EXPERIMENTAL INVESTIGATION OF THE EPITAXIAL LATERAL
OVERGROWTH OF GALLIUM NITRIDE AND SIMULATION OF THE GALLIUM
NITRIDE METALORGANIC CHEMICAL VAPOR DEPOSITION PROCESS

A dissertation presented to

the faculty of

the Fritz J. and Dolores H. Russ College of Engineering and Technology of
Ohio University

In partial fulfillment
of the requirement for the degree

Doctor of Philosophy

Wentao Ju
March 2003
This dissertation entitled

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BY

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ABSTRACT

JU, WENTAO Ph.D. March 2003. Chemical Engineering

Experimental Investigation of the Epitaxial Lateral Overgrowth of Gallium Nitride and Simulation of Gallium Nitride Metalorganic Chemical Vapor Deposition Process

(154pp.)

Director of Dissertation: Daniel A. Gulino

In this dissertation, the experimental investigation of the epitaxial lateral overgrowth of GaN and the simulation of the GaN MOCVD process are presented.

The effects of various parameters on the MOCVD and ELO process were examined. The crystal structures of both the GaN seeding layers and the ELO layers were examined by XRD 0-2θ scan and x-raying rocking curve. Significant film morphology improvement has been achieved by the ELO process. It was found that V/III ratio has no significant effect on GaN film growth in the MOCVD process. The use of a low temperature GaN buffer layer in the ELO process gave the best quality GaN film. The AlN buffer layer was found not suitable for the second growth of GaN from the seeding layer openings.

The modeling of the GaN MOCVD process has given a deep understanding of the growth process. Kinetik model describing both gas-phase and surface reactions were used in the simulation. The effect of thermal diffusion and radiative heat transfer were also taken into account. The transport phenomena for the gas mixture in the reactor chamber were studied under different operating conditions, such as susceptor rotation speed and ammonia flow rate at inlet, in different inner tube configurations. A detailed analysis of
the reactions and transport process was given. The bell-shaped inner tube configuration was predicted to give better growth rate distribution than the other two configurations. High susceptor rotation speed increases the film growth rate on the substrate, but very high susceptor rotation speed also decreases the desorption rate of the surfacr reaction products from the growth surface. The simulation also indicated that an optimal ammonia flow rate exists. The model was validated by experimental data, and was used to explain the observed unwanted deposits on the inner tube wall for the bell-shaped inner configuration.

Approved: Daniel A. Gulino

Associate Professor of Chemical Engineering
ACKNOWLEDGEMENTS

First of all, I would like to express my appreciation and gratitude to my advisor, Dr. Daniel Gulino. It has been my privilege to study under his direction and I thank him for providing me his invaluable and thoughtful guidance and encouragement.

I am personally deeply grateful to Mr. Ryan Higgins for his generous support on my experimental work and his advice and expertise on a variety of topics.

I would like to thank Dr. Wojciech Jadwisienczak, Mr. Emil Kowalczyk, and Dr. Lozykowski for helping me with the electron beam evaporation and photoluminescence experiments. I would also like to thank Dr. Jean Heremans for helping me with the photolithography experiments. I would also express thanks to Dr. Hugh Richardson for helping me with the FT-IR experiments. I am grateful to Dr. Khairul Alam and Dr. Bhavin Mehta for allowing me to use the simulation software.

My thanks also go to my committee members, Dr. Daniel Gulino, Dr. David Ingram, Dr. Valerie Young, and Dr. Douglas Goetz for their careful review of my dissertation.

Finally, I would express heartfelt thanks to all of my friends who have given help for the preparation of my dissertation during these three and a half years.
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LIST OF SYMBOLS

\(a\)     lattice parameter
\(\alpha\) absorption coefficient
\(c\)     lattice parameter
\(c\)     total mole concentration of the gas mixture
\(c_p\)   specific heat per unit mass
\(D_i\)   effective diffusion coefficient for the \(i\)th species
\(D_{ij}\) binary diffusion coefficient for the \(i\)th and \(j\)th species
\(D_i^r\) thermal diffusion coefficient of the \(i\)th species
\(E_g\)   band-gap energy
\(E_a\)   activation energy
\(f_i\)   mole fraction of the \(i\)th species
\(\vec{g}\) gravity acceleration vector
\(H_i\)   molar enthalpy of the \(i\)th species
\(I\)     radiation intensity, which depends on position \(\vec{r}\) and direction \(\vec{s}\)
\(I\)     unit tensor
\(\vec{j}_i\) total diffusion flux of the \(i\)th species
\(\vec{j}_i^C\) ordinary diffusion flux of the \(i\)th species due to concentration gradient
\(\vec{J}_i^C\) diffusive mole flux of the \(i\)th species, \(\vec{J}_i^C (= \vec{j}_i^C / M_i)\)
\(\vec{j}_i^T\) diffusion flux of the \(i\)th species due to thermal diffusion
$k_B$  \(\text{Boltzmann’s constant}\)

$k_k$  \(\text{forward reaction rate constant of the } k\text{th gas-phase reaction}\)

$k_{-k}$  \(\text{reverse reaction rate constant of the } k\text{th gas-phase reaction}\)

$M$  \(\text{average mole mass of a gas mixture}\)

$M_i$  \(\text{molar mass of the } i\text{th species}\)

$n$  \(\text{index of refraction}\)

$\vec{n}$  \(\text{unit vector}\)

$N_0$  \(\text{Avogadro’s number}\)

$p$  \(\text{pressure}\)

$r$  \(\text{position vector}\)

$R$  \(\text{universal gas constant}\)

$R_k^g$  \(\text{forward gas-phase reaction rate in the } k\text{th gas-phase reaction}\)

$R_{-k}^g$  \(\text{reverse gas-phase reaction rate in the } k\text{th gas-phase reaction}\)

$\vec{s}$  \(\text{direction vector}\)

$\vec{s}'$  \(\text{scattering direction vector}\)

$T$  \(\text{temperature}\)

$\vec{v}$  \(\text{velocity vector}\)

$\vec{v}_i$  \(\text{velocity vector of the } i\text{th species}\)

**Greek Symbols**

$\alpha_{il}$  \(\text{stoichiometric coefficients for the } i\text{th gaseous in the } l\text{th surface reaction}\)

$\beta_{jl}$  \(\text{stoichiometric coefficients for the } j\text{th solid species in the } l\text{th surface reaction}\)
\( \varepsilon \) the maximum energy of attraction between gas molecules.

\( \Phi \) phase function

\( \lambda \) thermal conductivity, wave length

\( \mu \) dynamic viscosity

\( \nu_{ik} \) stoichiometric coefficient of the \( i \)th species in the \( k \)th gas-phase reaction

\( \sigma \) collision diameter, Stefan-Boltzmann constant

\( \sigma_s \) scattering coefficient

\( \rho \) density

\( \tau \) viscous stress tensor

\( \omega_i \) mass fraction of the \( i \)th species

\( \Omega' \) solid angle

**Subscripts**

\( i,j \) with respect to the \( i \)th/\( j \)th species

\( k \) with respect to the \( k \)th gas phase reaction

\( l \) with respect to the \( l \)th surface reaction

**Superscripts**

\( o \) at standard temperature and pressure

\( c \) due to ordinary diffusion

\( \tau \) due to thermal diffusion
1. INTRODUCTION

Research in III-V nitrides is a burgeoning field. With increasing maturity in epitaxial growth and improvement in crystal quality, III-V nitrides are providing potential for the expansion of semiconductor technology. Gallium nitride (GaN) is being extensively investigated for microelectronic and optoelectronic device applications due to its wide direct band gap and good thermal, chemical and mechanical stability.

There are several ways to grow GaN, such as vapor phase epitaxy, molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). [1] The development of GaN materials and devices has suffered from the lack of availability of low-dislocation-density, lattice-matched native nitride substrates for device synthesis by MOCVD or MBE. [2] Due to the large lattice mismatches with the substrates, GaN epitaxial layers contain a large density of extended defects despite the use of a two-step growth method. [3]

A thin layer of typically aluminum nitride (AlN) or low temperature GaN is grown before the GaN epilayer growth and act as a compliant, or "buffer," layer to reduce the degree of crystalline defects and threading dislocations in the subsequently-grown GaN epilayer. The buffer layer plays an important role in reducing GaN film defects. However, the quality of the buffer layer structures is very sensitive to the details of the growth system, and the result is unavoidable three-dimensional growth that degrades the film quality. Recently, a significant reduction in the dislocation densities in GaN films was achieved via lateral mask overgrowth. The epitaxial lateral overgrowth (ELO) technique consists of partially masking a substrate or “seed” layer and subsequently regrowing over the masked substrate. [4]
Up to now little has been reported about the chemical mechanism of the hetero-
epitaxial growth of nitrides. No general growth model exists which takes into account the
influence of reactor geometry and parasitic reactions. A clear relationship between
growth parameters, film morphology, growth rate, and electrical and optical properties of
the material has not been reported yet. \[3\]

The purpose of this study is to experimentally and theoretically investigate the effect
of growth conditions on GaN film growth in MOCVD process. In the experimental study,
the effects of V/III ratio are studied for the MOCVD process of GaN. The effect of
different buffer layers are studied for the ELO process of GaN. A numerical simulation of
the MOCVD process of GaN is carried out to study how different reactor configurations
and growth conditions will affect the film growth rate.
2. OVERVIEW OF MOCVD AND ELO OF GaN

GaN is used for optoelectronic devices operating in short-wave-length and high temperature, high frequency, and/or high power electronic devices. Several epitaxial techniques have been used to grow GaN, such as vapor phase epitaxy, molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), and a number of plasma-assisted processes. Many studies have been undertaken on how to reduce the GaN film defects and dislocations due to the lattice mismatch and difference in thermal conductivity between GaN and the substrate. The potential of epitaxial lateral overgrowth (ELO) for extended defect reduction in the heteroepitaxial growth of III-V semiconductors has been demonstrated and utilized in the deposition of GaN.

2.1 Gallium Nitride and Its Application

GaN has a direct band gap of 3.39 eV at 300 K and forms a continuous alloy system with AlN and InN. [5] With a wide, direct band gap and excellent physical properties, GaN is a very promising material for fabricating blue light emitting devices, high density optical data storage, full color video-screens and even traffic lights. Significant progress in epitaxial growth of GaN has already led to commercially available, nitride-based, high brightness light emitting diodes and GaN blue lasers.

2.1.1 Crystal Structures and Properties

GaN is observed to nucleate in a multiple tetrahedrally-bonded polytype. [6] Predominantly, the GaN epitaxial layers crystallize in the most stable, hexagonal wurtzite structure (α-GaN), especially when grown on substrates with hexagonal symmetry. The films can also crystallize in a metastable zinc blende structure (β-GaN) grown on cubic
substrates. Table 2-1 lists some of the most important properties of the polytypes of GaN.

<table>
<thead>
<tr>
<th>Table 2-1 The fundamental properties of gallium nitride[^6]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wurtzite polytype</strong></td>
</tr>
<tr>
<td>Band-gap energy</td>
</tr>
<tr>
<td>$E_g$ (300K) = 3.39 eV</td>
</tr>
<tr>
<td>$E_g$ (1.6K) = 3.50 eV</td>
</tr>
<tr>
<td>Temperature coefficient</td>
</tr>
<tr>
<td>$\frac{dE_g}{dT} = -6.0 \times 10^{-4}$ eV/K</td>
</tr>
<tr>
<td>Pressure coefficient</td>
</tr>
<tr>
<td>$\frac{dE_g}{dP} = 4.2 \times 10^{-3}$ eV/kbar</td>
</tr>
<tr>
<td>Lattice constants</td>
</tr>
<tr>
<td>$a = 3.189$ Å</td>
</tr>
<tr>
<td>$c = 5.185$ Å</td>
</tr>
<tr>
<td>Thermal expansion</td>
</tr>
<tr>
<td>$\Delta a / a = 5.59 \times 10^{-6}$ K</td>
</tr>
<tr>
<td>$\Delta c / c = 3.17 \times 10^{-6}$ K</td>
</tr>
<tr>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$\lambda = 1.3$ W/cm·K</td>
</tr>
<tr>
<td>Index of Refraction</td>
</tr>
<tr>
<td>$n$ (1 eV) = 2.33</td>
</tr>
<tr>
<td>$n$ (3.38 eV) = 2.67</td>
</tr>
<tr>
<td>Dielectric constants</td>
</tr>
<tr>
<td>$\varepsilon_r \approx 9$</td>
</tr>
<tr>
<td>$\varepsilon_\infty = 5.35$</td>
</tr>
</tbody>
</table>

| **Zinc blende polytype**                                   |
| Band gap energy                                            |
| $E_g$ (300K) = 3.2 ~ 3.3 eV                               |
| Lattice constant                                           |
| $a = 3.189$ Å                                             |
| Index of refraction                                        |
| $n$ (3 eV) = 2.9                                          |

The high thermal conductivity and superior stability of GaN allow higher-power laser operation with less rapid degradation than in other semiconductors.

### 2.1.2 Applications

The followings are a brief review the applications of GaN.

Gallium nitride-based (GaN) materials have become the central focus for the development of blue and green semiconductor light emitting devices, using efficiently its direct energy band gap.[^7] By appropriately alloying GaN with AlN and InN, the energy band gap of the resulting Al (In) GaN can be altered for emission in the range of ultraviolet to yellow or even red. The first GaN LED was reported 32 years ago.[^8] Amino et al.[^9] demonstrated the first GaN p-n junction LED. In 1993, Nakamura[^10]
succeeded in making the first GaN-based blue LED with sufficient output power for applications.

GaN-based field effect transistors (FET) are projected to be highly useful for amplification and switching in high temperature and/or high power environments. Binari et al. \cite{11} reported on the microwave performance of GaN metal semiconductor field effect transistors (MESFET), and Si$_3$N$_4$/GaN metal insulator field effect transistors (MISFET). Pankove et al. \cite{12} reported on a new heterojunction bipolar transistor that used a heterojunction between GaN and SiC. The transistor exhibited an extremely high gain of ten million at room temperature, decreasing to 100 at 535 °C.

The use of UV sensitive GaN detectors will largely simplify the design of the spectroscopic monitoring equipment by substituting for the current Si photo-detectors, which require bulky band filters. GaN based photo-detectors also attract attention in monitoring gas combustion, where UV emission is a normal phenomenon.\cite{7}

Wide band gap nitrides can also find applications in the field of digital information storage. Significant gains in recording density can potentially be achieved by using GaN-based lasers that operate at shorter wavelength(s). The nitride-based materials system, when adapted to semiconductor laser in blue and UV wavelengths, offers a storage capacity of 27 GB on 5 inch single sided discs.
2.2 MOCVD AND ELO PROCESSES

Almost all III-V semiconductors and most of their alloys have been successfully grown using MOCVD. MetalOrganic Chemical Vapor Deposition (MOCVD) is a form of non-equilibrium CVD technique utilizing vapor transport of the precursors and subsequent reactions of metalorganic compounds and group-V hydrides in a heated zone. Alternative names include OM (Organo Metallic) CVD, MOVPE (Vapor Phase Epitaxy), and OMVPE. All mean essentially the same, except epitaxy is a special case of thin film deposition where the layer replicates the crystal structure of the substrate. \(^{[13]}\)

The overall MOCVD reaction describing the GaN deposition process is

\[
\text{Ga(CH}_3\text{)}_3(g) + \text{NH}_3(g) \rightarrow \text{GaN(s)} + 3\text{CH}_4
\]

The specific reaction path and reactive species are largely unknown. The main pathway controlling the GaN growth is still unknown and is believed to be the pyrolysis and diffusion of TMG through the boundary layer. Some possible parasitic side reactions will also decrease the growth rate. Much work is needed to understand the fundamentals of this crystal growth process.

High dislocation density is known to limit both the efficiency and lifetime of high-current GaN devices. \(^{[14]}\) ELO is used for defect reduction in GaN thin films. This technique has been employed previously to fabricate new microelectronic devices with better performance in Si, \(^{[15]}\) GaAs, \(^{[16]}\) and InP \(^{[17]}\) semiconductor materials. Studies have shown that threading dislocation density can be reduced by 3-4 orders of magnitude in the ELO film grown on Si (111) substrates compared to the traditional growth methods using MOCVD technique. \(^{[18]}\) ELO is expected to open a new and useful field in crystal growth.
Figure 2-1 is a schematic diagram showing the ELO of a GaN layer on a SiO$_2$ mask deposited with striped window openings on a substrate. The ELO GaN is obtained by performing a regrowth on a conventional GaN layer that is partially masked by an amorphous layer such as SiO$_2$. The basic concept of the process is to reduce defect propagation in masked regions of the substrate where the laterally overgrowing GaN is defect free.

![Figure 2-1](image)

There are various factors influencing epitaxial growth and the quality of the resulting films. These include parameters such as the rates of impingement of species, growth temperature, surface migration rates of reactants, the bond strengths and bond lengths of the substrate and overgrowth atoms, and the nucleation processes. Depending on the importance of these parameters, heteroepitaxial growth can take place under different modes which may be classified under three main categories: Frank-van der Merwe (FvdM) or layer-by-layer two-dimensional growth, Volmer-Weber (VW) or three-dimensional island growth, and Stranski-Krastinov (SK) or layer-by-layer plus island growth.
growth, as shown in Figure 2-2. These are the three structures observed when material is deposited onto a crystalline substrate under conditions with large surface mobility. The growth modes will determine the formation of the nucleation layer for GaN growth.

