Reaction and Transport Processes in OMCVD: Selective and Group III-Nitride Growth

by

Theodoros Mihopoulos

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Abstract

Researchers have continued to explore light sources that are brighter, cheaper, more reliable, and emit light closer to natural sunlight than conventional incandescent and fluorescent lighting. The most recent advance in this direction is the fabrication of light emitting diodes (LEDs), and laser diodes that can emit in the short wavelength region of the visible spectrum (from green to violet). By using organometallic chemical vapor deposition (OMCVD) to fabricate thin films of the group III nitride materials (GaN, AlN, and InN), LEDs with lifetimes over 10,000 hours are now commercially available while rapid progress is being made towards a laser diode structure with a similar lifetime. These devices, coupled with the existing red, yellow, orange, and amber LEDs (based on AlInGaP, also grown by OMCVD) whose light-emission efficiency is already superior to incandescent lamps can lead to full color solid-state light sources.

OMCVD of AlGaInN involves complex chemistry and flow phenomena, which determine the quality of the deposited layers. Incorporation of significant concentrations of Al and In have proven difficult to achieve. The understanding of the dominant reaction pathways and their interaction with transport phenomena has been insufficient for design and optimization of nitride deposition processes. This thesis describes coupled finite element simulations of fluid flow, heat and mass transfer with emphasis on constructing kinetic mechanisms that incorporate all the chemistry information known by experimental studies and quantum chemistry calculations.

A kinetic mechanism for GaN deposition is proposed. The model involves fast reaction between trimethylgallium and NH$_3$ to form a Lewis type acid-base adduct which can dissociate or decompose at higher temperatures. The decomposition fragments can subsequently react to form dimer or trimer complexes in the gas phase containing multiple gallium-nitrogen bonds. Reaction rate parameters are obtained from quantum chemistry calculations in the literature and analysis of experimental data. The reaction mechanism is shown to be consistent with individual experimental observations, flow-tube decomposition studies, and growth rate temperature and pressure dependence in a horizontal OMCVD reactor as well as growth rate data in a close-spaced OMCVD reactor. The growth rate appears to be limited by GaN formation at low temperatures, mass transport at intermediate temperatures and GaN decomposition at temperatures higher than 1000 °C. Dimer and trimer formation provide additional pathways of Ga supply to the surface at low temperatures and high pressures.

In order to simulate nitride growth in a new OMCVD reactor with close-spaced-injector, a hierarchical simulation approach of fluid flow and mass transfer in such reactors was initially performed. Three-dimensional calculations establish that there is complete mixing in the gas phase, while the individual gas injectors dissipate within 5-8 mm from the reactor inlet under typical operating conditions.
conditions. Two-dimensional parametric studies of growth rate and uniformity dependence on operating conditions and geometric factors were used to gain insight into the chamber performance. Regions of stagnation and rotating disk flows were delineated as a function of operating parameters. In the case of rotating disk flow, growth uniformity increases with pressure, contrary to the classical vertical rotating disk reactor response.

A mechanism for AlN growth is also described. Formation of dimers and trimers in the gas-phase is identified as the major pathway for decreased growth efficiency with decreasing pressure. An additional pathway involving nucleation and growth of oligomers from dimers and trimers, and ultimately particle formation, is consistent with decreased growth efficiency with increasing temperature. The kinetic model is consistent with experimental observations of temperature and pressure dependence of AlN growth rate in a horizontal hot-wall reactor and growth rate data for AlGaN in a close-spaced reactor. In agreement with experimental observations, the simulations predict AlN deposition in a close-spaced reactor under conditions that prohibit AlN growth in a horizontal reactor.

Thin films of In$_x$Ga$_{1-x}$N are used as the active region in the III-N devices. Thus, controlling the indium composition in a reproducible manner is imperative for III-N device fabrication. The solid indium mole fraction in InGaN is reported to independently depend on temperature, relative indium amount at the inlet, film growth rate, and carrier gas used. A simple trapping mechanism is proposed for InN growth in InGaN ternary alloys. In agreement with multiple experimental observations, the indium content appears to be controlled by competition between desorption kinetics and incorporation, the latter being determined by the GaN growth rate since InN is not stable under typical growth conditions. The effect of H$_2$ carrier gas on indium mole fraction is also discussed.

For laser diode fabrication in the III-Nitride system, selective area growth is used to deposit buffer layers with fewer dislocations. In addition to its recent use in the nitride system, selective area epitaxy has been pursued in OMCVD of III-V compound semiconductors in general. Quantitative understanding of selective epitaxy, in particular compositional variations arising in selective growth of ternary alloys such as InGaAs and InGaP that are currently not understood, is needed to realize advanced optoelectronic devices. A hierarchical modeling approach of selective area epitaxy is undertaken to identify the origins of growth rate enhancement and indium composition enrichment in the case of ternary InGa(As/P) growth. Simulations using the stagnant layer approach reveal that surface reaction rate differences give rise to the compositional modulation. A realistic fluid flow description in a vertical axisymmetric reactor is coupled with a simple kinetic mechanism for InGaAs/P deposition. Differences in homogeneous decomposition kinetics of In and Ga precursors give rise to different “effective” surface reaction rates that lead to the observed In-enrichment. The proposed model is in agreement with reports on the dependence of In-enrichment on operating parameters. Simulations show that, while the alloy deposition is limited by mass transport, differences in reaction rates are responsible for the composition variations in selective growth. Thus, the usefulness of reaction-transport models in elucidating the relative roles of different deposition pathways and gaining insight to the deposition process is demonstrated. Growth rate enhancement and In-enrichment model predictions are in excellent agreement with experimental data on lateral and axial dependence obtained in a horizontal reactor with a large masked area.

Research advisor: Klavs F. Jensen
Lammot Du Pont Professor of Chemical Engineering
To my parents, Γιώργο και Βουλα Μιχοπουλου
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Chapter 1. Introduction and motivation

Thin films of elemental and compound semiconductors find a wide range of applications in electronic and optoelectronic components. Devices such as light-emitting diodes, solid-state lasers, photovoltaics, infrared detectors, high-electron mobility transistors and heterojunction bipolar transistors can be fabricated. While silicon is the established material in electronic device technology, its indirect energy bandgap limits its use in optoelectronic device applications. III-V compound semiconductors, such as GaAs, AlAs, InP and their alloys are of particular interest since they are direct bandgap semiconductors that can emit coherent light for photonic applications. By varying the composition in ternary alloys, devices operating in a broad wavelength range can be fabricated as shown in Figure 1-1.

With the current drive for even smaller and faster devices, lateral as well as vertical shrinking of the crystalline films is required. The most successful approach to the vertical size reduction problem for compound semiconductors, has been through the application of advanced epitaxial growth techniques [1]. In epitaxial growth, a layer of the desired semiconductor (e.g. GaAs) is formed by co-deposition of the individual growth species on an existing single crystal surface. The substrate and the deposited crystal have the same crystallographic orientation. Out of the variety of epitaxial techniques currently available for III-V growth, organometallic chemical vapor deposition (OMCVD) possesses the advantage of large area growth, while also being the most versatile method. In OMCVD, the gaseous reactants, also called precursors, are introduced in a reactor at low temperature diluted in a carrier gas such as H₂ or N₂. These
precursors, reach a heated zone close to the substrate and undergo homogeneous and heterogeneous chemical reactions that lead to deposition of the desired material. Organometallic compounds such as (CH₃)₃Ga, (CH₃)₃Al and (CH₃)₃In are used as the group III precursors, lending their name to the epitaxial technique. The wide range of organometallic precursors available and the chemical similarities among them account for the high versatility of the process.

![Bandgap versus lattice constant of a variety of elemental and compound semiconductors.](image)

Figure 1-1. Bandgap versus lattice constant of a variety of elemental and compound semiconductors. Lines indicate the bandgap vs. lattice constant dependence of ternary alloys.

Chemical vapor deposition processes to grow epitaxial films are performed in numerous reactor configurations and a wide range of operating parameters. A recent review can be found in [2]. Optoelectronic device fabrication requires growth of successive epitaxial layers with a
tight control of layer properties such as thickness, uniformity, composition, morphology and ultimately electrical properties. Until the late 1980s, OMCVD was predominantly a research technique, focusing on new materials and the performance improvement of devices fabricated from these materials [3]. The recent transition to manufacture for a variety of III-V compound semiconductors (e.g. AlInGaP that leads to high-brightness visible light emitting diodes and lasers in the red to yellow-green region) places new requirements of controllability and reproducibility of the process. Thus, understanding of the multiple transport phenomena and chemical kinetic steps involved in OMCVD is necessary.

While OMCVD currently contributes about 15% of the material for devices in the optoelectronics industry, this amount is projected to increase to 25% by 2000 [4]. Light emitting diodes (LEDs), by far the largest component of this ~ $4.5 billion industry, used little if any of this technology in 1994, but by 1996 ~ 2% of the material was grown by OMCVD with projections of ~ 8% by 2000. These projections are spurred by the recent demonstration of LEDs and Laser Diodes (LDs) operating in the blue and green region of the spectrum that is fueling intensive research activity as well as general interest [5].

Ever since the invention of the incandescent bulb by Thomas Edison, researchers have striven for light sources that are brighter, cheaper, more reliable, and emit light closer to natural sunlight. The most recent advance in this direction is the fabrication of LEDs [6], and LDs [7] that can emit in the short wavelength region of the visible spectrum (from green to violet). These devices, coupled with the existing red, yellow, orange, and amber LEDs (based on AlInGaP, also grown by OMCVD) whose light-emission efficiency is already superior to incandescent lamps [8], can lead to full color solid-sate light sources. Although short wavelength LEDs and LDs have been fabricated with SiC and II-VI materials, their use is impaired by the very low
efficiency and short lifetime they exhibit. On the contrary, when the III-Nitride material system is used, LEDs with lifetimes over 10,000 hours are now commercially available while rapid progress is being made towards a Laser Diode structure with a similar lifetime [9]. These devices can find a number of applications in addition to full color electroluminescent displays, such as laser printers, read-write laser sources for high-density information storage on magneto-optical media, UV photo detectors etc. As a result, the column III nitride materials, gallium nitride (GaN), aluminum nitride (AlN), indium nitride (InN) and their alloys have been the focus of intense research over the last 4-6 years. These materials are excellent for bandgap engineering because they form a continuous range of superlattices with direct room-temperature bandgaps that range from 6.2 eV for AlN, to 3.4 eV for GaN, to 1.9 eV for InN.

In order to realize these devices, high-quality epitaxial films with low defect densities and controlled conductivity are needed. Although single crystalline GaN was first synthesized almost 30 years ago [10], the epitaxial growth of high quality films necessary for p-n junction fabrication has been hampered by a number of reasons:

- Lack of a suitable lattice-matched substrate. A variety of single crystals have been used as substrates. Sapphire, which is the most popular one, exhibits a ~14% lattice mismatch with GaN. This misfit coupled with differences in thermal expansion coefficient (7.5·10$^{-6}$/°C for sapphire vs. 5.6·10$^{-6}$/°C for GaN, 4.2·10$^{-6}$/°C for AlN and 4.0·10$^{-6}$/°C for InN) leads to epitaxial films with poor morphology and plenty of cracks and dislocations.

- Large n-type background carrier concentrations in the deposited nitride films as a result of defects and impurities. As grown GaN films typically contain a $10^{19}$-$10^{20}$ cm$^{-3}$ free electron concentration. Silicon or oxygen are typical contaminants identified to act as donors. As a result, p-type conductivity had been almost impossible to realize.
• Inability to grow bulk crystals of the nitrides from stoichiometric melts by standard crystallization methods such as Czochralski or Bridgman growth. This is due to the extremely high melting temperatures (~2800 °C for GaN, ~3500 °C for AlN) and very high decomposition N\textsubscript{2} pressures at melting (~45 kbar for GaN, 200 bar for AlN) [11]. The large equilibrium N\textsubscript{2} pressure necessary to suppress GaN decomposition even under typical growth conditions (~20 bar at 1000 °C, [12]) further hinders epitaxial growth. Additional difficulties are associated with the thermal dissociation of InN at temperatures > 600 °C.

• Severe pre-reactions between the commonly employed OMCVD precursors, trimethylgallium (TMGa) or trimethylaluminium (TMAI) with ammonia. Both metalorganic precursors readily form Lewis acid-base type adducts with ammonia upon mixing. The adducts have low vapor pressure and their presence leads to changes in the nature as well as gas phase depletion of the actual growth precursors that in turn can result in growth uniformity, quality and efficiency degradation. Moreover, since these reactions take place away from the heated substrate, additional parameters such as reactor geometry, reactant delivery, and inlet mixing design critically influence the epitaxial growth. In a typical statement on the effect of pre-reactions, Sasaki [13] notes that "when discussing the GaN growth mechanism, some process in the gas phase should not be overlooked", upon observing that the most important parameter in whether epitaxial growth is observed or not in his setup is the inlet nozzle-to-susceptor distance. Adduct pre-reactions are more severe in the case of AlN growth.

Although Pankove succeeded in fabricating the first GaN LED in 1971, [14], it was an \textit{m-i-n} structure since \textit{p}-type GaN was not available. Nearly all the imaginable GaN-based optical
devices are better realized using $p$-$n$ homojunctions or even better using heterojunctions. Due to
the problems mentioned above, GaN research slowly faded and development in nitride materials
was interrupted. It was not until the pioneering work of Isamu Akasaki in the mid-1980s that
many of these problems began to be overcome. The substrate mismatch problem was solved by
the use of a thin AlN buffer layer deposited on sapphire at low temperature ($\sim$ 500 °C) upon
which the actual III-N thick film is then grown at elevated temperatures ($\sim$1050 °C). Using this
approach, the first high quality GaN films, specular, free of cracks and with reduced background
electron concentration, were deposited by atmospheric pressure OMCVD on sapphire substrates
[15]. The buffer layer was shown to supply nucleation sites with low orientational fluctuation
and promote the lateral growth of GaN [16]. This breakthrough was followed by another: the
first successful production of $p$-type GaN by low-energy electron-beam irradiation (LEEBI) of
magnesium-doped GaN, which as-grown is highly resistive [17]. With all the components in
place, the first violet-blue $p$-$n$ junction GaN LED was demonstrated [18].

At around the same time, Shuji Nakamura at Nichia Chemical Company implemented
and extended many of these ideas. He first introduced a novel reactor design for the OMCVD
growth of the nitride materials. It has two different gas flows and is predictably called TF-
MOCVD [19]. The main flow carries the reactant gases parallel to the substrate similar to a
conventional horizontal reactor. The second flow (subflow) transports inactive ($H_2$ and $N_2$) gas
perpendicular to the substrate surface. Nakamura points out that this subflow is very important;
in its absence continuous nitride film cannot be grown because the reaction gas rises due to
natural convection. The subflow is used to urge the rising reaction gas downward to be brought
in contact with the substrate [20]. He then proposed the use of a thin GaN low-temperature
buffer layer instead of AlN and showed that for an optimum buffer layer thickness of 200 Å, the
resulting high temperature epitaxial film has superior electrical properties (e.g., very low background carrier concentration, high Hall mobility) [21]. He also succeeded in obtaining very low-resistivity, highly p-type GaN films by thermal annealing Mg-doped GaN films at temperatures above 700 °C under N₂ ambient or vacuum [22]. Nakamura et al. [23] then suggested that hydrogen passivation through the formation of electrically inactive Mg-H complexes during OMCVD was responsible for the compensated acceptors, a theory later validated by direct spectroscopic evidence of the Mg-H complex [24,25]. LEEBI treatment or thermal annealing dissociates these complexes and electrically activates the acceptor dopants, the latter process being capable of uniformly changing the entire thickness of the as-grown layer into a low-resistivity p-type GaN film [23]. In a span of three years Nakamura and his coworkers proceeded to demonstrate and commercialize high-brightness, high-efficiency blue and green LEDs based on double heterostructure [26], and single quantum well design [27,28] using a thin InGaN film as the active layer. Soon thereafter they demonstrated the first violet room temperature continuous-wave Laser Diode based on an InGaN multi-quantum-well active region, [29]. Continuous improvements in the deposition process have increased the LD lifetime sufficiently that its commercialization is imminent [9].

These advances have spurred extraordinary interest in the III-N material system with a lot of growth and device related work being reported [30-32]. Although a variety of deposition techniques using numerous precursors have been used (for a comprehensive review see [33]), the highest material quality III-N films to date have been grown by OMCVD [7,34,35]. This capability, coupled with the aforementioned potential for high throughput and abrupt interface growth has established OMCVD as the principal epitaxial technique for nitride growth. A typical growth procedure consists of a low temperature (500 °C - 700 °C) buffer layer growth on
a sapphire substrate followed by a high temperature (~1050 °C) epitaxial growth of the thin film. The precursors normally used are TMG, TMA and TMI as group III source and NH₃ as the nitrogen source in H₂ and/or N₂ carrier gas.

With the main aspects of the growth recipe based on an established technique like OMCVD in place, one would have expected fast progress towards commercialization of simpler devices such as LEDs and advances in more complex structures e.g., LDs, field effect transistors, and photodetectors. Yet, despite the large effort expended in recent years, many fundamental growth-related problems remain unsolved. One of the main challenges in the commercial development of GaN based devices is the optimal design and operation of OMCVD reactors capable of growing such materials. In contrast to typical III-V OMCVD growth, reactor design is of paramount importance in realizing device quality material in nitride growth. During a unofficial poll among researchers regarding their geometry of choice in a recent MRS symposium, more that one third “felt” that the two-flow design is the best, despite the fact that none present knew the details of its operation, or the reason it outperforms other designs. Clearly, Nakamura’s claim that the subflow succeeds in bringing the process gases in contact with the substrate cannot be the explanation, since all reactor designs can accomplish such a task. Although a lot of growth related work under similar conditions is being reported on a variety of different reactor configurations, such as vertical rotating-disk reactor (RDR) [36,37], “planetary” multiple-wafer reactor [38], and stagnation-flow close-spaced reactor [39], it is not understood why material quality significantly differs among them. Neither is it clear what are the problems (growth pathways / transport phenomena) that specific reactor designs help eliminate. This uncertainty stems from the fact that the kinetics of GaN formation is not well understood. Considering reaction kinetics, the high temperatures used lead to significant gas-
phase decomposition of the precursors. Moreover, since TMG and NH₃ react at low temperature, the reactor inlet design, and reactant residence time are important parameters. Considering transport phenomena, the large temperature gradients and large concentration of NH₃ lead to complex non-dilute mixed convection reactive flow fields. As a result, “the crystal grower is required to explore the crystal growth parameter space peculiar to the specific reactor geometry employed in order to determine the optimum conditions for the growth of both the buffer layer and the epitaxial film” [31].

For growth optimization to take place, it is imperative that growth conditions during epitaxy be well-identified and reproducible. Given the complexity of the deposition, physical-model-based simulations that combine transport phenomena and chemical kinetics become essential to understand and quantify the different rate processes controlling nitride growth. Such kinetic mechanisms should be able to predict the numerous growth variations observed. In addition, they should be able to provide insight into the origin of the film variations and elucidate the relative roles of different deposition pathways. No such study of nitride growth has been reported. Safvi et al. [40] reported on a model for the growth of GaN growth in a vertical reactor. They used an apparent chemistry model with a small number of species participating in a simple mechanism. The main reaction rate was fitted to experimental data. No pressure or temperature dependence was studied. Wide variation in the rate for the same reaction as a function of flow rate was needed in order to describe the experimental data. Of course, a reaction rate should not depend on flow rate. Thus, this study demonstrates the inability of apparent chemistry models to capture the many facets of nitride deposition.

For laser diode fabrication in the III-Nitride system, selective area growth is used to deposit buffer layers with fewer dislocations and address the substrate mismatch problem [9].
Epitaxial growth techniques, such as OMCVD, are usually considered as large-area deposition techniques that result in complete coverage of the substrate surface. In selective growth, parts of the substrate are covered with a stable dielectric material such as SiO$_2$ or Si$_3$N$_4$, and the process is manipulated so that growth is confined to openings in the mask. Atoms or molecules impinging on the masked surfaces desorb and reenter in the gas phase, where they can collide with other molecules, and be redirected towards the substrate surface, contributing thus to the growth rate. If they strike the mask again, they re-evaporate. Consequently, the growth rate is enhanced, the enhancement being higher closer to the substrate-mask interface.

In addition to its recent use in the nitride system, selective area epitaxy has been pursued in OMCVD of III-V compound semiconductors in general. Selective growth offers unique opportunities for device isolation and monolithic integration of electronic and photonic devices onto the same substrate, using fewer, self-aligned processing steps. As discussed earlier, OMCVD offers an established solution to the control of the film vertical dimension. When coupled with selective area growth, lateral dimensional control can also be achieved. Thus selective epitaxy has been used to fabricate tapered waveguides, quantum wire and quantum dot-like structures, and vertical multiple quantum structures that allow the construction of lasers, modulators, and low-loss waveguides in a single plane (see [41,42] for a recent review). These examples demonstrate the potential of selective area growth to become an important technology for the fabrication of tailored, optoelectronic devices. However, a quantitative understanding of the growth procedures is needed to fully utilize its potential. In particular, compositional variations arising in selective growth of ternary alloys such as InGaAs and InGaP are not currently understood and various explanations choosing gas-phase diffusion, surface migration, or gas-phase reaction differences are proposed. While these variations are mostly undesired
because they change the bandgap of the alloy, they can also be exploited to fabricate novel device structures such as multi quantum wells in a single growth step. Thus, quantitative understanding of selective epitaxy can be used to realize its substantial capabilities for advanced optoelectronic devices.

The objective of this thesis is to develop a systematic understanding of the processes underlying OMCVD growth in the III-Nitride system and selective OMCVD growth by combining physically accurate transport phenomena models with proposed gas-phase and surface chemistry mechanisms. Transport processes determine the access of precursors to the growth interface and control the degree of gas-phase reactions occurring prior to species participating in surface deposition reactions. A poor selection of design or operating parameters can lead to complex flow fields resulting in non-uniform film thickness and increased potential for particle formation. The importance of transport phenomena issues in reactor design and operating conditions has been realized and extensively studied (see [43] for a detailed review). These transport phenomena concepts have to be combined with models of chemical reaction mechanisms and species mass transport. Chemical mechanisms can account for different levels of the underlying chemistry. Simple models consisting of a few lumped rate expressions for the gas-phase and surface chemistry can be easily incorporated into transport simulations with modest requirements in computational resources. However, these models provide limited insight into the underlying chemistry and may not be used to extrapolate to new operating regimes. Mechanisms based on elementary reactions represent the other extreme by providing detailed understanding of the various deposition reaction pathways at the expense of significant computational effort.
Furthermore, formulation of the accurate detailed models for OMCVD systems is hindered by the complex nature of chemical interactions and the lack of available information on the reactivity of the precursors. In this work we aim to develop a model that is consistent with reported trends in GaN, AlN, and InN growth for several different studies, rather than a model that exhibits an exact agreement with only one particular set of data. In developing this mechanism, we incorporated all the known chemistry pertaining to the growth of III-Nitrides through either experimental studies or quantum chemistry calculations of thermochemical species data and kinetic parameters. Various levels of reactor fluid dynamics (idealized plug flow reactor, stagnant layer approach, two-dimensional axisymmetric and realistic three-dimensional reactor models) are used to determine the dominant kinetic pathways and obtain chemistry models for full-scale reactor design and optimization.

