 23. 3-D surface plot of $N$ vacancy concentration ($/cm^3$) versus temperature ($K$) and ECR power ($W$) for a flow rate of 6 $sccm$. 

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Figure 24. 3-D surface plot of $N$ vacancy concentration ($/cm^3$) versus temperature ($K$) and ECR power ($W$) for a flow rate of 9 sccm.
Figure 25. Experimental SIMS impurity levels vs. microwave power [119].
Figure 26. 3-D plot of GaN growth rate versus temperature (K) and ECR power (W) for a flow rate 3 sccm.
Figure 27. 3-D plot of GaN growth rate versus temperature (K) and ECR power (W) for a flow rate 6 sccm.
Figure 28. 3-D plot of GaN growth rate versus temperature \((K)\) and ECR power \((W)\) for a flow rate 9 \text{sccm}.
Figure 29. 3-D plot of floating layer of Ga coverage versus temperature \((K)\) and ECR power \((W)\) for the case of growth represented in Figure 26.
Figure 30. 3-D plot of floating layer of Ga coverage versus temperature (K) and ECR power (W) for the case of growth represented in Figure 27.
Figure 31. 3-D plot of floating layer of Ga coverage versus temperature (K) and ECR power (W) for the case of growth represented in Figure 28.
APPENDIX

ECR Plasma Simulation Output File Sample

The program is got from M. Meyyappan, NASA Ames Research Center, Moffett Field, California. Its name is SAMPR.
$READ1$

esolve = .true.,
tsolve = .false.,
$END$

$READ2$

ggeom = 2,
radius = 1.27,
cleng = 10.0,
wwf = 0.0,
wwarea = 0.0,
nrwall = 1,
$END$

$READ3$

press = 4.0,
power = 18.0,
tempgas = 350.0,
tempwl = 350.0,
tempwf = 350.0,
tinit = 350.0,
eldens = 2.0e11, eltemp = 2.0, eltin = 0.0,
$END$

$READ4$

ecinp(l) = 3, ecf(1) = 7.08e19,
chexcr(1) = 6.0e-15,
thcon = 5.0e-5,
gloor = .false.,
$END$

$READ5$

pwall(2) = 1.0e-1, asurf(1,2) = 0.5,
pwall(3) = 1.0, asurf(1,3) = 1.0,
pwall(4) = 1.0, asurf(2,4) = 1.0,
pwall(5) = 1.0, asurf(1,5) = 1.0,
pwall(6) = 1.0, asurf(1,6) = 1.0,
$END$

$READ6$

nt = 3000, dtmin = 1.0e4, dt = 1.0e4, dtmax = 1.0e4,
dtfac(7) = 1.0e6, 1.0e6,
gueswf(1) = 0.9, 0.50e-1.1.0e-3,1.0e-3,1.0e-2,1.0e-2,
$END$

$READ7$

isscnt = 100,
$END$

$SPECIES$

MW FLOW DBASE
N2 28.0 9.0 input
N 14.0 0.0 input
N2+ 28.0 0.0 input
N+ 14.0 0.0 input
N2V 28.0 0.0 input
N2E 28.0 0.0 input

$JANAFNL$

asispec(1,1,1) = 2.5,
asispec(1,2,1) = 2.5,
asispec(1,1,2) = 2.5,
asispec(1,2,2) = 2.5,
asispec(1,1,3) = 2.5,
asispec(1,2,3) = 2.5,
asispec(1,1,4) = 2.5,
asispec(1,2,4) = 2.5,
asispec(1,1,5) = 2.5,
 SPECIES INFORMATION

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<th>REF. MASS FRAC</th>
<th>REF. FLOW</th>
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THERMOCHEMICAL DATA FIT INFORMATION

\[ CP(I)/R = A1(I) + A2(I)*T + A3(I)*T^2 + A4(I)*T^3 + A5(I)*T^4 \]
\[ H(I)/RT = A1(I) + A2(I)*T + A3(I)*T^2 + A4(I)*T^3 + A5(I)*T^4 + A6(I) \]
\[ S(I)/R = A1(I)ln(T) + A2(I)*T + A3(I)*T^2 + A4(I)*T^3 + A5(I)*T^4 + A7(I) \]