![Figure 2-2 Schematic representation of the Frank-van der Merwe (FvdM), Volmer-Weber (VW), and Stranski-Krastinov (SK) growth modes for thin films.]

### 2.2.1 Substrates

GaN has been grown epitaxially on a variety of substrates such as silicon, spinel, silicon carbide, and various crystallographic orientations of sapphire. The relevant properties of GaN and AlN with those of the most popular substrate materials are compared in Table 2-2.

There is no ideal substrate material that is well lattice and thermally matched to GaN. Growth of GaN on foreign substrates is typically three-dimensional, which leads to rough surface morphology. Researchers have come to favor basal plane sapphire as the substrate of choice; however, substrates such as SiC, MgO, and ZnO, which have superior thermal and lattice matches to the nitrides, are increasingly available.

The crystal quality of GaN grown on silicon is still inferior to that of GaN layers.
grown on sapphire substrates. However, there is still much research on the growth of GaN on the silicon substrate because of its wide availability, ease of handling, simple pregrowth cleaning requirements, stability at the elevated temperatures, and low price. As can be seen in Table 2-2, the lattice and thermal mismatch between silicon and GaN is quite large, resulting in considerable strain after postgrowth cooling which limits successful heteroepitaxy. Nevertheless, GaN has been successfully applied on silicon substrates with a suitable buffer layer.

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>Lattice parameters</th>
<th>Thermal conductivity</th>
<th>Coefficients of thermal expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>a = 3.189 Å, c = 5.185 Å</td>
<td>1.3 W/cm·K</td>
<td>5.59 × 10^-6 K^-1</td>
</tr>
<tr>
<td>AlN</td>
<td>a = 3.112 Å, c = 4.982 Å</td>
<td>2.0 W/cm·K</td>
<td>4.2 × 10^-6 K^-1</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>a = 3.08 Å, c = 15.12 Å</td>
<td>4.9 W/cm·K</td>
<td>4.2 × 10^-6 K^-1</td>
</tr>
<tr>
<td>Sapphire</td>
<td>a = 4.758 Å, c = 12.99 Å</td>
<td>0.5 W/cm·K</td>
<td>7.5 × 10^-6 K^-1</td>
</tr>
<tr>
<td>ZnO</td>
<td>a = 3.252 Å, c = 5.213 Å</td>
<td>2.9 W/cm·K</td>
<td>4.75 × 10^-6 K^-1</td>
</tr>
<tr>
<td>Si</td>
<td>a = 5.301 Å</td>
<td>1.5 W/cm·K</td>
<td>3.59 × 10^-6 K^-1</td>
</tr>
<tr>
<td>GaAs</td>
<td>a = 5.6533 Å</td>
<td>0.5 W/cm·K</td>
<td>6 × 10^-6 K^-1</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>a = 4.36 Å</td>
<td>4.9 W/cm·K</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>a = 4.216 Å</td>
<td></td>
<td>10.5 × 10^-6 K^-1</td>
</tr>
</tbody>
</table>

**2.2.2 Buffer Layer**

GaN films are usually grown by a two-step process in which a buffer layer is used. Improvement has been made by introducing an initial buffer layer, especially on silicon
substrates, but also on sapphire, SiC, and GaAs.

Akasaki et al. \cite{20} have studied in detail the role of AlN as buffer layer, reporting that a low growth temperature causes the buffer layer to be amorphous but cover the substrate uniformly. When heating the layer to the normal growth temperature, the AlN crystallizes and provides an excellent template for epitaxy. Later researchers usually have grown GaN of equal or better quality by using GaN buffer layer grown at low temperature. Boo et al. \cite{21} have attempted to use highly oriented polycrystalline hexagonal BN as buffer layer to GaN films on silicon substrates. However, the GaN films grown were polycrystalline.

2.2.3 Pressure

Continuous GaN films cannot be grown under atmospheric pressure according to the study of the effects of the partial pressure of the carrier gas (hydrogen gas) in GaN growth by Sasaki. \cite{22} While under lower pressure, increasing the carrier gas partial pressure will change the morphology of the GaN film from pyramid-like to truncated-pyramid like. However, further increasing the hydrogen gas partial pressure will cause discontinuous island growth and even result in no film growth.

2.2.4 Temperature

Generally, growth rate and crystalline quality increase with growth temperature \cite{19}. The typical growth temperature is 950°C or higher. However, excessively high temperatures (greater than 1200°C) result in significant dissociation of the deposited film. The high growth temperature also causes large temperature gradients in a cold wall reactor, which may cause poor fluid dynamic conditions. Due to the large difference in the thermal expansion coefficient between GaN and the substrates, the stress that
accumulates in the epilayer during the cooling process may cause a very high density of dislocations or even cracks in the epilayer.

Yu et al. [1] studied the MOCVD of GaN on both silicon and sapphire substrates over the temperature range of 370 to 1050 °C. The crystallinity and surface morphology of the films varied with the deposition temperatures. Neibuhr et al. [5] reported the effects of variation of the growth temperature (700 ~ 1000 °C) that shows a weak increase in growth rate with temperature.

2.2.5 V/III Ratio

V/III ratio is a critical parameter for MOCVD of GaN and is intimately related to the chemistry of the process. Understanding of the chemical mechanism can lead to accurate control of film properties and increased reactor efficiencies in the MOCVD of GaN. However, up to now, little is reported about the chemistry involved in this process.

Tarsa et al. [23] investigated the growth-related characteristics (e.g., structure, morphology, etc.) of MBE-grown GaN layers as a function of the V/III ratio during growth. GaN layers grown with a low V/III ratio (N-stable growth) have been found to display a rough, faceted surface morphology and a tilted columnar structure with a high density of stacking faults. In contrast, films grown with a high V/III ratio (Ga-stable growth) displayed comparable structure to the underlying MOCVD-grown template.

Neibuhr et al. [5] reported the effects of variation of the V/III ratio (150 ~ 2500) for GaN growth on sapphire by MOCVD, which shows a distinct effect on the growth rate, i.e., with decreasing V/III ratio, an increasing growth rate was found. Marchand et al. [24] reported the effect of varying V/III ratio on lateral growth rate in a two-step process lateral epitaxial growth of GaN from $<10\overline{1}0>$-oriented stripes to produce vertical
(1120) sidewalls. The growth is initiated at a low V/III ratio, and is subsequently raised to get high lateral growth rate.

### 2.2.6 Nitrogen Source Precursors

So far, ammonia is the most commonly used nitrogen precursor in GaN layer growth with MOCVD technique. However, due to the decomposition of ammonia at the high growth temperatures, very high V/III ratios (~$1 \times 10^4$) are usually required to provide enough active species to achieve suitable epilayers. Many efforts have been made to replace ammonia with other nitrogen precursors.

Linnen et al. [25] have reported the successful use of HN$_3$ as in the low temperature deposition of GaN. Precursors like hydrazine (N$_2$H$_4$) or dimethylhydrazine have been proposed as alternative sources to ammonia. [26] The disadvantages of these precursors are their toxic nature as well as carbon incorporation into the resulting films. Beside these compounds, it is also possible to grow GaN films using single source precursor without an additional nitrogen source. The azides such as [(C$_2$H$_5$)$_2$GaNH$_2$]$_3$ have been already used successfully to grow GaN by Park et al. [27] Devi et al. [28] also reported the growth of GaN thin films using a single source precursor, bisazido-dimethylaminopropyl-gallium (BAZIGA), in a cold wall horizontal CVD reactor. The GaN films grown have a structural quality that is reasonable close to the materials grown with the standard process.

### 2.2.7 Other Factors for Epitaxial Lateral Overgrowth

There are several other factors influencing ELO processes besides the above introduced factors that affect general MOCVD processes. The manipulation of these factors will determine how the initial growth features converge and coalescence into
continuous films, which has a direct effect on optical quality and uniformity of the resulting film.

(a) Mask Opening Types for ELO

Growth from stripe openings allows the study of orientation-dependent lateral growth without favoring the development of slow growth facets. The stripes can be parallel or in a star patterned shape. \[^{29}\]

There is also research using hexagonal openings. Haffouz et al. \[^{3}\] studied the hexagonal opening patterns in the mask (used as a pattern for the study) achieved by photolithography and dry etching techniques. Gibart et al. \[^{30}\] have investigated GaN overgrown from hexagonal openings.

Rectangular openings are commonly adopted when using selective area lateral epitaxial overgrowth (SALEO). Using square mask pattern windows surrounded by a SiO\(_2\) mask, Shibata et al. \[^{31}\] studied the epitaxial overgrowth of GaN upon the hydride vapor phase epitaxy growth (HVPE) conditions, and growth direction, rectangular window area shape change.

Using a sub-micron SiO\(_2\) dot pattern fabricated by laser holography, Matsushima et al. \[^{32}\] realized a sub-micron GaN structure with selective area growth using MOVPE.

(b) Stripe Orientations

Marchand et al. \[^{33}\] have grown stripes of ELO GaN aligned along the GaN \(<1\overline{1}00>\) direction by low pressure MOCVD. The stripe morphology is reported to be dependent on the growth temperature as well as on the pattern geometry.

Hiramatsu et al. \[^{34}\] studied the effects of growth parameters on the epitaxial lateral overgrowth via low pressure MOCVD for the ELO GaN on different directions of SiO\(_2\).
stripes along the GaN $<1\overline{1}20>$ and $<1\overline{1}00>$ directions. For the stripes along $<1\overline{1}00>$, decreasing the reactor pressure has similar effects on the ELO GaN structures as increasing the growth temperature. For the stripes along $<1\overline{1}20>$, the shapes were found independent of the reactor pressures as well as the growth temperatures.

Kapolnek et al. \cite{35} reported the orientation-dependent selective epitaxy of GaN and the effect of growth parameter variation on the lateral (in-plane) growth rate anisotropies. The orientation dependence of GaN growth rates was studied using a large star pattern. This pattern consists of mask opening line pairs oriented at different values of degree rotational increments.

(c) **Coalescence Bridge (Void Area)**

Hiramatsu et al. \cite{34} reported the existence of triangular voids on the SiO$_2$ mask of trapezoidal shape from the cross-sectional TEM image of the ELO layer on the $<1\overline{1}00>$ line pattern and its magnified image. It was believed that the void comprises energetically more stable facets than an interface between GaN and SiO$_2$ where the void does not occur. Kawaguchi et al. \cite{36} did not observe the triangular voids in the SAG-GaN grown by MOVPE on a tungsten mask. It is not clear at present why these differences occur.

(d) **Ambient Gas Effect**

To date, the effect of ambient gas remains unclear. Tadatomo et al. \cite{37} investigated the effects of hydrogen gas, nitrogen gas and their mixture on the ELO of GaN via atmospheric MOVPE. In hydrogen ambient, the ELO-GaN with a smooth surface was obtained using the $<1\overline{1}00>$ stripe pattern, but the layer became rough on the $<1\overline{1}20>$ stripe pattern. In nitrogen ambient, the lateral overgrowth rate was very fast, but it was difficult to realize a smooth ELO layer surface. The fast lateral overgrowth rate and the
smooth surface were simultaneously achieved by using a mixture ambient.

(e) Techniques for Masking and Openings

The most commonly used masking material is silicon dioxide, though there are studies using different masking materials.\cite{36} Various methods exist to prepare SiO$_2$.\cite{38} Plasma enhanced chemical vapor deposition (PECVD) and electron beam evaporation are the commonly used methods. The samples deposited with a silicon dioxide film are patterned by standard photolithography or laser holography. Wet chemical etching method is commonly applied to etch the oxide to leave an oxide mask outside the growth area using the buffered oxide etchant (BOE).
2.3 Characterization

Characterization analysis is required to fully understand the properties of the films and the effects of changes in the growth parameters. A large number of analysis techniques can be used for this purpose, each of which usually offers information on only one aspect of the materials properties.

2.3.1 Optical Characterization

(a) Scanning Electron Microscopy (SEM)

The surface of the specimen is scanned with an electron beam that causes the emission of electrons and X-rays. These emitted electrons are collected and used to produce an image on a cathode ray tube. The SEM may be used in the electron beam induce current (EBIC) mode to look at variation in the current flowing in various parts of the sample. This highlights the presence of extended defects and other leakage paths, a particularly useful feature for examining heteroepitaxial material.

(b) Photoluminescence (PL)

Photoluminescence spectroscopy is a non-contact, non-destructive method of examining the electronic structure of semiconductors. The sample is illuminated with light of wavelength appropriate for exciting transitions of carriers from band-to-band, or from impurities in the material to either band. The absorbed light imparts excess energy into the material and causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released by the sample through the emission of light called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties.
Selective photoluminescence (SPL) has been demonstrated to be a powerful tool to study localized and extended states in finite band gap semiconductors, in particular, by evidencing the excited states or vibrational spectra of impurities and defect centers \cite{40}.

2.3.2 Structural Analysis

(a) X-ray Diffraction (XRD)

X-ray diffraction provides a measure of the substrate orientation and of the average quality of the epilayer by the analysis of the angular position and intensity of x-rays diffracted from the sample.

(b) Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is usually used to measure film thickness. IR spectra are collected on a spectrometer using unpolarized light with a reflectance angle of zero degree from the normal.
3. OVERVIEW OF CVD MODELING

3.1 MOTIVATION AND GOAL OF THIS RESEARCH

CVD modeling is now recognized to be an essential and integral part of CVD research. In this research, we focus on the MOCVD system that is located at Ohio University. This CVD system is designed for depositing gallium nitride from trimethylgallium and ammonia.

Instead of attempting to model the overall behaviors of this system by considering all constituent physical mechanisms, the goal of this research was to develop a simplified but accurate, multi-dimensional transport model that is capable of describing the observed reactor behavior and can be used to improve the operating parameters. Different reactor configurations were studied and the results were used in designing the inner tube type of the reactor. The effects of susceptor rotation speed and the ammonia flow rate were also studied to give guidance and reference for determining experimental operating parameters.

3.2 LITERATURE REVIEW

Chemical vapor deposition process characteristics are determined by many factors related to hydrodynamics and chemical kinetics. Optimizing and improving the CVD process is often expensive and time consuming. Computer simulation of CVD processes offers the possibility of a deeper understanding of underlying physicochemical processes leading to a systematic approach to reactor and process design. The use of these models in reactor design and process optimization will greatly reduce the time and expense.

CVD modeling began to receive broad attention in the early 1980s. Although considerable progress has been made in the development of mathematical models for
CVD reactors, computation of film growth rates and material properties is limited by the lack of knowledge of the gas-phase and surface chemistry. Accurate description of the chemistry in CVD processes requires hundreds of elementary chemical reactions. By studying the CVD process from various aspects, the CVD models are becoming more and more commonly used to improve reactor designs and process characteristics.

In this section, a short survey of the published CVD equipment modeling studies is given.

### 3.2.1 Fundamentals of CVD Processes

Chemical vapor deposition is the formation of a film on a surface from a volatile precursor (vapor or gas) as a result of heterogeneous chemical reactions that change the state of the precursor. Homogeneous gas-phase reactions also take place, either preceding, parallel to, or in competition with the heterogeneous surface reactions.

A CVD process is the combination of fluid transport phenomena and chemical reaction kinetics, particularly in the gas-phase near the gas/wafer interface and on the wafer surface. The major transport and reaction sequences that generally occur during a deposition process are summarized as follows,

1. Chemical reactions in the gas-phase from reactants that generate new reactive intermediates and byproducts;
2. Convective and diffusive transport bringing the gas species to the wafer surface;
3. Adsorption and/or chemisorption of those gas species on the wafer surface;
4. Heterogeneous surface reactions on the surface, leading to the solid film formation, initiated by the high wafer temperature;
5. Desorption of gaseous products resulted from the surface reactions;
6. Convective and/or diffusive transport of reaction products away to bulk gas-phase.

Various configurations have been employed for chemical vapor deposition. Two commonly used CVD reactor designs are shown schematically in Figure 3-2 and 3-3. The horizontal reactor in Figure 3-2 is mostly used in research and in compound semiconductor epitaxial growth. The vertical reactor in Figure 3-3 is usually operated with a single wafer on a rotating susceptor.

Figure 3-1 Schematic representation of basic steps in CVD\textsuperscript{[41]}

![Figure 3-1 Schematic representation of basic steps in CVD](image-url)
3.2.2 Flow Regime

Horizontal duct reactors are commonly used for the evaluation of comprehensive CVD models. Jensen and coworkers \cite{42} characterized the general flow properties roughly with the Reynolds number and the Grashof number. The growth rate in horizontal ducts decreases exponentially along the flow direction.

Axisymmetric vertical reactors are also widely used for epitaxial growth at near-atmospheric pressures. In vertical reactors, the susceptor surface is usually rotating to average out small asymmetries in the reactor and the flow. The gases are introduced to the reactor either at the top of the reactor or from below. At high rotation rates (100–1000rpm), the rotating susceptor has a strong pumping effect on the flow conditions in the reactor. Figure 3-4 shows the basic flow regimes \cite{43} in vertical rotating disk CVD reactors. The three flow regimes are dependent on the inlet flow and susceptor rotation rate. For very low inlet gas flow and low susceptor rotation rate, the buoyancy effects are dominant. If the inlet gas flow is very high, it can strongly influence the flow in the reactor. Susceptor rotation at high rates can induce recirculation zones at the edge of susceptor.
Reaction mechanism plays an important role in epitaxial deposition processes in vertical reactors and the film growth rate is usually determined by transport limitations of the reactive species on the susceptor surface. Thermal diffusion is also an important issue.