In Chapter 2 the governing equations describing conservation of total mass, momentum, energy along with mass balances for individual chemical species are presented. The finite element method is used to solve this nonlinear set of partial differential equations along with appropriate boundary conditions. Due to the non-dilute nature of the carrier gas (H₂/N₂ and NH₃ in comparable amounts) in III-Nitride OMCVD, the implementation of multicomponent diffusion is discussed in detail. Chapter 3 presents a hierarchical simulation approach of fluid flow and mass transfer in a novel OMCVD reactor design that finds extensive use in III-Nitride growth. Two- and three-dimensional calculations are used to map the growth rate and uniformity reactor performance with respect to operating conditions and geometric factors. In Chapter 4, the kinetic model for GaN deposition is presented while Chapter 5 discusses kinetic models for AlGaN and InGaN growth. The issue of compositional and growth rate variations in
selective growth of ternary InGa(As/P) alloys is addressed in Chapter 6. Finally Chapter 7 summarizes the contributions of this work and provides recommendations for further study.
1.1 References


Chapter 2. Model formulation and solution method

2.1 Introduction

The mathematical models presented in this thesis are constructed to quantitatively describe the complex interaction between the gas-phase fluid dynamics and the heat and individual species transport in OMCVD reactors. The models consist of a set of partial differential equations (PDEs) with appropriate boundary conditions, describing the fluid flow, the transport of energy and species and the chemical reactions in an OMCVD reactor. Several transport properties of gas species and mixtures enter in these equations. Their values depend on the temperature, pressure and composition of the gas mixture. The chemical reactions in the gas-phase and at the substrate surface are described in a general way that is applicable to many different semiconductor materials. Knowledge of the specific chemical mechanisms and kinetics is necessary for the actual modeling of a particular compound system. This knowledge must be attained from experimental observations and theoretical considerations on the chemistry of that process. Development of such kinetic models is the focus of this thesis. The usefulness of the simulations lies in the accuracy of the predicted solutions as well as in the capability of the numerical algorithms used to solve the set of governing equation. Therefore, care needs to be taken when making assumptions in order to simplify the physics of the process and reduce the computation time to tractable levels.
Numerical methods are required to solve the nonlinear set of governing equations. In this thesis the equations are solved via the finite element method (FEM), which is a naturally suited approach to solving the coupled, nonlinear PDEs arising in fluid flow, heat and mass transfer calculations. In the FEM procedure, a mesh is generated by tessellating the computational domain into many regularly shaped elements. Piecewise polynomials represent the solution. By applying a Galerkin approximation, the PDEs governing transport phenomena and reaction are converted in a set of coupled algebraic equations in the unknown node values of the polynomial approximation. The resulting system of equations is then solved by using Newton's method.

Detailed models of CVD processes based on the finite element method have been presented in recent years and ample reference exists on the framework for developing the equations and solving them numerically [1-4]. Emphasis here is placed on the implementation of the multicomponent diffusion formulation in the constitutive relation for the diffusive flux in individual species transport. The principal assumptions involved in the derivation of the PDEs describing transport phenomena and chemistry in the reactor enclosures are discussed in section 2.2. The PDEs themselves are presented in section 2.3, while section 2.4 contains the boundary conditions associated with these equations. The numerical methods used to solve the PDEs are outlined in section 2.5 along with mesh generation procedures. Specifically, the discretization of the dependent variables and algebraic equation formulation over the computational domain along with methods for solving the resulting linear problem are described. Finally, section 2.6 presents a method to compute gas-mixture properties and implement multicomponent diffusion.
2.2 Model assumptions

A number of important assumptions are employed to reduce the computational effort required for solving the modeling equations. These assumptions are generally justified for typical CVD conditions and essentially do not limit the accuracy and pertinence of the model for CVD applications. These key assumptions are listed below:

- *The gas mixture behaves as a continuum.* This approach is appropriate because the Knudsen number, the ratio of the mean free path to the length scale over which macroscopic changes in properties occur, is smaller than 0.1 when operating under reduced or atmospheric pressures characteristic of most OMCVD systems. As a point of reference, the mean free path length at 76 torr and 400 °C is approximately 2.6 and 1.6 μm in H₂ and N₂ carrier gas, respectively.

- *The gases follow the ideal gas law.* This is a valid assumption for the types of gases, and at the low pressures and high temperatures used in CVD. The ideal gas law provides the gas density dependence on temperature, that is needed to capture gas expansion effects due to density changes caused by the large temperature differences (~ 600 – 1000 K) between the hot substrate and the cold walls.

- *The gas flow in the reactor is laminar.* This is a valid assumption for the Reynolds number range typically encountered in CVD. The Reynolds number is a measure of the relative importance of convective (inertial) and viscous forces and typically takes values in the 1-100 range. This range is much lower than the values at the onset of turbulence in a reactor (= 2300 for pipe flow, = 1000 for free jet flow).

- *The gas density depends only on temperature.* The very low Mach numbers, i.e., the ratio of the gas velocity in the reactor to the speed of sound, encountered in CVD justify this
assumption. Furthermore, since the pressure drop in CVD reactors is very small ($\approx 10^{-6}$ atm), the pressure imposed at the reactor outlet is assumed to be a constant and is used in the ideal gas law to calculate the density.

- A steady-state formulation is used. This assumption is valid because the time scale for deposition of thin semiconductor films (growth rates $\sim 1 \mu\text{m/hr}$) is much longer than the time scale for convective and diffusive transport processes in the gas which is on the order of seconds. Thus, transient terms can be safely dropped from the modeling equations of steady-state deposition processes. Similarly, the thin film length scale on the order of microns is much smaller than the characteristic length scale of gas flow in the reactor, and the time evolution of the film profile can be neglected.

- The fluid flow and heat transfer are decoupled from the mass transfer. The reactant species and the reaction products are present in low concentrations on the order of $10^{-5}$ mole fraction in a carrier gas, typically H$_2$ or N$_2$. Thus the properties of the gas mixture present in the reactor remain constant and equal to those of the carrier gas. Even in the case of III-Nitride deposition (where comparable amounts of H$_2$ (or N$_2$) and NH$_3$ are used) the organometallic precursors and the reaction products are still present in trace amounts. As will be discussed in Chapter 4, negligible homogeneous NH$_3$ decomposition occurs, and thus the carrier gas can be assumed to be a constant-composition mixture of H$_2$(N$_2$) and NH$_3$. Mixing rules are used to compute the “effective” carrier gas transport properties (viscosity, thermal conductivity, heat capacity) that are used in the fluid flow and heat transfer calculations. These mixing rules are presented in section 2.6. Since the mass loss due to deposition is negligible, no source/drain terms are present in the total mass conservation equation and it may then be decoupled from the chemistry. The
energy conservation equation can also be decoupled from the chemistry, since, due to the dilute nature of the reactants, heat consumption or dissipation by gas-phase reactions can be neglected.

2.3 Governing equations

The CVD equations are based on conservation equations for the total mass, momentum, energy, and individual gas-phase species along with constitutive relations for momentum, heat, and species fluxes. These transport equations can be readily found in fluid dynamics texts such as [5]. The simplifying modeling assumptions described in the previous section are used to derive the following set of governing equations. Since two- and three-dimensional calculations were performed in this thesis, the equations will be given in vector notation for simplicity.

Conservation of total mass is represented by the continuity equation:

$$\nabla \cdot (\rho \mathbf{v}) = 0, \quad (2.1)$$

where $\rho$ is the mass density of the gas mixture and $\mathbf{v}$ is the vector of mass averaged velocities.

The density is given by the ideal gas law:

$$\rho = \frac{p \overline{M}}{RT}, \quad (2.2)$$

where $p$ is the ambient pressure, $\overline{M}$ is the average molecular weight of the gas, $T$ is the temperature, and $R$ is the universal gas constant.

The conservation of momentum is given by:

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \nabla \cdot \mathbf{v} + \rho g, \quad (2.3)$$
where $g$ is the vector of gravitational force. The tensor $\tau$ denotes the viscous stress tensor and for a Newtonian fluid mixture is given by:

$$\tau = \mu[\nabla v + (\nabla v)^T] - \frac{2}{3} \mu (\nabla \cdot v) I,$$  \hspace{1cm} (2.4)

where $\mu$ is the viscosity of the gas mixture and $I$ is the identity tensor.

Conservation of energy in the reactive flow system is described by the following equation:

$$\rho C_p \nabla v \cdot \nabla T = \nabla \cdot \lambda \nabla T,$$  \hspace{1cm} (2.5)

where $\lambda$ and $C_p$ are the mixture-averaged thermal conductivity and constant pressure heat capacity of the gas respectively. In deriving equation (2.5), effects of heating due to viscous dissipation, energy flux due to concentration gradients, and gas heating through radiation have been neglected in addition to the assumptions discussed in the previous section. The energy equation for solid materials is given by:

$$\nabla \cdot K_j \nabla T + S = 0,$$  \hspace{1cm} (2.6)

where $K_j$ is the thermal conductivity of solid material $j$, and $S$ is a volumetric heat source term. This term is zero for all solid materials unless a resistive reactor heater (inductive or resistive) is included in the calculation of the temperature field.

The conservation equation for individual species $k$ can be expressed as follows:

$$\nabla \cdot (\rho v Y_k) = -\nabla \cdot j_k + M_k \cdot \dot{R}_k \hspace{0.5cm} k = 1, \ldots, N_g - 1,$$  \hspace{1cm} (2.7)

where $Y_k$ is the mass fraction of species $k$, $M_k$ is the molecular weight, $\dot{R}_k$ is the net molar rate of species $k$ production form homogeneous gas-phase reactions, and $j_k$ is the multicomponent diffusive flux for species $k$. Constitutive equations for $j_k$ will be presented in detail in section
2.6. $N_g$ denotes the number of gas-phase species. Only $N_g - 1$ continuity equations for the individual species need to be solved; given that the mass fractions $Y_k$ must sum to unity:

$$\sum_{k=1}^{N_g} Y_k = 1.0,$$

the remaining unknown mass fraction can be calculated from (2.8). Therefore, that single species in the reaction mechanism, usually the last one, has generally a larger discretization error than the other species. To minimize errors in this “effective conservation equation”, that species is chosen to be the one with the largest mass fraction.

At steady state there is no net generation of surface species, however, a new film is formed. The loss of species to film is balanced by the formation of new vacant sites so that the overall balance is given by:

$$\sum_{j=1}^{N_{\text{react}}} \nu^*_{ij} R^*_j = 0,$$

where $N_{\text{react}}$ is the total number of adsorption, desorption and surface reactions, $R^*_j$ is the rate of reaction $j$, and $\nu^*_{ij}$ is the stoichiometric coefficient of species $i$ participating in surface reaction $j$. For the $l$th type of site, overall site balances are used to compute the fraction of free sites $\theta^l_v$:

$$\theta^l_v = 1.0 - \sum_{i=1}^{N_l} \theta^l_i,$$

where $\theta^l_i$ is the fractional coverage of adsorbed species $i$ on site type $l$, and $N_l$ is the total number of such species existing on type $l$ sites.

In all surface reactions that represent adsorption of a single gas-phase species followed by dissociation, the sticking coefficient concept is used. In the sticking coefficient formulation, the reaction rate is broken down into a term representing the collision rate of the molecule with
the surface and a term representing the probability that a collision at the surface will result in a reaction. The collision rate is estimated from the kinetic theory of gases leading to the following expression for the adsorption/reaction rate of gas-phase species \( k \):

\[
R' = \gamma_{k} \frac{p_{k}}{\sqrt{2\pi M_{k}T}},
\]

where \( p_{k} \) is the partial pressure of species \( k \) and \( \gamma_{k} \leq 1 \) is the sticking coefficient. In general, \( \gamma_{k} \) is not constant and often an Arrhenius-type temperature dependence expression is used.

### 2.4 Boundary conditions

The governing equations described in the previous section have to be solved with appropriate boundary conditions. Boundary conditions are prescribed for the velocity, the temperature, and the species concentrations on solid non-reacting walls, on the reactive surfaces and at the reactor inlet and outlet. Boundary conditions are of three types: Dirichlet, where the value of the dependent variable is specified, Neumann, where the normal flux of the dependent variable is set to zero, and Robin, where a condition on the normal derivative of the dependent variable is imposed. The implementation of these constraints within the finite element framework is presented in the remainder of this section.

#### 2.4.1 Reactor inlet

At the inlet the flow is assumed to be either fully developed or plug so that a velocity profile can be assigned. The velocity has only a component normal to the inlet direction, the absolute value of which is obtained from the prescribed flow rate and the inlet area. Expressions
for the velocity profiles of fully developed flow in a duct, cylinder, or concentric cylinder can be found in [5]. The temperature and the mass fraction of each species are prescribed at the inlet. This inlet species condition implies that the Peclet number for mass transfer, defined as the ratio of convective to diffusive flux, is sufficiently large (> 10) so that diffusive flux at the inlet can be neglected. The accuracy of this idealized approximation to the flow fields at the reactor inlet (and outlet) is rendered less critical by taking the inflow and outflow boundaries of the computational domain to be far from the deposition region.

2.4.2 Reactor outlet

Fully developed flow is assumed at the reactor outlet:

\[ p - \rho g z \cdot t n + \mu [\nabla v + (\nabla v)^T] \cdot n = 0, \]  \hspace{1cm} (2.12)

where \( t \) and \( n \) are the tangential and normal vectors, respectively, and \( z \) refers to the vertical height at that location [6]. Zero heat and species diffusion fluxes are assumed at the outlet:

\[ \nabla T \cdot n = 0, \quad \nabla Y_k \cdot n = 0. \]  \hspace{1cm} (2.13)

2.4.3 Reactor surfaces

2.4.3.1 Mass and momentum balance equations

On solid surfaces in the reactor, the no-slip and impermeability conditions for the velocity vector are assumed:

\[ v = 0. \]  \hspace{1cm} (2.14)

The no-slip condition breaks down only at high Knudsen numbers (very low pressure). While the normal velocity at the deposition surfaces is non-zero due to the adsorption of growth
precursors and desorption of volatile surface species, the dilute reactant levels typical of OMCVD processes render the no-penetrations velocity condition a reasonable assumption.

### 2.4.3.2 Energy balance equation

Boundary conditions for the temperature field play a critical role in determining the gas flow behavior in a CVD reactor by controlling the degree of gas-phase reactions and ultimately governing the nature and access of precursors to the growth interface. In general, a constant substrate temperature is a reasonable approximation for the different susceptor heating methods unless the resistive heater elements are included in the calculation (see Eq. 2-6). In that case, the heater power is the boundary condition imposed. For a solid surface in the interior of the reactor adjacent to the gas where the velocity field is being solved for, the temperature is calculated by an energy balance between conduction through the solid, conduction from the gas, and radiation exchange with the reactor enclosure. For a surface $i$ of material type $j$, the balance of the net heat flux is given by the following equation:

$$K_j \nabla T_i \cdot \mathbf{n} = \lambda \nabla T_i \cdot \mathbf{n} + \sigma \sum_{k=1}^{N_{\text{bands}}} \left[ \left( \alpha_j \sum_{m=1}^{N_j} \epsilon_m R_{m}^{k} T_{m}^{4} \right) - \phi_{i \rightarrow m}^{k} \epsilon_{i}^{k} T_{i}^{4} \right]; \quad (2.15)$$

$N_s$ is the total number of surfaces in the reactor enclosure; $\sigma$ is the Stefan-Boltzmann constant; $\epsilon$ and $\alpha$ are the emissivity and absorptivity of each surface; and $R_{im}$ is the radiative exchange factor. This factor represents the fraction of energy emitted from surface $i$ which is incident on surface $m$ after all possible intervening specular and diffuse reflections. The superscript $k$ refers to a particular radiation band and $N_{\text{bands}}$ denotes the total number of bands. Each band is characterized by a wavelength range and a characteristic temperature. The bands are used to capture the essential components of radiative heat transfer, namely the change in radiation properties of quartz. While quartz is transparent to radiation whose wavelength is below 4.0 $\mu$m,
it is virtually opaque at longer wavelengths. Thus, a two-band model is used in all the reactor simulations. In band 1 ($0 < \lambda < 4.0 \, \mu m$), all quartz surfaces are assumed to be transparent and are excluded from the exchange factor calculation, while in band 2 ($\lambda > 4.0 \, \mu m$), they are present as opaque material. The term $\phi_{\lambda-T}$ that appears in (2.15) represents the fraction of blackbody energy associated with the characteristic temperature $T$ within the wavelength range $\lambda$ of a band. In the case of two bands employed here, $\phi_{\lambda-T}^2 = 1 - \phi_{\lambda-T}^4$. The typical wafer temperature of 1000 K is used as the characteristic temperature for both bands. The above discussion on radiation exchange in CVD reactors follows the work of Merchant for radiation exchange in Rapid Thermal Processing systems [4]. The approach presented there is also used in this thesis and the reader is referred to [4] for a detailed description of the theory and computation of radiative heat transfer in CVD reactors.

For solid surfaces exposed to the external ambient, an energy balance between conduction though the solid, convective heat loss to the ambient and radiative heat loss to the ambient determines the temperature boundary condition:

$$K_j \nabla T \cdot \mathbf{n} = h(T - T_{\text{amb}}) + \sigma \varepsilon (T^4 - T_{\text{amb}}^4),$$

where $T_{\text{amb}}$ is the ambient temperature, and $h$ is the ambient heat transfer coefficient which is estimated from correlations for natural and forced convection in vertical cylinders and horizontal plates [7].

2.4.3.3 Mass balance equation

The chemical species boundary conditions on solid surfaces depend on the reactivity of the surface. At non-reactive surfaces, zero net mass flux to the surface for each of the species is assigned:
For boundary conditions at solid surfaces where reactions are occurring, the flux of gas-phase species $k$ to the wall is equated to the negative of the net production rate of that species due to surface reactions:

$$ (\rho v Y_k + j_k) \cdot n = -\sum_{j=1}^{N_{\text{re}}} v_{kj}^s M_k R_j^s. $$

The molecular weight of the species appears in the equation because the reaction rates are computed in molar units while $j_k$ is in mass units.

### 2.5 Finite element approximation of the governing equations

The PDEs with appropriate boundary conditions described in the previous two sections are solved using the finite element method [8]. The primitive variable formulation is used so that the unknown variables, the three components of the velocity vector $\mathbf{v}$, the pressure $p$, the temperature $T$, and the mass fraction $Y_k$ of each species, are solved for directly from the governing equations. In the finite element method, the physical domain is divided into a number of small elements to form a mesh. Within each of these elements, the unknown variables are interpolated by low-order continuous polynomials, in terms of values to be determined only at the set of mesh points, also called nodes.

#### 2.5.1 Mesh generation

In order to simulate realistic OMCVD reactors of increased complexity in a feasible time frame, a commercial mesh generator, ICEM-CFD [9], is used to convert a Computer Aided
Design (CAD) drawing file of a reactor into a finite element mesh. Within the mesh generator, the CAD file can be modified, simplified or completely regenerated. After the mesh has been generated, a scheme has to be devised to specify all the material properties and boundary conditions on domains, surfaces, and nodal points, so that solution of the equations can be obtained. Such translation software was developed in [4] and is used in this work as well. Thus, each solid element carries appropriate attributes such as quartz, graphite, stainless-steel etc., and each surface element carries an identification tag corresponding to the appropriate boundary condition. In addition, bookkeeping arrays that contain the connectivity information between domains, surfaces, and nodal points are generated. The mesh preprocessor program developed in [4] was extended to create bookkeeping arrays that aid in eliminating Dirichlet boundary conditions during the assembly of the algebraic equations. This extension reduces the size of the resulting nonlinear problem, especially when three-dimensional simulations are performed.

2.5.2 Finite element discretization

Within each element the mixture velocity, temperature, and species mass fractions are approximated by the following expansions:

\[ v(x) = \sum_{i=1}^{N_v} v^i \Phi^i(\xi) \]  
\[ T(x) = \sum_{i=1}^{N_T} T^i \Phi^i(\xi) \]  
\[ Y_k(x) = \sum_{i=1}^{N_y} Y_k^i \Phi^i(\xi) \] 

where \( x \) is the global coordinate vector and \( \xi \) is a vector of local coordinates of a unit isoparametric element of sides \( 0 \leq \xi \leq 1, 0 \leq \eta \leq 1, 0 \leq \zeta \leq 1 \). Each basis function \( \Phi^i(\xi) \) is a
quadratic Lagrangian polynomial function. Basis functions have highly localized support. They are defined on each particular element, with their value being 1 at one node of that element and identically zero at all other nodes. The quantity \( N_Q \) denotes is the total number of nodes where quadratic basis functions exist in an element; it is identically equal to the total number of nodes in an element, 27 in three dimensions and 9 in two. Since only first order gradients exist in pressure, while all other variables have second order derivatives in the governing PDEs (2.1), (2.3), (2.5), and (2.7), the pressure interpolating terms have to be one order lower than the corresponding velocity, temperature and species interpolating functions [10]. Consequently, the pressure is interpolated using linear polynomial Lagrangian functions \( \Psi^i(\xi) \):

\[
p(x) = \sum_{i=1}^{N_L} p^i \Psi^i(\xi) ,
\]

where \( N_L \) is the number of nodes within an element where pressure is an unknown, 8 in three dimensions and 4 in two. Isoparametric mapping is used to interpolate the spatial coordinates within the element. Thus, the coordinate vector \( x \) is interpolated quadratically and the following equation is used to transform physical coordinates \( (x) \) to reference coordinates \( (\xi) \):

\[
x = \sum_{i=1}^{N_0} \xi^i \Phi^i(\xi) .
\]

### 2.5.3 Weak form of the governing equations

The method of weighted residuals in the Galerkin finite element formulation employed in this thesis involves the solution of an approximate integral form, also known as the 'weak' form of the governing equations. The differential equations are weighted with a set of orthogonal functions so that the error within each element is minimized. The weighting functions are taken to be the same as the interpolating basis functions. Thus, the continuity equation, assigned to the
calculation of the pressure field, is weighted by $\Psi'(\xi)$, while the other conservation equations are weighted by $\Phi'(\xi)$. The derivation of the weak form is illustrated here for the case of the heat balance equation. Consider the solution over the domain $\Omega$ with differential volume $dV$:

$$\rho C_p v \cdot \nabla T = \nabla \cdot \lambda \nabla T$$

(2.24)

with mixed boundary conditions $\lambda \nabla T \cdot n = f(T)$ on boundary $\partial \Omega$ with differential area $dS$.

First, we integrate the PDE over the computational domain to obtain the integral form:

$$\int_{\Omega} \rho C_p v \cdot \nabla T \Phi_i dV = \int_{\Omega} \nabla \cdot \lambda \nabla T \Phi_i dV .$$

(2.25)

Then by integrating by parts and applying Green's theorem to compute the integral over the boundary we obtain:

$$\int_{\Omega} \rho C_p v \cdot \nabla T \Phi_i dV = -\int_{\partial \Omega} \lambda \nabla T \cdot \nabla \Phi_i dV + \int_{\partial \Omega} \lambda \nabla T \cdot n \Phi_i dS .$$

(2.26a)

This formulation readily allows the inclusion of the flux boundary conditions:

$$\int_{\Omega} \rho C_p v \cdot \nabla T \Phi_i dV = -\int_{\Omega} \lambda \nabla T \cdot \nabla \Phi_i dV + \int_{\partial \Omega} f(T) \Phi_i dS .$$

(2.26b)

By dropping the last term in (2.26a), zero normal flux at that boundary is automatically assigned.

The interpolation expressions (2.19) and (2.20) are substituted in (2.26a) and Gaussian quadrature is used to numerically evaluate the integrals. This results in a set of $N_Q$ equations in $N_Q$ unknowns for each finite element. This process is repeated to yield (in the temperature case) a global set of $N$ nonlinear algebraic equations in $N$ unknowns, where $N$ is the total number of nodes in the mesh.
2.5.4 Solution of the nonlinear algebraic equations

Since the system of equations is nonlinear, iterative procedures are needed to solve for the unknowns. In this work, a Newton-Raphson scheme is used to iteratively solve the residual equations. At each iteration, the correction \( \Delta y^{n+1} \) to the initial guess \( y^0 \) of the vector containing the unknowns is obtained by solving the following linear set of equations:

\[
J(y^n)\Delta y^{n+1} = -R(y^n),
\]

where \( n \) is the iteration number, \( R \) is the vector of residual equations, and \( J \) is the global Jacobian matrix whose entries \( J_{ij} = \frac{\partial R_i}{\partial y_j} \) represent the sensitivity of the residual equations to perturbations in the unknowns. The unknown vector \( y \) is updated by:

\[
y^{n+1} = y^n + \Delta y^{n+1}.
\]

While quadratic convergence of Newton's method (i.e., \( \|\Delta y^{n+1}\| \leq \|\Delta y^n\|^2 \)) is guaranteed close to the solution [11], the initial guess has to be sufficiently close to the actual solution for the method to converge. Continuation from a known, or at least easily solvable initial solution is used. In addition, when mass transfer simulations are performed, the problem is decomposed according to gas-phase and surface reactions in the early stages of the iteration sequence. Furthermore, as will be discussed in the following section, the Jacobian matrix has to be exact at each iteration step for the asymptotic quadratic convergence rate to be achieved. If the matrix is inaccurate, the same solution is obtained but with linear asymptotic rate of convergence. While the Jacobian matrix entries can be computed by numerical differentiation, analytical differentiation needs to be done whenever possible since it is always more accurate and requires significantly fewer computations.
At each Newton iteration, the Jacobian matrix has to be assembled on an element by element basis and the linear system of equations (2.27) has to be solved. The frontal method originally developed by Irons [12] and Hood [13] performs both operations simultaneously resulting in a reduction in both computation time and storage. The frontal method takes advantage of the localized nature of the finite element basis functions and eliminates unknowns as soon as possible. The frontal solver is a robust solver for the asymmetric, non-positive definite linear system that arises from the finite element discretization of the governing equations.