SPECIES N2 - INFORMATION GENERATED BY USER INPUT

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Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
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**SPECIES N2E** - INFORMATION GENERATED BY USER INPUT

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SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2+. 
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv1.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv2.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv3.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv5.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv7.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-nv8.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e1.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e2.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e3.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e5.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e7.
SUCCESSFULLY OPENED FILE: INFILE = /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e8.
SUCCESSFULLY OPENED FILE: INFILE - 10 /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e9
SUCCESSFULLY OPENED FILE: INFILE - 10 /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e10
SUCCESSFULLY OPENED FILE: INFILE - 10 /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e11
SUCCESSFULLY OPENED FILE: INFILE - 10 /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e12
SUCCESSFULLY OPENED FILE: INFILE - 10 /ul/unlv/coe/ee/fuw/plasma/rama/n2-n2e13

REACTION RATE COEFFICIENTS

\[ K(T) = A T^B \exp(-C/T) \]

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TIME STEP NO. = 300  TIME = 3.00000E+06  DT = 1.00000E+04

TIME STEP NO. = 400  TIME = 4.00000E+06  DT = 1.00000E+04

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**Final Reactor Results**

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SUM OF MASS FRACTION CHECK = 1.000000

OUTFLOW IN sccm FOR CASCADING

SPECIES | MW | FLOW | DBASE  
--- | --- | --- | --- |
N2      | 28.00 | 8.93 | INPUT |
N       | 14.00 | 1.17 | INPUT |
N2+     | 28.00 | 0.01 | INPUT |
N+      | 14.00 | 0.15 | INPUT |
N2V     | 28.00 | 0.44 | INPUT |
N2E     | 28.00 | 0.44 | INPUT |

ELECTRON OUTFLOW = 7.4116880E-03 sccm

TOTAL OUTFLOW RATE = 1.0698391E+01 sccm

FINAL TOTAL NUMBER DENSITY = 1.1035885E+14 cm**-3

FINAL GAS DENSITY = 4.8458611E-09 gm/cm**3

MASS OUT FLOW = 1.8748886E-04 gm/s

FINAL SPECIES NUMBER DENSITY cm**-3
N2      | 9.2123456E+13 |
N       | 1.2088992E+13 |
N2+     | 7.6452823E+10 |
N+      | 2.1555150E+06 |
N2V     | 1.4993190E+12 |
N2E     | 4.4942406E+12 |

ELECTRON DENSITY = 7.6454979E+10 cm**-3
ELECTRON TEMPERATURE = 4.1924798E+00 eV
VP minus VF = 2.3127245E+01 Volts

APPLIED POWER DISTRIBUTION, fraction

INELASTIC COLLISION LOSS = 0.7266
ELASTIC COLLISION LOSS = 0.0231
ELECTRON ENERGY OUTFLOW = 0.0002
AMBIPOlar WALL LOSS = 0.0666
ION POWER DEPOSITION = 0.1836

DATE AND TIME
START OF JOB | Sun Apr 9 19:43:47 2000 |
END OF JOB | Sun Apr 9 19:43:47 2000 |
MACHINE NAME | atom |

ELAPSED TIME, IN SECONDS
START OF JOB | 0.0012 |
END OF JOB | 0.1497 |
MACHINE NAME | 0.0149 |

TOTAL |
0.1700 |
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Thesis Examination Committee:
Chairperson, Dr. Rama Venkat, Ph.D.
Committee Member, Dr. Sahjendra Singh, Ph.D.
Committee Member, Dr. Henry Selvaraj, Ph.D.
Graduate Faculty Representative, Dr. John Wang, Ph.D.