The first two-dimensional simulation of a vertical CVD reactor was performed with a finite volume numerical technique by solving the flow equations in stream function vorticity formulation for a stagnation flow/impinging jet configuration.\[44\]

Due to the inefficient use of expensive precursor gases and limited pump capacity, high gas flow rates are not desirable to operate chemical vapor deposition reactors. A general preference has developed for the use of laminar flow conditions in the operation of CVD reactors. However, some studies on cold wall CVD reactors show that buoyancy effects can cause turbulence. Giling\[45\] reported the gas flow pattern and temperature profiles in horizontal CVD reactors with heated susceptor at the bottom wall and a cooled top wall. An unstable turbulent boundary layer on top of a stable laminar boundary layer was demonstrated by using the interference holography method.
Using the large eddy simulation technique, Santen et al.\cite{46} simulated the turbulent flow caused by the buoyancy effect inside a cold wall vertical rotating disk reactor. The simulation result of the instantaneous temperature distribution and flow field is shown in Figure 3-5. Crystal growth kinetics and radiative heat transfer were not included in the modeling. Whether or not such buoyancy inducing turbulence effect is favorable to film growth in CVD processes still needs further study.

![Figure 3-5 Instantaneous temperature field and projection of the velocity field in a horizontal cross-section at dimensionless height 0.3 above the wafer](image)

### 3.2.3 Chemistry

Although several essential features of the GaN growth have been studied experimentally and numerically modeled, it is still not possible to give a complete reaction model of GaN growth based on studies published in the literature.
For the GaN growth by MOVPE in a horizontal tube reactor, the modeling proposed by Karpov and coworkers\textsuperscript{[47]} includes the following heterogeneous reactions:

\begin{align}
\text{TMG(g)} + \text{NH}_3(g) & \rightarrow \text{GaN(s)} + 3\text{CH}_4(g) \quad (3-1) \\
\text{MMG(g)} + \text{NH}_3(g) & \rightarrow \text{GaN(s)} + \text{CH}_4(g) \quad (3-2) \\
2\text{GaN(s)} & \rightarrow 2\text{Ga(g)} + \text{N}_2(g) \quad (3-3) \\
2\text{Ga(g)} + \text{H}_2(g) & \rightarrow 2\text{GaH(g)} \quad (3-4) \\
2\text{NH}_3(g) & \rightarrow \text{N}_2(g) + 3\text{H}_2(g) \quad (3-5)
\end{align}

The gas species include the precursors gases TMG (trimethylgallium) and NH\textsubscript{3}, the carrier gas H\textsubscript{2}, and the products of TMG decomposition – MMG (monomethylgallium) and CH\textsubscript{4}. Figure 3-6 shows a comparison between theoretically predicted and experimentally measured GaN growth rate. This model by Karpov, et al.\textsuperscript{[47]} didn’t predict growth rate accurately below 600 °C. Also for temperature above 1100 °C, the model was not verified. It is also reported the ammonia decomposition on GaN surfaces are non-equilibrium as compared to thermodynamic expectations.\textsuperscript{[26]} This model did not include the important adduct formation kinetics between TMG and NH\textsubscript{3}. Reactions (3-1), and (3-2) are heterogeneous reactions with two gaseous species reactants, which are very unlikely in practice. No radiative heat transfer modeling was reported.

The adduct formation reaction between TMG and NH\textsubscript{3} reaction was studied only by few groups, and the results are often contradictory. The relative contribution of the reaction to the GaN growth is not clearly understood because of very little kinetics data and knowledge on the nature of adduct-derived species.
The reaction between TMG and NH$_3$ was experimentally studied by Thon et al.\(^{[48]}\) at high temperature (100-800 °C) by means of in situ mass spectroscopy in an isothermal flow tube reactor. The study indicated that almost no TMG exists in the growth environment under most MOCVD growth conditions (1-760 torr). The main gas-phase species is [(CH$_3$)$_2$Ga:NH$_2$]$_3$, which is resulted from the adduct formation followed by elimination of methane. The process can be described by the following reactions.

\[
\text{Ga(CH}_3)3 + \text{NH}_3 \rightarrow (\text{CH}_3)_3\text{Ga:NH}_3
\] 

\[
3(\text{CH}_3)_2\text{Ga:NH}_3 \rightarrow [(\text{CH}_3)_2\text{Ga:NH}_2]_3 + 3\text{CH}_4
\]

The principal mechanism is believed to be decomposition of [(CH$_3$)$_2$Ga:NH$_2$]$_3$.

Bergmann et al.\(^{[49]}\) also studied the reactions between TMG and ammonia in a heated flow tube reactor. The gallium- and nitrogen-containing intermediates were detected with the isotopic distribution in the mass spectra obtained from the experiments. It was reported that the oxygen contamination in GaN films was possibly caused by the small amount of water presenting the ammonia (99.98%).
Theoretical research on the adduction reactions was performed by Watwe et al. \cite{50} by the use of quantum chemical calculations employing density functional theory techniques. The research identified the reactive intermediates and reaction pathways. The changes in electronic energies, enthalpies, standard state entropies and standard state Gibbs free energies for the formation of the intermediate species were also reported.

Sun et al. \cite{51} proposed a kinetic model comprised of five gas-phase reactions to model the GaN growth process in a vertical MOCVD cold wall reactor. The surface reactions were assumed to be very rapid and deposition processes were assumed diffusion-limited. The gas-phase reactions included adduct formation, decomposition, oligimerization and dissociation, which were believed to be the four main growth pathways that determine the nature of the growth. The model is shown in Table 3-1.

<table>
<thead>
<tr>
<th>Reaction Steps</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adduct formation</td>
<td>$\text{TMG} + \text{NH}_3 \rightarrow \text{TMG:NH}_3$</td>
</tr>
<tr>
<td>Decomposition</td>
<td>$\text{TMG:NH}_3 \rightarrow \text{TMG} + \text{NH}_3$</td>
</tr>
<tr>
<td></td>
<td>$\text{TMG:NH}_3 \rightarrow \text{DMGNH}_2 + \text{CH}_4$</td>
</tr>
<tr>
<td>Oligimerization</td>
<td>$3\text{DMGNH}_2 \rightarrow \text{TGNCY}$</td>
</tr>
<tr>
<td>Product of oligimer decomposition</td>
<td>$\text{TGNCY} \rightarrow 3^<em>\text{Ga-N}^</em> + 6\text{CH}_4$</td>
</tr>
</tbody>
</table>

*DMGNH$_2$ symbols (CH$_3$)$_2$Ga:NH$_2$ and TGNCY [(CH$_3$)$_2$Ga:NH$_2$]$_3$.

The modeling study was performed using the multi-purpose computational fluid dynamics software, CFD-ACE™. The simulation shows that a high temperature flow zone exists above the growth front, inside which a chemically stratified gas-phase structure is formed. The growth rate data obtained under the modeled growth conditions are in qualitative agreement with the modeling results. The modeling of surface reactions
is not sufficient to describe the film growth process. Furthermore, the model didn’t include radiative heat transfer.

Pawlowski et al. [52] reported another fundamental reaction-transport model describing the MOVPE of GaN from TMG and ammonia. The proposed reaction mechanism includes six gas-phase reactions and seven gas-surface interactions leading to stoichiometric film growth. Some reaction parameters are estimated from kinetic collision theory. The model has been tested against experimental data from research scale and industrial scale reactors. The model was found to slightly over-predict the growth rates but it could capture accurately all observed variations of growth rate with temperature in the region where GaN films are typically grown.

Theodoropoulos et al. [53] used the same kinetic model to study the effect of inlet design and reactor operating conditions in axisymmetric vertical stagnation flow and rotating disk reactors. The growth rate variations over the substrate were studied under different design and operating parameters. The simulation gives the optimal cases which lead to uniform films over the substrates. Neither research included a simulation of the radiative heat transfer. Much research activity is needed in the scale-up and understanding of the mechanisms of gallium nitride growth by MOCVD.

3.2.4 Heat Transfer

Unlike the conduction and convective heat transfer, the energy of radiative heat transfer is carried by photons. Figure 3-7 shows the electromagnetic wave spectrum. For thermal radiation the wavelengths are between 0.1µm and 100 µm. The complete treatment of radiation can be extremely complex, since photons can reflect off multiple
surfaces and follow complex paths. Various assumptions have been made to model radiative heat transfer.

![Figure 3-7 Electromagnetic wave spectrum](image)

Accurate calculation of the temperature field in CVD reactors is extremely important. The most complex part of the heat transfer modeling in CVD reactors is the radiative heat exchange inside the reactor chamber between reactor walls, wafers, and heated susceptors. The analysis may become even more complicated when dealing with three-dimensional reactor geometries, and the spectral and temperature dependence of the optical properties of materials such as silicon and quartz.

Durst et al. [54] presented a numerical approach for studying the effect of radiative heat transfer in the epitaxial growth of GaAs in a horizontal MOCVD reactor. The models also included the simulation of thermal diffusion and chemical reactions. The
radiative heat transfer was coupled with convection and conduction heat transfer by
assuming a non-participating medium and semi-transparent gray-diffusive quartz walls.
The temperature distribution predicted by the two-dimensional model achieved a good
agreement with experimental temperature measurements.

However, the gray-diffusive approximation for the quartz walls is very coarse
considering that the absorption coefficient of quartz is not constant with different
wavelength regions. A three-band modeling of the absorption coefficient of quartz walls
was presented by Kadinski et al.\textsuperscript{[55]} Using the model, a numerical study of the radiation
heat transfer was conducted in a horizontal CVD quartz reactor. The three-band model
can describe the change of radiative properties of the reactor wall due to the formation of
the deposits on wall surface. The value of the emittance and reflectance are calculated in
each wavelength band on the wall surfaces. The upper wall temperature distribution was
found to be influenced by the film deposited on the surface of the reactor wall and
susceptor.

Durst et al.\textsuperscript{[56]} further developed a 14-band model for a more accurate modeling of
radiative heat transfer in the same horizontal CVD reactor geometry used in Kadinski’s
research. The effect of radiative heat transfer on the upper wall temperature and the
formation of thin films of GaAs have been studied in detail. The multi-band model was
used because of the strong interference phenomena, which occur when monochromatic
radiation passes through a thin film and the radiative properties are oscillation functions
of the wavelength and the film thickness. It is shown that the interference phenomena in
the GaAs layer deposited on the reactor upper wall leads to a significant decrease of the
wall temperature, which slows down the GaAs deposition rate on the wall.
A simulation of two types of commercial CVD reactors, AIX 200 and AIX 2000 planetary reactor™, was performed by Talalaev, et al. [57] The global transport model for the MOVPE of InGaN growth includes detailed radiative heat transfer, multi-component diffusion and homogeneous and heterogeneous chemical reactions. The modeling is validated experimentally and used for process improvements. It was shown that the model described the growth process with a reasonable agreement with the experimental data at lower gas-phase composition of TMIn. However, disagreement between theory and experiment became significant at higher TMIn compositions.
4. EXPERIMENTS AND RESULTS

The process of the epitaxial lateral overgrowth (ELO) of GaN has been experimentally investigated. In the ELO process, a layer of GaN layer was first grown on silicon substrate using MOCVD. The effect of different V/III ratios on film growth in this growth step was studied. In the regrowth step, different buffer layers were used to get epitaxial lateral overgrown GaN. The objective of the ELO experiments was to determine which buffer layer was suitable for GaN regrowth. The GaN films were characterized by various methods.

4.1 PROCESS OF EPITAXIAL LATERAL OVERGROWTH OF GaN

In this section, the general experimental parameter setup is given as well as the description of the experiment procedure.

4.1.1 MOCVD System Configuration

The MOCVD system at Ohio University is a commercial system fabricated by CVD Equipment Corporation. The system consists of a gas handling system, the CVD reactor, computer control system, MO sources supplies, and exhaust system. Figure 4-1 is an overview of the MOCVD system and Figure 4-2 is a close-up view of the CVD reactor.

![Figure 4-1](image_url)

**Figure 4-1** Basic structure of the MOCVD system
The CVD reactor is of vertical rotating-disk, cold-wall and single-wafer type. The substrate wafer is supported by a rotating 1 inch diameter molybdenum susceptor to assure the symmetry of the deposited film. The susceptor is set on the top of a hollow quartz shaft which is driven by a motor to rotate the susceptor during operation. Radio frequency (RF) inductive heating is used to heat the susceptor to growth temperatures. The susceptor temperature is measured by a thermocouple embedded within the top of the hollow shaft. The thermocouple wires are inside the hollow shaft. The reactor wall is made of quartz and is water-cooled by a water chiller.

A closed loop vacuum control system enables the reactor to be operated over a
pressure range of 10–760 torr. A high vacuum load lock is interfaced to the reactor tube to isolate the tube from the ambient environment during wafer loading and unloading operations.

The gases can be fed to the reactor from two inlets. A gas mixture of group-III precursor (trimethylgallium or trimethylaluminum) carried by hydrogen gas and ammonia enters the reactor chamber through the top inlet. A nitrogen gas flow is input to the reactor through the side inlet if an inner tube is used in the reactor configuration. This nitrogen gas flow is called tube purge flow and is to prevent unwanted depositions on the reactor walls.

The carrier gas, hydrogen, is purified using a hydrogen purifier at 400°C after removing of oxygen and moisture. Nitrogen, used as a purge gas and backfill gas, and ammonia, the nitrogen precursor, are purified using a Nanochem activated resin before entering the system. The temperature of the trimethylgallium and trimethylaluminum bubbler is set at -6 °C and 25 °C, respectively, by separate temperature-controlled baths. A hydrogen push flow is applied to push the group-III precursors entrained by the carrier gas before entering the reactor. The group-III and group-V precursors mix with each other just before entering the reactor.

Although sapphire is the most commonly used substrate, (111) silicon wafers were used as substrate in this study because it has been less thoroughly investigated experimentally, but is actually more desirable due to its low price and easy availability.

4.1.2 MOCVD Growth Parameter Setup

The system operation is done by using an editable multi-step operating recipe. The recipe defines processing sequences including the choice of reactant gases, gas flow rates,
chamber pressure, and wafer temperature setpoints, etc. Recipes are created and edited by CVDEDIT program and executed by CVDPRC program. The controlling parameters of susceptor rotation, load lock evacuation and backfill, and metalorganic compounds bubblers are set on the control panel of the equipment. The growth process can proceed automatically by running the recipe after the growth parameters are correctly set up.

4.1.3 Reagents and Materials

- Acetone, semiconductor grade (Alfa Aesar)
- Ammonia, 99.99994% (AGA Gas, Inc.)
- Buffered oxide etchant 100:1 (ATMI Materials Inc.)
- Deionized water, resistivity 18.3 MΩ (Department of Chemical Engineering at Ohio University)
- Hydrogen gas, 99.999% (AGA Gas, Inc.)
- Nitrogen gas, 99.995% (AGA Gas, Inc.)
- Silicon substrates: Si (111) n-types (Virginia Semiconductor, Inc.)
- Silicon dioxide, fused, pieces, <4mm, 99.99% (Fisher Scientific Inc.)
- Trimethylgallium, 99% (Polishing Corp of America)
- Trimethylaluminum, 98% (Polishing Corp of America)

4.1.4 Experiment Methods

In this section, the experimental procedure is described for the epitaxial lateral overgrowth of GaN in this study.

(a) Substrate Preparation

A simple method was used to clean the silicon substrate by putting it in a hot bath of acetone solution for about 4 minutes and rinsing with deionized water. This cleaning of
substrate is done before loading it in the reactor. The substrate is further cleaned in the reactor prior to growth with a hydrogen flow at 1040 °C for 20 to 40 minutes to remove oxides on the substrate surface.

(b) Growth Conditions of GaN

The GaN epilayers were grown under various conditions in the MOCVD reactor. The detailed operating procedure for the MOCVD system is listed in the appendix section.

Two types of buffer layers were used: low temperature grown GaN (650 °C) and high temperature grown AlN (1040 °C). The ammonia flow rate is from 0.4 to 0.9 slpm. The growth temperature changes from 650 to 1040 °C. The growth pressure, TMG flow rate, and growth time are fixed at 76 torr, 2.1 µmol/min, and 45 minutes, respectively. The susceptor rotation speed is set to 70 rpm. The hydrogen flow rate is 1.0 slpm. The nitrogen flow enter from the side inlet is set to be 0.2 slpm.

(c) Masking and Patterning

Silicon dioxide masks were used in the selective growth. Thin layers of SiO$_2$ were deposited on MOCVD GaN seeding layers by electron beam evaporation method using MDC e-Vap 4000 electron beam evaporation System. The SiO$_2$ mask layer thickness is 100~200nm.

The patterning of the SiO$_2$ film was achieved using standard photolithography techniques and etching with buffered oxide etchant. A positive photoresist AZ5206 was first deposited on the SiO$_2$ deposited wafer. The wafer was spun at 4000 rpm which spreads the photoresist into a uniform layer about 0.6 µm thick. The photoresist coated wafer is exposed to single wavelength UV light passing through a reticle. After exposure, wafers are dipped in developer solution to remove the exposed areas of
photoresist. Once the exposed photoresist is removed, the wafer is baked at a temperature of 100 °C to harden the remaining photoresist.