2.6 Mixture properties and multicomponent diffusion

In principle, the transport and physical properties of the mixture depend on the local values of $T$ and $Y_k$. These are the density $\rho$, the viscosity $\mu$, the heat capacity $C_p$, the thermal conductivity $\lambda$, and the average molecular weight $\overline{M}$. As was mentioned in section 2.2, while non-dilute carrier gas mixtures are simulated, the reactants are present in trace amounts and decoupling of fluid flow and heat transfer from mass transfer calculations is justified. Thus, the following expressions are used to determine the mixture properties from the pure species properties. Pure species properties are evaluated at a reference temperature $T_o$ using the kinetic gas theory methods described in [14]. The composition of the mixture at the inlet is used for the calculations.

2.6.1 Viscosity

To compute the viscosity $\mu$, the semi-empirical Wilke formulation [14] is used:
\[ \mu = \sum_{k=1}^{N_k} \frac{X_k \mu_k}{\sum_{j=1}^{N_k} X_j \Phi_{kj}}, \]  

\[ \Phi_{kj} = \frac{[1 + \sqrt{\frac{X_k}{X_j}} \frac{M_j}{M_k}]^2}{\sqrt{8(1 + \frac{M_k}{M_j})}}. \]

The complicated temperature dependence arising from the kinetic theory is replaced in the governing equations by the following power law approximation:

\[ \mu(T) = \mu \left( \frac{T}{T_o} \right)^{0.7}. \]

### 2.6.2 Thermal conductivity

The thermal conductivity of the multicomponent mixture is approximated by [15]:

\[ \lambda = \frac{1}{2} \left( \sum_{k=1}^{N_k} X_k \lambda_k + \frac{1}{\sum_{k=1}^{N_k} \frac{X_k}{\lambda_k}} \right), \]

with a temperature dependence similar to that of viscosity:

\[ \lambda(T) = \lambda \left( \frac{T}{T_o} \right)^{0.7}. \]

### 2.6.3 Heat capacity

Finally, the heat capacity of the gas mixture is computed by:
\[ C_p = \sum_{k=1}^{N_k} X_k C_{p,k} \]  \hspace{1cm} (2.34)

### 2.6.4 Constitutive relations for the diffusive flux, \( j_k \)

In order to solve the individual species mass balances (2.7), the diffusion flux \( j_k \) must be connected to the mass fractions though appropriate constitutive relations. \( j_k \) expresses the flux of species \( k \) relative to the mass-average velocity vector \( v \), arising from ordinary diffusion (flux driven by concentration gradients) and thermal diffusion (flux driven by thermal gradients). It is given by:

\[ j_k = \rho Y_k V_k, \]  \hspace{1cm} (2.35)

where \( V_k \) is the diffusion velocity of species \( k \) given by [16]:

\[ V_k = \frac{1}{X_k M} \sum_{i \neq k}^{N_k} M_i D_{ik} d_i - \frac{D_k^T}{\rho Y_k} \nabla (\ln T), \]  \hspace{1cm} (2.36)

where \( d_i \) is the diffusion driving force for species \( i \), \( D_{ik} \) are the ordinary multicomponent diffusion coefficients that depend on temperature, pressure, and mixture composition, while \( D_k^T \) is the multicomponent thermal diffusion coefficient for species \( k \). The coefficient \( D_k^T \) is a function of the temperature and composition of the gas mixture but it is independent of pressure. \( D_k^T > 0 \) for heavy molecules and \( D_k^T < 0 \) for light molecules. The driving force for thermal diffusion is the logarithm of the temperature gradient. Nevertheless, the significant mass difference between reactant sources such as group III organometallic compounds and the carrier gas, when combined with the large temperature gradients in OMCVD reactors, results in significant contribution to the mass transfer from thermal diffusion. The heavy reactants are
driven away from the hot substrate resulting in reduced deposition rates. Thus an accurate
description of thermal diffusion, in addition to ordinary diffusion, needs to be obtained.

The multicomponent diffusion coefficients presented above satisfy the following
constraints:

\[
\sum_{j=1}^{N_k} M_j D_{jk} = 0, \forall k, \quad \sum_{k=1}^{N_k} D_{ik}^T = 0 \tag{2.37}
\]

that guarantee that the diffusion fluxes sum to zero:

\[
\sum_{k=1}^{N_k} Y_k V_k = 0 . \tag{2.38}
\]

A rigorous expression for the diffusion fluxes due to concentration gradients in a
multicomponent gas mixture is given
by the Stefan-Maxwell equations [17]. They are given
below in terms of \( \mathbf{d}_k \) [18]:

\[
\mathbf{d}_k = \sum_{j=1}^{N_k} \left( \frac{X_k X_j}{D_{jk}^n} \right) \left( V_k - V_j \right) + \nabla \left( \ln T \right) \sum_{j=1}^{N_k} \frac{X_k X_j}{\rho D_{jk}^n} \left( \frac{D_{jk}^T}{Y_j} - \frac{D_{ik}^T}{Y_k} \right), \tag{2.39}
\]

where \( D_{jk}^n \) is the binary diffusion coefficient for gas species \( j \) and \( k \). As can be seen, the
diffusion velocities are implicitly defined in (2.36) and (2.39) requiring an iterative solution of
the \( N_k \times N_k \) set of equations within each element in order to compute the diffusive fluxes needed
for the mass transfer governing equation. This approach is extremely computationally expensive
to implement numerically, and approximate treatments of comparable accuracy have been
developed [19,20].

In this work the mixture-averaged diffusivity formulation suggested by Coffee and
Heimerl [19] is used. Equation (2.36) is replaced by the simpler expression:

\[
V_k = -\frac{D_k^M}{X_k} \mathbf{d}_k - \frac{D_{ik}^T}{\rho Y_k} \nabla \left( \ln T \right), \tag{2.40}
\]
where $D_k^M$ is called the mixture averaged diffusivity of species $k$, and is given by:

$$D_k^M = \frac{1 - Y_k}{\sum_{j=1}^{N_k} \frac{X_j}{D_{jk}^B}}.$$  \hspace{1cm} (2.41)

The driving force in equation (2.40) is given simply by:

$$\mathbf{d}_k = \nabla X_k$$ \hspace{1cm} (2.42)

in the absence of significant pressure gradients and transport of neutral gases. Both assumptions are appropriate for CVD simulations.

While the $D_k^M$ formulation is rigorous in the binary and dilute limits, it does not ensure that the diffusion fluxes sum to zero. This problem is addressed by adding a correction velocity vector to the diffusion velocity vector:

$$\mathbf{V}_k' = \mathbf{V}_k + \mathbf{V}^C, \text{ where } \mathbf{V}^C = -\sum_{i=1}^{N_k} Y_i \mathbf{V}_i.$$ \hspace{1cm} (2.43)

The mixture-averaged diffusion velocity formula (2.40) greatly reduces the coupling between mass-transfer equations and allows the analytical computation of the Jacobian matrix entries. The addition of the correction velocity to the diffusive flux expression significantly increases the coupling by distributing the total error caused by the mixture-averaged approximation among all the species. This necessitates the calculation of the entire diffusion term by numerical differentiation. Whenever processes with multicomponent gas mixtures are simulated in this thesis, trace amounts of reactants in a mixture of carrier gases (H$_2$ and NH$_3$) are used. Therefore, accurate prediction of the NH$_3$ concentration profile (the species with the highest mass fraction) is not needed for accurate computation of the growth rates. Thus, the velocity correction method mentioned above is not implemented and the ammonia mass fraction is computed via equation (2.8). Kleijn [21] compared this approach to solving the rigorous
Stefan-Maxwell equations and found that, while overall computational time savings of more than 50% are realized, accurate growth rate predictions of CVD of Si from SiH₄ in hydrogen/nitrogen mixtures can be obtained. Furthermore, the uncertainty in the estimation methods of the Lennard-Jones parameters of reactant species that are needed to compute the binary diffusion coefficients in (2.41) outweighs the importance of including an entirely rigorous formulation for multicomponent diffusion.

Since inlet composition, reaction rates, and the ordinary diffusion driving force (2.42) are given in terms of species mole fractions, while species mass fractions are the unknowns solved for, the following formulas are used for the conversions:

\[ X_k = \frac{\overline{M}}{M_k} Y_k, \quad \text{where} \quad \overline{M} = \sum_{k=1}^{N_x} X_k M_k = \left( \sum_{k=1}^{N_x} \frac{Y_k}{M_k} \right)^{-1}. \]  (2.44)

Substituting for \( j_k \) in (2.7) the expression obtained via (2.42), (2.40), (2.35) and using (2.44) results the governing equation for individual species mass transfer:

\[ \nabla \cdot (\rho v Y_k) = \nabla \cdot \left( \rho D^M_k \nabla Y_k \right) + \nabla \cdot \left( D^T_k \nabla \ln T \right) + M_k \dot{R}_k. \]  (2.45)

An expression for the “effective” mixture-averaged coefficient of ordinary multicomponent diffusion, \( D^M_k \), was described earlier (see (2.41)). Approximations for the multicomponent thermal diffusion coefficient are presented below. In an \( N_g \) component gas mixture, exact equations for calculating multicomponent thermal diffusion coefficients involve the evaluation of one determinant of size \( 2N_g \times 2N_g \) and \( N_g \) determinants of size \( (2N_g+1) \times (2N_g+1) \) determinants. Each element of these determinants is a \( T \)-dependent function of the mole fractions and Lennard-Jones parameters of all species [17], whose computation is prohibitively expensive. Instead, the “effective mixture thermal diffusion coefficient” \( D^T_k \), proposed by Chapman and Cowling [22] is used:

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\[ D_{k}^{T,M} = \sum_{i \neq k} \frac{N_{k}}{N_{i}} D_{k}^{T,\text{Bin}}, \] (2.46)

where \( D_{k}^{T,\text{Bin}} \) is the binary thermal diffusion coefficient of species \( k \) in a gas comprised of just \( k \) and \( i \). Binary thermal diffusion coefficients are often expressed in terms of a quantity called the thermal diffusion ratio \( k_{ki} \) [5]:

\[ D_{k}^{T,\text{Bin}} = \frac{p}{MRT} M_{k} M_{i} k_{ki}, \] (2.47)

where \( k_{ki} = \alpha_{ki} X_{k} X_{i} \) and \( \alpha_{ki} \) is called the thermal diffusion factor. The thermal diffusion factor is a \( T \)-dependent, complex expression of the individual species Lennard-Jones parameters and mole fractions [17].

These expressions apply for binary gas mixtures where the species mole fractions are uniquely defined. In (2.46), however, where summation is carried over all binary pairs in a multicomponent mixture, it is not clear whether the mole fractions in the mixture of \( N_{g} \) species or the corresponding mole fractions in binary pairs are to be used. There is clearly a significant difference among the two. The original reference where the effective \( D_{k}^{T,M} \) was proposed [23], is not clear on this matter either, but appears to imply that the actual mole fractions are used to compute \( k_{ki} \) and the reduced binary mole fractions are used to compute \( \alpha_{ki} \). To verify this, the thermal diffusion coefficients of a typical gas-phase mixture used in GaN growth were computed with both approaches and compared to the correct values, computed using the rigorous approach involving the \( N_{g}+1 \) determinants. Using the actual mole fractions to calculate \( k_{ki} \) and the reduced ones to compute \( \alpha_{ki} \) resulted in < 1% deviation from the correct values for all species. Deviations of \( \approx 30\% \) for the main carrier gases (NH\(_{3}\), H\(_{2}\), N\(_{2}\)) and of \( \approx 300 - 500\% \) for the
reactants (TMGa, dimer, trimer) were observed when the actual mole fractions were also used in
the \( \alpha_{ki} \) evaluation. Therefore, the reduced mole fractions:

\[
X_k' = \frac{X_k}{X_k + X_i}, \quad X_i' = 1.0 - X_k'
\]  

(2.48)

are used in this thesis to estimate the effective thermal diffusion coefficients. Since the actual
mole fractions are used to compute \( k_{ki} \), substituting (2.47) in (2.46) and using (2.44) gives:

\[
D_{ki}^{TM} = \rho Y_k \sum_{i=k}^{N} Y_i D_{ki}^{B} \alpha(X_k', X_i') .
\]  

(2.49)

The binary diffusion coefficients \( D_{ki}^{B} \) are computed at a reference temperature and
pressure using the Chapman-Enskog equation [14], and the temperature and pressure dependence
are included by the following power law:

\[
D(T, p) = D_p \left( \frac{T}{T_*} \right)^{1.7}.
\]  

(2.50)

The thermal diffusion factors \( \alpha(X_k', X_i', T) \) for all binary pairs are precomputed as a
function of \( X_k' \in [0,1] \) and \( T \in [300,1300] \) and may be fitted fairly accurately by using a
relation of the following form:

\[
\alpha(x, T) = c_o \left( 1 + c_1 x + c_2 x^2 + c_3 x^3 \right) \left( 1 + c_4 T + c_5 \frac{1}{T} \right) .
\]  

(2.51)

Substituting the expression for the effective thermal diffusion coefficient (2.49) in the
species balance equation (2.45) results in an extremely complicated dependence on the various
species mass fractions since the reduced mole fractions (2.48), extracted through (2.44) from the
solution vector, are to be used in (2.51). Exact analytic differentiation of the species balance
residual with respect to the mass fractions is practically unfeasible. However, accurate
evaluation of the Jacobian terms is necessary to achieve quadratic error convergence. Thus, we investigated the following alternatives of including the \( \frac{\partial D_{k}^{T,M}}{\partial Y_i} \) dependence in the Jacobian terms.

The norm of the correction vector \( \|\Delta y'\| \) was monitored, while simulating trace TMGa diffusion in a H\(_2\)/NH\(_3\) mixture \( (X_{NH3} = 0.25) \) in a vertical OMCVD reactor:

- **Method A**: The concentration dependence of the thermal diffusion coefficient is neglected, \( \frac{\partial D_{k}^{T,M}}{\partial Y_i} = 0, \forall k, i \in [1, N_g - 1] \), and the remaining Jacobian entries are computed analytically.

- **Method B**: Only the concentration dependence of \( D_{i}^{T,M} \) with respect to same species, \( \frac{\partial D_{k}^{T,M}}{\partial Y_i}, i = k \), is included via numerical differentiation. The remaining Jacobian entries are computed analytically.

- **Method C**: The concentration dependence \( \frac{\partial D_{k}^{T,M}}{\partial Y_i} \) \( \forall k, i \in [1, N_g - 1] \) is included via numerical differentiation. The remaining Jacobian entries are computed analytically.

- **Method D**: The Jacobian entries for all the terms in the governing equation (2.45) are computed numerically.

- **Method E**: For comparison purposes, simulations were done invoking the dilute approximation routinely used in CVD simulations [24], where all gases are assumed to be present in trace amounts in H\(_2\) carrier gas in the calculation of the diffusion fluxes. Explicit analytical evaluation of the Jacobian terms is feasible in this formulation.

Results are shown in Figure 2-1. The norm of the correction vector after each non-linear Newton iteration is plotted as a function of the iteration number. The quadratic convergence of
Newton's algorithm is demonstrated. As expected, method C, with the most rigorous evaluation of the Jacobian entries outperforms the other approaches. However, all three methods that account in some fashion for the concentration dependence of the thermal diffusion coefficient (methods B, C, D) exhibit similar error performance. By neglecting this dependence (method A), quadratic convergence is not achieved and additional iterations are required to arrive at the solution. By neglecting entirely the mixture nature of the gas-phase (method E), quadratic convergence cannot be achieved. In addition, the algorithm based on this oversimplifying approximation does not converge to the correct solution.

Figure 2-1. Dependence of Newton's method convergence behavior for various approximations of the Jacobian entries associated with the thermal diffusion coefficient.

The differences between methods B, C, and D do not merit the selection of one over the others. However, the differences in required computational time presented in Figure 2-2 do. The
CPU time for this 5,000 unknown problem is normalized by the time needed for the analytical Jacobian evaluation, namely method A. It is shown that while Case C slightly outperforms the other approaches, it does so at a significant cost. It is also shown that for this problem, using entirely numerical differentiation results in a ~ threefold increase in the computation time over the analytic Jacobian approach. Based on the findings presented in Figures 2-1 and 2-2, method B represents the best trade-off between accuracy and speed of computation and is the method used in this thesis.

![Figure 2-2. Dependence of CPU time needed for 4 non-linear iterations on the method of Jacobian entry calculation. Times are normalized with the CPU time needed in Case A.](image)
2.7 Summary

A solution strategy for simulating complex reacting-flow problems related to OMCVD processes has been briefly described. The PDEs governing transport phenomena and chemistry within the reactors, heat transfer in the reactor walls and solid materials, along with boundary conditions for these equations have been presented. Application of the Galerkin finite element method to solve these equations numerically has been discussed. Modeling equations for mass transfer in a multicomponent, ideal gas mixture have been presented. An "effective multicomponent diffusion coefficient" approximation to the computationally expensive multicomponent transport equations has been implemented. The approximation is used for both ordinary and thermal diffusion.

Figure 2-3. GaN growth rates as a function of susceptor radius in a vertical OMCVD reactor. Comparison among multicomponent and dilute treatments for mass transfer simulations.
Figure 2-3 demonstrates the importance of including the multicomponent diffusion formulation in the simulations of OMCVD growth of GaN and related materials. Although the kinetic mechanism for OMCVD growth of GaN will be discussed later in Chapter 4, these results are included here to qualitatively illustrate the significance of the techniques presented in section 2.6. The results shown are obtained in a vertical axisymmetric reactor, a substrate temperature of 900 °C, and a 1:1 H₂/NH₃ carrier gas mixture. If the gas mixture is assumed to have the transport properties of hydrogen, (i.e. equations (2.29), (2.32), and (2.34) are not used), the growth rate is underestimated by > 50% even if the mass transfer problem is solved using the multicomponent formulation. When the mixture transport properties are used to compute the fluid flow and heat transfer, using the conventional dilute approximation of CVD modeling leads to either substantial overprediction (H₂ carrier gas) or underprediction (NH₃ carrier gas) of the growth rate. These large deviations due to inexact description of the underlying transport phenomena would mask any growth rate variations arising from differences in kinetic pathways. Thus, implementation of multicomponent diffusion, at least at the level of approximation presented in this section, is mandatory given the focus of this thesis on chemical mechanism development.
2.8 References


Chapter 3. Simulation of flow and growth phenomena in a close-spaced reactor

3.1 Introduction

Superlattice and quantum-well structures of compound semiconductors for optoelectronic applications require the growth of successive epitaxial layers with a high degree of uniformity along the layer and very abrupt interfaces between the layers. OMCVD is a very promising technology in this area, as evidenced in the extensive use it finds in existing [1] and new material systems (III-Nitrides [2]). As mentioned in Chapter 1, high wafer throughput and excellent crystal and interface properties are typical advantages of OMCVD. For epitaxial growth of III-V semiconductors to be commercially viable, run-to-run reproducibility and well-characterized reactor performance are also necessary. Reactor design is the key factor that determines the degree of uniformity and interface abruptness of the deposited layers. These considerations lead researchers to investigate either novel or altered designs of the conventional vertical and horizontal reactor configurations. One such design finding increasing use is the close-spaced reactor with [3], or without [4] separate injection of the group III and group V precursors. It is essentially a vertical cold wall reactor with a water-cooled injection showerhead that is placed very close (10-20 mm) to the heated substrate. Due to this close proximity, the reactor design is routinely assumed to yield stagnation point flow where the boundary layer thickness remains
unchanged along the susceptor. Potential advantages of this design include: enhanced interface abruptness due to the reduced residence time of the reactants over the substrate, improved uniformity due to the suppression of the natural convection induced recirculation cells, circumvention of undesired upstream pre-reactions due to separate precursor injection, and increased process parameter window due to the insensitivity of growth uniformity on operating conditions.

Figure 3-1. Schematic diagram of the close-spaced reactor geometry used in the simulations (after [5]).

The objective of this chapter is to relate layer uniformity and deposition growth rate to control parameters such as reactor height, carrier flow rate, operating pressure, susceptor temperature, and susceptor rotation rate in a close-spaced reactor. Due to the recent introduction
of the close-spaced reactor design in OMCVD processes, there is a need for a general understanding of the flow behavior and growth rate uniformity of this design. An additional incentive to this study is the expanding usage of this design in III-Nitride deposition processes that are the primary focus of this thesis.

Numerical calculations of gas flow, heat transfer, and species transport, as outlined in the previous chapter are performed. The specific reactor design studied is depicted in Figure 3-1. It has been shown to achieve excellent uniformity results (± 2% over a 48 mm wafer) in either the 3x2" (for AlGaAs/GaAs and InGaAs(P)/InP growth [3]) or the 1x2" (for InGaN/GaN growth [5]) configuration. Since the showerhead is comprised of hundreds of individual jets positioned close to the substrate, the typical assumption of axisymmetry employed in vertical reactor simulations cannot be used \textit{a priori}; it needs to be investigated through a hierarchical modeling approach. Three-dimensional calculations are first carried out with a twofold goal: i) determine the degree of mixing between group III and V precursors and ii) establish whether the individual jets can locally influence chemistry and deposition uniformity. The growth is shown indeed axisymmetric. Based on these findings, detailed two-dimensional calculations are then used to conduct the parametric study.

3.2 Jetting studies

A useful dimensionless number in analyzing flows from impinging jets is the jet Reynolds number, Re$_j$:

$$\text{Re}_j = \frac{\rho_j u_j D_j}{\mu_0},$$
where $\rho_0$ and $\mu_0$ are the values of the gas density and viscosity evaluated at the temperature $T_o$ and pressure $p$ of the inlet. The length scale $D_j$ is the nozzle diameter, while $u_j$ is the gas velocity at each nozzle. Circular jets are characterized as dissipated laminar if $Re_j < 300$, fully laminar if $300 < Re_j < 1000$, transition jets for $Re_j$ up to 3000 and fully turbulent at higher Reynolds numbers [6]. The ratio $H/D_j$ is another important dimensionless number, where $H$ is the distance between the jet and the impingement surface. Enhanced heat (and mass) transfer occurs underneath the jet at high values of $Re_j$ and low $H/D_j$ ratios. In studies of laminar jets, typical values of these parameters are $150 < Re_j < 950$ and $H/D_j < 6$. For instance, operating at $Re_j = 450$ and $H/D_j = 2$ gives an increase of the local Nusselt number underneath the jet by a factor of 8 [6]. In contrast, for a close-spaced reactor with a typical height of $H = 16$ mm, operating at $p = 76$ torr with 10 slm H$_2$, these numbers are $Re_j = 5$ and $H/D_j \equiv 25$. Therefore, based on the dimensionless analysis, the jets are expected to dissipate completely within the reactor and leave the deposition surface unaffected.

In order to confirm these findings, investigate reactant mixing, and study the flow patterns due to the individual jets, we carried out three-dimensional fluid flow and mass transfer calculations in a close-spaced reactor. A secondary goal of this study was to establish whether two-dimensional simulations could be used to describe the reactor performance in a more efficient computational approach. The transport model used in this work was based on numerical solution of the partial differential equations representing the conservation of momentum, energy, total mass and individual species using the finite element method, as outlined in the previous section. The dilute approximation in computing diffusive fluxes was invoked, since simulations with a single carrier gas were performed.
A complete 3-D simulation of the reactor showerhead that contains \( 650 \) jets requires enormous amounts of computation and is beyond the scope of this study. Instead, a water-cooled reactor and showerhead containing \( 25 \) jets was simulated. The computational domain along with the temperature and flow streamlines is depicted in Figure 3-2.

![Figure 3-2](image)

Figure 3-2. Finite element computational domain along with temperature profile and flow streamlines (black lines) in a close-spaced reactor. Substrate temperature is \( 650 \) °C. Wall and inlet temperature is \( 27 \) °C. Operating pressure is 76 torr. Gas velocity at the nozzles is \( 5 \) m/sec.

The excellent scalability of this reactor design [7] further justified the use of a scaled-down version. The nozzle diameter and the spacing between adjacent jets found in the actual reactor were used. Symmetry considerations mean that only a quarter of the reactor needs to be
simulated. The flow rate was adjusted to give inlet gas velocities similar to the ones achieved in the actual reactor (e.g. \( u_j = 5 \text{ m/s} \) for 6 slm \( \text{H}_2 \) at 76 torr).

The predicted velocity profiles across the reactor radius are shown in Figure 3-3 at different heights. A height of 16 mm corresponds to the showerhead location, while 0 mm denotes the susceptor location. A uniform velocity profile is established within 5-6 mm from the showerhead nozzles and, as predicted, the jets do not penetrate close to the susceptor.

![Figure 3-3](image)

Figure 3-3. Vertical gas velocity along the reactor radius at different heights in the close-spaced reactor denoted by different colors. The velocities are extracted from the 3-D calculations at different heights along a radius that passes though the centerline of the jets as shown by the line in the figure insert. The inlet is at 16mm. (---): 16 mm, (---): 15mm, (---): 10 mm, (---): 1mm.

Once the flow and temperature profile is computed, a one species kinetic model assuming that growth is limited by the gas-phase mass transport of trimethylgallium (TMGa) is used. The use of a simple kinetic model is justified in order to prevent kinetic limitations overshadowing
transport issues. TMGa is added to the carrier gas in alternating jets to reflect the separate group III and V plenums used in an actual close-spaced reactor.

Figure 3-4. (a) Concentration map of TMGa in the reactor. (b) TMGa mole fraction in the reactor as a function of position away from the inlet underneath a group III nozzle (solid line) and a group V nozzle (dashed line). The individual jets can be also seen, as well as the supply of TMGa in alternating jets.

The TMGa mole fraction profile in the gas phase is shown in Figure 3-5(a). In addition to the composition variations at the inlet, the depletion of TMGa due to surface reaction close to the substrate is observed. TMGa mole fractions in the gas phase as a function of reactor height are extracted and shown in Figure 3-4(b) for two cases: (a) underneath a group III nozzle and (b) underneath a group V nozzle. Thus, the dependence of gas-phase mixing on reactor height and total flow rate is studied. It can be seen that for a typical reactor height, $H > 15$ mm, there is
complete mixing in the gas phase before the reactants adsorb on the substrate. The individual jets did not penetrate close to the substrate even for the case of a total flow of $= 25$ slm, much higher than the typical operating range of 6 - 15 slm. Consequently, the growth rate predicted under mass transfer-limited-conditions (see Figure 3-5) is free of local variations, and the deposition is indeed axisymmetric. The use of two-dimensional axisymmetric calculations that assume uniform distribution of precursors in the inlet is therefore warranted.

![Figure 3-5. Growth rate (in μm/hr) map under mass transport limited conditions in a close-spaced reactor. Flow rate is 8 slm H₂, pressure is 76 torr, reactor height is 16 mm.](image)

3.3 Summary of vertical reactor hydrodynamics
The hydrodynamics of vertical rotating-disk reactors has been the subject of numerous numerical simulation and flow visualization studies [8-13]. The fluid flow is characterized by the interaction of forced convection by the injected carrier gas, natural convection related to the temperature difference between the heated substrate and the carrier gas, and pressure gradients associated with the disk rotation. The following three main flow regimes have been identified: (a) forced convection dominated flow, where the gas flows over the substrate without any recirculation in the reactor, (b) natural convection dominated flow, where buoyancy forces induce recirculations in the gas, and (c) rotation induced flow, where a recirculation vortex forms near the reactor wall at the substrate level.

A classical method of analyzing the strength of the various forces is the use of dimensionless numbers that arise from the Navier-Stokes equations. The Reynolds number:

\[
\operatorname{Re}_Q = \frac{\rho_v u_0 H}{\mu_v},
\]

scales the inertia introduced by the flow through the inlet and is a measure of the forced convection in the reactor. The value of \(\operatorname{Re}_Q\) is independent of pressure at constant mass flow rate and depends linearly on total flow rate. When forced convection dominates, the reactor operates in a Stagnation Flow (SF) regime that occurs when the fluid impinges normally on the substrate and moves radially out. Assuming uniform injection velocity at the inlet and a disk of infinite radius, this flow produces a uniform boundary layer the thickness of which varies as \(\operatorname{Re}_Q^{-1/2}\) [14]. Due to the finite radius of the susceptor and the presence of the reactor walls, this similarity solution breaks down towards the edge of the substrate [15]. Under mass-transport-limited growth conditions, the growth rate is inversely proportional to the boundary layer thickness and
therefore scales as $\sqrt{Re_Q}$. Since $Re_Q$ is independent of pressure, constant mass flow can produce equal growth rate and uniformity at reduced and atmospheric pressure.

Vertical reactors cannot achieve stagnation flow because substrate heating results in strong buoyancy forces. Natural convection scales with the Grashof number:

$$Gr = \rho g H^3 (T_s - T_0) / T_0 \mu_o^2,$$

where $g$ is the acceleration of gravity and $T_s$ is the substrate temperature. The dependence of natural convection on pressure is $Gr \propto p^2$ through the linear dependence of density on pressure. Strong recirculations can be observed, given the cubic dependence on reactor height, and typical vertical reactor heights in the range 10 - 25 cm. The recirculation cells can be suppressed by increasing the forced convection through a flow rate increase. The ratio of the two effects varies as $Gr/Re_Q^2$. A flow rate increase, however, leads to poor reactant utilization and can eliminate the recirculations only at reduced operating pressures.

Rotating the disk provides a second mechanism for achieving flow stability. At high rotation rates, susceptor rotation causes centrifugal pumping that pulls gas down along the centerline and pushes it out radially along the substrate. The rotational Reynolds number:

$$Re_\Omega = \frac{\rho \omega R^2}{\mu_o},$$

characterizes forced convection due to rotation. The length scale $R$ represents the susceptor radius and $\omega$ is the susceptor rotation rate. In the ideal case of an infinitely large disk rotating in an isothermal fluid, a boundary layer of uniform thickness is obtained. The thickness scales with $Re_\Omega^{1/2}$ [14] and in the absence of recirculation cells, the mass-transfer-limited growth will increase as $\sqrt{Re_\Omega}$, or equivalently, $\sqrt{\omega p}$. This operating regime is sometimes called Rotating
Disk Reactor (RDR). The growth rate depends primarily on rotation rate and operating pressure. Although both growth rate and uniformity are expected to increase with increasing pressure, in reality growth is carried out at reduced pressures to avoid recirculations driven by natural convection. The \( \text{Gr}/\text{Re}^2_\Omega \) scaling analysis holds for an ideal flow field. The presence of walls and related thermal boundary conditions modify this dependence. The mixed convection parameter \( \text{MCP} = \text{Gr}/\text{Re}^{3/2}_\Omega \) was introduced as a measure of flow stability in the RDR regime \[10,11\]. Alternatively, Biber et al. \[12\] proposed \( \text{Gr} \leq \text{Re}_Q \cdot \text{Re}_\Omega \) as the criterion separating buoyancy-dominated from recirculation-free flow. The susceptor radius is the characteristic length scale used in both the Grashof and Reynolds numbers in these studies. Consequently, these criteria contain no dependence on reactor height, or any length scale for that matter. That limits their usefulness in characterizing reactor behavior without additional information. Flow stability also breaks down if the susceptor is rotated too fast. A counter-clockwise rotating eddy forms at the wall due to the interaction of the radial outflow with the reactor wall. Although this cell has little effect on growth rate uniformity, its presence limits run-to-run reproducibility and makes it difficult to achieve sharp junctions. The critical rotation rate at which the recirculating cell forms depends on the gas flow rate, reactor pressure and the relative positions of the reactor wall and the susceptor edge. Rotation-induced cells weaken with increasing flow rate and decreasing pressure at fixed spin rate.

Simulation studies of close-spaced reactors have been limited. Joh and Evans \[7\] studied heat transfer and flow stability using 1-D and 2-D calculations. They introduced the dimensionless inlet velocity, \( \text{SP} = \frac{u_o}{\sqrt{\nu_o}} \), where \( \nu_o \) is the gas kinematic viscosity evaluated at the inlet. They showed that the effect of SP on the radial variation of heat transfer is greater for larger values of reactor height. For all heights studied, there is greater radial variation of heat
transfer at larger values of SP. The heat transfer uniformity was shown to be only slightly affected when varying the reactor aspect ratio \( (AR = R_w/R) \), \( R_w \) being the reactor wall radius.

### 3.4 Parametric study – results and discussion

In the following we present finite element numerical simulations used to determine the influences of many operating parameters and geometric factors on close-spaced reactor performance. Two-dimensional axisymmetric simulations are performed based on the reactor geometry described in Figure 3-1. The carrier gas is hydrogen. The susceptor radius \( R \) is 37 mm and the substrate radius \( R_s \) is 25 mm. The reactor radius \( R_w \) is 49 mm, unless effects of the reactor aspect ratio \( AR \) are studied when it is varied accordingly. The showerhead and stainless steel walls are kept at 25 °C. The temperature on the quartz inner reactor walls is determined by the energy balance of thermal radiation, conduction through the wall and conduction from the adjacent gas as described in the previous chapter. A one species kinetic model assuming mass-transfer-limited growth is used for the epitaxial growth calculations. Transport parameters for TMGa/H\(_2\) were taken from [16]. In all the simulations, the TMGa mole fraction at the inlet is kept at a constant value of \( 1\times10^{-4} \). Higher flow rates will therefore carry higher amounts of TMGa in the reactor. This is done to eliminate dilution effects from the calculations, so that changes in the hydrodynamics under different conditions are not masked by changes in concentration. The numerical experiments are conducted over a wide range of flow rates, reactor pressures, disk rotation rates, substrate temperatures, reactor radii and reactor heights as given in Table 3-I. The results will be shown in terms of centerline growth rate and growth uniformity. Uniformity is reported in percentage radius of the substrate where the growth rate stays within ±1% of the centerline growth rate. So a uniformity of 80 means that the growth rate remains
within ± 1% of the centerline growth rate over a radius of \(0.80 \times 25 = 20\) mm. On some graphs, uniformity within ± 5% of the centerline growth rate is reported.

Centerline growth rate predictions were compared to experimental observations [17] of GaAs and AlAs deposition carried out in a reactor similar to the one depicted in Figure 3-1. Excellent agreement is obtained for both material systems (see Figure 3-6) for the growth rate dependence on group III precursor supply, as the growth rate is mass-transport-limited.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume flow rate</td>
<td>(Q)</td>
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<td>15</td>
<td>slm</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>(P)</td>
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<td>760</td>
<td>torr</td>
</tr>
<tr>
<td>Susceptor rotation rate</td>
<td>(\omega)</td>
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<td>800</td>
<td>rpm</td>
</tr>
<tr>
<td>Susceptor temperature</td>
<td>(T_s)</td>
<td>650</td>
<td>1050</td>
<td>°C</td>
</tr>
<tr>
<td>Reactor height</td>
<td>(H)</td>
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<td>74</td>
<td>mm</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>(R_w)</td>
<td>48</td>
<td>67</td>
<td>cm</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>(Re_Q)</td>
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<td>10</td>
<td></td>
</tr>
<tr>
<td>Rotational Reynolds number</td>
<td>(Re_\Omega)</td>
<td>0</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>(AR)</td>
<td>1.3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Axial velocity ratio</td>
<td>(SP)</td>
<td>0</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-6. Comparison of simulation (lines) and experimental (points) [17] predictions of centerline growth rates as a function of carrier gas flow though the group III bubbler, in a close-spaced reactor. Reactor height is 16 mm, pressure is 76 torr and substrate temperature is 750 °C.

Figure 3-7 presents a compilation of runs at the baseline reactor configuration (AR = 1.3, \( H = 16 \) mm, \( T_s = 750 \) °C. Growth rate and uniformity dependence on flow rate, pressure and rotation rate is shown. In all cases, the gas flow is free of any recirculations.
Figure 3-7. Growth rate and growth rate uniformity dependence on flowrate as a function of pressure. Substrate temperature is 750 °C. (---): $p = 76$ torr, (---): $p = 150$ torr, (---): $p = 300$ torr. (a): No rotation, (b): $\omega = 120$ rpm, (c): $\omega = 400$ rpm, (d): $\omega = 800$ rpm.

A close-spaced reactor achieves a true stagnation flow regime at low rotation rates, $\omega < 120$ rpm. The growth rate and uniformity in Figs 3-7(a), (b) remain virtually unchanged by pressure or rotation variations. The growth rate depends only on flow rate; specifically growth rate increases as $\sqrt{\omega}$, the indicative signature for a SF regime, as discussed earlier. Moreover, as can be seen by the uniformity plots, this dependence holds true for a large part of the substrate (e.g. 75% at 12 slm). As the rotation rate increases, the transition to an RDR regime is observed.
in Figs 3-7(c) and (d). Growth rate dependence on flow rate weakens. Increasing pressure or rotation leads to an increase of both uniformity and growth rate. Figure 3-8 demonstrates this dependence more clearly at a fixed flow rate.

Figure 3-8. Growth rate and growth rate uniformity dependence on flow rate as a function of rotation rate. Substrate temperature is 750 °C. (—): \( p = 76 \) torr, (—): \( p = 150 \) torr, (—): \( p = 300 \) torr. (a): \( Q = 4 \) slm, (b): \( Q = 8 \) slm.

At pressures higher than 150 torr and spin rates higher than 400 rpm, the growth rate is seen to increase as \( \sqrt{\omega p} \), as predicted by the similarity analysis for flows dominated by rotation-induced forced convection. As discussed earlier, in a “classical” RDR, increasing pressure degrades uniformity because the magnitude of natural convection increases as \( p^2 \). Counteracting that is forced convection, which increases as \( \omega p \). The higher pressure exponent on natural convection dictates low \( p \) and high \( \omega \) for good uniformity. However, Figs. 3-7(c) and (d) and
Figure 3-8 clearly indicate that in a "close-spaced" RDR, increasing the pressure increases uniformity. For small reactor heights, natural convection is not important and leaves the \( \omega p \) dependence on forced convection to dominate, indicating high uniformity at high pressure. On the other hand, close spacing does not eliminate rotation-driven recirculations.

Figure 3-9. Temperature profile and flow streamlines in a close-spaced reactor with (a) \( H = 16 \) mm, and (b) \( H = 37 \) mm. The pressure is 500 torr, the temperature is 750 °C, the flow rate is 8 slm \( \text{H}_2 \), and the rotation rate is 800 rpm.

Figure 3-9 depicts temperature profiles and flow streamlines in the reactor at \( p = 500 \) torr, \( \omega = 800 \) rpm for two values of the reactor height, (a) 16 mm, and (b) 37 mm. A high rotation
rate (800 rpm) gives rise to counter-rotating eddies even at the smallest reactor height studied, \( H = 16 \text{ mm} \), for \( P > 300 \text{ torr} \). While these recirculations may increase the growth rate uniformity by shrinking the boundary layer, operating under these conditions would be undesirable due to reproducibility and interface abruptness considerations. Our understanding of this geometry indicates that intermediate disk spin rates may be used to expand the operating parameter window of stable flow, with minimal penalty in uniformity.

Another difference between “classical” and “close-spaced” RDR is that no velocity matching is necessary for the latter. That is, the fluid velocity in the inlet does not have to be greater or equal to the asymptotic value for the axial velocity of an infinite rotating disk, \( \sqrt{\omega v_o} \). Velocity matching is required in a “classical” RDR and leads to increased demands on the carrier flow rate. In contrast, for a reactor height of \( H = 16 \text{ mm} \), no velocity matching is necessary. For example, in the case \( p = 300 \text{ torr} \), \( Q = 4 \text{ slm} \), and \( \omega = 800 \text{ rpm} \), the inlet velocity is one fourth of the “ideal” matched velocity. Nevertheless, the reactor gives excellent uniformity (> 80) without any recirculations. In summary, a close-spaced reactor with \( H = 16 \text{ mm} \) can achieve a true SF regime controlled either by inlet flow inertia or susceptor rotation. In both cases, excellent uniformity is achieved. The effect of changing the reactor height is studied next to determine the extent of this favorable operating regime.

Pressure dependence on uniformity of \( \pm 5\% \) for various reactor heights is reported in Figure 3-10. The substrate temperature is 750 °C. The inlet flow rate is kept at an intermediate value of 8 slm. The rotation rate is 400 rpm, indicating the reactor is in the RDR regime.
Figure 3-10. Dependence of ± 5% uniformity on pressure for different reactor heights at 750 °C and 400 rpm. Reactor heights are as follows: (---) 16 mm, (---) 25 mm, (---) 37 mm and (---) 74 mm.

An excellent demonstration of the transition from rotation-induced stagnation flow to “classical” RDR flow is captured. In the 16-mm case, the reactor retains its SF character even at atmospheric pressure with a continuous increase of uniformity. Neither buoyancy- nor rotation-driven recirculations are present over the entire pressure range at this height. As the susceptor-to-inlet gap increases, uniformity initially increases and then drastically drops off with increasing pressure. The initial rise is due to the transition from stagnation flow to a “close-spaced” RDR-type flow that increases the forced convection ($\alpha p$). At higher pressures, flow recirculations appear and uniformity plummets. That transition shifts to lower pressures with increasing height. In the 25-mm case, the reactor performs equally well to the 16-mm case for pressures up to 500 torr. Such a design may be favored if a larger height is dictated by non-hydrodynamic
reasons. Avoiding showerhead deposits and lowering temperature of the reactor sidewall are examples of such reasons.

When the substrate temperature is increased to 1050 °C (see Figure 3-11) the 16- and 25-mm cases are shown to retain their characteristics, but absolute uniformity drops by \( \approx 5 \). It should be noted that flow recirculations are inherently time-dependent three-dimensional phenomena that cannot be captured exactly by the axisymmetric simulations presented here. Therefore, the actual heights/pressures for the transition may be different from those presented in Figs 3-10 and 3-11.

![Graph showing dependence of \( \pm 5\% \) uniformity on pressure for different reactor heights at 1050 °C and 400 rpm.](image)

**Figure 3-11.** Dependence of \( \pm 5\% \) uniformity on pressure for different reactor heights at 1050 °C and 400 rpm. Reactor heights are as follows: (---) 16 mm, (-->) 25 mm, (---) 37 mm and (---) 74 mm.
The simulations presented above illustrated the transition among various operating modes as the reactor height is increased at a constant rotation rate. An intermediate value of $\omega = 400$ rpm was selected. Henceforth, the reactor behavior at the limits of no and very high rotation is addressed. At high rotation rates, rotation-induced recirculations appear even at very low susceptor-showerhead gap (16 mm) and reduced pressure (300 torr) as shown in Figure 3-9. At the opposite limit of no rotation, the pressure dependence on uniformity at 750 °C is depicted in Figure 3-12.

![Figure 3-12](image.png)

Figure 3-12. Dependence of $\pm 1\%$ uniformity on pressure for different reactor heights at 750 °C and no susceptor rotation. Reactor heights are as follows: (---) 16 mm, (---) 25 mm, (---) 37 mm and (---) 74 mm.

For the 16-mm case, stagnation flow is observed with a continuous increase in uniformity with increasing pressure. The growth rate remains within $\pm 1\%$ of the centerline growth rate.
over 75% of the substrate at atmospheric pressure. Given the $p^2$ and $H^3$ dependence on natural convection, recirculations cannot be avoided at heights larger than 25 mm considered in this study. A representative flow and temperature field at $H = 37$ mm and $p = 400$ torr is shown in Figure 3-13. The natural convection induced cell, rising along the reactor centerline and descending along the cold reactor wall, is displayed.

![Temperature profile and flow streamlines in a close-spaced reactor with $H = 37$ mm. The pressure is 400 torr, the temperature is 750 °C, the flow rate is 8 slm H₂, and there is no susceptor rotation.](image)

Considering the nearly ideal stagnation flow behavior exhibited by the 16-mm gap close-spaced reactor, it is worthwhile to study the dependence of uniformity on dimensionless numbers
for this case. Since natural convection is suppressed at all conditions for this small height, the value of the Grashof number is not important when it is small. Reynolds number can be used as a measure of forced convection in the reactor, Re_Q for the inlet inertia case and Re_Q' for the susceptor rotation case. \( \text{Re}_Q = H \sqrt{\alpha v_o / \nu} \), defined slightly different from the common notation. This expression used the axial velocity caused by the centrifugal pumping as the velocity scale, rather than the radial velocity at the susceptor edge (\( \alpha R \)). Figure 3-14 illustrates that there is no clear correlation of predicted growth uniformity with Re_Q or Re_Q' separately.

![Figure 3-14](image)

**Figure 3-14** Dependence of ± 1% uniformity on Re_Q or Re_Q'. Reactor height is 16 mm and substrate temperature is 750 °C. Compilation of simulation results at various combinations of operating pressure, flow rate and susceptor rotation rate.

When the higher of the two numbers at each condition, \( \text{max}[\text{Re}_Q, \text{Re}_Q'] \) is used, however, a clear trend is observed (Figure 3-15). The use of an axial velocity scale for Re_Q' enables direct comparison between the two Reynolds numbers. The SP number, used by [7,10] corresponds to the ratio Re_Q/Re_Q'. As is also shown in Figure 3-15, it does not offer by itself insight to actual growth rate uniformity. Nevertheless, it can be used as an indication of the controlling
stagnation flow regime. When SP is less than one, rotation-induced SF is established, therefore rotation rate and/or pressure should be manipulated for better results. In contrast, when SP is larger than one, classical SF is established and flow rate should be manipulated.

![Graphs showing uniformity vs. Re Q, Re Ω and 1/SP.]

Figure 3-15. Dependence of ± 1% uniformity on max[Re Q , Re Ω'] and SP. Conditions are as in Fig. 3-14. The trendline is added for visual aid.

3.5 Summary

A hierarchical simulation approach of fluid flow and mass transfer in close-spaced reactors for OMCVD has been presented. Three-dimensional calculations establish that there is complete mixing in the gas phase, while the individual gas injectors dissipate within 5-8 mm from the reactor inlet under typical operating conditions. Two-dimensional parametric studies of growth rate and uniformity dependence on operating conditions and geometric factors were used to gain new insight into the chamber performance. Either forced-convection dominated or rotation dominated stagnation flow can be achieved. In the latter case, growth uniformity increases with pressure, contrary to the classical vertical rotating disk reactor response.
3.6 References

Chapter 4. Kinetic modeling of OMCVD growth of GaN

4.1 Introduction

In this chapter we focus on the development of a systematic understanding of the processes underlying OMCVD growth of GaN by combining physically accurate transport phenomena models with proposed gas-phase and surface chemistry mechanisms. The development of such models depends heavily on the availability of data for elementary reaction steps in the gas phase and on the surface. Experimental studies yield information about the individual steps of the reaction mechanism, which must be consolidated in an overall kinetic model. The development of a kinetic model for OMCVD of GaN is a challenging task because of the large number of possible gas phase and surface reactions involved. The problem is compounded by the lack of experimental data for many reaction rate constants that then must be estimated by thermochemical methods (e.g., [1,2]) and quantum chemistry techniques [3]. In this work we aim to develop a model that is consistent with reported trends in GaN growth for several different studies, rather than a model that exhibits an exact agreement with only one particular set of data. In developing this mechanism, we tried to incorporate as much known chemistry pertaining to the growth of GaN as possible, while trying to keep the mechanism simple, given the lack of a general understanding of the underlying pathways. There is considerable understanding of the homogeneous decomposition of TMGa, both experimentally [4,5], and through detailed kinetic models for the growth of GaAs [6,7]. Ammonia gas phase
decomposition chemistry is largely known through combustion studies. This information is used as a starting point for the kinetic model for GaN growth. Although several elementary steps are unknown, we believe there is presently sufficient information for developing and testing kinetic models for GaN growth from TMGa and NH₃. Values of unknown reaction parameters are resolved by incorporating the model in detailed transport phenomena simulations of realistic reactor geometries and comparing with experimental data.