The reticle used in the photolithography experiments is an optically clear quartz substrate with a chrome pattern. Figure 4-3 shows the patterning of the wafer surface after photoresist baking. The pattern contained 4 µm wide stripe openings spaced with 6 µm distance and oriented along the GaN $<1 \bar{1} 00>$ direction. This is done by aligning the stripe direction perpendicular to the $<1 \bar{1} 0>$ direction indicated by the silicon wafer flat. The method is based on the fact that wurzite GaN layers formed on Si (111) substrate takes the crystalline relationship of GaN $<0001>||$ Si$<111>$ and GaN $<11\bar{2}0>||$ Si $<1 \bar{1} 0>$. [58]
Buffered oxide etchant (BOE) 100:1, prepared from hydrofluoric acid buffered with ammonium fluoride, was used to remove silicon dioxide without etching away the underlying GaN layer. The photoresist is removed from the wafer using acetone.

(d) Epitaxial Lateral Overgrowth of GaN

The second growth of GaN by MOCVD is performed to obtain the epitaxial lateral overgrowth of GaN onto the SiO\textsubscript{2} film on the initial grown GaN (occurring only on the window areas).

4.1.5 GaN Film Characterization

The following characterization techniques will be used to examine the quality of the GaN films.

(a) X-ray Diffraction (XRD)

X-ray diffraction was performed using a Rigaku Geigerflex DMAX-B powder x-ray diffractometer. The diffraction pattern in the θ-2θ scan is used to identify the components and crystal orientation of the epitaxial film. The structural quality of the films is determined by the full width at half maximum of the x-ray rocking curve for the GaN (0002) peak.

(b) Scanning Electron Microscopy (SEM)

Morphology of the film was characterized using JSM-5300 scanning electron microscope.

(c) Fourier Transform Infrared Reflectance (FT-IR)

Film thickness is measured by FT-IR experiments using Perkin-Elmer Spectrum 2000 spectrometer. The film thickness is calculated by
\[ d = \frac{\Delta m}{2(v_1 - v_2)\sqrt{n^2 - \sin^2 \theta}} \]  

(4-1)

Where:

- \( d \) — film thickness
- \( \Delta m \) — the number of fringes in the frequency interval
- \((v_1 - v_2)\) — the frequency interval
- \( n \) — refractive index
- \( \theta \) — the angle of incidence

(d) Photoluminescence (PL)

Photoluminescence was carried out to characterize the optical properties of the grown films. Photoluminescence was excited by a He-Cd laser beam and captured by a Princeton Instruments TEA-CC-512 TK back illuminated charge coupled device (CCD) with a UV/AR coating.

4.2 EXPERIMENTAL RESULTS AND DISCUSSION

A comparative study of GaN seeding layers grown on (111) silicon substrate with AlN buffer layer and epitaxial laterally overgrown GaN layers on the seeding layers by MOCVD is presented. Results for specific samples are discussed in this chapter.

4.2.1 GaN Seeding Layers

The investigation of the crystal structure and film orientation of the seeding layers is given by the analysis of \( \theta-2\theta \) scan of x-ray diffraction spectra and the value of the full width at half maximum (FWHM) for the GaN (0002) peak from the x-ray rocking curve spectra of GaN films. For wurtzite GaN, screw dislocations with a Burgers vector \(<0001>\) result in a tilt of lattice planes, which in turn reflects itself in the FWHM
values. The GaN films are deposited by MOCVD at different V/III ratios with similar other growth conditions.

Figure 4-4 shows the results of a GaN film grown by MOCVD at 1040 °C on (111) silicon substrate with a high temperature AlN buffer layer. The growth pressure is 76 torr. The thickness of the AlN buffer layer is 50nm. A V/III ratio of 11000 and susceptor rotation speed 70 rpm were used in the MOCVD process.

As one can see, the film shows strong XRD peaks that are attributed to GaN (0002) at a 2θ angle of 34.5°, and GaN (0004) at a 2θ angle of 73.0°. This indicates the film is single crystal because the GaN grows only in single c-axis orientation in alignment with the orientation of the underlying AlN buffer layer. There are also other peaks which are attributed to Si (111) at a 2θ angle of 28.3°, and AlN (0002) at a 2θ angle of 36.1°, respectively. This film is designated as sample A.

\[ \text{Figure 4-4 XRD 0-2θ scan results of sample A} \]
The XRD $\theta$-2$\theta$ scan results for two other films are grown under different V/III ratios with other growth conditions unchanged are shown in Figure 4-5 and Figure 4-6. The films also show strong XRD peaks that are attributed to GaN (0002) and GaN (0004) as indicated in the figures, which indicate the films are also single crystal. For the film grown at V/III ratio of 7600, a Si (222) peak can be identified at a $2\theta$ angle of 58.5° from the spectrum. A peak of AlN (0004) can also be identified at a $2\theta$ angle of 76.7°. For the film grown at V/III 15000, there are also the peaks that are attributed to Si (222) and AlN (0004). The silicon peaks are stronger compared with the XRD $\theta$-2$\theta$ scan profile of sample A.

Figure 4-5 XRD $\theta$-2$\theta$ scan results of film grown at V/III ratio 7600
Figures 4-7 to 4-9 are the x-ray rocking curves for the GaN (0002) peak of the samples. The full width at half maximum (FWHM) of the rocking curves of sample A and the sample grown at V/III ratio 7600 are 0.61°, and 0.60°, respectively. The FWHM of rocking curve of the film grown at V/III ratio 15000 is larger, 1.0°. The larger FWHM value indicates that the structural quality of the film is not as good as the other two samples.

It can be concluded that the V/III ratio has no significant effect on the film quality in the range of the experiments.
Figure 4-7 X-ray rocking curve of sample A

Figure 4-8 X-ray rocking curve of film grown at V/III ratio 7600
There are also no significant morphological differences among the films. The microstructure and the surface morphology of the films were examined by SEM. Although the films are mirror-like, there are some micro-cracks in the central portion of all the samples. The cracks are induced by the lattice mismatch and the difference of thermal expansion coefficient between the silicon substrate and the GaN layer. As an example, SEM picture of the surface growth morphologies of the central area of sample A is shown in Figure 4-10.
The film thickness was calculated from the IR fringes. The IR reflectance spectrum for Sample A is shown in Figure 4-11.
The radial distribution of the film thickness of sample A is shown in Figure 4-12. The growth rate gradually increases along the radial distance on the substrate. This is the typical feature of the growth rate distribution along the radial distance on film surface for most GaN seeding layers. The growth rate distributions are usually used in validating CVD simulations.

![Growth rate distribution in radial distance on substrate](image)

**Figure 4-12** Growth rate distribution in radial distance on substrate

The photoluminescence spectrum of sample A at 15 K is shown in Figure 4-13. Only a strong yellow band emission is observed. The yellow luminescence is a broad band centered around 589 nm. The cause of the yellow luminescence is attributed to intrinsic crystal defects and to impurities such as carbon, to a Ga-site vacancy and related complexes.
4.2.2 *Epitaxial Lateral Overgrowth of GaN*

Significant improvement in film morphology is achieved by the epitaxial lateral overgrowth (ELO) of GaN. The characterization results of three samples are presented.

The ELO process took place in a rectangular area on the substrate which is composed of parallel stripes of exposed GaN windows separated by stripes of SiO$_2$. The stripes were oriented along the $<1\overline{1}00>$ GaN crystal direction. The common growth conditions of the samples are: growth temperature 1020 °C, TMG flow rate 2.13 µmol/min., V/III ratio 11000, and susceptor rotation 70 rpm. Other ELO conditions of the samples are listed in Table 4-1.

<table>
<thead>
<tr>
<th>Table 4-1 Different ELO conditions</th>
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<tbody>
<tr>
<td>Buffer layer</td>
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<td>---</td>
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<tr>
<td>Seeding layer</td>
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</tbody>
</table>
Figure 4-14 is the SEM picture showing the ELO morphologies of GaN films with a low temperature AlN buffer layer. As one can see, the surface morphology is rough, and the average domain size is sub-µm. The reason for the poor quality of the ELO film is not clearly understood. But it is believed to be related to the poor growth of AlN on the exposed GaN windows.

![SEM image of ELO GaN with AlN buffer layer, sample B](image)

**Figure 4-14** SEM image of ELO GaN with AlN buffer layer, sample B

If a low temperature GaN film is used as buffer layer, the growth morphology of the GaN epilayer grown on top of the buffer layer improves dramatically. The surface of the film becomes much smoother than with an AlN buffer layer. Figure 4-15 shows the SEM image of ELO GaN with a low temperature GaN buffer layer. The GaN growth over the window areas is almost two-dimensional. The lateral side walls, i.e., the GaN (11\(\overline{2}0\)) planes, of the ELO GaN have spread onto the SiO\(_2\) stripes. The lateral overgrowth is completed and the adjacent GaN layers near the centers of the SiO\(_2\) stripes contact.
The morphology of the GaN films grown without buffer layers in ELO processes does not show very smooth and uniform surfaces along the direction of \( <1\bar{1}00> \). But the films are better than those grown with an AlN buffer layer. The SEM picture of Sample D is shown in Figure 4-16.
Figures 4-17 to 4-20 are the XRD \( \theta \rightarrow 2\theta \) scan results and x-ray rocking curves of GaN (0002) diffraction peak for sample C and sample D. For the epitaxial laterally overgrown films not using AlN as buffer layer, only the GaN (0002) and GaN (0004) peaks were observed. The XRD pattern of a GaN film grown on Si (111) along the GaN \(<1\overline{1}00>\) direction clearly displays one intense peak at \(2\theta = 34.4^\circ\), corresponding to the GaN (0002) peak, and a weak peak of GaN (0004). The results suggest that, in this the ELO process, the GaN film is grown with a highly preferred orientation in the \(<0001>\) direction. Compared with the results with the seeding layers, the film quality is improved.

X-ray rocking curves of GaN (0002) peak are used to further analyze the quality of the epitaxial laterally overgrown films. The value of the full width at half maximum (FWHM) from the rocking curve of the epitaxial laterally overgrown GaN film was found to be 0.46° and 0.32° for sample C and sample D, respectively. The values of the
x-ray rocking curves FWHM are smaller than those for the GaN seeding layers. This indicates that the ELO films have better structural properties than their seeding layers.

Figure 4-17 XRD 0-2θ scan results of sample C

Figure 4-18 X-ray rocking curve of sample C
Some cracks were also observed on some ELO samples as shown in Figure 4-21. The shape of the cracks in the ELO samples look quite different from the cracks in the MOCVD process for the seeding layers. The irregular shaped cracks were caused by the
quick heating/cooling process of SiO\textsubscript{2} deposition in the electron beam evaporation process.

![Figure 4-21 Cracks on an ELO GaN film](image)

The PL spectrum of sample C is shown in Figure 4-22. The broad band of yellow luminescence is observed again. There is a band edge emission peak at 359 nm, which is attributed to donor-bound exciton emission.\textsuperscript{[59]} The PL spectrum indicates that the optical property of Sample C is better than its seeding layer, Sample A.
Figure 4-22 Photoluminescence spectrum of Sample C at 12K
5. MODELING THE MOCVD OF GaN

5.1 MATHEMATICAL MODEL

The modeling of chemical vapor deposition processes generally includes the simulation of laminar multi-component ideal gas flow with chemical reactions, heat and mass transfer. Many difficulties need to be overcome to accurately model the CVD process. Some of the main problems are the multi-component nature of the gas mixture, unknown transport properties for less commonly used gases, large temperature gradients, and chemical reactions, etc. In this section, the necessary modeling components and solution steps for developing a complete CVD equipment-process model will be discussed.

5.1.1 Basic Assumptions

As indicated by Kleijn [41], several general assumptions should be made to simplify the modeling problem and the solution computational effort for typical CVD processes.

1. The gas mixture is usually treated as a continuum.
2. For the pressures and temperatures commonly used in CVD, the gases behave as ideal gases that satisfy the ideal gas law and Newton’s law of viscosity.
3. Gas flows in the CVD reactor can be assumed laminar.

5.1.2 Governing Equations

The governing equations represent the transport of mass, momentum, energy and other quantities for a fluid continuum. The equations form a set of partial differential equations.

(a) Balance Equations for Mass, Momentum, Energy

The gas flow in the CVD reactor can be described by the continuity equation and momentum balance equation (Navier-Stokes equation).
\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) \quad (5-1)
\]
\[
\frac{\partial \rho \vec{v}}{\partial t} = -\nabla \cdot (\rho \vec{v} \vec{v}) + \nabla \cdot \tau - \nabla p + \rho \vec{g} \quad (5-2)
\]

where, viscous stress tensor \( \tau \) takes the form
\[
\tau = \mu (\nabla \vec{v} + (\nabla \vec{v})^\top) - \frac{2}{3} \mu (\nabla \cdot \vec{v}) I \quad (5-3)
\]

The above flow equations are coupled to the energy balance equation.

\[
c_p \frac{\partial}{\partial t} (\rho T) = -c_p \nabla \cdot (\rho \vec{v} T) + \nabla \cdot (\lambda \nabla T) + \nabla \cdot \left( RT \sum_{i=1}^{N} \frac{D_i^T}{M_i} \nabla (\ln f_i) \right) \\
\begin{align*}
\text{(Temperature variations)} & \quad \text{(Convective and conduction heat transfer)} & \quad \text{(Heat transfer by Dufour effect)} \\
\text{(species interdiffusion)} & \quad \text{(Heat transfer by species interdiffusion)} & \quad \text{(Heat production from gas-phase reactions)} \\
\end{align*}
\quad + \sum_{i=1}^{N} \frac{H_i}{M_i} \nabla \cdot \vec{j}_i - \sum_{i=1}^{N} \sum_{k=1}^{K} H_i v_{ik} (R_k^x - R_k^y) \quad (5-4)
\]

The first term in the energy equation shows the transient temperature variation which is determined by the convective and conductive heat transfer, the heat transfer resulting from concentration gradient (Dufour effect), and the heat flux generated by species interdiffusion and gas-phase chemical reactions.

In most CVD processes, the Dufour effect and species interdiffusion effect on heat transfer can be neglected. The gas-phase heat production is usually negligible when the reactants are highly diluted in an inert carrier gas.

(b) Species Transport Equations

The fluid properties in the above equations are functions of temperature, pressure, and the composition of the gas mixture, therefore, the above equations are coupled with the
species transport equations. In terms of mass fractions and diffusive mass fluxes, the balance equation of the $i$th gas species is:

$$\frac{\partial (\rho \omega_i)}{\partial t} = - \nabla \cdot (\rho \vec{v} \omega_i) - \nabla \cdot \vec{j}_i + M_i \sum_{j=1}^{K} \nu_{ij} (R_{ij}^e - R_{ij}^w)$$

(5-5)

where, the mass averaged velocity and the diffusive mass flux are defined as

$$\vec{v} = \sum_{i=1}^{N} \omega_i \vec{v}_i$$

(5-6)

$$\vec{j}_i = \rho \omega_i (\vec{v}_i - \vec{v})$$

(5-7)

The first term of species transport equation represents the transient variation in concentration, which is determined by the convective and diffusive species mass transport and the generation/destruction of gaseous species from gas-phase reaction.

The high temperatures and large temperature gradients inside CVD reactors cause a coupling effect between the heat transfer and the mass diffusion to become significant. The effect of temperature gradients on mass flux is known as thermal diffusion. Therefore, the diffusive mass flux defined by equation (5-7) is composed of two parts, the ordinary diffusion fluxes due to concentration gradients, and the diffusion fluxes due to thermal diffusions:

$$\vec{j}_i = \vec{j}_i^C + \vec{j}_i^T$$

(5-8)

Fick’s law is used to give the ordinary diffusion fluxes for a binary gas mixture. For a multi-component ($N$=2) gas mixture, the ordinary diffusion fluxes are given by iteratively solving the following equation
\[ j_i^C = -\rho D_i \nabla \omega_i - \rho \omega_i D_i \nabla (\ln M) + M \omega_i D_i \sum_{j \neq i}^{N} \frac{j_j^C}{M_j D_{ij}} \]  

(5-9)

with

\[ D_i = \left( \sum_{j \neq i}^{N} \frac{f_i}{D_{ij}} \right)^{-1} \]  

(5-10)

where, the average mole mass of the mixture is calculated from

\[ M = \sum_{i=1}^{N} f_i M_i \]  

(5-11)

The thermal diffusion flux for the \( i \)-th species is given by

\[ j_i^T = -D_i^T \nabla (\ln T) \]  

(5-12)

with \( D_i^T \) is the multi-component thermal diffusion coefficient for the \( i \)-th species. In general thermal diffusion causes large, heavy gas molecules to move to cold regions of the reactor (\( D_i^T > 0 \)), whereas small, light molecules move to hot parts of the reactor (\( D_i^T < 0 \)).