### 4.2 Reaction mechanism development

The proposed simple gas-phase and surface chemical mechanism for crystal growth of GaN is presented in Table 4-I. It includes 11 gas-phase and 3 surface species participating in 7 gas-phase and 9 surface reactions. The corresponding reaction rate parameters are also given in Table 4-I. The mechanism revolves around the formation and decomposition of the TMGa:NH₃ adduct, the decomposition of TMGa, along with surface adsorption of all gas-phase species, GaN formation and decomposition. In the following, a detailed description of the kinetic model is presented.

#### 4.2.1 Trimethylgallium decomposition

The gas phase reactions of both TMGa and NH₃ separately, are well understood. The thermal decomposition of TMGa starts at 410 °C and takes place in sequential first order reactions. One Ga-CH₃ bond is broken at each step, with the apparent activation energy being \( \sim 59 \) kcal/mole for the first methyl group, and \( \sim 35 \) kcal/mole for the second [4]. These activation energies measured for decomposition in toluene are essentially the same for the case of H₂ carrier gas (\( \sim 58 \) kcal/mole) [5].
Table 4-I. Gas-phase and surface reaction mechanism for GaN growth from trimethylgallium and ammonia

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{Rate} = k_0 \times \exp\left(-\frac{E_a}{RT}\right) )</th>
<th>( k_0 )</th>
<th>( E_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[G1] Ga(CH(_3))(_3)</td>
<td>( \rightarrow ) GaCH(_3) + 2 CH(_3)</td>
<td>( 3.5 \times 10^{15} )</td>
<td>59.5</td>
</tr>
<tr>
<td>[G2] Ga(CH(_3))(_3) + NH(_3)</td>
<td>( \leftrightarrow ) Ga(CH(_3))(_3):NH(_3)</td>
<td>( 1.0 \times 10^{12} )</td>
<td>0.0</td>
</tr>
<tr>
<td>[G3] Ga(CH(_3))(_3):NH(_3)</td>
<td>( \leftrightarrow ) Ga(CH(_3))(_3) + NH(_3)</td>
<td>( 9.5 \times 10^{9} )</td>
<td>19.0</td>
</tr>
<tr>
<td>[G4] Ga(CH(_3))(_3):NH(_3)</td>
<td>( \rightarrow ) Ga(CH(_3))(_2)NH(_2) + CH(_4)</td>
<td>( 1.0 \times 10^{13} )</td>
<td>32.0</td>
</tr>
<tr>
<td>[G5] Ga(CH(_3))(_3):NH(_3) + NH(_3)</td>
<td>( \rightarrow ) Ga(CH(_3))(_2)NH(_2) + CH(_4) + NH(_3)</td>
<td>( 1.0 \times 10^{12} )</td>
<td>15.0</td>
</tr>
<tr>
<td>[G6] 3 Ga(CH(_3))(_2)NH(_2)</td>
<td>( \rightarrow ) [Ga(CH(_3))(_2)NH(_2)](_3)</td>
<td>( 1.0 \times 10^{21} )</td>
<td>0.0</td>
</tr>
<tr>
<td>[G7] [Ga(CH(_3))(_2)NH(_2)](_3)</td>
<td>( \rightarrow ) 3 &quot;Ga-N&quot; + 6 CH(_4)</td>
<td>( 4.0 \times 10^{15} )</td>
<td>60.0</td>
</tr>
<tr>
<td>[S1] Ga(CH(_3))(_3) + S</td>
<td>( \rightarrow ) Ga* + 3 CH(_3)</td>
<td>( s = 0.1 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S2] Ga(CH(_3))(_3):NH(_3) + S</td>
<td>( \rightarrow ) Ga* + 3 CH(_3) + NH(_3)</td>
<td>( s = 0.1 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S3] GaCH(_3) + S</td>
<td>( \rightarrow ) Ga* + CH(_3)</td>
<td>( s = 1.0 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S4] Ga(CH(_3))(_2)NH(_2) + S</td>
<td>( \rightarrow ) Ga* + 2 CH(_4)</td>
<td>( s = 1.0 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S5] &quot;Ga-N&quot; + S</td>
<td>( \rightarrow ) GaN*</td>
<td>( s = 1.0 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S6] [Ga(CH(_3))(_2)NH(_2)](_3) + 3 S</td>
<td>( \rightarrow ) 3 GaN* + 6 CH(_4)</td>
<td>( s = 1.0 )</td>
<td>0.0</td>
</tr>
<tr>
<td>[S7] Ga*</td>
<td>( \rightarrow ) [GaN](_s) + S</td>
<td>( 1.0 \times 10^{10} )</td>
<td>37.0</td>
</tr>
<tr>
<td>[S8] GaN*</td>
<td>( \rightarrow ) [GaN](_s) + S</td>
<td>( 2.0 \times 10^{8} )</td>
<td>22.0</td>
</tr>
<tr>
<td>[S9] [GaN](_s)</td>
<td>( \rightarrow ) ( \frac{1}{2} ) N(_2)</td>
<td>( 2.0 \times 10^{3} )</td>
<td>75.0</td>
</tr>
</tbody>
</table>

It has also been established that monomethyl-gallium (MMGa) is the most stable product of homogeneous TMGa decomposition [8]. The step wise thermal decomposition of TMGa to
MMGa has been lumped in reaction [G1] with rate parameters those of the first step, since the
decomposition of the dimethylgallium intermediate occurs at a much higher rate. The methyl
radicals produced can subsequently react to form methane and ethane as the final gas-phase
products of TMGa pyrolysis. These reactions are well known [6,7] and have no effect on the
GaN deposition. Thus, they are neglected within the scope of this study.

4.2.2 Homogeneous ammonia decomposition

The thermal decomposition of ammonia has been the subject of several experimental
studies in combustion chemistry. Detailed kinetic mechanisms have been developed and
validated by comparison with quantitative measurements of the component species concentration
[9,10]. Ammonia is stable for temperatures up to 800 °C. Gas phase decomposition proceeds in
a second order reaction with high activation energy (~ 95 kcal/mole) [10]. Therefore, negligible
ammonia decomposition is expected under typical conditions of nitride growth. Ban [11]
reported on ammonia pyrolysis in a quartz flow tube while studying halide Vapor Phase Epitaxy
of GaN. Less than 4% decomposed at 950 °C. In a consistent observation, Liu and Stevenson
[12] reported that only 6% of ammonia dissociates at 1150 °C when flowing in a quartz tube.
When a graphite liner was used either uncoated, or coated with a GaN film, the extent of
decomposition remained under 10%. Beaumont et al. [13] studied the nitrogen precursors in
nitride growth in order to determine the nature of the active species at the growth temperature.

Assuming that the following reaction,

\[ \text{NH}_3 \leftrightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \]  

[4-1]

is under thermodynamic equilibrium, they concluded that complete dissociation of NH\(_3\) to stable
N\(_2\) and H\(_2\) occurs at growth temperatures of 900-1100 °C, and therefore, high V/III ratios are
required to provide enough active N species. Their study is a demonstration of the perils associated with applying \( a \ priori \) thermodynamic equilibrium arguments in an inherently dynamic process like crystal growth. Pressure, residence time and kinetic rate constants, along with thermodynamic data, must be used in predicting the gas-phase composition under growth conditions. Based on thermodynamics, ammonia is unstable at elevated temperatures since the \( \Delta G^\circ_{\text{NH}_3} = 20 \text{ kcal/mole} \) at 1000 °C [14].

Figure 4-1 depicts the partial pressures of \( \text{NH}_3 \), \( \text{N}_2 \), and \( \text{H}_2 \) under thermodynamic equilibrium as a function of temperature. \( P_{\text{tot}} = 1 \text{ atm} \).

Ammonia is completely decomposed at \( T > 300 \text{ °C} \). Under thermodynamic equilibrium, no GaN growth at all would occur since the only nitrogen source reaching the hot zone of the reactor would be stable \( \text{N}_2 \). However, the large kinetic barrier for decomposition indicates that most of ammonia would arrive undecomposed at the growth surface and can participate in surface reactions leading to nitride growth. The pyrolysis
mechanism presented in [10] that includes nine species participating in 21 reactions, was used in a plug-flow reactor model. Gas-phase mole fractions of the main species at 1000 °C and 1 Atm are shown in Figure 4-6. Hydrogen is used as the carrier gas and the ammonia mole fraction at the inlet is $X_{NH_3} = 0.3$.

![Figure 4-2. Mole fraction time histories for all major species in ammonia pyrolysis kinetic model [10]. Modeled conditions are $T = 1000$ °C, $P = 1$ Atm, $[NH_3]_o = 0.3$, and $[H_2]_o = 0.7$.](image)

Less than 1% of $NH_3$ decomposes at atmospheric pressure with $N_2$ and $H_2$ as the major products. The extent of $NH_3$ dissociation is much smaller at reduced pressures. The accuracy of the calculations was tested by studying $NH_3$ decomposition at 2500 °C and 1 Atm, the conditions used in the results presented in [10]. Simulation results are shown in Figure 4-3. Significant
ammonia decomposition is observed. The mole fraction time histories for all species are in good agreement with the published results.

![Figure 4-3](image)

Figure 4-3. Mole fraction time histories for all major species in ammonia pyrolysis kinetic model [10]. Modeled conditions are $T = 2500 \, ^\circ C$, $P = 1 \, \text{Atm}$, $[\text{NH}_3]_o = 0.003$, and $[\text{H}_2]_o = 0.0$

Methyl radical attack on ammonia to produce $\text{CH}_4$ and $\text{NH}_2$ is known to proceed with a very low kinetic barrier ($\sim 10 \, \text{kcal/mole}$) [15,16]. Such a pathway could be significant in OMCVD growth by initiating $\text{NH}_3$ decomposition. However, as will be shown in the next section, virtually no TMGa exists in the heated zone of the reactor and methyl radical formation is entirely suppressed in nitride growth. Gas phase dissociation of $\text{NH}_3$ at growth conditions can thus be seen as a minor competing pathway that merely reduces the amount of precursor
available. Since a large excess of ammonia is typically used, we do not include these gas-phase reactions in the proposed mechanism.

4.2.3 TMGa:NH₃ adduct reactions

The adduct formation between TMGa and NH₃ is well documented. Trimethylgallium is electron-deficient since the central Ga atom has an empty p-orbital, and can accept an electron pair from a donor molecule to form Lewis-type acid-base adducts. Ammonia has electron lone-pairs and can readily donate them acting as the Lewis base in the following reaction:

\[
\text{TMGa} + \text{NH}_3 \leftrightarrow \text{TMGa : NH}_3
\]  

[4-2]

Leib et al. [17] measured the strength of the Ga-N coordination bond to be 18.5 kcal/mole. Zaouk et al. [18] estimated that bond strength to be 21.1 kcal/mole by using an empirical equation for correlating enthalpies of Lewis acid-base interactions developed by Drago [19]. The value of the bond strength is very important when considering nitride growth, since it can be also interpreted as the dissociation enthalpy of the adduct. If the bond strength is low, then the adduct upon reaching the heated zone of the reactor will dissociate to regenerate TMGa and NH₃, with no consequence to the growth. If the bond strength is high, an alternative decomposition pathway may be favored, thus entirely altering the chemistry of the epitaxial growth.

Coates [20] synthesized the white crystalline adduct and reported that it has a melting point of 32°C and a low vapor pressure of ~ 0.95 Torr at room temperature. Upon heating, the adduct is stable up to 70 °C where it begins to evolve methane. At 90 °C the adduct was found to decompose to methane and the cyclic compound [Ga(CH₃)₂NH₂]₂. Almond et al. [21] determined the molecular structure of the adduct by gas-phase electron diffraction at room temperature. In a subsequent study [22], they reported that thermal decomposition of the solid adduct at 120 °C under a nitrogen atmosphere yields the trimeric species [Ga(CH₃)₂NH₂]₃ and
one CH₄ molecule per Ga atom. The trimer was characterized by single-crystal X-ray analysis, and was found to exist as a six-member ring in both the solid and the gas phase. No kinetic information on the adduct decomposition can be extracted from their data, since the adduct was heated for 1 h prior to product characterization.

A number of recent studies have focused on the gas-phase reactions of TMGa and NH₃ and their impact on nitride growth. No direct spectroscopic evidence on the presence or not of the dimer/trimer species in an OMCVD reactor exists. Mazzarese et al. [23] studied the reaction by in-situ FTIR. Their results, however, do not appear to be reliable, since in a calibration run the homogeneous TMGa decomposition in H₂ was measured to proceed with an activation energy of 10 kcal/mole. Sywe et al. [24] also used FTIR spectroscopy to study the adduct formation. They reported the adduct vapor pressure at room temperature to be ~ 0.92 Torr, in excellent agreement with the earlier study [20]. At room temperature the formation reaction occurs instantaneously upon mixing, and proceeds to completion within 0.2 sec. The pressure in the gas cell was less than 20 Torr. When ammonia is in excess, the IR absorption spectrum lacks all the characteristic peaks of TMGa, while peaks assigned to gaseous TMGa:NH₃ are observed. Alternatively, if the mixing takes place at 150 °C, peaks associated with both TMGa and TMGa:NH₃ are recorded. It appears that complete consumption of the limiting reactant (TMGa) is not favored, and a chemical equilibrium in reaction [4-2] is established within 2 min of mixing. The same IR spectrum is obtained if TMGa and ammonia are mixed at 25 °C and the mixture is subsequently heated to 150 °C, further validating the conclusion of thermal equilibrium. The peak intensities associated with CH₄ begin to increase 30 min after mixing at 150 °C with a corresponding decrease in the TMGa:NH₃ peaks, indicating that adduct dissociation is much faster than decomposition.
Thon and Kuech [25] studied the high temperature gas phase reactions between TMGa and NH₃ in H₂ carrier gas by means of in situ mass spectrometry within a flow tube isothermal reactor operating at 76 Torr and a residence time of 1 sec. An immediate reaction between TMGa and NH₃ resulting in the elimination of a single methane molecule at all T > 200 °C is observed. The product of this reaction is thermally stable up to 500 °C. Their system could not determine the exact nature of this species. Upon complete decomposition at T > 700 °C, three CH₄ molecules per initial TMGa molecule are produced. Their results do not provide any further insight in the onset of adduct decomposition because the lowest temperature studied was 200 °C. When TMGa/ND₃/H₂ was used, only CH₃D was detected. Similarly, only CH₄ was observed when the mixture was TMGa/NH₃/D₂. These results clearly indicate that the gas-phase production of methane comes exclusively from an intramolecular adduct reaction, or a reaction between the adduct and the excess ammonia. In conclusion, this study demonstrated that the implications of the adduct-related pre-reactions in nitride growth go beyond typical considerations of precursor loss due to adduct condensation. The evolution of methane at low temperature, low pressure and very short residence time suggests that adduct-derived species are the actual growth precursors in nitride epitaxy. The kinetics of adduct formation/ decomposition/ dissociation will determine the nature and amount of the growth species. Furthermore, since these gas-phase pre-reactions can take place at low temperature, parameters such as residence time, pressure, inlet mixing design, temperature distribution, and effectively reactor configuration, would be important.

The mechanistic details of the methane elimination are not known. The same is true for the dimer/trimer formation. Based on studies of analogous Al-containing species [26], the following reaction sequence is proposed:
\[ \text{TMGa : NH}_3 \rightarrow \text{Ga(CH)}_2\text{NH}_2 + \text{CH}_4 \]  \[4-3\]

\[ 2 \text{Ga(CH)}_2\text{NH}_2 \leftrightarrow [\text{Ga(CH)}_2\text{NH}_2]_2 \]  \[4-4\]

\[ \text{Ga(CH)}_2\text{NH}_2 + [\text{Ga(CH)}_2\text{NH}_2]_2 \rightarrow [\text{Ga(CH)}_2\text{NH}_2]_3 \]  \[4-5\]

While the trimer was shown to be the prevalent species at 120 °C in [22], those results were obtained after equilibrium was attained. In an OMCVD reactor where residence times are ~ 1-5 sec, a mixture of adduct (Ga(CH\text{3})_2:NH\text{3}), monomer (Ga(CH\text{3})_2NH\text{2}), dimer ([Ga(CH\text{3})_2NH\text{2}]_2), and trimer ([Ga(CH\text{3})_2NH\text{2}]_3) may be present. Reaction [4-3] implies that the first Ga-C bond (~ 58-60 kcal/mole) can be broken at \( T > 100 \) °C in the presence of ammonia. The activation energy for this elimination reaction was estimated to be 49 kcal/mole [18]. Clearly, the actual activation energy must be much lower for the reaction to take place at low temperature.

Simka [27] performed quantum chemistry calculations utilizing density functional theory (DFT) methods, such as the Becke 3-parameter density functional theory using the Lee-Yang Parr correlation functional (B3LYP), to investigate the structure and reactivity of the TMGa:NH\text{3} adduct. The structure and electron-density plot of the adduct is shown in Figure 4-4, and is in excellent agreement with the gas-phase electron diffraction results [21]. Significant electron density is shared by the Ga and N atoms.
The molecular structures of the monomer, dimer and trimer were also determined and are shown in Figure 4-5. The calculated structure for the trimer matches the structure derived experimentally [22].

Figure 4-5. Structures of the gas-phase species arising from TMGa:NH₃ adduct decomposition [27]. (red = Ga, blue = N, green = C, gray = H)
The thermodynamics of adduct formation were also computed. Figure 4-6 depicts the Gibbs free energy of reaction, $\Delta G_{\text{rxn}}$, of reactions [4-2], [4-3] and [4-4] as a function of temperature.

![Diagram of Gibbs free energy vs. temperature]

Figure 4-6. $\Delta G_{\text{rxn}}$ for the reactions of: (a) adduct formation (reaction [4-2]), (b) dimer formation (reaction [4-4]), and (c) methane elimination (reaction [4-3]). After [27].

Formation of TMGa:NH$_3$ is energetically favorable for temperatures up to 220 °C. $\Delta G_f$ for adduct formation is positive at $\approx 250$ °C, indicating that in reactor configurations where TMGa and NH$_3$ are mixed at elevated temperatures, the formation of the adduct is not thermodynamically favored and may thus be completely avoided. However, the presence of the irreversible decomposition pathway via methane elimination may deplete the adduct, and shift the equilibrium towards adduct formation even at elevated temperatures. Dimerization of the monomer is energetically favored up to temperatures as high as 700 °C, while methane
elimination from the adduct is thermodynamically favorable. In addition to estimating thermodynamic quantities, Simka investigated possible reaction pathways for the elimination of methane from the adduct. Two possible pathways were identified as illustrated in Figure 4-7[27].

![Diagram of possible pathways](image)

Figure 4-7. Possible pathways for CH₄ elimination from TMGa:NH₃ adduct. (green = Ga, blue = N, black = C, white = H)

One pathway is the intramolecular H transfer from the NH₃ fragment to one of the methyl groups; the other pathway involves a bimolecular reaction of the adduct molecule with an unreacted NH₃ molecule. DFT calculation results suggest that the intramolecular pathway proceeds through a four-center transition-state configuration with an activation barrier of 32 kcal/mole. The activation barrier for the bimolecular reaction pathway is about 15 kcal/mole.

Reactions [G2-G3] represent the adduct formation equilibrium. Multiple experimental observations that the reaction goes to completion almost instantaneously at room temperature indicate a negligible kinetic barrier (i.e. Eₐ = 0.0) for the forward reaction, [G2]. The reaction
The rate is bound by the collision rate, which for TMGa and NH₃ was estimated to be ~ 1.3×10¹⁴ cm³/sec/mole at room temperature. Actual rates for gas reactions between molecules of any complexity are lower than the collision limits by several orders of magnitude [2]. The rate of the reverse reaction, [G3], is computed using: \( r_{G3} = \frac{r_{G2}}{K_p} \), where \( K_p \) is the equilibrium constant of the adduct formation and is computed using the equation \( \Delta G_f = -RT \ln K_p \). Values of \( \Delta G_f \) are taken from Figure 4-6. Adduct dissociation is calculated to proceed with an activation energy of \( \approx 20 \) kcal/mole, which agrees with the early estimates of the Ga-N bond strength [17,18]. Adduct decomposition is represented in reactions [G4]-[G5]. Following Simka [27], intramolecular methane elimination, [G4], proceeds with barrier of 32 kcal/mole, while the second order reaction with excess ammonia, [G5], has a 15 kcal/mole barrier. According to transition state theory [1], the pre-exponential factor for reaction [G4] is given by:

\[
A = \frac{k_B T Q^*}{h Q_{adduct}}
\]

where \( k_B \) and \( h \) are the Boltzmann and Planck constants respectively, and \( Q^*, Q_{adduct} \) are the partition functions for the transition state and the adduct respectively. Based on the DFT calculations of the adduct and transition state structure, the pre-exponential factor was estimated to be \( A_{300K} = 5.0 \times 10^{12} \) sec⁻¹ and \( A_{600K} = 8.0 \times 10^{12} \) sec⁻¹. Dimer formation from the reactive intermediate \( \text{Ga(CH}_3)_2\text{NH}_2 \), as well as the subsequent trimer formation, is expected to proceed with no kinetic barrier. The rate of the reverse reaction, dimer dissociation, is computed from the equilibrium constant as described above and is shown to proceed with an activation energy of 54.7 kcal/mole. Reactions [4-2] through [4-5] address the main effects observed when TMGa and NH₃ are mixed, i.e. adduct formation, dissociation, decomposition and formation of a stable cyclic species containing Ga-N bonds. At the elevated temperatures used in nitride growth,
dimer and trimer species can decompose to a number of \([(\text{CH}_3)_y \text{GaN}_x \text{H}_y]\) reactive fragments and, therefore, contribute similarly to the film deposition. Since only methane is observed in the gas-phase at temperatures higher than 500 °C, [25], the dimer and trimer species are assumed to decompose to \((\text{GaN})_x\) fragments and \(\text{CH}_4\) with kinetic parameters similar to those of TMGa decomposition. The possible formation of a stable gaseous oligomer that does not contribute to the growth by either particle formation or wall deposition, needs also to be explored. Such a pathway would depend strongly on overall reactor pressure, being more dominant at higher pressures. In this work we have neglected this mechanism, based on the minimal pressure dependence of the GaN growth efficiency reported in the literature, [28]. However, the oligomer formation pathway will also strongly depend on reactor residence time and reactor configuration. Thus, the assumption to neglect it needs to be reevaluated once additional experimental data is available.

In order to estimate the reaction pre-exponential factors, the expanded gas-phase kinetic mechanism shown in Table 4-II is implemented in a simple plug flow reactor (PFR) model to emulate the tubular hot wall reactor used in [25]. Since the reactor tube is isothermal and the residence time is very short \((\tau = 1 \text{ sec})\), the assumption of plug flow is warranted. The batch reactor formulation is also used to emulate the stainless-steel gas cell used in the spectroscopic study reported in [24].
Table 4-II. Gas-phase mechanism used in plug-flow and batch reactor studies

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate = $k_o \times \exp (-E_a / RT)$</th>
<th>$k_o$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4-2]_r Ga(CH$_3$)$_3$ + NH$_3$ ↔ Ga(CH$_3$)$_3$:NH$_3$</td>
<td>1.0x10$^{12}$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[4-2]_r Ga(CH$_3$)$_3$:NH$_3$ ↔ Ga(CH$_3$)$_3$ + NH$_3$</td>
<td>9.5x10$^{9}$</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>[4-3] Ga(CH$_3$)$_3$:NH$_3$ → Ga(CH$_3$)$_2$NH$_2$ + CH$_4$</td>
<td>1.0x10$^{13}$</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>[4-6] Ga(CH$_3$)$_3$:NH$_3$ + NH$_3$ → Ga(CH$_3$)$_2$NH$_2$ + CH$_4$ + NH$_3$</td>
<td>1.0x10$^{12}$</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>[4-4]_r 2 Ga(CH$_3$)$_2$NH$_2$ ↔ [Ga(CH$_3$)$_2$NH$_2$]$_2$</td>
<td>1.0x10$^{12}$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[4-4]_r [Ga(CH$_3$)$_2$NH$_2$]$_2$ ↔ 2 Ga(CH$_3$)$_2$NH$_2$</td>
<td>1.0x10$^{17}$</td>
<td>54.7</td>
<td></td>
</tr>
<tr>
<td>[4-5] [Ga(CH$_3$)$_2$NH$_2$]$_2$ + Ga(CH$_3$)$_2$NH$_2$ → [Ga(CH$_3$)$_2$NH$_2$]$_3$</td>
<td>1.0x10$^{12}$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[4-7] [Ga(CH$_3$)$_2$NH$_2$]$_2$ → 2 “Ga-N” + 4 CH$_4$</td>
<td>4.0x10$^{15}$</td>
<td>60.0</td>
<td></td>
</tr>
<tr>
<td>[4-8] [Ga(CH$_3$)$_2$NH$_2$]$_3$ → 3 “Ga-N” + 6 CH$_4$</td>
<td>4.0x10$^{15}$</td>
<td>60.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-8 illustrates the time dependence of TMGa and adduct mole fractions in a batch reactor operating at 20 Torr and 27 °C, for three different rates of the adduct formation reaction, [4-2]_r. The initial TMGa mole fraction is 0.4 while that of NH$_3$ is 0.6. The time needed for complete adduct formation strongly depends on the rate of reaction [4-2], with a rate of 1.0x10$^{11}$ giving the closest agreement with the experimentally measured time for complete reaction under those conditions, 0.2 sec. Yet, the same reaction rate can lead to unequal times of reaction completion for different levels of ammonia excess, as demonstrated in Figure 4-9. Since the exact amount of NH$_3$ excess used is not known and time measurement may be swayed by incomplete mixing, direct comparison to experiments is inconclusive.
Figure 4-8. TMGa and adduct mole fractions as a function of time in a batch reactor. T=27 °C. P_{tot}=20 torr. [TMGa]_o = 0.4, [NH3]_o = 0.6. The rate of reaction [4-2]_f is: (a) 1.0×10^{12}, (b) 1.0×10^{11}, and (c) 1.0×10^{10}. 
Figure 4-9. TMGa and adduct mole fractions as a function of time in a batch reactor. 
$T=27 \, ^\circ\text{C}$. $P_{\text{tot}}=20$ torr. The rate of reaction [4-2]$_r$ is $1.0 \times 10^{12}$. The initial TMGa/NH$_3$ mole fraction ratio is: (a) 0.1/0.9, (b) 0.4/0.6, and (c) 0.5/0.5.

Figure 4-10 illustrates the mole fraction time histories when mixing occurs at 150 $^\circ$C for different rates of reaction [4-2]$_r$. In agreement with experimental observations, the adduct formation does not proceed to completion; rather, equilibrium between TMGa, adduct and ammonia is reached. The simulations using the mechanism of Table 4-II show no methane production for long mixing times (<10 min) at 150 $^\circ$C, also in agreement with [24].
Figure 4-10. TMGa and adduct mole fractions as a function of time in a batch reactor. T=150 °C. P_{tot}=20 torr. The initial TMGa/NH₃ mole fraction is 0.5/0.5. The rate of reaction [4-2] is: (a) 1.0×10¹², and (b) 1.0×10¹⁰.

A reaction rate of 1.0×10¹² for [4-2], and corresponding rate for [4-2], that is consistent with experimental observations, is two orders of magnitude lower than the maximum collision rate of TMGa and NH₃ and leads to “instantaneous” reaction at room temperature, was assumed. The mechanism was then utilized in an isothermal plug-flow-reactor model. Figure 4-11 depicts the temperature dependence of decomposition in the TMGa/NH₃/H₂ system. The operating conditions reported in [25] were used in the simulations; namely P = 76 Torr, τ = 1 sec, [TMGa]₀ = 0.05, [NH₃]₀ = 0.35, and [H₂]₀ = 0.60. Separate simulations at different temperatures are used to generate the temperature dependence shown. Mole fractions of all pertinent species are presented; ammonia and hydrogen are in excess and are omitted.
Trimethylgallium is entirely consumed to form the adduct which is stable up to 150 °C under these conditions. Both adduct dissociation to regenerate TMGa, and adduct decomposition to produce methane occur at temperatures higher than 200 °C. One methane molecule per TMGa molecule is produced at temperatures higher than 350 °C. Coexistence of monomer, dimer and trimer is observed, with the trimer being the dominant species and major group III precursor since each trimer molecule accounts for three Ga atoms. Trimer and dimer species decompose to form “Ga-N” and methane at temperatures higher than 500 °C according to reactions [4-7] and [4-8]. The increased presence of monomer at temperatures higher than 450 °C is owed to the shift of the monomer-dimer equilibrium (reaction [4-4]) towards the monomer. Dimer, and subsequently, trimer formation is not favored under these conditions. Unfortunately, this
advantageous behavior does not occur in an OMCVD reactor. In contrast to the isothermal flow simulations used in this study, precursors in an OMCVD reactor face a wide temperature distribution ranging from inlet room temperature to the high temperatures of nitride growth. As seen in Figure 4-11, the irreversible trimer formation will consume most of the monomer before the latter reaches the favorable thermal environment. When comparing with the experimental flow tube study [25], we note the similar temperature and CH₄ behavior at the onset of trimer/dimer decomposition. Since the exact nature of the Ga-containing species could not be determined experimentally, further comparison cannot be performed. Regarding the onset of low-temperature adduct decomposition, we note that the production of one CH₄/TMGa molecule is experimentally observed at lower temperature (200 °C) than predicted by simulations based on the mechanism in Table 4-II, (350 °C). Due to the low pressure and very short residence time used, adduct decomposition proceeds primarily though the unimolecular pathway [4-3] with high Eₐ, rather than the bimolecular reaction with the low kinetic barrier [4-6]. Adding a second bimolecular pathway that involves autocatalytic adduct decomposition as seen experimentally during the pyrolysis of the similar Al(CH₃)₃:NH₃ adduct [26,29], cannot lower the temperature onset of methane evolution. This autocatalytic pathway will be discussed in more detail in the following chapter. A high pre-exponential factor (1.0×10¹⁶) for reaction [4-3] needs to be used in order for one CH₄/TMGa to be produced at 200 °C. In this case however, significant methane production would occur at reduced pressure and very short contact times at temperatures as low as 100 °C, in contrast to many experimental observations. This slight discrepancy between the simulations based on the kinetic model and the observations in [25] may be due to inaccurate description of the transport in the experimental setup by the PFR model, or enhanced decomposition in the experiments via surface reactions. Furthermore, the sensitivity of the
decomposition kinetics on operating parameters is demonstrated in Figure 4-12, where the simulations were carried out for an increased residence time (5sec), while keeping all other parameters constant.

![Graph showing temperature dependence of decomposition within the TMGa/NH₃/H₂ system.](image)

*Figure 4-12. Temperature dependence of decomposition within the TMGa/NH₃/H₂ system. P = 76 Torr, τ = 5 sec, [TMGa]₀ = 0.05, [NH₃]₀ = 0.35.*

Complete adduct decomposition and 1:1 CH₄ production is now observed at 300 °C. Comparing to the τ = 1 sec simulation results, a decrease in dimer mole fraction and significant increase in the high temperature methane production at longer residence times is also noted. Better agreement with the experimental results for the high temperature CH₄ production indicates that a residence time τ > 1 sec may have been actually achieved. A closer study of the results in [25], reveals that although the onset of TMGa decomposition in the presence of ammonia is ~ 70 °C
higher than in its absence, the reported kinetic barrier (48.7 kcal/mole) is lower in the TMGa/NH₃/H₂ case than in the TMGa/H₂ case (51.4 kcal/mole) with similar pre-exponential factors. Due to this inconsistency, kinetic parameters similar to those of TMGa decomposition [4], were used in reactions [4-7] and [4-8] and good agreement with the results in [25] was obtained.

![Graph showing temperature dependence of decomposition](image)

**Figure 4-13.** Temperature dependence of decomposition within the TMGa/NH₃/H₂ system. P = 1 Atm, τ = 1 sec, [TMGa]₀ = 0.05, [NH₃]₀ = 0.35.

Simulations were also carried out at atmospheric pressure and the results are shown in Figure 4-13. Comparing to the low-pressure results (Figure 4-11), absence of TMGa and the dimer at all temperatures, an increase in CH₄ production, and a decrease of monomer mole fraction at high T is shown.
In summary, adduct related pre-reactions were shown to be highly dependent on pressure, temperature, residence time, and ammonia excess. The proposed kinetic model is in agreement with multiple experimental observations and captures the main elements of this chemistry. This model is represented by reactions [G2]-[G7] in the overall GaN kinetic mechanism introduced in Table 4-I. In order to reduce the computational cost of the realistic OMCVD reactor simulations using this mechanism, the dimer and trimer species are lumped and represented by the trimer. This assumption is justified since the dimer species is continuously depleted to form the trimer and is always present in very small amounts, as shown in Figs. 4-11, 4-12 and 4-13. Furthermore, given the similar decomposition kinetics assumed for these ring species, inclusion of the dimer will only change the relative amounts of each growth precursor without affecting the deposition. As was discussed above, if the group III and V precursors were mixed at temperatures higher than 500 °C the dimer-monomer equilibrium will be important yielding substantial amounts of the monomer. No OMCVD reactor used for nitride deposition operates under these conditions, thus enabling the trimer/dimer lumping.

4.2.4 Surface reactions

The development of a surface reaction mechanism for GaN growth is complicated by the large number of possible gaseous species that can adsorb on the surface and the lack of studies on the nature these adsorbates, especially at the elevated temperatures used in nitride growth. In the absence of surface science studies, detailed surface mechanisms including many reactions and species succeed only in providing enough fitting parameters for comparison with experiments. In this initial attempt to model nitride growth, we use simplified surface kinetics to
describe GaN formation and decomposition. In the following, nitrogen availability on the surface through NH₃ decomposition and the energetics of GaN deposition will be discussed.

4.2.4.1 Heterogeneous ammonia decomposition

The heterogeneous thermal decomposition of ammonia is well documented. Activation energies for the catalyzed NH₃ decomposition on a variety of materials are given in Table 4-11. Decomposition normally proceeds by the initial dissociative chemisorption of NH₃ at low T followed by fast H₂ desorption. At moderate temperatures, NH₂* and NH* decompose and a surface nitride film is formed with adsorbed N* being the most abundant surface species. Desorption of molecular nitrogen ensues at higher temperatures. Two mechanisms are typically observed. In the first, the rate of decomposition is proportional to the ammonia partial pressure and the mechanism represents a dynamic balance between supply and consumption of surface nitrogen with no single rate-determining step. Decomposition on W [30], Mo [31], VN [32] follows this mechanism. Decomposition on Fe [33] and Pt [34] favors this mechanism at high temperatures and/or low ammonia pressures.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Eₐ (kcal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>93.5</td>
<td>[10]</td>
</tr>
<tr>
<td>Tungsten</td>
<td>38 – 41</td>
<td>[2]</td>
</tr>
<tr>
<td>Platinum</td>
<td>4 – 22</td>
<td>[34]</td>
</tr>
<tr>
<td>Vanadium Nitride</td>
<td>32</td>
<td>[32]</td>
</tr>
<tr>
<td>Iron</td>
<td>4 – 50</td>
<td>[33]</td>
</tr>
<tr>
<td>Quartz sand</td>
<td>35</td>
<td>[35]</td>
</tr>
</tbody>
</table>
In the second mechanism, desorption of N\(_2\), or equivalently decomposition of the surface nitride is rate limiting and the surface is saturated with N*. Low temperatures and/or high ammonia pressures favor this mechanism on Ni, Fe [33], or Pt [34]. Under this mechanism, quasi-equilibrium between gaseous ammonia, chemisorbed nitrogen and gaseous hydrogen is assumed. Since significant N* exists while direct chemisorption of N\(_2\) is negligible, the nitrogen coverage is determined by employing a quantity called “virtual pressure” of nitrogen, (P\(_{N_2}^\diamond\)) [36]. This virtual pressure is that pressure of nitrogen, which would be in equilibrium with the pressures of ammonia and hydrogen observed in the ambient gas:

\[
P_{N_2}^\diamond = \frac{1}{K_{NH_3}} \frac{P_{NH_3}^2}{P_{H_2}^3}
\]

where \(K_{NH_3}\) is the equilibrium constant of the reaction N\(_2\)(g) + 3 H\(_2\)(g) ⇌ 2 NH\(_3\)(g). The virtual N\(_2\) pressure is essentially a measure of the ability of NH\(_3\) to provide N* to the surface, and will be discussed later in the context of nitride growth.

Inefficient cracking of NH\(_3\) on the GaN surface is often sited as the reason for the high temperatures and large V/III ratios necessary during nitride OMCVD. This assumption is often attributed to the high temperature study of Liu and Stevenson [12] where GaN was shown to have little effect on ammonia decomposition (< 10% at 1100 °C). Similar results were obtained for decomposition on graphite, whereas coexistence of Ga and GaN induced significant catalytic decomposition (~ 60% at 1000 °C) [12]. Sedgwick and Smith [37] used Raman spectroscopy to monitor the NH\(_3\) concentration in the vicinity of the susceptor in a CVD reactor. The extent of decomposition was ~ 100% close to the graphite susceptor at 950 °C and dropped to less than 12% 1 cm higher. The results of the two studies may be reconciled by considering that only
integral effects were measured in the first study where the total amount of unreacted ammonia was measured at the outlet.

In a surface science study of ammonia interactions with a semiconductor surface, Yates and coworkers [38] studied the adsorption on Si(100) by thermal desorption spectroscopy. Ammonia was found to dissociatively adsorb onto Si dimers at -150 °C to produce NH₂* and H*. NH₂* remains on the surface up to ~ 400 °C where it primarily decomposes to N* and H*. In a minor pathway, a recombination reaction leads to ammonia desorption. Recently, Chiang et al. [39] studied the hydrogen desorption and ammonia adsorption on polycrystalline GaN using time-of-flight scattering and recoil spectroscopy. They observed two different states for H₂ desorption, presumably from Ga sites (~ 525 K) and N sites (~ 775K). All hydrogen was desorbed by 600 °C. Ammonia was found to dissociatively adsorb on both clean and hydrogen terminated GaN surfaces at room temperature. Ga-H and N-H species are formed and the same hydrogen desorption states are observed. The ammonia reactions on single crystalline GaN were studied by Shekhar and Jensen [40] using temperature programmed desorption (TPD). Dissociative chemisorption of ammonia on GaN to produce NH₂* and H* species was observed. While H₂ desorbed starting at ~ 200 °C and N₂ was detected at ~ 580 °C, the main pathway involved recombination and ammonia desorption at ~ 300 °C. Nevertheless, up to 5% ammonia decomposition was observed at temperatures as low as ~ 400 °C.

Further indication on NH₃ decomposition can be found in the detailed study on the effect of thermal annealing on GaN resistivity and p-type conductivity by Nakamura et al. [41]. Mg-doped GaN grown by TF-OMCVD was annealed under different ambient gases at temperatures ranging from 25 °C to 1000 °C. Low-resistivity films showed no change in resistivity when annealed under N₂ ambient or vacuum. When NH₃ ambient was used, an increase in resistivity
started at $T > 400 \, ^\circ C$ and highly resistive ($\sim 10^6 \, \Omega \cdot cm$, similar to as-grown films) were obtained at $T > 600 \, ^\circ C$. The results were almost the same whether NH$_3$/N$_2$ or NH$_3$/H$_2$ were used. A mechanism where atomic hydrogen produced by ammonia decomposition on GaN at temperatures above 400 $^\circ C$ forms neutral Mg-H complexes and passivates the acceptors was proposed. Moreover, these experiments suggest NH$_3$ decomposition on GaN films under conditions (high pressure / flowrate) very similar to the actual growth environment.

In light of these observations, the assumption of poor NH$_3$ cracking efficiency on GaN needs to be reconsidered. The ability to routinely grow GaN films by OMCVD at temperatures as low as 500 $^\circ C$ provides additional indirect evidence on sufficient ammonia decomposition. The amorphous or polycrystalline nature of these films indicates inadequate energy for the adsorbed species to migrate to their preferred crystalline location at these low temperatures. In fact, given the very high melting points of the III-Nitrides, the high temperatures needed to achieve epitaxial growth may be owed to this requirement for increased mobility and not poor NH$_3$ cracking. Consistent with this assumption is the demonstrated inability to grow epitaxial films of comparable quality to OMCVD when using low temperature growth with a variety of alternative precursors containing Ga-N bonds, activated N sources, etc [42]. Consequently, we assumed that NH$_2^*$ is in excess and the growth rate is determined by the rates of arrival and reaction of the Ga-containing species.

4.2.4.2 Gallium nitride: thermal stability

A number of experimental studies have reported on the thermal stability of GaN and the main findings will be summarized briefly in chronological order in the following. Sime and Margrave [43] investigated the evaporation of GaN and Ga metal in the temperature range 950 – 1150 $^\circ C$ at 1 atm pressure of N$_2$, NH$_3$, and H$_2$. They determined the heat of evaporation to be 62
kcal/mole and proposed the existence of [GaN]ₙ polymers in the gas phase. Lorenz and Binkowski [44] reported that annealing GaN powder in a sealed quartz tube at 1150 °C resulted in an explosion, indicating a dissociation pressure of several atmospheres. They subsequently quantified the decomposition at lower temperatures by measuring the time dependence of the increase in N₂ pressure. They found a minimum value of 616 °C with extremely slow rates. Even at 850 °C negligible decomposition occurred after ~ 4 days. Schoonmaker et al. [45] studied the vaporization of gallium nitride by weight loss and torsion effusion techniques. At 916 °C and 3h, little decomposition occurred for pure GaN. The rate of vaporization is markedly enhanced in the presence of metallic gallium. The measured N₂ pressures are in both cases much lower than the values calculated by thermodynamic data indicating that the vaporization coefficient is much lower than unity. Munir and Searcy [46] obtained similar results using the same technique and estimated the activation energies for GaN sublimation to be 109.3 kcal/mole and GaN decomposition to be 19.5 kcal/mole at 1300 K. The formation and decomposition of GaN in the presence of NH₃ and H₂ respectively, was first studied by Thurmond and Logan [47] by analyzing the exiting gas stream in a quartz furnace tube by chemical methods. They determined the minimum NH₃ partial pressures at which GaN can be formed from liquid Ga, as well as the, surprisingly high, NH₃ pressures generated when H₂ is passed over GaN. All measurements were consistent with a calculated equilibrium curve for GaN formation/decomposition that will be discussed in detail in a later section. Morimoto [48] reported on the weight loss of GaN crystals as a function of temperature in N₂, air and H₂ atmosphere. No weight loss could be detected and no change of the crystal surface was observed up to 1000 °C in N₂ or air. Significant weight loss and small Ga droplets on the surface were observed at temperatures higher than 800 °C in a H₂ atmosphere after a 20-min anneal. No
kinetic parameters were ascertained. Groh et al. [49] studied the decomposition of GaN under
vacuum by thermogravimetry and by measuring the amount of N₂ developed during the
decomposition using mass spectrometry. Definitive weight loss started only above 980 °C.
Only N₂ was found in the gas phase analysis while a metallic deposit left on the quartz tube after
decomposition was Ga metal. Although the equilibrium constant or enthalpy of dissociation
could not be determined from their dynamic system, they estimated the activation energy for
GaN decomposition by equaling the rate of N₂ evolution to that of decomposition. Using an
Arrhenius expression, the barrier is 74.7 kcal/mole. Recently, Ambacher et al. [50] by using the
same technique determined this barrier to be 90 kcal/mole. Pisch and Schmid-Fetzer [51]
studied the GaN decomposition by in-situ optical microscopy of thermally annealed thin films
under Ar/H₂ and N₂/H₂ mixtures at atmospheric pressure. No decomposition of pure GaN was
observed at temperatures as high as 800 °C, while adding droplets of Ga metal caused
dissociation at temperatures 720 °C irrespective of gas mixture used.

In summary, substantial decomposition of GaN occurs at temperatures higher than 850 –
900 °C and proceeds with a large kinetic barrier. Liquid gallium and H₂ atmospheres have the
potential to lower this barrier.

4.2.4.3 Gallium nitride: thermodynamics

The thermodynamics of the Ga-GaN-N₂ system at elevated temperatures and high N₂
pressure was studied by Karpinski and Porowski [52]. By measuring the equilibrium pressure of
nitrogen over GaN, the standard Gibbs free energy, enthalpy and entropy of formation of GaN
were calculated. GaN formation/decomposition is described by the following reaction:

\[ \text{Ga (l)} + \frac{1}{2} \text{N}_2 \ (g) \leftrightarrow \text{GaN (s)} \]  \[4-9\]
where Ga (l) is the equilibrium phase of gallium at the temperature range of interest (800 – 1100 °C). For this reaction, \( \Delta H_{\text{rxn}}^\circ = -37.7 \text{ kcal/mole} \) and \( \Delta G_{\text{rxn}}^\circ = -37.7 + 0.03243 \times (T/K) \text{ kcal/mole} \) [52]. The enthalpy value is in good agreement with the one reported in the previous section [53]. The Gibbs free energy is plotted as a function of temperature in Figure 4-14 along with data from the experimental study of Thurmond and Logan [47] and a database [54]. Quite good agreement is observed; the data from [52] will be used to describe the GaN thermodynamics.

![Figure 4-14](image)

Figure 4-14. Temperature dependence of the Gibbs free energy of GaN formation according to references (a): [47], (b): [52], and (c): [54].

As can be seen in Figure 4-14, \( \Delta G_{\text{GaN}}^\ell \) is positive for \( T > 900 \) °C indicating that GaN is thermodynamically unstable at the temperatures of OMCVD growth. Conditions that enhance
the GaN stability, or lower its decomposition rate, must prevail during OMCVD growth for deposition of high quality crystalline material to occur. Nitrogen pressures higher than the equilibrium N$_2$ pressure (or N$_2$ dissociation pressure $P_{N_2}^{diss}$) are required to suppress the GaN decomposition according to reaction [4-9]. $P_{N_2}^{diss}$ can be calculated from the equilibrium constant according to the following formula:

$$\exp(-\Delta G_{GaN}^f / R T) = K_p = \frac{1}{\sqrt{P_{N_2}^{diss}}}$$

and is depicted as a function of temperature in Figure 4-15.

Figure 4-15. Temperature dependence of N$_2$ pressures over GaN. (a): $P_{N_2}^{diss}$, (b): $P_{N_2}^\circ$ over a 3:1 H$_2$:NH$_3$ mixture at 76 Torr, (c): $P_{N_2}^\circ$ over a 3:1 H$_2$:NH$_3$ mixture at 1 Atm, and (d): $P_{N_2}^\circ$ over a 99:1 H$_2$:NH$_3$ mixture at 1 Atm.
Also included in that figure is the "virtual" N₂ pressure \( P_{N_2}^\circ \) that is owed to the presence of ammonia and was introduced in section 4.2.4.1. \( P_{N_2}^\circ \) depends on the gas composition and pressure and is shown for various conditions representative of OMCVD growth. The N₂ dissociation pressure over GaN is \( \sim 30 \) Atm at 1000 °C. The partial pressure of nitrogen present in an OMCVD reactor as the carrier gas or the product of catalytic ammonia decomposition cannot be higher than 1 Atm. Therefore, nitrogen gas in any inlet composition cannot suppress GaN decomposition. However, if the concept of virtual nitrogen pressure supplied by the presence of ammonia is applied to GaN growth, sufficient N₂ overpressure is obtained under typical growth conditions as seen in Figure 4-15. Even a 99:1 H₂/NH₃ gas mixture close to the substrate can supply enough nitrogen to suppress GaN decomposition. This is due to the high thermal instability of NH₃ coupled with the large kinetic barrier for NH₃ decomposition, as discussed in section 4.2.2.

An equivalent way of analyzing the effect of ammonia and hydrogen in the thermodynamics of GaN formation/decomposition starts with the assumption that the following equilibrium reaction represents GaN growth:

\[
\text{Ga (l) + NH}_3 (g) \leftrightarrow \text{GaN (s) + } \frac{3}{2} \text{H}_2 (g) \quad [4-10]
\]

with \( \Delta G_{rxn}^\circ = \Delta G_{GaN}^f - \Delta G_{NH_3}^f \), which is negative over the whole temperature range of interest. The reversibility of reaction [4-10] was established in the study by Thurmond and Logan [47] where ammonia partial pressures very close to the ones predicted by thermodynamic equilibrium were observed when hydrogen passed over GaN. The reverse reaction under OMCVD growth can be interpreted as etching by H₂. Almost complete ammonia dissociation close to the substrate must occur however, for this reaction to take place as seen in Figure 4-15(d).
4.2.4.4 Gallium nitride: kinetics and the role of hydrogen

The above discussion of GaN formation and decomposition, NH₃ stabilization, and H₂ etching revolved around the thermodynamics of growth. Very often though, the kinetics of various competing reactions determine the deposition behavior, especially in dynamic systems with very short contact times like an OMCVD reactor. As an example, the GaN formation will probably not proceed according to reaction [4-10] because the coexistence of Ga(l) and GaN(s) would lead to significant GaN decomposition at temperatures as low as 700 °C as seen in many experimental studies. The inability to deposit GaN at low V/III ratios that could lead to Ga-droplet formation on the surface also provides indirect supportive evidence. As a second example, when H₂ was passed over heated GaN in [47], constant ammonia pressure in the outlet was recorded only 1 hr after initiation. Such a slow process would not be applicable in nitride growth.