### 5.1.3 Gas-Phase Reactions

The general reaction for a total number of \( K \) homogeneous gas-phase reactions can be written as

\[ \sum_{i=1}^{N} k_i \nabla A_i \xrightarrow{k_{i-}} \sum_{i=1}^{N} \nabla A_i \]  

(5-13)

with \( A_i \) (\( i=1, N \)) representing the different gaseous species, \( k_i \) the forward reaction rate constant, and \( k_{-i} \) the reverse reaction rate constant of the \( k \)-th gas-phase reaction (\( k=1, K \)).
and $v_{ik}$ the stoichiometric coefficient for the $i$th species in the $k$th gas-phase reaction. By taking $v_{ik} > 0$ for the products of the forward reaction and $v_{ik} < 0$ for the reactants of the forward reaction, and by defining

$$\|v_{ik}\| = \frac{1}{2} (|v_{ik}| + v_{ik})$$

The reaction rates can be expressed as

$$R_k^\circ = k_k \prod_{i=1}^{N} c_i^{v_{ik}} = k_k \prod_{i=1}^{N} \left( f_i \frac{P}{RT} \right)^{v_{ik}} (5-14)$$

$$R_{-k}^\circ = k_{-k} \prod_{i=1}^{N} c_i^{v_{ik}} = k_{-k} \prod_{i=1}^{N} \left( f_i \frac{P}{RT} \right)^{v_{ik}} (5-15)$$

Substitute the above expression, and the expression for the thermal diffusion $\vec{j}_i^T$ to the species transport equation, the following equation for the species concentrations can be obtained.

$$\frac{\partial (\rho \rho_i)}{\partial t} = -\nabla \cdot (\rho \vec{v} \omega_i) - \nabla \cdot (\rho \rho_i \nabla \omega_i) + \rho \omega_i D_i \nabla (\ln M) - \nabla \cdot \left( M \omega_i D_i \sum_{j=1}^{N} \frac{\vec{j}_j^c}{M_j D_j} \right)$$

$$+ \nabla \cdot (D_i \nabla (\ln T)) + M \sum_{j=1}^{K} v_{ik} \left( k_k \prod_{i=1}^{N} c_i^{v_{ik}} - k_{-k} \prod_{i=1}^{N} c_i^{v_{ik}} \right)$$

(5-16)

### 5.1.4 Surface Reactions

Surface chemistry can be expressed in similar way to the gas-phase reactions. Assume a total number of $L$ surface reactions will take place at the wafer surface.

$$\sum_{i=1}^{N} \alpha_{ij} \|A_j (g)\| + \sum_{j=1}^{M} \beta_{ji} \|B_j (s)\| \rightarrow \sum_{i=1}^{N} \alpha_{ij} \|A_i (g)\| + \sum_{j=1}^{M} \beta_{ji} \|B_j (s)\|$$

(5-17)
with $A_i$ the gaseous reactants and reaction products ($i=1, N$) and $B_j$ the solid reactants and reaction products ($j=1, M$). The $\alpha_i$ and $\beta_j$ represent the stoichiometric coefficients for the $i$th gaseous and the $j$th solid species in the $l$th surface reaction ($l=1, L$).

The growth rate of the $j$th solid species may be calculated from the reactions that deposit the bulk species:

$$
G_j = \frac{M_j}{\rho_j^s} \frac{\partial}{\partial t} \left[ \frac{\partial [B_j]}{\partial t} \right] = \frac{M_j}{\rho_j^s} \sum_{j=1}^{L} R_i^s \beta_j
$$

(5-18)

Unlike gas-phase reactions, surface reactions do not appear in the species transport equations. The deposition due to surface reactions enters the model equations as a boundary condition rather than source terms.

### 5.1.5 Radiative Transfer Equation (RTE)

The equation of radiative transfer may be obtained from the Boltzmann transport equation for photons where it is assumed the interactions between photons can be ignored. For an absorbing, emitting, and scattering medium, the radiative transfer equation (RTE) at position $\vec{r}$ in the direction $\vec{s}$ is:

$$
\frac{dI(\vec{r}, \vec{s})}{ds} + (a + \sigma_s) I(\vec{r}, \vec{s}) = an^2 \frac{\sigma T^4}{\pi} + \frac{\sigma_s}{4\pi} \int_{0}^{4\pi} I(\vec{r}, \vec{s'}) \Phi(\vec{s} \cdot \vec{s'}) d\Omega'
$$

(5-19)

where, $\vec{r}$ — position vector

$\vec{s}$ — direction vector

$\vec{s'}$ — scattering direction vector

$a$ — absorption coefficient

$n$ — refractive index

$\sigma_s$ — scattering coefficient
$\sigma$ — Stefan-Boltzmann constant ($5.672 \times 10^{-8}$ W/m$^2$K$^4$)

$I$ — radiation intensity, which depends on position $\vec{r}$ and direction $\vec{s}$

$T$ — local temperature

$\Phi$ — phase function

$\Omega'$ — solid angle

Several radiation numerical methods are available to solve equation (5-19). The method used in this study for solving the equation of radiative heat transfer is the discrete ordinates (DO) method. The method can deal with non-isothermal, non-homogeneous, anisotropically-scattering, non-gray media in complex geometries. The general transfer relations are replaced by a discrete set of equations for the average intensity over a finite number of discrete solid angles. The solution method is identical to that used for the fluid flow and energy equations.

### 5.1.6 Boundary Conditions

The solution of the foregoing equations can be determined only when the boundary and initial conditions are specified.

(a) **Non-reacting Wall Boundary Conditions**

On non-reacting walls, the condition of no-slip and impermeability are satisfied, i.e., the normal and tangential components of velocity must vanish:

$$\bar{v} = 0$$  \hspace{1cm} (5-20)

The total mass flux vector normal to a non-reacting surface is assumed to be

$$\bar{n} \cdot (\bar{j}_i^C + \bar{j}_i^T) = 0$$  \hspace{1cm} (5-21)

where $\bar{n}$ is a unity vector normal to the surface of the wall.
Temperature and/or its gradient at the boundaries should also be specified. Temperature boundary conditions are given by prescribing wall temperature and zero-temperature gradients normal to the wall for isothermal and adiabatic walls, respectively.

\[ T = T_{wall} \quad \text{(isothermal walls)} \]  
\[ \vec{n} \cdot \nabla T = 0 \quad \text{(adiabatic walls)} \]  

(b) Reacting Wall Boundary Condition

Surface reaction appears as boundary condition in the model. The velocity component normal to the wafer surface is expressed by

\[ \vec{n} \cdot \vec{v} = \frac{1}{\rho} \sum_{i=1}^{N} M_i \sum_{j=1}^{L} \alpha_{ij} R_i^S \]  

with \( \vec{n} \) a unity vector normal to the reacting surface.

The tangential component of the velocity is given by

\[ \vec{n} \times \vec{v} = \vec{0} \quad \text{(no-slip condition)} \]

For wall surface reactions, the calculation of the species concentration at reacting surfaces is based on a balance of the convection and diffusion of each species to or from the surface and the rate at which it is consumed or produced at the surface. On the substrate surface (where surface reactions take place), the net total mass flux of the \( i \)th species normal to the wafer surface is

\[ M_i \sum_{j=1}^{L} \alpha_{ij} R_i^S = \vec{n} \cdot (\rho \omega_i \vec{v} + \vec{j}_i^C + \vec{j}_i^T) \]  

Usually, the reacting wafer surfaces is assumed to be isothermal, leading to

\[ T = T^S \]  

where, \( T^S \) is the wafer surface temperature.
(c) **Inflow Boundary Conditions**

The inflow boundary conditions are given by

\[ \vec{n} \cdot \vec{v} = v_{in} \]  \hspace{1cm} (5-28)

\[ \vec{n} \times \vec{v} = \vec{0} \]  \hspace{1cm} (5-29)

\[ T = T_{in} \]  \hspace{1cm} (5-30)

(d) **Outflow Boundary Conditions**

In the outflow, boundary conditions are given by assuming zero gradients for the total mass flux, heat flux and species diffusion fluxes in the direction normal to the outflow opening.

\[ \vec{n} \cdot (\rho \vec{v}) = 0 \]  \hspace{1cm} (5-31)

\[ \vec{n} \times \vec{v} = \vec{0} \]  \hspace{1cm} (5-32)

\[ \vec{n} \cdot (\lambda \nabla T) = 0 \]  \hspace{1cm} (5-33)

\[ \vec{n} \cdot (\vec{j}_i^C + \vec{j}_i^\tau) = 0 \]  \hspace{1cm} (5-34)

### 5.1.7 **Equation of State**

In order to close this system of equations, it is necessary to establish relationships between the thermodynamic variables and to relate the transport properties to them. Such relations are known as equations of state. For ideal gases, the equation of state is

\[ p = \rho RT \]  \hspace{1cm} (5-35)

where, \( R \) is the gas constant.

### 5.1.8 **Thermodynamic and Transport Properties**

The properties of the gas mixture play a very important role in the mathematical and numerical modeling of the CVD process. The ranges of some process variables are
usually large enough to make it necessary to consider the thermodynamic and transport property variations. Usually, the dependence of the properties on temperature is the most important effect. Most CVD processes require the solution of the full variable property problem for accurate predictions of the resulting transport.

For common gases like hydrogen and nitrogen, experimental data on transport properties as a function of temperatures are available in the published literature. In the absence of experimental data, the transport properties of the less common gas species and of gas mixtures maybe calculated from kinetic theory. The form of the intermolecular potential energy function \( \phi(r) \) is assumed to be the Lennard-Jones potential

\[
\phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]  

(5-36)

where \( r \) is the distance between the molecules, \( \sigma \) the collision diameter of the molecules and \( \varepsilon \) the maximum energy of attraction.

(a) Viscosity

The dynamic viscosity \( \mu_i \) of the \( i \)th species from the kinetic theory is given by

\[
\mu_i = \frac{5}{16} \frac{(\pi M_i R T_i)^{1/2}}{\pi \sigma_i^2 N_0 \Omega_{\mu} (T_i^*)}
\]

(5-37)

with \( M_i \) the mole mass and \( \sigma_i \) the collision diameter of the \( i \)th species, \( R \) the universal gas constant, and \( N_0 \) Avogadro’s number.

For the gas mixture, the viscosity is computed as

\[
\mu = \sum_i \frac{f_i \mu_i}{\sum_j f_j \phi_{ij}}
\]

(5-38)
where,

\[
\varphi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2}{8 \left(1 + \frac{M_i}{M_j}\right)^{1/2}}
\]  

(5-39)

\(f_i\) is the mole fraction of species \(i\), and \(\mu_i\) is the material's viscosity

(b) Thermal Conductivity

A reasonably accurate expression for gas thermal conductivity is given by

\[
k_i = \frac{15}{4} \frac{R}{M_i} \mu_i \left[\frac{4}{15} \frac{c_{p,j}M_i}{R} + \frac{1}{3}\right]
\]  

(5-40)

where, \(R\) is the universal gas constant, \(M_i\) is the molecular weight, \(\mu_i\) is the material's viscosity, and \(c_{p,j}\) is the material's specific heat capacity.

For an ideal gas mixture, the thermal conductivity is computed by

\[
k = \sum_i f_i k_i / \sum_i f_i \varphi_{ij}
\]  

(5-41)

where, \(\varphi_{ij}\) and \(f_i\) are the same as in the equation for calculating viscosity

(c) Mass Diffusion Coefficient

A modification of the Chapman-Enskog equation \(^{[60]}\) has been used to compute the diffusion coefficient:

\[
D_{ij} = 0.0188 \frac{T^3 \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{3/2}}{p \sigma_{ij}^2 \Omega_D}
\]  

(5-42)
where, \( p \) is the absolute pressure, and \( \Omega_D \) is the diffusion collision integral, which is a measure of the interaction of the molecules in the system. \( \sigma_{ij} \) is calculated as

\[
\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j)
\]  
(5-43)

For the diffusion dominated flows, a simulation of chemical species diffusion in the species transport and energy equations is very important. The multi-component diffusion model gives the diffusive mass flux as

\[
\vec{j}_i = - \sum_{j=1}^{N} \rho D_{ij} \nabla \omega_j - D_{ij}^T \frac{\nabla T}{T}
\]  
(5-44)

where, \( \omega_j \) is the mass fraction of species \( j \). Other terms are defined as follows:

\[
D_{ij} = [D] = [A]^{-1} [B]
\]  
(5-45)

\[
A_{ij} = \left( \frac{f_i M}{D_{ij}^NN} + \sum_{j \neq i} f_j M_{i} \right)
\]  
(5-46)

\[
A_{ij} = f_i \left( \frac{1 M}{D_{ij}^NN} + \frac{1 M}{D_{ij}^NN} \right)
\]  
(5-47)

\[
B_{ii} = f_i \left( \frac{M}{M_j} + (1 - f_i) \frac{M}{M_i} \right)
\]  
(5-48)

\[
B_{ij} = f_i \left( \frac{M}{M_j} \right)
\]  
(5-49)

where, \([A]\) and \([B]\) are \((N-1) \times (N-1)\) matrices and \([D]\) is an \((N-1) \times (N-1)\) matrix of the Fick's law diffusion coefficients \( D_{ij} \).
(d) **Thermal Diffusion Coefficients**

An empirically-based composition-dependent expression is used to calculate thermal diffusion coefficients: \[^{[61]}\]

\[
D_i^T = -2.59 \times 10^{-7} T^{0.659} \left[ \frac{\sum_{i=1}^{N} M_i^{0.511} f_i}{\sum_{i=1}^{N} M_i^{0.511} f_i} \right] \left[ \frac{\sum_{i=1}^{N} M_i^{0.511} f_i}{\sum_{i=1}^{N} M_i^{0.511} f_i} \right]
\]

\(5-50\)

(e) **Specific Heat Capacity**

The gas specific heat capacity can be defined using kinetic theory as

\[
c_{p,i} = \frac{1}{2} \frac{R}{M_i} (3n + 2)
\]

\(5-51\)

where \(3n\) is the number of degrees of freedom for a molecule of species \(i\) with \(n\) atoms.

From the equipartition theorem, all degrees of freedom have the same average energy and the average energy associated with each quadratic term in the kinetic or potential energy is equal to \(\frac{1}{2} k_B T\). Complicated molecules like benzene can be treated in this manner, with some success. The mixture's specific heat capacity is computed as a mass fraction average of the pure species heat capacities:

\[
c_p = \sum_i \omega_i c_{p,i}
\]

\(5-52\)

5.1.9 **Dimensionless Characteristic Groups**

Several characteristic dimensionless groups, appearing in the transport equations by scaling all variables with reference values, are used to characterize the general features of CVD processes. They are listed in Table 5-1. Each of the dimensionless numbers may be interpreted as the ratio of the magnitudes of two physical mechanisms. The importance of
different processes can be easily estimated by the value of the dimensionless numbers. In this study, the Reynolds number values were used to determine whether the flow in the CVD reactor is laminar.

**Table 5-1 Dimensionless groups in atmospheric pressure CVD**

<table>
<thead>
<tr>
<th>Dimensionless groups</th>
<th>Physical interpretation</th>
<th>Definition</th>
<th>Typical Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynolds ($Re$)</td>
<td>inertia forces/viscous forces</td>
<td>$\frac{\rho u L}{\mu}$</td>
<td>$10^2$-$10^3$</td>
</tr>
<tr>
<td>Grashof ($Gr$)</td>
<td>buoyancy forces/viscous forces</td>
<td>$\frac{g \rho L^4 \Delta T}{\mu^2 \rho L}$</td>
<td>$10^2$-$10^3$</td>
</tr>
<tr>
<td>Prandtl ($Pr$)</td>
<td>momentum diffusivity/thermal diffusivity</td>
<td>$\frac{\mu c_p}{\lambda}$</td>
<td>0.7</td>
</tr>
<tr>
<td>Gas-phase Arrhenius ($Arrh_g$)</td>
<td>activation energy/potential energy</td>
<td>$\frac{E_g}{RT}$</td>
<td>0-100</td>
</tr>
<tr>
<td>Surface Arrhenius ($Arrh_s$)</td>
<td>activation energy/potential energy</td>
<td>$\frac{E_s}{RT_s}$</td>
<td>0-100</td>
</tr>
<tr>
<td>Knudsen ($Kn$)</td>
<td>mean free path length/typical dimension</td>
<td>$\frac{L}{L}$</td>
<td>$10^{-6}$-$10^{-5}$</td>
</tr>
<tr>
<td>Thermal Peclet ($Pe_T$)</td>
<td>convective heat transfer/conductive heat transfer</td>
<td>$Re \cdot Pr$</td>
<td>$10^2$-$10^3$</td>
</tr>
</tbody>
</table>

5.1.10 Modeling of Chemical Reaction Mechanism and Kinetics

With only the transport phenomena model equations, the simulation cannot be completed. A chemistry model of the gas-phase and surface reactions in the reactor chamber must be specified. There is very limited experimental information on the reaction mechanisms of CVD processes. This is a bottleneck for the modeling of CVD processes. Much research is accomplished by assuming one single overall chemical reaction with the rate constant determined from empirical correlations. But such
simulations cannot be used when the operating conditions, such as temperature, pressure or concentrations, are different, or on different type of reactors. The possible important influence of the intermediate reaction products is also neglected. The design and optimization of CVD reactors and processes require a more detailed description of the chemical reaction mechanisms involved through extensive experimental and theoretical research.

(a) Gas-phase Chemistry

Gas-phase reactions appear as a source term in the general species concentration. Gas-phase chemistry plays an important role in atmospheric pressure CVD processes. In the literature, experimental data are generally not available. Reaction rates are estimated by using theoretical kinetics. For example, collision theory can be used in the prediction of the rates of bimolecular and termolecular reactions. \[52\]

Using kinetic theory, the gas-phase reaction rate constant and its dependence on temperature can be determined. \[62\] Consider an elementary bimolecular reaction between two gases A and B:

\[
A + B \rightarrow \text{products} \tag{5-53}
\]

According to collision theory, the rate coefficient is given by

\[
k = \left[ N_0 \sigma_{AB} \left( \frac{8\pi R}{M_{AB}} \right)^{\frac{1}{2}} \right] \frac{1}{T^2} \tag{5-54}
\]

where, \(N_0\) is Avogadro’s constant, \(M_{AB}\) is the reduced molecular mass, and \(\sigma_{AB}\) is the collision diameter between A and B molecules. This is equivalent to the modified Arrhenius Law.
\[ k = k_0 T^\beta e^{\frac{E_a}{RT}} \quad (5-55) \]

where, \( k_0 = N_0 \sigma_{AB} \left( \frac{8\pi R}{M_{AB}} \right)^{\frac{1}{2}} \), \( \beta = \frac{1}{2} \), and \( E_a = 0 \).