Drawing conclusions on chemistry from experimental studies of OMCVD growth is equally challenging. At the elevated temperatures used, mass transport of precursors to the surface is typically the rate-limiting step. Since the kinetic processes are masked by the slower mass transport, any kinetic mechanism can give good agreement with growth rate data and no conclusions on chemistry can be inferred. The enormous potential for misleading conclusions is demonstrated in a recent study of GaN growth by Briot et al. [55]. The temperature dependence of the growth rate in the 500-1000 °C range showed an activation energy of ~ 4 kcal/mole. Although this barrier is the signature of mass-transport-limited growth and reflects the temperature dependence of gas-phase diffusion, the authors assumed complete decomposition of the TEGA precursor and attributed the barrier to the heterogeneous ammonia decomposition.
Similar arguments can be made regarding the effect of H₂ in GaN deposition where conclusions obtained by switching between N₂ and H₂ carrier gases are convoluted by the large change in transport parameters accompanying this switch. All the growth studies reported in the literature use substantial amounts of H₂ carrier gas and hydrogen can be produced in-situ by catalytic NH₃ decomposition. Hashimoto et al. [56] deposited GaN films at 1000 °C using a N₂ carrier gas with and without H₂. Growth rates using only N₂ were significantly higher than those using a N₂/H₂ mixture at the same total flow rate. Since a vertical reactor was used, the change in carrier gas and the subsequent change in Reynolds number resulted in a change in the gas flow pattern and the boundary layer thickness. The flow pattern change was verified by TiO₂ smoke traces.

Ambacher et al. [57] studied the role of hydrogen in the growth of GaN thin films on sapphire in the 600-1100 °C temperature range. The thermally induced hydrogen effusion from GaN was also studied. Use of H₂/NH₃ resulted in lower growth rates overall than in N₂/NH₃ and a decrease in the growth rate at temperatures higher than 850 °C. When D₂/NH₃ was used, no change in the growth rate relative to the H₂/NH₃ case occurred. However, although the same total concentration of hydrogen effused at high temperatures, no deuterium was measured. Thus, even if hydrogen has a strong influence in the growth mechanism of GaN, these reactions probably involve hydrogen from the catalytic ammonia decomposition. Changes in the carrier gas will therefore affect the growth either through variations in transport parameters, or through thermodynamic arguments concerning the total partial pressure of H₂ close to the substrate. Unfortunately, the extent of ammonia decomposition close to the substrate during growth is not known. An in-situ spectroscopic study of the relative amounts of H₂ and NH₃ present close to
the substrate similar to that in [37] would provide valuable information towards an enhanced understanding of nitride growth.

Two recent studies have reported on the temperature dependence of GaN growth at elevated temperatures. Chen et al. [28] used a horizontal OMCVD reactor to study the growth on sapphire substrates in a wide temperature and pressure range. They reported a significant drop-off in GaN growth at temperatures higher than 1000 °C. Scholz et al. [58] also used a horizontal OMCVD reactor operated at low pressure (76 Torr) to study GaN growth in the 800–1100 °C range. They similarly reported a gradual increase in growth rate with increasing temperature up to 1000 °C followed by a drastic drop-off at even higher temperatures. In light of these reports, the decomposition of GaN was included in the kinetic mechanism and is represented by reaction [S8] in Table 4-I. The kinetic barrier of 75 kcal/mole reported in [49] was used. The decomposition products (most probably Ga(g)) are postulated not to subsequently contribute to growth and are not included in the mechanism. The underlying assumption in including reaction [S8] is that the growth environment cannot suppress the GaN decomposition. Under operating conditions or reactor designs that no temperature decrease is observed, this reaction may be omitted.

To determine the kinetic barrier for GaN synthesis, the rates of formation and decomposition were assumed to follow the Arrhenius dependence with the kinetic barriers related through the formula:

\[ E_{f,GaN} = E_{d,GaN} + \Delta H_{f,GaN}, \]

where \( \Delta H_{f,GaN} \) is the standard enthalpy of formation. Using \( E_{d,GaN} = 75 \) kcal/mole [49], and \( \Delta H_{f,GaN} = -37.7 \) kcal/mole [52], a kinetic barrier of 37 kcal/mole was calculated for the GaN synthesis represented in reaction [S6]. This single-step GaN formation reaction between
adsorbed Ga* species and the assumed excess of N*/NH* species obviously involves several elementary reactions (e.g. nucleation, surface diffusion, incorporation) but there exists no data to provide additional mechanistic details at this stage. Mizuta et al. reported on the low temperature growth of GaN by OMCVD using hydrazine [59] or ammonia [60]. They used separate inlets for TMGa and the group V source and found minimal adduct formation. They reported activation energy of 35 kcal/mole for the kinetically limited regime observed at temperatures lower than 600 °C. The same barrier was observed irrespective of the group V source. If we assume that GaN formation from Ga* and excess N*/NH* is indeed the rate-limiting process at low temperature, similar kinetic barriers for growth using NH₃ and N₂H₄ are justified. Furthermore, the kinetic barrier measured experimentally compares very favorably to the activation energy computed above.

Gallium arrives at the surface though adsorption of all the Ga-containing precursors. Reactions [S1]-[S5] involve the dissociative adsorption of all the reactive species present in the gas phase. As described in Chapter 2, the rates of all adsorption reactions are assumed to be equal to the rate of collision of gas-phase species with the surface estimated by kinetic theory and modified by the corresponding sticking coefficient. Sticking coefficients of unity are assumed for all species except TMGa and TMGa:NH₃ where the initial Ga-C bond is not broken and a sticking coefficient of 0.1 is used. Trimer (and dimer) species that already contain a ring of Ga-N bonds are postulated to yield a different surface intermediate, GaN* upon adsorption. The exact nature of the surface products of trimer and dimer adsorption is unknown. Methyl or methane elimination from the adsorbed species will lead to Ga-N complexes that can be directly incorporated in the growing film. Therefore, growth from this surface intermediate is assumed to proceed with a lower kinetic barrier of 22 kcal/mole, similar to the 23 kcal/mole activation
energy seen for the low temperature growth of GaN from the TMGa:N₂H₄ adduct [61]. Although deposition of GaN may be possible via this adduct-related route, distinction between epitaxial and polycrystalline or amorphous film growth cannot be made in this simple kinetic mechanism. It is reasonable to assume that GaₓNᵧ species would have limited mobility on the surface and their incorporation in the film would lead to misfit dislocations, rough surfaces and impurity incorporation.

4.3 Reaction-transport simulation results and discussion

In developing a chemical mechanism for a deposition process, it is imperative to be able to compare model predictions with experimental data. Experiments carried out at different reactor pressures and temperatures are particularly valuable for this task. Despite the large volume of contributions reported in the literature, few studies have reported on parametric investigations of nitride growth. An accurate description of the temperature distribution and fluid flow in the actual reactor configuration is also required before any chemical mechanism can be tested. This is particularly important in GaN growth considering the growth performance variations among different reactor designs.

Chen et al. [28] studied the OMCVD growth of GaN and AlN at atmospheric and reduced pressure (85 Torr) over a wide temperature range (400-1100 °C). They used a horizontal hot-wall quartz reactor with a rectangular cross section. The temperature dependence of the growth rate exhibits a kinetically limited regime at \( T < 600 \) °C, and a mass transport-limited regime at \( T < 1000 \) °C, followed by a decrease in growth rate at even higher temperatures. The authors reported minimal loss of growth efficiency with increasing pressure and concluded that parasitic
adduct formation between TMGa and NH₃ is negligible. On the other hand, substantial drop-off in the case of AlN growth was observed and will be discussed in detail in the following chapter.

The kinetic model in Table 4-I is used to simulate GaN growth in the horizontal OMCVD reactor. The steady state flow and temperature distributions are first computed using the methods described in Chapter 2. They are then used to solve the individual species mass balances and predict the growth rate. We simulated a detailed representation of the reactor configuration to allow quantitative comparison of kinetic results to experimental data. Two-dimensional simulations along the centerline of a 5cm x 2cm rectangular channel are performed. The distance between reactor entrance and heated susceptor is 10 cm [28]. A 2” substrate is positioned on top of the 10-cm long susceptor. Deposition is assumed to occur only on the substrate. A mixture of ammonia and hydrogen is used as the process gas in the fluid flow and heat transfer simulations. Constant TMGa, NH₃, and H₂ mole fractions are assumed at the inlet similar to those used in the experiments.

Figure 4-16 depicts temperature and flow fields in the reactor at reduced and atmospheric pressure. As can be seen, the susceptor and the quartz flow tube are included in the simulation. Conduction to stagnant ambient air is used as the boundary condition for the energy equation on the outside quartz surfaces. The inlet is assumed to be at room temperature. The susceptor temperature is 1000 °C. The gas flow rate is 4 slm (H₂/NH₃ = 3:1) at 85 Torr and 8 slm (H₂/NH₃ = 3:5) at 780 Torr as used experimentally [62]. As the gas reaches the heated edge of the susceptor, it expands and partially blocks the flow, which in the high-pressure case gives rise to a recirculation cell in the reactor. The temperature profiles show a cold finger over the upstream half of the susceptor caused by the radiative heating of the reactor top wall. The extent of the
cold finger is more pronounced in the 780 Torr case due to the higher flowrate and increased NH$_3$ mole fraction used.

![Temperature profiles and flow streamlines in the horizontal reactor](image)

Figure 4-16. Temperature profiles and flow streamlines in the horizontal reactor used in [28]. Substrate temperature is 1000 °C. (a): P = 85 torr, total flowrate is 4 slm, H$_2$/NH$_3$ = 3:1, (b) P = 780 torr, total flowrate is 8 slm, H$_2$/NH$_3$ = 3:5.

The sensitivity of the relative amounts of Ga-containing species to temperature variations was established earlier though PFR calculations. Therefore, accurate prediction of the reactor temperature distribution is important in simulations of GaN growth. Since conjugate heat transfer is included in our simulations (i.e. heat transfer to the walls through conduction, convection, and radiation) the reactor wall temperatures need not be set a priori. That is, the assumption of adiabatic or water-cooled top wall often used in reactor scale simulations is not made. Rather, the wall temperature profiles are computed by the simulations. The top wall temperature is very important in GaN growth because it affects the gas-phase chemistry as well as precursor depletion though thermal diffusion. Thermal diffusion of heavier species away from
the heated substrate is important due to the large temperature gradients and bulky gaseous species present in nitride growth.

\[ \text{TMGa} \quad X_{\text{max}} = 2.5 \times 10^{-4} \]

\[ \text{MMGa} \quad X_{\text{max}} = 3.7 \times 10^{-11} \]

\[ \text{Adduct} \quad X_{\text{max}} = 3.2 \times 10^{-4} \]

\[ \text{Monomer} \quad X_{\text{max}} = 1.2 \times 10^{-4} \]

\[ \text{Trimer} \quad X_{\text{max}} = 7.6 \times 10^{-5} \]

\[ \text{"Ga-N"} \quad X_{\text{max}} = 2.0 \times 10^{-4} \]

Figure 4-17. Mole fraction profiles of the main species in the horizontal reactor. Pressure is 85 Torr, temperature is 1000 °C. Reactor dimensions are in cm, and the maximum mole fraction for each species is given.
The mole fraction profiles of trimethylgallium, monomethylgallium, adduct, monomer, trimer, and "Ga-N" are shown in Figures 4-17 and 4-18 for the 85 Torr and 780 Torr cases respectively. Susceptor temperature is 1000 °C.

<table>
<thead>
<tr>
<th>Species</th>
<th>( X_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa</td>
<td>( 1.2 \times 10^{-4} )</td>
</tr>
<tr>
<td>MMGa</td>
<td>( 6.0 \times 10^{-11} )</td>
</tr>
<tr>
<td>Adduct</td>
<td>( 1.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Monomer</td>
<td>( 1.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>Trimer</td>
<td>( 4.6 \times 10^{-5} )</td>
</tr>
<tr>
<td>&quot;Ga-N&quot;</td>
<td>( 8.7 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Figure 4-18. Mole fraction profiles of the main species in the horizontal reactor. Pressure is 780 Torr, temperature is 1000 °C.
Trimethylgallium reacts at the inlet with the ammonia excess to form the adduct and is present in negligible amounts close to the susceptor. Gallium is transported close to the heated area of the reactor in the form of the adduct. Decomposition of the adduct to form monomer and trimer occurs when the temperature exceeds 230 °C. The trimer subsequently decomposes to yield the gaseous “Ga-N” species.

Figure 4-19 compares the predicted temperature dependence of the GaN growth rate with the one reported experimentally over the entire temperature range at 85 Torr. Similar comparison for the 780 Torr case is shown in Figure 4-20. The growth rate at the substrate midpoint is reported.

Figure 4-19. Simulated (line) and experimental (points)[28] GaN growth rates in a horizontal reactor as a function of temperature at 85 Torr. Total flow rate is 3 slm H₂ and 1 slm NH₃. [TMGa]_{inlet} = 2.5×10⁻⁴.
Figure 4-20. Simulated (line) and experimental (points)[28] GaN growth rates in a horizontal reactor as a function of temperature at 780 Torr. Total flow rate is 3 slm H₂ and 5 slm NH₃. [TMGa]ₐₐₐₐ₁ₐₐ = 1.2×10⁻⁴.

Very good agreement is observed over the whole parameter space. The kinetic model is able to capture the main features of the growth rate behavior. Consistent with this mechanism then, the following regions can be identified: i) at temperatures higher than 1000 °C the growth is limited by GaN thermal decomposition, ii) at the intermediate range of 600 °C - 1000 °C the growth is limited by the mass transfer of Ga-containing species to the surface where they undergo fast surface reaction, and iii) at temperatures lower than 600 °C the growth is limited by surface kinetics of Ga* and GaN* species with the excess NH* to form gallium nitride. As can be seen in the experimental data, the mass transport limited regime extends to lower temperatures at 780 Torr. This effect is captured by the simulations and can be clearly observed
in Figure 4-21 where the experimental and simulation data are depicted in an Arrhenius-type format.

![Graph showing growth rate dependence as a function of inverse temperature at 85 and 780 Torr. Simulation predictions (solid lines) and experimental data (solid: 780 Torr, open: 85 Torr). Conditions are as in Figs. 4-19 and 4-20.](image)

Figure 4-21. Growth rate dependence as a function of inverse temperature at 85 and 780 Torr. Simulation predictions (solid lines) and experimental data (solid: 780 Torr, open: 85 Torr). Conditions are as in Figs. 4-19 and 4-20.

The bimolecular dimer and trimer formation reactions are enhanced at high pressure and provide an additional channel of growth species to the surface. Growth from GaN* species is assumed to proceed with a lower kinetic barrier, and explains the extension of the mass-transport-limited regime to lower temperature at higher pressures. Figure 4-22 shows the percentage of adduct chemistry contribution to the rate as a function of temperature and pressure. Specifically, the contribution percentage is the relative rate of GaN growth occurring through the trimer formation pathway and is computed by the relative rates of reactions [S8] and
The growth is dominated by the trimer formation pathway at high pressure. Up to 75% of the growth occurs via this pathway at reduced pressure. As mentioned earlier, correlation between experimental observations on film quality and predicted AC% under the same conditions can be used to infer whether dimer/trimer formation is detrimental to the deposition of device quality material. Although the film quality was not reported in [28], Scholz et al. [58] similarly used a horizontal reactor for GaN deposition and reported epitaxial growth at 85 Torr and T > 900 °C, while only polycrystalline films were grown at atmospheric pressure.

\[ \text{AC} = \frac{r_{\text{ss}}}{r_{\text{ss}} + r_{\text{d}} \times 100} \]

Figure 4-22. Adduct contribution to the growth rate as a function of temperature at 780 Torr (solid line) and 85 Torr (dashed line).

Growth resulting from the surface reactions involving products of dimer/trimer adsorption can be assumed to lead to polycrystalline films due to incomplete elimination of the
C$_n$H$_y$ groups and limited mobility on the surface. However, the reactive product of trimer decomposition "Ga-N" present at elevated temperatures must lead to epitaxial growth since GaN films of highest quality are grown under conditions that favor its presence. This is illustrated in Figure 4-23 where the percentage of growth occurring directly through the trimer adsorption is depicted. The trimer contribution is calculated by: $TC\% = \frac{3\times r_{[G]}^6}{r_{[SS]} + 3\times r_{[SS]}^6} \times AC\%$.

![Figure 4-23. Trimer contribution to the growth rate as a function of temperature at 780 Torr (solid line) and 85 Torr (dashed line).](image)

Almost complete trimer decomposition in the gas-phase at $T > 900 \, ^\circ C$ is seen. However, [G7], the single-step decomposition reaction used, may lead to enhanced decomposition in comparison to the successive CH$_4$ elimination that actually takes place. Such successive elimination reactions may be included in future improvements of the reaction model. If a correlation
between film quality and AC% or TC% is established, the kinetic mechanism proposed can be used in detailed reaction-transport simulations to investigate effects of reactor geometry and operating conditions on film quality. As an example, the reduction in dimer/trimer formation observed when TMGa and NH3 are mixed at T > 450 °C in PFR simulations can be investigate in a realistic OMCVD reactor.

![Graph showing GaN growth rates vs. pressure](image)

Figure 4-24. Simulated (line) and experimental (points)[28] GaN growth rates in a horizontal reactor as a function of pressure at 600 °C. Total flow rate is 3 slm H2 and 1 slm NH3. [TMGa]inlet = 2.5×10^4.

Comparison of predicted and experimental growth rates as a function of pressure is depicted in Figure 4-24. Again, the proposed kinetic model is consistent with the experimental data. As was shown earlier, a significant proportion of growth occurs though adduct related pre-reactions. The minor efficiency loss with increasing pressure observed is attributed to the
absence of any pathways leading to oligomeric complex/ particle formation rather than total absence of any chemical interaction between TMGa and NH\textsubscript{3}.

The kinetic mechanism in Table 4-I was also used to simulate GaN growth during deposition of AlGaN in a close-spaced reactor. The results are shown in the following chapter that considers AlN growth in detail. Although no temperature or pressure dependence data were available, very good agreement is obtained for the growth rate dependence of GaN on the TMGa inlet partial pressure at conditions of epitaxial growth (76 Torr, 1060 °C).

4.4 Summary

The chemistry underlying OMCVD growth of GaN was studied and a kinetic mechanism was proposed. The model involves fast reaction between TMGa and NH\textsubscript{3} to form a Lewis type acid-base adduct which can dissociate or decompose at higher temperatures. The decomposition fragments can subsequently react to form dimer or trimer complexes in the gas phase containing multiple gallium-nitrogen bonds. Reaction rate parameters were obtained through quantum chemistry calculations and analysis of experimental data. The reaction mechanism was shown to be consistent with individual experimental observations, flow-tube decomposition studies, and growth rate temperature and pressure dependence in a horizontal OMCVD reactor as well as growth rate data in a close-spaced OMCVD reactor. GaN growth was proposed to be limited by GaN formation at low temperatures, mass transport at intermediate temperatures and GaN decomposition at temperatures higher than 1000 °C. Dimer and trimer formation can lead to an additional pathway of Ga supply to the surface at low temperatures and high pressures. A correlation between quality of deposited film, and growth through this trimer pathway was proposed and its validity can be tested by comparison of reaction-transport simulations with
qualitative experimental observations on film properties. The extent of catalytic ammonia
decomposition close to the growing surface, and direct spectroscopic evidence on the nature of
the gaseous species present in the reactor were identified as important issues for future
experimental study.
4.5 References


Chapter 5. Kinetic modeling of OMCVD growth of AlGaN and InGaN

5.1 Introduction

The technological importance of the InGaAlN material system in realizing a wide variety of devices such as LEDs and LDs was referred to in an earlier chapter. The direct energy bandgap of this alloy system covers the wavelength range from the red (InN) to the ultraviolet (AlN). In addition to the GaN binary, growth of AlN, AlGaN and InGaN in particular is essential in device fabrication. While AlN is electrically insulating and is primarily used as a buffer layer for GaN-based devices, the AlGaN alloys are widely used as the wide band gap portion of double heterostructure (DH) LEDs, double heterostructure and quantum well lasers and heterojunction Field Effect Transistors [1]. The InGaN alloy is used as the active region in DH LEDs [2,3], single quantum well LEDs [4,5] and multiple quantum well LEDs [6] and LDs [7]. By changing the indium alloy composition used in the quantum well, the wavelength of the devices can be tuned in the $450 < \lambda < 600$ nm range (i.e., from blue to yellow). Thus, controlling the indium composition in a reproducible manner is imperative for III-N device fabrication.

In this chapter, we expand upon the kinetic mechanism for GaN deposition to account for OMCVD growth of ternary AlGaN and InGaN films. An approach similar to that for the GaN mechanism was used for AlN growth. Partially due to the technological importance of InGaN,
very few published experimental studies on InGaN deposition have focused on understanding the underlying processes. The majority of InGaN-related studies report on device fabrication with limited information on the details of the deposition process. Thus, an initial attempt at correlating indium composition with operating parameters is presented in this thesis through a phenomenological model.

5.2 AlGaN deposition

Similarly to GaN, OMCVD growth of AlN is complicated by pre-reactions between the common group III and V precursors, trimethylaluminum (TMAI) and ammonia at low temperature. In the original feasibility study of AlN and GaN growth by organometallic sources, [8], Manasevit et al. reported the formation of a white solid addition compound upon mixing TMAI and NH₃. They observed formation of AlN powder away from the substrate and used a coaxial tube and high carrier flow rate to deliver the reactants separated close to the substrate. Koide et al. [9] observed that the Al distribution coefficient (x_d/x_v where \( x_v = \frac{[TMAI]}{[TMAI] + [TMGa]} \)) in OMCVD growth of AlₓGa₁₋ₓN depends strongly on total flow rate. When the reactants were fed at a slow velocity (~ 0.02 m/sec) the solid Al composition was independent of the vapor-phase composition. In addition, some white deposits were observed in the epilayers that were shown to have higher Al content than the epilayer itself. Under similar conditions, no white deposits were observed for GaN growth, indicating that TMAI:NH₃ may be more reactive than TMGa:NH₃. When, on the other hand, a high velocity was used (~ 1.1 m/sec) distribution coefficients around unity were observed, i.e. nearly 1:1 correlation between gas-phase and solid composition. The growth rate was found independent of temperature in the 970 – 1120 °C
range. Hirosawa et al. [10] used a hot-wall horizontal reactor operating at atmospheric pressure with two flow channels and delivered TMAI/TMGa and NH₃ separately at a high velocity. At a typical growth temperature of 1050 °C, they reported linear dependence of $x_s$ on $x^v$ with a distribution coefficient slightly larger than unity. Their results indicate minimal parasitic reactions leading to precursor loss under these conditions. In contrast, Chen et al. [11] studied AlN and AlGaN growth in a hot-wall horizontal reactor and reported substantial drop-off of AlN growth rate (or corresponding Al solid fraction in AlGaN) with increasing temperature and pressure. The parasitic reactions in the gas-phase were severe enough to prohibit AlN growth at pressures higher than 270 torr or temperatures higher than 1000 °C. Killeen et al. [12] used a close-spaced reactor similar to the one described in Chapter 3 and reported AlGaN growth at 1050 °C over the entire composition range with a distribution coefficient slightly less than unity. Finally, Ruffenach-Clur et al. [13] successfully grew AlGaN at 1000 °C with a distribution coefficient larger than one in an undisclosed OMCVD reactor. The authors were able to model the dependence of $x_s$ on $x^v$ by using a simple stagnant layer model [14] that was also used to model Al incorporation in AlGaAs OMCVD. They attributed differences in incorporation efficiency to differences in gas-phase diffusion coefficients of Al- and Ga-containing species. The wide variation of Al incorporation efficiency in different OMCVD reactors operating under similar conditions and using the same growth precursors, demonstrates the need for reaction-transport simulations that quantify the relative roles of transport phenomena and various deposition pathways.