(b) Surface Reaction Chemistry

In many chemistry models the surface chemistry is simplified into one or more irreversible reactions with only gaseous reactants and apart from the deposited species. One semi-empirical approach, the so-called “reactive sticking coefficient” concept is often used to estimate the surface reaction rate. The method is usually used to give surface reaction rate of a monomolecular surface dissociation reaction \[ (5-56) \]

\[ A(g) \rightarrow B(s) + C(g) \]

The reactive sticking coefficient is defined as the mole flux of species \( B \) which is incorporated to the deposited film divided by the mole flux of species \( A \) colliding with the surface. From kinetic theory, the colliding mole flux of species \( A \) with the surface is

\[ F_A = \frac{P_A}{\sqrt{2\pi M_A RT_S}} \quad (5-57) \]

The surface reaction rate becomes

\[ R^S = \gamma_A \frac{P_A}{\sqrt{2\pi M_A RT_S}} = \gamma_A C_A \sqrt{\frac{RT_S}{2\pi M_A}} \quad (5-58) \]

where, \( \gamma_A \) is the reactive sticking coefficient for species \( A \) and \( \gamma_A \leq 1 \), and \( C_A \) is the mole concentration.

Relating this to the expression of the surface reaction rate expression

\[ R^S_A = kC_A \], the rate constant is given by
This is equivalent to the Arrhenius Law expressed by equation (5-55), provided

$$k = \gamma_A \sqrt{\frac{R}{2\pi M_A}} \frac{1}{T^\beta}$$  

(5-59)

Because the interactions between gas-phase and surface species are much more complex compared to those between gas-phase molecules, the prediction of reaction pathways and rate constants for heterogeneous reactions is considerably more difficult than for gas-phase reactions. More fundamental approaches to surface chemistry modeling, similar to those used in gas-phase kinetics, are just beginning to emerge.

5.1.11 Numerical Techniques for the Solution of CVD Model Equations

In general, it is not possible to solve the mathematical model analytically. The coupled nonlinear partial differential equations can be solved numerically with boundary conditions. Two main numerical techniques are finite element analysis and finite volume difference. A description of both methods can be found in Kleijn’s work [41]. Table 5-2 is his subjective vision on the respective strengths and weaknesses of finite volume and finite element techniques.
Table 5-2 Comparison between the strengths and weaknesses of Finite Element and Finite-Volume Techniques[41]

<table>
<thead>
<tr>
<th></th>
<th>Finite-Volume Method</th>
<th>Finite-Element Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plus</td>
<td>+mathematically simple and conceptually intuitive</td>
<td>+easy to apply to complex geometries</td>
</tr>
<tr>
<td></td>
<td>+easy coding</td>
<td>+mathematically well founded</td>
</tr>
<tr>
<td></td>
<td>+small memory requirements</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+inclusion of new physical models easy and straightforward</td>
<td></td>
</tr>
<tr>
<td>Minus</td>
<td>-more difficult handing of complex geometries</td>
<td>-large memory requirements</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-mathematically more complex and conceptually non-intuitive</td>
</tr>
</tbody>
</table>

In this study of the GaN MOCVD process, the finite volume method was chosen because this is the only technique provided by FLUENT™ to convert the governing equations to algebraic equations that can be solved numerically.

(a) Introduction to Finite Volume Method

This section gives only a brief introduction on how to discretize the governing equations based on the finite volume formulation. More detail for this method can be found in some very good references.[63]

It is highly desirable if a general algorithm can be applied to the governing equations. Based on the common features in the governing equations, a generalization is possible to make. Equation (5-60) gives the general appearance of the transport equations for variable \( \phi \).

\[
\frac{\partial \rho \phi}{\partial t} = -\nabla (\rho \nabla \phi) + \nabla (\Gamma_{\phi} \nabla \phi) + S_{0}^{\phi} + S'_{\phi} \phi
\]

(5-60)

Here, \( \phi \) is the variable to be solved, \( \Gamma_{\phi} \) its generalized diffusion coefficient, and

\[S = S_{0}^{\phi} + S'_{\phi} \phi\]

is the generalized source term, linearized in \( \phi \). The differential equation
expresses the conservation of the dependent variable $\phi$ in the control volume. It is easy to verify that the governing equations can all be transformed to the format of the general transport equation. Equation (5-60) is formulated for $\phi$ equal to the velocity components, the thermal energy $c_pT$, and the species mass fraction $\omega_i$.

The above transport equation for variable $\phi$ can be written in the integral form over a volume $V$ as

$$\frac{\partial}{\partial t} \int_V \phi dV + \oint_F \vec{F} \cdot d\vec{A} = \int_V Q dV \quad (5-61)$$

Here, $\vec{F}$ is the vector flux of the quantity $\phi$ crossing the volume surface $S$ that defines volume $V$, and $Q$ is the source of $\phi$ within the control volume.

The conservation equations represented by equation (5-61) are directly discretized in the spatial domain that is subdivided into a finite number of contiguous control volumes. The FVM consists of integrating the governing equations about each control volume, yielding discrete equations that conserve each quantity on a control volume basis. The transport variables at each discrete node are determined by applying the conservation laws to the corresponding control volume. The general formulation of FVM can be obtained by writing the above equation for the discretized control volume $V_a$ with $\phi_a$:

$$\frac{\partial}{\partial t} (\phi_a V_a) + \sum_{\text{sides}} \vec{F} \cdot d\vec{S} = Q_a V_a \quad (5-62)$$

where, the sum for the flux terms refers to all the external sides for the control volume $V_a$ and should span the whole domain. To ensure the conservative character of the FVM, the computation of the fluxes along a cell surface is independent of the considered cell [64].

The final form of the discretized equations all takes the following form:
This equation says the point $p$ value is related to its neighboring values and the residual term $b$. The coefficients and $b$ are decided according to certain discretization criteria.

(b) Discretization of Radiation Transfer Equation (RTE)

There are several methods to solve the radiative transfer equation numerically. The discrete ordinates (DO) method is one of them. It can deal with non-isothermal, non-homogeneous, anisotropically-scattering, non-gray media. It is capable of solving radiative heat transfer problems from surface-to-surface radiation to participating radiation with relatively good accuracy and moderate computing resources.

In the DO model, the general transfer relations are replaced by a discrete set of equations for the average intensity over a finite number of discrete solid angles. The solution method is identical to that used for the fluid flow and energy equations.

Gray-band models are usually used to model the radiative heat transfer in non-gray media. The radiation spectrum is divided into a number of wavelength bands. For each band, the gray body behavior is assumed. The scattering coefficient $\sigma_s$, the scattering phase function $\Phi$, and the refractive index $n$ are assumed independent of wavelength $\lambda$. Thus, the RTE for the spectral intensity $I_\lambda$ can be written as

$$\nabla \cdot (I_\lambda (\vec{r}, \vec{s}) \vec{s}) + (a_\lambda + \sigma_s) I_\lambda (\vec{r}, \vec{s}) = a_\lambda n^2 I_{b\lambda} + \frac{\sigma_s}{4\pi} \int_{0}^{4\pi} I_\lambda (\vec{r}, \vec{s}') \Phi (\vec{s} \cdot \vec{s}') d\Omega'$$  \hspace{1cm} (5-64)

Here $a_\lambda$ is the spectral absorption coefficient, and $I_{b\lambda}$ is the black body intensity given by the Planck function. The radiant energy contained in the wavelength band $\Delta\lambda$ is expressed as $I_\lambda \Delta\lambda$. Transport equations for the variable $I_\lambda \Delta\lambda$ can be obtained by
integrating the RTE over each wavelength interval. The total intensity \( I(\vec{r}, \vec{s}) \) in each direction \( \vec{s} \) at position \( \vec{r} \) is computed using

\[
I(\vec{r}, \vec{s}) = \sum_k I_{2k}(\vec{r}, \vec{s})\Delta\lambda_k
\]

(5-65)

where, the summation is over the wavelength bands.

The polar angles \( \theta \) and azimuthal angles \( \phi \) composed an angular space \( 4\pi \), as shown in Figure 5-1. Each octant of the angular space at any spatial location is discretized.

![Angular coordinate system](image)

**Figure 5-1** Angular coordinate system

For non-gray radiation, the boundary intensity for all outgoing directions \( \vec{s} \) in the band \( \Delta\lambda \) at the wall is given by

\[
I_{0,\lambda} = \frac{q_{\text{out},\lambda}}{\pi\Delta\lambda}
\]

(5-66)

where, \( q_{\text{out},\lambda} \) is the net radiative flux leaving the surface in the band \( \Delta\lambda \) and is calculated from

\[
q_{\text{out},\lambda} = (1 - \varepsilon_{\text{in},\lambda}) q_{\text{in},\lambda} + \varepsilon_{\text{in},\lambda} \left[ F(0 \rightarrow n\lambda_2 T_w) - F(0 \rightarrow n\lambda_1 T_w) \right] n^2 \sigma T_w^4
\]

(5-67)
with $\varepsilon_w$ the wall emissivity in the band and the incident radiative heat flux $q_{in,\lambda}$ in the band $\Delta\lambda$ at the wall which is given by

$$q_{in,\lambda} = \Delta\lambda \int_{\frac{1}{\lambda} \geq 0} I_{in,\lambda} \bar{s} \cdot \bar{n} d\Omega$$  \hspace{1cm} (5-68)

At specular walls, all the energy incident on the interface is reflected. The direction of the reflected radiation $\bar{s}_r$ corresponding to the incoming direction $\bar{s}$ is given by

$$\bar{s}_r = \bar{s} - 2(\bar{s} \cdot \bar{n})\bar{n}$$  \hspace{1cm} (5-69)

The intensity of the reflected radiation equals the incident one, i.e.,

$$I_w(\bar{s}_r) = I_w(\bar{s})$$  \hspace{1cm} (5-70)
5.2 Model Description

The objective of this research is to model the MOCVD of GaN in the CVD reactor at Ohio University. The numerical investigation will be used to determine inner tube effect and optimize operating parameters of the process. The numerical simulation is performed using the commercial software FLUENT™.

5.2.1 CVD Reactor Geometry

Figure 5-2 depicts the CVD reactor configuration. Two types of quartz inner tubes are studied in the simulation: the straight-pipe inner and bell-shaped inner tube. The geometry of the reactor is accurately represented. The CVD reactor geometry and measurements are shown in Figure 5-2 and Figure 5-3 for the configuration with bell-shaped inner tube.
Figure 5-2 Sketch of the MOCVD reactor chamber
Figure 5-3 The measurements of CVD reactor chamber with a bell-shaped inner tube used in the simulation

Gas-phase reactions occur in the reaction chamber and the surface reactions take place on the top of the substrate wafer.
5.2.2 Previous Work

Gao [65] proposed a model to simulate the fluid dynamic effects on the MOCVD process for this CVD reactor using CFX-4 software. A highly simplified reactor geometry is used in the study. The shape of reactor walls is quite different from the actual one. The shaft is not included in the geometry, and only the upper part of the susceptor is considered. The reactor geometry and computational grid structure are shown in Figure 5-4 and Figure 5-5.

Effects of susceptor geometry, growth pressure, susceptor rotation, and inlet configuration were considered in the modeling study. A susceptor geometry modification is done base on experiments. Its effect on flow patterns and temperature distributions was then numerically studied. The simulation showed that the susceptor geometry differences only affect the axial velocity distribution in the reactor but have almost no effect on radial velocities and the temperature distribution. The model also showed that different inlet
configuration may influence the velocity field in the reactor. However, the effect on influencing the temperature distribution was reported.

No chemistry kinetic model was included in the model. The surface reactions on the substrate were related only to TMG. The growth rate was calculated from the net arrival rate of TMG on the reactive surface based on the concept of reactive sticking coefficient. An arbitrary value of 0.06 for the reactive sticking coefficient was used because of the occurrence of solution divergence for larger values. Thermal and mass diffusion effects were not considered and the gas mixture properties other than viscosity and thermal conductivity were all set to be constant. Radiative heat transfer was not modeled, either.

5.2.3 Model Description

In this work, the simulation is a modeling of three-dimensional steady laminar flow with heat transfer in several complex CVD reactor geometries. The heat transfer includes the radiative heat transfer inside the reactor, which becomes significant for the very high growth temperature. The multi-component diffusion modeling, including thermal diffusion and mass diffusion, are employed in the study. A reaction mechanism of GaN growth including gas-phase and surface reactions is included in the simulation.

(a) Computational Grid

Three reactor geometry configurations were used in the simulations: reactor with a straight-pipe inner tube, reactor with a bell-shaped inner tube and reactor without inner tube. The two inner tube configurations have been used by Gao experimentally.\textsuperscript{[65]} However, no conclusive results were reported on how the geometry will influence the film growth. In this study, the effects of these different reactor configurations on film
growth were studied theoretically to determine which configuration can achieve uniform film growth on the substrate surface.

The computation grid generation is done using Gambit 2.0 software, which supports unstructured mesh. The reactor geometry is represented as structured and unstructured meshes containing approximately $1.0 \times 10^6$ nodes. The non-uniform grid arrangement for the whole reactor geometry with the bell-shaped inner tube is shown in Figure 5-6.

Figure 5-6 Display of computational grid used for the entire simulation domain for reactor configuration with the bell-shaped inner tube
Figure 5-7 is a close-up view of the grid arrangement near the susceptor for reactor with bell-shaped inner tube. The grid cut on the axial vertical plane for reactor configurations with straight-pipe inner tube and with no inner tube are shown in Figure 5-8, and Figure 5-9.

**Figure 5-7** A close-up view of the grid arrangements of reactor near the susceptor for bell-shaped inner tube configuration
Figure 5-10 shows the grids arrangements for the bell-shaped inner tube. Figure 5-11 shows grid arrangement of the susceptor and the shaft. The conduction heat transfer inside the inner tube and shaft is coupled with both the radiative heat transfer and the convective heat transfer with ambient gas. The term ‘conjugate heat transfer’ is used to describe such coupled heat transfer. The conjugate heat transfer was included in this study.
The grids arrangement for the susceptor is shown in Figure 5-12 and Figure 5-13. The grids on the top of the susceptor are the combination of structured and unstructured grids. This arrangement is adopted in order to give more uniformly distributed grids.

Both structured and unstructured meshes are used. The main difference between the structured grid system and the unstructured grid system is in the identification of the
points forming the computational cell and its neighbors. The structured grid stands in a line regularly, and its form in generally cubic. In contrast to the structured grid system, the mesh points in an unstructured grid system are not organized in an orderly manner.

Figures 5-14 and 5-15 show the grid arrangements for the upper side inlet and the bottom outlet part of the reactor. The combination of structured and unstructured grids can give a more uniform grid volume and shape distribution in the areas where the side pipes connect with the vertical cylinders. Using a structured grid in these parts, there would be drastic changes in the grid volumes and shapes.

![Figure 5-14](image1.png) The structured grid and unstructured grids in the lower part of reactor

![Figure 5-15](image2.png) The structured and unstructured grids in the upper part of reactor

In this study, the numerical analysis employed to discretize the equation is based on the finite volume formulation. The solution of the equations is approximated by a power law upwind differencing scheme in order to minimize numerical diffusion. The pressure-velocity coupling is treated using the Semi-Implicit Method for Pressure Linked Equations (SIMPLE) algorithm of proposed by Patankar \[63\]. The real difficulty in calculating the velocity field lies in determining the unknown pressure field. In the SIMPLE algorithm, the pressure field is indirectly specified by the continuity equation.
The velocity and pressure fields are all solved on a staggered differential grid arrangement to prevent the pressure-velocity coupling that links the continuity and the momentum equations.

Radiation is the dominant mode of heat transfer in the MOCVD reactor. The radiative energy loss from the hot susceptor determines the temperature distribution of the quartz inner tube and shaft. The absorption coefficient of quartz strongly depends on the wavelength and temperature. Three spectral bands can be distinguished from studies on the quartz absorption coefficient dependence on the wavelength of photon:

(1) \( \lambda < 3.5 \mu m \), where the quartz wall of the reactor is nearly transparent;

(2) \( 3.5 < \lambda < 4.5 \mu m \), where the absorption coefficient increases rapidly;

(3) \( \lambda > 4.5 \mu m \), where the quartz wall can be considered to be opaque.

In this study, discrete ordinates method discussed in 5.1.11(b) was used to model the radiation transport.

(b) Boundary Conditions

In the model the temperature of the susceptor is assumed to be constant because of the high efficiency of RF heating. The reactor wall is also assumed to have a uniform temperature distribution, which is common in CVD simulations and reasonable since no large temperature gradients are expected because of the water cooling. Otherwise we have to face the formidable numerical simulation challenge to accurately model the water cooling process coupled with the inside heat transfer process. The temperature of the water-cooled reactor wall is set to be 313 K, which is the average temperature of water flows in and out the water chiller.
Different operating conditions are simulated for different reactor configurations. The operating conditions are the same as those used in the GaN seeding layer growth process. Three reactor configurations are studied: reactor with bell-shaped inner tube, reactor with straight-pipe inner tube and reactor without inner tube. The flow rate of the TMG under all of the operating condition is set to a fixed value: 2.13 µmol/min. Hydrogen gas enters the reactor with a volumetric flow rate 1.0 slpm. The temperature of the gas mixture entering from the top inlet is 323K. The different ammonia flow rate at the top inlet of the reactor gives different V/III ratios. Other operating parameters studied are summarized in Table 5-3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Variations studied in the simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia flow rate at top inlet</td>
<td>0.4 slpm  0.6 slpm  0.8 slpm</td>
</tr>
<tr>
<td>Nitrogen flow rate at side inlet</td>
<td>0.2 slpm  0 slpm**</td>
</tr>
<tr>
<td>Susceptor rotation speed</td>
<td>0 rpm  70 rpm  300 rpm</td>
</tr>
</tbody>
</table>

* For reactor configurations with an inner tube.  
** For reactor configurations with no inner tube.

The heat transfer on the inner tube walls and shaft walls were set to be coupled to the conduction heat transfer inside the inner tube and shaft, and the convective heat transfer between the wall and the gas phase, i.e., the heat transfer is directly calculated from the solution in the adjacent cells. This conjugate heat transfer of the inner tube and shaft must be included to predict the temperature distribution along and inside the inner tube and shaft. The temperature profiles on the walls of the inner tube and shaft have to be obtained from the thermal energy balance accounting for heat conduction in the wall.
material and conductive, convective, and radiative heat exchange between the wall and its surroundings.

(c) **Kinetic Model for MOCVD of GaN**

A kinetic model describing the growth of GaN from trimethylgallium and ammonia is listed in Table 5-4. The kinetic model includes gas-phase reactions (i) to (iv) and surface reactions (v) to (vii). The reaction rate constants are given by the modified Arrhenius expression

\[ k = k_0 T^\beta e^{\frac{E_a}{RT}} \quad (5-55) \]

<table>
<thead>
<tr>
<th>Reactions</th>
<th>(k_0)</th>
<th>(E_a)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) TMG + NH₃ → TMG:NH₃</td>
<td>(1.258 \times 10^{10} \text{ m}^3\text{kmol}^{-1} \cdot \text{s}^{-1} \cdot \text{K}^{-0.5})</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>(ii) TMG:NH₃ → TMG + NH₃</td>
<td>(9.5 \times 10^9 \text{s}^{-1})</td>
<td>7.955 \times 10^7 \text{ J/kmol}</td>
<td>0</td>
</tr>
<tr>
<td>(iii) TMG:NH₃ → DMGNH₂ + CH₄</td>
<td>(1 \times 10^{14} \text{s}^{-1})</td>
<td>2.052 \times 10^8 \text{ J/kmol}</td>
<td>0</td>
</tr>
<tr>
<td>(iv) 3DMGNH₂ → TGNCY</td>
<td>(2.202 \times 10^9 \text{ m}^6\text{kmol}^{-2} \cdot \text{s}^{-1} \cdot \text{K}^{-0.5})</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>(v) TMG:NH₃ + 2S → GaN(s) + 3CH₄</td>
<td>(3.167 \text{ m/s}^{-1} \cdot \text{K}^{-0.5})</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>(vi) DMG:NH₂ + 2S → GaN(s) + 2CH₄</td>
<td>(3.380 \text{ m/s}^{-1} \cdot \text{K}^{-0.5})</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>(vii) TGNCY + 6S → 3GaN(s) + 6CH₄</td>
<td>(1.951 \text{ m/s}^{-1} \cdot \text{K}^{-0.5})</td>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Reaction (i) is the formation of the adduct coordination compound trimethylgallium-monamine (TMG:NH₃) between TMG and ammonia. TMG is the electron acceptor (Lewis acid), while ammonia is the electron donor (Lewis base). The zero activation energy shows that the reaction is spontaneous. The reaction rate is assumed to be controlled by the rate of collisions between the two molecules. The value of the rate
constant and its dependence on temperature is estimated from the bimolecular collision rate as described in section 5.1.3. The measured strength of the Ga-N coordination bond is $7.955 \times 10^7$ J/kmol. \[66\] Because the Ga-N bond is weak, the decomposition of the adduct back to its constituents can take place easily in the heated zone of a MOCVD reactor as described by reaction (ii). The kinetic parameters of reactions (ii) are reported by Sun et al. \[51\] The reaction activation energy is the value of the Ga-N bond strength. The rate constant is assumed to be $9.5 \times 10^9$ s$^{-1}$.

Reaction (iii) is the methane-elimination reaction with the subsequent release of a single methane molecule. This reaction forms a thermally stable adduct $(\text{CH}_3)_2\text{Ga}:\text{NH}_2$ (DMGNH$_2$). The kinetic parameters are taken from the study of Theodoropoulos et al. \[53\] The activation energy for this reaction is reported to be $2.052 \times 10^8$ J/kmol. The value of the rate constant is reasonable for complex fissions. Reaction is followed by the oligimerization of DMGNH$_2$ into cyclic trimer, cyclotrimimidiohexamethyltrigallium (TGNCY) as described in reaction (iv). The rate constant is estimated from the kinetic theory of three-body collisions rate:

\[ k = \left( \frac{N_0}{\pi} \right)^2 \sigma_{TGNCY}^2 \left( \frac{8R}{\pi M_{TGNCY}} \right)^{\frac{1}{2}} T^{\frac{3}{2}} \quad (5-71) \]

Here, $\sigma_{TGNCY}$ is the collision diameter of TGNCY given in Table 5-5, $N_0$ is Avogadro’s constant, $R$ is ideal gas constant, and $M_{TGNCY}$ is the mole mass of TGNCY. The ring form of TGNCY was found to be more energetically favorable than a chain structure. \[67\] TGNCY is very unlikely to decompose in the gas-phase even at the high temperatures commonly used for GaN growth.
The surface reactions of the interactions of gas-phase species containing Ga and N with the reactive surface are described by reactions (v) to (vii). Because there is no experimental data available for the reactive sticking coefficient, the rate constants for these reactions are calculated with a unity reactive sticking coefficient. This assumes that once a reactive molecule collides with the substrate surface, it will react on the surface to give film growth. Zero activation energies are also assumed, thus making the estimated growth rates the maximum possible.

The chemistry is a simplification that might be replaced by considering more complex reaction kinetics. This would, however, require accurate data for the kinetic reactions.

(d) Thermodynamic and transport properties of gas mixture

The gas mixture properties are calculated by ideal gas mixing laws as described in section 5.1.8. The mass diffusion coefficient and thermal diffusion coefficient are calculated from kinetic theory for lack of experimental data for the intermediate species.

Most of the thermodynamic and transport properties of hydrogen gas, nitrogen gas, ammonia, and methane used in the model are from the FLUENT software database. However, FLUENT does not provide temperature dependence of the viscosity and thermal conductivity for ammonia and methane. Since large temperature gradients exist in the CVD reactor, the variation of the thermodynamic and transport properties of the chemical species and some materials must be considered. In order to include the temperature dependent character of the properties, the viscosity and thermal conductivity of ammonia and methane are calculated using kinetic theory.
The thermodynamic properties of TMG, TMG:NH₃, DMGNH₂, and TGNCY, such as the standard enthalpy and entropy, are taken from the database reported by Przhevalskii et al. [68]

The viscosity, thermal conductivity and specific heat of TMG, TMG:NH₃, DMGNH₂, and TGNCY are not available in the literature. These properties can be estimated using kinetic theory as described in section 5.1.8. The mass diffusion coefficient of the gas mixture is also calculated from the kinetic theory. Table 5-5 lists the values for $\sigma$ and $\epsilon$ for the gas species in MOCVD processes for GaN growth.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molecular Weight (kg/kmol)</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon / k_B$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(CH₃)₃</td>
<td>114.824</td>
<td>5.470</td>
<td>378.2</td>
<td>[53]</td>
</tr>
<tr>
<td>(CH₃)₃Ga:NH₃</td>
<td>131.855</td>
<td>5.89</td>
<td>228.9</td>
<td>[53]</td>
</tr>
<tr>
<td>(CH₂)₂Ga:NH₂</td>
<td>115.812</td>
<td>5.387</td>
<td>209.9</td>
<td>[53]</td>
</tr>
<tr>
<td>((CH₃)₃Ga:NH₂)₃</td>
<td>347.436</td>
<td>7.631</td>
<td>279.2</td>
<td>[53]</td>
</tr>
<tr>
<td>NH₃</td>
<td>17.030</td>
<td>2.92</td>
<td>481</td>
<td>[41]</td>
</tr>
<tr>
<td>N₂</td>
<td>28.013</td>
<td>3.798</td>
<td>71.4</td>
<td>[41]</td>
</tr>
<tr>
<td>H₂</td>
<td>2.016</td>
<td>2.827</td>
<td>59.7</td>
<td>[41]</td>
</tr>
</tbody>
</table>
5.3 Modeling Results and Discussion

The results of the simulation of MOCVD of GaN are presented. The effects of various parameters on the MOCVD process are examined. The solution of the model is very time consuming. For a typical run with a full modeling of radiative heat transfer and chemical reactions, it could take 14 to 30 days to get a fully converged solution using FLUENT on a Pentium Xeon 833MHz workstation.

5.3.1 Description of Typical Three-Dimensional Flow Field

The entire flow field in the reactor is three-dimensional and exhibits strong asymmetric character near the side inlet and the outlet in reactors with different inner tube configurations. But the side inlet flow of nitrogen gas has little to do with the flow region around the susceptor since it is blocked by the inner tube from entering the hot zone or is set to zero for the reactor with no inner tube. Figure 5-16, 5-17 show the pathlines for the flow field in reactor with bell-shaped inner tube with different susceptor rotation speeds. No flow recirculation zones are observed. The stagnation zones are also not obvious.
Figure 5-16 Flow pathlines with zero rotation speed for the bell-shaped inner tube reactor configuration
Figure 5-17 Flow pathlines with rotation speed at 70 rpm for the bell-shaped inner tube reactor configuration

The local flow fields around the susceptor are almost axisymmetric for different reactor configurations. The axisymmetric characters of the local flow are very clearly shown in figures 5-18 to 5-20 by the contours of velocity magnitude near the susceptor in the reactors with different inner tube configurations.
Figure 5-18 Contours of velocity magnitude on the axial vertical plane near susceptor for bell-shaped inner tube configuration, rotation speed 70 rpm

Figure 5-19 Contours of velocity magnitude on the axial vertical plane near susceptor for straight-pipe inner tube configuration, rotation speed 70 rpm
Figure 5-20 Contours of velocity magnitude on axial vertical plane near susceptor for reactor with no inner tube, rotation speed 70 rpm

Also from the above figures, we can see the velocities in the reactor chambers near the susceptor are small. The cell Reynolds number distributions are shown in Figure 5-21 to Figure 5-23 for different inner tube configurations. Cell Reynolds Number is the value of the Reynolds number in a cell, which is defined as

$$Re = \frac{d u \rho}{\mu}$$

(5-72)

Here, $\rho$ is density, $u$ is velocity magnitude, $\mu$ is viscosity, and $d$ is the cubic root of cell volume. The maximum calculated cell Reynolds number is 7.15, confirming the laminar flow in the chamber.
Figure 5-21 Cell Reynolds number values in reactor with no inner tube

Figure 5-22 Cell Reynolds number values in reactor with straight-pipe inner tube
To further understand the three-dimensional flow, the velocity vector field near the susceptor is shown in figures 5-24 and 5-25.
Figure 5-24 Flow field near the susceptor illustrated with fix length velocity vectors colored by velocity magnitude

Figure 5-25 A close-up view of the velocity distribution on a plane 1mm above the top surface of susceptor
5.3.2 Typical Three-Dimensional Temperature Distribution

Very large temperature gradients exist in the CVD reactor for each of the three reactor configurations. For each configuration, there is a high temperature zone around the susceptor in which temperature is much higher than other zones in the reactor chamber. The thickness of the high temperature zones above the susceptor is about several centimeters. The bulk temperature of the gas-phase is much lower. Figures 5-26 to 5-29 show the temperature distributions within the reactor under typical operating conditions for different inner tube configurations.

![Figure 5-26](image) Temperature distribution of in the reactor with bell-shaped inner tube
Figure 5-27 Close-up view of the temperature distribution in the reactor with bell-shaped inner tube

Figure 5-28 Temperature distribution in the reactor with no inner tube
As one can see, just like the flow field, the temperature distributions are also nearly axisymmetric around the susceptor for each of the three reactor configurations as shown in the figures.

It is found that different operating conditions, such as susceptor temperature, susceptor rotation speed, and ammonia flow rate at the top inlet, will have effects on changing the temperature distribution for each of the three reactor configurations. However, these effects have little influence on the typical shapes of the temperature profiles.
5.3.3 Thermal Diffusions in the Reactor

Because of the large temperature gradient in the reactor chamber, the thermal diffusion effect is very obvious. Thermal diffusion causes small, light molecules move to the high temperature zone around the susceptor. The thermal diffusion effect was found in every reactor configuration. For the bell-shaped inner tube configuration, Figure 5-30 shows that hydrogen concentrates in the zone around the hot susceptor.

![Figure 5-30](image)

*Figure 5-30* Hydrogen concentrates in the high temperature zone due to thermal diffusion effect. The mole fraction of hydrogen distribution on the axial vertical plane for the bell-shaped inner tube configuration, rotation speed 70 rpm.

The thermal diffusion effect can be seen more clearly by comparing the TGNCY mole fraction distributions shown in Figure 5-31. Figure 5-31(a) shows the TGNCY mole fraction distribution when neglecting thermal diffusion. As one can see, TGNCY
concentrates in the region near the susceptor and the radial gradient of the mole fraction is not very large. However, when including thermal diffusion in the simulation, the mole fraction gradient along the radial direction becomes much greater as shown in Figure 5-31(b). Near the inner tube wall, the mole fraction is large while near the high temperature susceptor the mole fraction is small. This shows that the thermal diffusion causes TGNCY to concentrate in the low temperature regions.

**Figure 5-31** Mole fraction distribution of TGNCY on the axial vertical plane: (a) neglecting thermal diffusion effect. (b) considering thermal diffusion effect.
5.3.4 The Effect of Reactor Configurations on the MOCVD Process

Two different types of inner tubes were used in the reactor system to get better velocity and temperature distribution for film growth. The simulations have shown that the geometry of the inner tube will greatly influence the flow field and temperature profile in the reactor. The different gaseous species concentration distributions are also presented.

(a) Straight-Pipe Inner Tube Configuration

For the reactor configuration with straight-pipe inner tube, susceptor rotation rate 70 rpm, and susceptor temperature 1300K, the species mole fraction distribution in the reactor hot zone are shown in Figure 5-32 to Figure 5-35. The simulation results indicate that the instant reaction of TMG with ammonia in high excess rapidly consumes all the TMG fed into the reactor at the inlet. Figure 5-32 shows that the TMG:NH$_3$ is formed upstream of the high temperature zone and decomposes before reaching the reactive wafer surface on the top of susceptor.

The decomposition increases the mole fraction of TMG close to the susceptor top as shown in Figure 5-33. Not all of the TMG:NH$_3$ will decompose; however, some TMG:NH$_3$ will form the thermally stable DMGNH$_2$ with elimination of methane molecules. The mole fraction of TMG decreases again near the susceptor top because the formation of DMGNH$_2$ from TMG:NH$_3$ decreases the TMG:NH$_3$ concentration to an extent that the reaction balance favors the reforming of the TMG:NH$_3$ through reaction (i).

The formation of DMGNH$_2$ from TMG:NH$_3$ is followed by its formation of TGNCY. This explains why the mole fraction of DMGNH$_2$ increases and then decreases above the
substrate top as shown in Figure 5-34. Because DMGNH$_2$ concentrates in above the center of the substrate surface, large amount of DMGNH$_2$ and the trimer TGNCY formed by DMGNH$_2$ is expected to take part in the surface reaction on the substrate surface and results in a high growth rate in the substrate center area.

Only a fraction of the TGNCY will reach the wafer surface and go through a surface reaction to give GaN deposition. Because of the thermal diffusion effect, the TGNCY concentrates in the low temperature regions of downstream. This is shown in Figure 5-35.
The axial distributions of the mole fraction of TMG:NH$_3$, DMGNH$_2$, and TGNCY are shown in Figure 5-36. The mole fraction of DMGNH$_2$ is greater than that of TMG:NH$_3$ and TGNCY above the substrate surface. This indicates that DMGNH$_2$ is the main species that takes part in the surface reaction and contributes to the GaN growth.
Figure 5-36 Mole fraction distributions of adduct TMG:NH₃ and adduct-derived species DMGNH₂ and TGNCY along axial distance from substrate surface for straight-pipe inner tube configuration.

(b) Bell-Shaped Inner Tube Configuration

The species mole fraction distributions for the bell-shaped inner tube configuration are quite different from that for the straight-pipe inner tube configuration. The spatial mole fraction distributions of the species are shown in Figure 5-37 to Figure 5-40. The susceptor rotation rate is 70 rpm, and susceptor temperature is 1300 K.

The process of the formation of TMG:NH₃ and its decomposition, the formation of DMGNH₂ and TGNCY are similar as described for the straight-pipe inner tube configuration.

However, the intermediate species are distributed in a much broader region above the substrate surface. Because of the thermal diffusion effect, DMGNH₂ and TGNCY species have a tendency to diffuse from high temperature zone around susceptor toward the low temperature inner wall of the inner tube. Both species concentrate near the inner wall surface of the inner tube as shown in Figure 5-39 and 5-40. This makes less of the species...
to come onto the substrate surface and take part in the surface reaction. The result is low growth rate, especially on the substrate center area. However, stratified concentration flow sheets of DMGNH₂ and TGNCY are formed above the growth front. This will increase the uniformity of growth rate on the substrate surface, which is very important to improve the film quality.

**Figure 5-37** Spatial distribution of the mole fraction of TMG:NH₃ in reactor with bell-shaped inner tube

**Figure 5-38** Spatial distribution of the mole fraction of TMG in reactor with bell-shaped inner tube
Figure 5-39 Spatial distribution of the mole fraction of DMGNH₂ in reactor with bell-shaped inner tube

Figure 5-40 Spatial distribution of the mole fraction of TGNCY in reactor with bell-shaped inner tube

Figure 5-41 shows the mole fraction distributions of TMG:NH₃, DMGNH₂ and TGNCY along the axial distance from the substrate surface. It is clearly shown that near the substrate surface top, the concentrations of DMGNH₂ and TGNCY decrease quickly due to the surface reactions.
The spatial mole fraction distributions of the species for the reactor with no inner tube are shown in figures 5-42 to 5-45. The susceptor rotation rate is 70 rpm, and susceptor temperature is 1300 K.

The process of the gas-phase reactions is similar as described for the straight-pipe and bell-shaped inner tube configurations. Both DMGNH$_2$ and TGNCY will contribute to the GaN growth on substrate surface. However, because of the low wall temperature, the spatial distributions of the intermediate species are quite different from the other two inner tube configurations. DMGNH$_2$ is confined to a small region near the susceptor top. There is no significant thermal diffusion effect on the DMGNH$_2$ distribution. But the thermal diffusion effect on TGNCY distribution is very strong. The species concentrates near the reactor wall but not the susceptor top. This will lower the film growth rate on
substrate surface. Above the substrate top, there is no stratified concentration flow sheet of DMGNH$_2$. The stratified concentration flow sheet of TGNCY still exists.

**Figure 5-42** Spatial distribution of the mole fraction of TMG:NH$_3$ in reactor with no inner tube

**Figure 5-43** Spatial distribution of the mole fraction of TMG in reactor with no inner tube
Figure 5-46 shows the mole fraction distributions of TMG:NH₃, DMGNH₂ and TGNCY along the axial distance from the substrate surface. Near the substrate top, the mole fraction of TGNCY is greater than that of DMGNH₂ and TMG:NH₃, which is different from the reactor configurations with bell-shaped or straight-pipe inner tube. TGNCY is the main species that contributes the GaN growth.
(d) Growth Rate

The growth rates for the three reactor configurations are compared in Figure 5-47. For each configuration, the rotation speed of susceptor is the same, 70 rpm, and the susceptor temperature is 1300 K.

The straight-pipe inner tube configuration gives a highly non-uniform distribution of the growth rate on the center area of substrate surface. As already discussed in section 5.3.3(a), the model predicted a higher growth rate on the center area of the substrate.

Although the configuration with no inner pipe gives a fairly uniform distribution of the growth rate on the top of substrate wafer, the growth rate values are comparatively low. Another drawback of this configuration is that there is unwanted deposition on the reactor walls during operation. This effect, however, is not modeled because the deposition process is quite different from that on the substrate surface.

Figure 5-46 Mole fraction distributions of adduct TMG: NH₃ and adduct-derived species DMGNH₂ and TGNCY along axial distance from substrate surface for reactor configuration with no inner tube.
The uniformly distributed growth rate on most area of the substrate is also predicted in the reactor with the use of a bell-shaped inner tube. The growth rate gradually increases along the radial distance and the highest growth rate is obtained on the substrate edge. Compared with the growth rate in reactor with no inner tube, the growth rate is much higher. The growth rate is also more uniformly distributed than in reactor with straight-pipe inner tube.

From above analysis of the gas reactions and the growth rate comparison, it can be concluded that the bell-shaped inner tube configuration is better than the other two reactor configurations. The bell-shaped inner tube has been used for most of the experiments of MOCVD of GaN in this study.
5.3.5 Operating Parameter Effect

(a) Susceptor Rotation speed

Three susceptor rotation speeds, 0, 70, and 300 rpm, were studied. In Figure 5-16 and Figure 5-17, the pathlines of different susceptor rotation speed are displayed. It can be seen that the rotation of the susceptor and the shaft greatly change the flow in the reactor compared with no rotations. The GaN growth rate changes with different susceptor rotation speeds. Figure 5-48 shows the growth rate distributions along the substrate radial distance for three different susceptor rotation speeds.

![Figure 5-48 Predicted GaN growth rate distribution along the radial distance of substrate at different susceptor rotation speeds for bell-shaped inner tube configuration](image)

From Figure 5-48, the deposition rate of GaN increases when the susceptor rotation speed increases. This may be because the disk rotation may have an effect on determining the residence time of the reactant above the substrate wafer. Figure 5-49 is a close-up view of the pathlines of the flow around susceptor. It can be seen that gaseous species
arrived on the substrate surface will stay above and move along with the rotating surface for a certain amount of time. The higher the susceptor rotation speed, the longer the residence time above the substrate surface for gaseous species that transports near the reactive surface. Therefore, the substrate rotation is favorable for surface reactions during film growth, since the species will have more time to diffuse on to the reaction zone.

However, because the surface reaction products will also stay longer with the rotating reactive surface, a very high rotation speed will also result in a lower desorption rate of the surface reaction products from the wafer surface. This explains why the growth rate difference is smaller between 70 rpm and 300 rpm than that between 0 rpm and 70 rpm. Very high susceptor rotation speed may also cause fluid recirculation zones in the reactor as is shown in Figure 3-4(c).

**Figure 5-49** A close-up view of pathlines near the substrate top with susceptor rotation speed 70 rpm
(b) **Ammonia Flow Rate at Inlet**

Because the flow of TMG is fixed at the inlet in this study, changing the ammonia flow will change the V/III ratio. The maximum allowed ammonia flow rate of the MOCVD system is 0.9 slpm because of the limitation of the system hardware. The minimum allowed ammonia flow rate is 0.2 slpm. Three ammonia flow rates, 0.4 slpm, 0.6 slpm, and 0.9 slpm are chosen in the simulation to investigate their effects on the CVD process.

The growth rate distributions along substrate radial distance for different ammonia flow rates are predicted by simulation. The results are shown in figures 5-50.

![Figure 5-50](image.png)

**Figure 5-50** Predicted GaN growth rate distribution along the radial distance of substrate with different ammonia flow rate for bell-shaped inner tube configuration

From the comparison of the growth distributions, the growth rate is the highest when the ammonia flow rate at 0.6 slpm. This is slightly greater than the growth rate at 0.4 slpm. The little increase in the growth rate may be caused by the more intermediate species, such as DMGNH$_2$ and TGNCY, are produced from gas-phase reactions due to
the more excess of ammonia in the gas-phase. However, for the ammonia flow rate at 0.9 slpm, the growth rate decreases about 10 to 20%. This may be because high ammonia flow will push the intermediate species to leave the region above the substrate surface more quickly, resulting less surface reactions due to the decrease of species residence time. The existence of an optimal ammonia flow rate in the MOCVD of GaN growth was also reported in Gao’s [65] experimental study.

The ammonia flow rate effect can be further examined by analyzing the species concentration distribution along the axial distance from substrate. Figures 5-51 and 5-52 show the mole fraction distributions of DMGNH$_2$ and TGNCY along the reactor axis above the substrate surface at different ammonia flow rates.

Generally, the mole fraction of DMGNH$_2$ decreases as ammonia flow rate increases because of the dilution effect of ammonia to DMGNH$_2$. However, in the axial distance range below 1 mm, the DMGNH$_2$ mole fraction becomes greater for 0.6 slpm ammonia flow than that for 0.4 slpm.
Figure 5-51 Mole fraction distribution of DMGNH$_2$ along the reactor axis above the substrate surface at different ammonia flow rates for bell-shaped inner tube configuration.

The same tendency of mole fraction changing along the axial distance can be found for TGNCY in Figure 5-52.

Figure 5-52 Mole fraction distribution of TGNCY along the reactor axis above the substrate surface at different ammonia flow rates for bell-shaped inner tube configuration.
The mole fraction of TGNCY is higher when ammonia flow is at 0.6 slpm, compared with the situations when ammonia flow is 0.4 slpm or 0.9 slpm. The prediction of higher DMGNH$_2$ and TGNCY mole fraction indicates that more of the two species will take part in the surface reactions when ammonia flow is at 0.6 slpm. The reason for why the modeling predicts higher DMGNH$_2$ and TGNCY mole fraction near the substrate surface when ammonia flow is 0.6 slpm is due to the combination effect of the species residence time and the extent of how much ammonia is in excess.

(c) Model Validation

The growth rate distribution predicted by the simulation is compared with the experimental data in Figure 5-53 and Figure 5-54. Figure 5-53 shows the GaN growth rate distribution on the radial distance along substrate surface compared to the experimental data. The susceptor rotation speed is 70 rpm; the ammonia flow is 0.6 slpm; the substrate temperature is 1020 °C.

![Figure 5-53](image)

**Figure 5-53** Comparisons between experimental data and model predictions in reactor with bell-shaped inner tube. Susceptor rotation speed is 70 rpm.
Figure 5-54 shows the GaN growth rate distribution on the radial distance along substrate surface compared to experimental data taken from Gao’s experiments.\cite{65} The ammonia flow is 0.6 slpm; the substrate temperature is 1020 °C. The susceptor rotation speed is 40 rpm.

![Figure 5-54](Image)

**Figure 5-54** Comparisons between experimental data and model predictions in reactor with straight pipe inner tube.

As one can see, the predicted growth rates are much lower than the observed ones. The low predicted growth rates might be caused by the inaccuracy of the kinetic model which does not include the homogenous decomposition of TMG and its reaction on the substrate to deposit Ga. The Ga will further react with N form GaN on the substrate surface. The N is deposited from the surface reaction of ammonia with the substrate surface.

However, the model captured the observed variation trends in the growth rate. For the bell-shaped inner tube configuration, the model predicted that the lowest growth rate was
in the substrate center and gradually increased along the radial distance of substrate. The experimental data verified the same changing trend as shown in Figure 5-30(a). For the straight-pipe inner tube configuration, the model predicted that the growth rate decreased along the radial distance of substrate surface. The experimental data also confirmed the prediction.

From the comparison between the experimental and the simulated GaN growth rate, we can conclude that the model cannot give a quantitative prediction but it can give a reasonable qualitative prediction. The predicted growth rate is in reasonable agreement with the experimental data. Qualitatively, the model can provide reasonably good predictions for investigating effects of operating parameters.

The surface feature of the actual film is compared with the simulated growth rate contour on the substrate surface in Figure 5-55 and Figure 5-56.

![Figure 5-55](image1.png) A photo of the surface feature of the actual GaN film  

![Figure 5-56](image2.png) GaN growth rate contour on the substrate surface

An application of the model is to explain the existence of the unwanted deposits found on the bell-shaped inner tube. From the experimental observations, some deposits were found on the middle part of inner tube wall facing the susceptor. It is not clear what
the deposits are. However, it may be related to the high temperature on the inner tube surface. Although there is no applicable method to measure the actual temperature distribution of the inner tube, the unwanted deposits can be explained by the results from simulations. The inner tube temperature distributions predicted are shown in Figure 5-57 and Figure 5-58.

**Figure 5-57** Inner tube temperature distribution with radiative heat transfer modeling, ammonia flow rate 0.6 slpm and susceptor rotation speed 70 rpm
The temperature distribution in Figure 5-57 is predicted considering the radiative heat transfer, and the temperature distribution in Figure 5-58 is predicted without modeling the radiation exchange. A high temperature area can be seen on the part of inner tube wall that is near the heated susceptor. The highest temperature predicted including radiative heat transfer modeling is 637 K, which is higher than that predicted without considering radiative heat transfer, 582 K. The high temperature on the inner tube indicates that the magnitude of temperature gradients is smaller than that in other reactor configurations, which is beneficial to get more uniformly grown films.

According to experimental observation, the unwanted deposits are located in the predicted high temperature area. Therefore, it can be concluded qualitatively that the predicted temperature distributions are in agreement with the real ones. The simulation
considering radiative heat transfer gives higher temperature, which seems more reasonable.

5.4 Concluding Remarks

In this chapter, the simulation results are presented for the continuum modeling of the macroscopic gas flow heat transfer, species diffusion, and chemical reactions in the MOCVD process of GaN. The model can give valuable insights on the MOCVD process that cannot be provided by experimental study. The model gives a further understanding of some important basic aspects of the MOCVD process.

There is still largely unknown chemistry of the MOCVD process of GaN. Future work should deal with the integration of more detailed chemistry mechanisms in reactor models.
6. CONCLUSIONS

In this work, a systematic experimental research on the effects of growth condition on the quality of MOCVD GaN film has been carried out in a vertical rotating-disk MOCVD reactor. A model for simulating the MOCVD of GaN has been developed.

The effects of different ELO conditions have been studied experimentally. The experimental results of the effects of different growth conditions were compared. The ELO process can greatly improve the GaN film quality. The regrowth of GaN with a low temperature GaN buffer layer gives the best ELO film. An AlN buffer layer is not suitable for the second growth of GaN.

In the CVD reactor modeling, a kinetic model has been used to describe the gas-phase reactions and surface reactions in the MOCVD process of GaN. Radiative heat transfer and multi-component diffusion including mass diffusion and thermal diffusion were also taken into account. The transport phenomena inside the reactor was studied in different conditions. The simulation has been used to study the operating parameter effects on film growth. Different ammonia flow rate, susceptor rotation speed, and different inner tube type will influence the growth process. The model predictions were compared with experimental results. The results of this work have increased the understanding of the growth process.
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APPENDIX: MOCVD SYSTEM OPERATING PROCEDURE

1. PREPARATION

*Prepare Substrate.*

Heat substrate wafer in acetone for 5 minutes using the CORNING hot plate heater. Then, rinse substrate with DI water and blow dry with nitrogen gas. Clip substrate to susceptor and place susceptor in loadlock chamber.

*Evacuate and Backfill Loadlock with Nitrogen Gas.*

(a) **Start the CVDPRC Program**

On the computer monitor screen type the following commands under MS-DOS prompt:

```
C:\CVD\cvdprc
```

MANUAL MODE: M

On the monitor screen, check for “Low N2 Press Alarm”. The inlet and outlet valves of N₂ purifier need to be opened if there is such an alarm.

(b) **Evacuate Load Lock**

Set “Load Lock N2” setpoint (SETPT) to 0.0. Press [START] button on the “Load Lock Evacuate Start” panel to start evacuating the loadlock. After “Load Lock Vacuum Gauge” reads below 1 torr, wait 4 minutes for the evacuating to proceed.

(c) **Backfill Load Lock**

Set “Load Lock N2” setpoint to 10. Press [STOP] button (“Load Lock Evacuate Stop”) to backfill N₂. Wait 3–4 minutes. Repeat (b) and (c) steps for three more times.
(d) **Load the Sample into Reactor Chamber**

After the 3~4 minutes’ backfill with “Load Lock N2” at 10, set it to 0.0 (verify that the value is 0 and the load lock pressure is 1.1×10^3 torr). Press the [LOAD] button on the process panel. Wait until the sample is fully loaded.

(e) **Prepare Gas Sources and Cooling Water**

Turn on the exhaust fan. Open valve of H2 tank and Set H2 Purifier switch to the “NORMAL” position. Open valve of NH3 tank. Start water chiller. Reset alarms and all alarm LED’s should extinguish.

2. **DEPOSITION PROCESS**

Select the menu bar “NEW RECIPE” (or “NEW RCP”) on screen, then specify operating mode to be automatic, input recipe name and lot number, and input other required information. The following message will appear after the above inputs: “BEGIN PROCESS/TERMINATE SESSION <B/T>: “. The recipe is loaded by pressing “B”. Wait for the first menu bar ABORT to change to “GO AHEAD”. Then select menu bar “GO AHEAD” and hit <Enter> key.

Set bubbler#2 pressure controller to Auto Mode (if applicable). Check the bubbler#2 pressure during AlN growth. If it reaches 900 torr, abort the recipe.

3. **SHUT-DOWN PROCEDURE**

Be certain that the recipe is completed, and all set points are at 0. Press the [UNLOAD] button. Wait until sample is fully unloaded. Flip H2 Purifier switch back to “PURGE” (up) position and close the valve on H2 tank. Close the valves on N2 Purifier. Close the valve on ammonia tank. Turn off H2O chiller. Check the readouts of bubbler#2
pressure controller; set the controller to manual mode and the valve opening percentage to 0.0. Wait 2 minutes after purging the H₂ purifier to turn off exhaust fan. Opening load lock door and take out the sample.

4. Maintenance

**Restarting the Computer**

When the computer needs to be restarted, press Ctrl-Alt-Delete to restart. A boot disk should be in the floppy disk drive. After restarting the computer, change directory to C:\CVD and run CVDGO command to install the interrupt drivers. Then start CVDPRC program.

**Refilling Gases**

To order a refill, contact Pallini Industries Inc. at (740) 594-7730.

To change UHP hydrogen tank, first make sure the tank valve and system hydrogen inlet valve HV1 are closed. Disconnect tank from pipeline and connect the newly refilled tank to pipeline. Open HV1 valve and check leakage with combustible gas detector.

For the liquid nitrogen dewar, note that the level indicator tends to stick. The dewar is probably close to empty when the indicator reads below 1/2. Check the N₂ purifier valves are closed. Close the valve of dewar that is connected to the system. Disconnect the dewar from pipeline. Cover up the outlet of dewar and the system pipeline inlet. When the newly refilled arrives, reconnect it to the pipeline and check the pressure. Make sure the pressure is higher than 80psi.