5.2.1 Thermodynamic analysis

Growth under thermodynamic equilibrium has been widely used to explain the dependence of $x_s$ on $x^v$ in OMCVD of ternary alloys [15,16]. Such arguments do not apply to
AlGaN growth because variation in Al incorporation is observed under constant temperature, pressure, and inlet composition – the independent parameters in thermodynamic analysis. A more detailed explanation follows. Equilibrium at the interface yields two mass action expressions:

\[
\frac{a_{\text{GaN}}}{P_{\text{Ga}}P_{\text{N}_2}^{3/2}} = K_{\text{GaN}},
\]

where \( K_{\text{GaN}} = \exp(-\Delta G_{\text{GaN}}^I/RT) \) and

\[
\frac{a_{\text{AlN}}}{P_{\text{Al}}P_{\text{N}_2}^{3/2}} = K_{\text{AlN}},
\]

where \( K_{\text{AlN}} = \exp(-\Delta G_{\text{AlN}}^I/RT) \).

The solid activities can be calculated using

\[
a_{\text{GaN}} = x_{\text{GaN}}^s \exp\left(\frac{(1-x_{\text{GaN}}^s)^2}{RT}\right),
\]

where \( \Omega \) is the semi-empirical interaction parameter in a Delta Lattice Parameter model [17].

The equilibrium phases of the III-Nitrides are wurtzite and not zinc-blende for which the DLP model was developed, and fitting to experimental data is needed to determine an empirical constant in the \( \Omega \) expression. Thus, following Ho and Stringfellow [18], a modified Valence Force Field model can be used and \( \Omega_{\text{AlGaN}} \) estimated to be 0.88 kcal/mole. The driving force for the group III species incorporation is then \( (P_{\text{III}}^o - P_{\text{III}}) \) where \( P_{\text{III}}^o \) denotes the input partial pressures. It is well established that for OMCVD of ternary alloys with mixing in the group-III sublattice and high V/III ratio, the equilibrium \( P_{\text{III}} \ll 0 \). The solid mole fraction then becomes a linear dependence of the input mole fraction modified by the appropriate ratio of diffusion coefficients [15]. Furthermore, for the AlGaN system, AlN is thermodynamically more stable.
than GaN since at 1050 °C, $\Delta G_{GaN}^f = 5.2$ kcal/mole [19] and $\Delta G_{AlN}^f = -42.2$ kcal/mole [20]. That corresponds to $K_{GaN} = 0.14$ and $K_{AlN} = 9.5 \times 10^6$ at 1050 °C. Therefore, if thermodynamic equilibrium were established, AlN incorporation would be significantly favored over GaN incorporation, contrary to experimental observations. As a point of reference, when variations of the group V distribution coefficient in the InAsSb or GaAsSb ternary alloys are explained by thermodynamic equilibrium arguments, the relative equilibrium constants at 600 °C are $K_{InSb} = 244$ and $K_{InAs} = 638$, or $K_{GaAs} = 440$ and $K_{GaSb} = 260$ [15]. Clearly thermodynamic equilibrium arguments cannot explain this wide variation of Al incorporation efficiency at the similar temperatures and large V/III ratios used in the different experimental studies.

5.2.2 Reaction mechanism development

A kinetic mechanism for AlN (and AlGaN) deposition consisting of both gas-phase and surface reactions is proposed. The AlN portions of the mechanism are presented here. The mechanism for GaN deposition presented in the previous chapter is used for Ga species and adducts. Although some experimental evidence exists that the presence of TMAI and related TMAI:NH$_3$ adducts may lower the GaN growth rate [21], this effect is neglected in this study and Al- and Ga-containing species do not interact during simulation of AlGaN growth. The mechanism for AlN consists of 11 gas-phase reactions and 7 surface reactions (see Table 5-I and Figure 5-1). Quantum chemistry computations using the density functional theory (DFT) methods such as the Becke 3-parameter density functional theory using the Lee-Yang Parr correlation functional (B3LYP) were performed to investigate the structure and reactivity of the Lewis acid-base adducts formed by TMAI with NH$_3$ [22,23].
Table 5-I. Gas-phase and surface reaction mechanism for AlN growth from trimethylaluminum and ammonia.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Rate Coefficient</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>[G1] Al(CH₃)₃</td>
<td>→ AlCH₃ + 2 CH₃</td>
<td>$3.5 \times 10^{15}$</td>
<td>66.5</td>
</tr>
<tr>
<td>[G2] Al(CH₃)₃ + NH₃</td>
<td>↔ Al(CH₃)₃:NH₃</td>
<td>$3.0 \times 10^{12}$</td>
<td>0.0</td>
</tr>
<tr>
<td>[G3] Al(CH₃)₃:NH₃</td>
<td>↔ Al(CH₃)₃ + NH₃</td>
<td>$5.0 \times 10^{10}$</td>
<td>22.0</td>
</tr>
<tr>
<td>[G4] Al(CH₃)₃:NH₃</td>
<td>→ Al(CH₃)₂NH₂ + CH₄</td>
<td>$2.0 \times 10^{12}$</td>
<td>27.0</td>
</tr>
<tr>
<td>[G5] Al(CH₃)₃:NH₃ + NH₃</td>
<td>→ Al(CH₃)₂NH₂ + CH₄ + NH₃</td>
<td>$2.0 \times 10^{12}$</td>
<td>13.0</td>
</tr>
<tr>
<td>[G6] 2 Al(CH₃)₂NH₂</td>
<td>→ [Al(CH₃)₂NH₂]₂</td>
<td>$4.0 \times 10^{11}$</td>
<td>0.0</td>
</tr>
<tr>
<td>[G7] Al(CH₃)₃:NH₃ + [Al(CH₃)₂NH₂]₂</td>
<td>→ [Al(CH₃)₂NH₂]₃ + CH₄</td>
<td>$1.0 \times 10^{11}$</td>
<td>0.0</td>
</tr>
<tr>
<td>[G8] Al(CH₃)₂NH₂ + [Al(CH₃)₂NH₂]ₙ</td>
<td>→ [Al(CH₃)₂NH₂]ₙ₊₁</td>
<td>$1.0 \times 10^{10}$</td>
<td>0.0</td>
</tr>
<tr>
<td>[G9] [Al(CH₃)₂NH₂]₂ + [Al(CH₃)₂NH₂]ₙ</td>
<td>→ [Al(CH₃)₂NH₂]ₙ₊₂</td>
<td>$1.0 \times 10^{10}$</td>
<td>0.0</td>
</tr>
<tr>
<td>[G10] [Al(CH₃)₂NH₂]₂</td>
<td>→ AlN (particle)</td>
<td>$1.0 \times 10^{11}$</td>
<td>40.0</td>
</tr>
<tr>
<td>[G11] [Al(CH₃)₂NH₂]₃</td>
<td>→ AlN (particle)</td>
<td>$1.0 \times 10^{11}$</td>
<td>40.0</td>
</tr>
<tr>
<td>[S1] Al(CH₃)₃ + S</td>
<td>→ Al⁺ + 3 CH₃</td>
<td>s = 0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>[S2] Al(CH₃)₃:NH₃ + S</td>
<td>→ Al⁺ + 3 CH₃ + NH₃</td>
<td>s = 0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>[S3] AlCH₃ + S</td>
<td>→ Al⁺ + CH₃</td>
<td>s = 1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[S4] Al(CH₃)₂NH₂ + S</td>
<td>→ Al⁺ + 2 CH₄</td>
<td>s = 1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[S5] [Al(CH₃)₂NH₂]₂ + 2 S</td>
<td>→ 2 AlN⁺ + 4 CH₄</td>
<td>s = 1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[S6] Al⁺</td>
<td>→ [AlN]⁺ + S</td>
<td>$6.0 \times 10^{6}$</td>
<td>20.0</td>
</tr>
<tr>
<td>[S7] AlN⁺</td>
<td>→ [AlN]⁺ + S</td>
<td>$6.0 \times 10^{6}$</td>
<td>20.0</td>
</tr>
</tbody>
</table>
5.2.2.1 Trimethylaluminum decomposition

TMAI is known to exist in an equilibrium between the monomer form AlMe$_3$ and the dimer form Al$_2$Me$_6$, with the heat of dissociation of the one mole of dimer into two moles of monomer being 20.3 kcal/mole [24,25]. At typical bubbler conditions (17-25 °C, 500-800 torr) the equilibrium is dominated by the dimer form. However, upon dilution with the carrier gas the partial pressure of the Al-containing species decreases significantly and, according to the Le Chatelier principle, the equilibrium shifts towards the monomer. Diluting 20 sccm H$_2$ transporting = 0.15 sccm Al$_2$Me$_6$ with 4 SLM carrier gas implies that more than 85% of the Al-containing species will be in the monomer form. Furthermore, the adduct formation between TMAI and NH$_3$ (which is in excess) occurs instantaneously upon mixing, (reaction [G2]), further depleting the TMAI and shifting the equilibrium towards the monomer state. Reaction [G1] represents the unimolecular decomposition of TMAI. The rate constant has been obtained by taking the activation energy equal to the reported Al-C bond strength [26], and assuming that the
pre-exponential factor will be similar to the one obtained from TMGa decomposition studies [27]. TMAI decomposition has been proposed to occur through the loss of CH₃ radicals, and the loss of the first CH₃ radical has been taken to be the rate-limiting step.

5.2.2.2 TMAI:NH₃ adduct reactions

The TMAI:NH₃ adduct is a white crystalline solid which upon heating at 70 °C eliminates CH₄ to give DMAI-NH₂ [28]. TMAI:NH₃ has also been isolated on argon matrices from a merged jet of TMAI and ammonia [29]. Irradiation of matrix-isolated TMAI:NH₃ yields methane and DMAI-NH₂ [30]. The alkyl-aluminum amide, DMAI-NH₂, has been shown to exist as a trimer, both in the solid phase as well as the gas-phase [28]. The formation of these intermediate species such as TMAI:NH₃ followed by thermal elimination of CH₄ plays a significant role in AlN deposition. AlN has been successfully deposited from single source precursors, TMAI:NH₃ [31] and [DMAI-NH₂]₃ [32], giving further support to the importance of these species. The reader is referred to [33] for a recent thorough review of III-Nitride deposition by alternative precursors.

Reaction [G2] is the adduct formation reaction between TMAI and NH₃. The forward reaction rate parameters have been estimated from collision theory and the reverse rate parameters [G3] have been computed by using the Kₚ values estimated from quantum chemistry calculations [22]. The Gibbs free energy for TMAI:NH₃ adduct formation is −16 kcal/mole which, when compared to the −7.9 kcal/mole value for TMGa:NH₃ formation (see Figure 4-9), gives a six orders of magnitude difference of the corresponding equilibrium constants. Thus, the Lewis acid-base interaction in TMAI:NH₃ is stronger than in TMGa:NH₃ in agreement with experimental observations for more severe parasitic reactions and particle formation in AlN growth. Reactions [G4] and [G5] represent the CH₄ elimination reactions for the adduct. The
CH₄ elimination reaction from the Lewis acid-base adduct has been studied experimentally in solution [34]. The ΔH_rxn was measured as -19.6 kcal/mole. Quantum chemistry calculations (at the B3LYP/6-31G(d,p) level) gave ΔH_rxn in the gas-phase as -4.2 kcal/mole. The difference in the heat of reaction could be due to effects of solution, phase change, and inaccuracies in the quantum chemistry calculations. Using quantum chemistry techniques, the activation energy for this intra-molecular reaction pathway was determined to be 27 kcal/mole (reaction [G4]). Coordination with a second NH₃ molecule further lowers the activation energy for the loss of CH₄ to 13 kcal/mole (reaction [G5]). This is consistent with the lower ΔH_rxn value obtained from quantum chemistry. The same experimental study also found the CH₄ elimination reaction to be catalyzed by excess TMA1 and DMA1-NH₂, with the DMA1-NH₂ catalyzed pathway being suppressed in the presence of excess NH₃. Under typical nitride growth conditions, the NH₃/TMA1 ratio is ~5000 and TMA1 is not present in excess. Thus, both the TMA1 and DMA1-NH₂ catalyzed pathways should not be important in OMCVD and are ignored in this mechanism.

The monomeric species, DMA1-NH₂ can form dimers (reaction [G6]), which can further undergo polymerization reaction to form trimers (reaction [G7]) and higher n-mers (reactions [G7] and [G8]). Both monomer and dimer are postulated to contribute to growth. Although the trimer has been employed as a precursor to deposit AlN [32], such growth runs were successful only using Low Pressure MOCVD (~ 10⁻² torr), and resulted in polycrystalline films. The vapor pressure of these species is very low, thereby making growth from these species unlikely at typical growth conditions. Hence, it has been postulated that the trimers and higher n-mers either deposit on the walls or are swept out of the reactor and do not contribute to growth. The polymerization/agglomeration reaction would lead to a sharp fall-off in the growth rate with increasing pressure. All n-mers with n ≥ 3 have been lumped as a single component in this
model. This allows us to represent the polymerization reaction in a few simple steps in the absence of more detailed kinetic information.

The strong bond in the adduct-derived dimer and trimer ring species in AlN leads to the possibility of gas-phase nucleation and particle formation in the reactor (reactions \([G9]\) and \([G10]\)). It is postulated here that at high temperatures, the dimers have sufficient energy to lose the methyl groups to form AlN particles. These particles are carried away from the deposition zone by thermophoresis and they therefore do not contribute to the growth. This results in a further depletion of growth species from the reactor.

5.2.2.3 Surface reactions

The surface mechanism consists of chemisorption reactions for the reactive species from the gas phase and growth reactions. As was discussed in the previous chapters, the rate of the chemisorption reactions is given by the rate of the collision of the gaseous species with the surface modified by a sticking coefficient. The sticking coefficient is taken to be 0.1 for TMAI and TMAI:NH\(_3\) and unity for all other species. Reaction \([S6]\) represents the growth resulting from the decomposition of TMAI or the adduct, while \([S7]\) represents the growth from the adduct-derived route. Similarly to the GaN mechanism, these reactions assume that there is excess of active N species available for growth at the surface. In the absence of any experimental data on the kinetics of AlN formation, the rate parameters for the two growth reactions have been taken to be the same to minimize the number of fitting parameters. In contrast to the GaN mechanism, AlN decomposition was neglected. That is because the equilibrium partial pressure of N\(_2\) over AlN is orders of magnitude lower than corresponding N\(_2\) pressures necessary for stability of GaN [35,36]. This is due to the very high bonding energy (2.88 eV/bond) in the AlN crystal lattice that greatly lowers the chemical potential of N in the
crystal. As a reference, the corresponding bonding energies for GaN and InN are 2.2 and 1.94 eV/bond respectively. Furthermore, in their study of group III-Nitride thermal stability, Ambacher et al. [37] reported that AlN decomposition starts at ~ 1050 °C with a very high activation barrier of 100 kcal/mole.

Finally, although the presence of H₂ may affect the growth of AlN there is scarce experimental evidence for this chemical interaction. Conclusions on chemistry from experimental studies of switching between N₂, H₂, and NH₃ carrier gases are convoluted by the large change in transport parameters accompanying this switch (see Figure 2-3). Detailed transport simulations coupled with kinetic mechanisms of increasing complexity, such as the one proposed in this chapter, may elucidate this complex interaction.

5.2.3 Simulation results and discussion

As was mentioned earlier, different reactor designs yield different results of AlN growth at similar operating conditions. Thus, meaningful comparison between experimental data and simulation predictions can only be done for well-described reactor configurations. The horizontal reactor used in [11] is such a reactor. Temperature profiles and flow streamlines for this reactor along with temperature and pressure dependence of GaN growth were presented in the previous chapter. Similarly, Figures 5-2 and 5-3 show model predictions for AlN growth rate dependence on temperature and pressure respectively. Excellent agreement is observed over the whole parameter space.
Figure 5-2. Comparison of predicted (solid line) and experimentally observed [11] (points) growth rates of AlN in a horizontal reactor, as a function of temperature ($p = 85$ torr).

Formation of dimers and trimers is identified as the major pathway leading to decreasing growth rate with increasing pressure. A pathway involving nucleation and growth of oligomers from dimers and trimers, and ultimately particle formation, is consistent with decreasing Al-incorporation efficiency with increasing temperature. Similarly to the experimental observations, no AlN growth is predicted at $T > 900$ °C or $p > 300$ torr.
Figure 5-3. Comparison of predicted (solid line) and experimentally observed [11] (points) growth rates of AlN in a horizontal reactor, as a function of pressure (T = 600 °C).

The same kinetic mechanism was also included in mass transfer simulations in a close-spaced reactor similar to that used in [12] for AlGaN OMCVD. The detailed study of the fluid flow in such a reactor presented in Chapter 3 established that two-dimensional axisymmetric calculations can be used to describe transport phenomena. Comparison of simulation results with the available experimental growth rate data at a fixed temperature (1060 °C) and pressure (85 torr) is shown in Figures 5-4 and 5-5. The kinetic model is found to be consistent with this experimental data set as well. While the growth rate of GaN varies linearly with the inlet flow rate (or equivalently inlet mole fraction since the total flow rate is constant) of the TMGa, the growth rate of AlN increases sub-linearly with the inlet mole fraction of TMAI. It should be noted that for this reactor design, significant growth rate of AlN is predicted by the kinetic
mechanism at $T > 900$ °C, in agreement with experimental observations. Comparing to the results for the horizontal reactor, the reactor efficiencies can be compared.

Figure 5-4. Growth rates of GaN and AlN in a closed-spaced reactor as a function of the inlet flowrate of TMGa and TMAI respectively. Operating conditions: $T = 1060$ °C, $p = 76$ torr. Comparison of predicted (lines) growth rates and experimental data [12] (points).

Growth efficiency is defined as the growth rate divided by the Group III molar flow rate. While the absolute growth efficiency varies with the reactor configuration and depends on operating conditions, such as the carrier gas flow rate and pressure, the relative AlN/GaN growth efficiency can serve as an indication of the ability of a reactor to incorporate Al in the nitride film. Table 5-II shows the relative Al incorporation efficiency for the two different reactor configurations. For the close-spaced reactor, upon increasing the substrate temperature from 800 °C to 1060 °C, the relative Al-incorporation efficiency drops to almost half, from 0.91 to 0.40.
For the hot-wall horizontal reactor, the relative Al incorporation is lower compared to the close-spaced reactor at 800 °C, and drops to zero at higher temperatures. These results underscore the importance of reactor geometry and operating conditions in the growth of AlN based materials. The closed-spaced reactor, which has a thin thermal boundary layer and short residence time, is less affected by adduct reactions and achieves higher Al incorporation than the horizontal reactor under similar conditions.

In summary, the proposed mechanism coupled with accurate transport phenomena simulations is in agreement with available experimental observations of AlN growth and appears to capture the main deposition aspects. Additional information, through experiments or
quantum-chemistry calculations, on the probable interactions among Ga and Al adduct-derived species is necessary for an improved understanding of AlGaN deposition. Furthermore, the numerical description of particle nucleation and growth though homogeneous reactions is a very challenging task, which has not yet been fully solved in CVD environments.

Table 5-II. Relative Aluminum Incorporation Efficiency for AlGaN growth

<table>
<thead>
<tr>
<th>Reactor Configuration</th>
<th>AlN/GaN Growth Efficiency</th>
<th>800 °C</th>
<th>1060 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed-space injector (76 torr)</td>
<td></td>
<td>0.91</td>
<td>0.40</td>
</tr>
<tr>
<td>Horizontal (85 torr)</td>
<td></td>
<td>0.70</td>
<td>0.00</td>
</tr>
</tbody>
</table>

5.3 InGaN deposition

As was earlier mentioned, uniform growth of thin In$_x$Ga$_{1-x}$N films with reproducible amounts of indium incorporation is one of the key requirements in the fabrication of optoelectronic devices with superior photoluminescence and electroluminescence characteristics in the blue and green regions of the visible spectrum. The indium composition in InGaN determines the emission wavelength of the LED or laser diode. The technological importance of InGaN deposition has limited the majority of experimental publications to device results after InGaN growth at a particular set of operating conditions. Thus, considerations of InGaN growth and simulation results are preceded by a summary of experimental data sets presented below.
5.3.1 Summary of published reports on InGaN deposition

Nakamura and coworkers are using a specially designed two-flow OMCVD reactor [38]. H₂ and N₂ at equal amounts (10 slm) are used in the subflow during GaN and InGaN growth. Triethylgallium (TEGa) replaces trimethylgallium (TMGa) and N₂ replaces H₂ in the main flow when the growth is switched from GaN to InGaN [2,39-41]. The group III and group V precursors are fed to the reactor using the same inlet. The growth is conducted at atmospheric pressure, and in the 720 – 830 °C temperature range. High inlet indium/(total group III) ratios ($x'_\text{In} = 0.9$) are used in all the published experimental results. Growth rates vary in the 5 - 35 Å/min range. The authors report that the indium incorporation in InGaN consistently decreases with increasing temperature under a constant [TMIn/(TMIn+TEGa)] flow rate ratio. They also report that the crystal quality of the film degrades with increasing indium mole fraction. From their discussion, however, it is not clear if this is due to the low temperature that is needed to grow crystals with high indium content. A comparison of crystal quality (e.g. Full Width at Half Maximum of X-ray rocking curves) of InGaN films with equal indium content grown at different temperatures has yet to appear in the literature.

Indium incorporation is known to be strongly dependent on growth rate in addition to temperature as will be discussed in detail below. This issue, however, is somewhat disguised in publications Nakamura et al. As can be seen in Table 5-III, where the major experimental results are summarized, growth rates vary from 30 Å/min at 830 °C to 5 Å/min at 720 °C without an explanation or justification. At these elevated temperatures, the growth rate is typically limited by mass-transport as shown in the previous chapter for GaN growth. The growth rate should exhibit negligible temperature dependence, and be linearly dependent to group III inlet partial pressure. The growth rate increase at 830 °C can be thus explained by two possibilities: i)
growth is indeed mass-transport-limited and the inlet group III partial pressures are adjusted, or

\(ii)\) the two-flow reactor has increased mass transport capabilities that allow kinetics to control the
growth even at these elevated temperatures. This latter explanation is, however, highly unlikely.

A kinetic process with very high activation energy is required for kinetic-limited growth at 800
\(\text{oC}\). Furthermore, reactors operating under such conditions would have significant uniformity and
reproducibility problems even for slight temperature variations. In an earlier study, Nakamura et al. [42] report growth rates of \(\approx 50 \, \text{Å/min}\) in the 780 – 830 \(\text{oC}\) range when the group III inlet
partial pressures are kept constant. We therefore conclude that their reactor is operating under
mass-transport conditions in this temperature range, and that significant growth rate changes are
due to respective changes of the inlet partial pressures. The effects of V/III ration on indium
incorporation and indium droplet formation are not discussed.

### Table 5-III. InGaN experimental growth results.

Values denoted by (c) were not explicitly reported by the authors, rather computed based on figures and relevant presented information.

<table>
<thead>
<tr>
<th>Group</th>
<th>Reactor</th>
<th>Pressure</th>
<th>Tempe</th>
<th>Growth</th>
<th>(X_{\text{In}}^g)</th>
<th>(X_{\text{In}}^s)</th>
<th>(f_{\text{TMMg}})</th>
<th>(f_{\text{TMMGAs}})</th>
<th>V/III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakamura [41]</td>
<td>Two Flow</td>
<td>1 Atm</td>
<td>720 °C</td>
<td>5</td>
<td>0.90</td>
<td>0.33</td>
<td>unknown</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>Nakamura [41]</td>
<td>&gt;&gt;</td>
<td>800 °C</td>
<td>20</td>
<td>0.90</td>
<td>0.18</td>
<td>unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nakamura [41]</td>
<td>&gt;&gt;</td>
<td>830 °C</td>
<td>30</td>
<td>0.90</td>
<td>0.13</td>
<td>unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nakamura [2]</td>
<td>&gt;&gt;</td>
<td>800 °C</td>
<td>~ 33</td>
<td>0.94</td>
<td>0.16</td>
<td>17</td>
<td>1</td>
<td>10 (c)</td>
<td></td>
</tr>
<tr>
<td>Nakamura [2]</td>
<td>&gt;&gt;</td>
<td>810 °C</td>
<td>~ 33</td>
<td>0.94</td>
<td>0.11</td>
<td>17</td>
<td>1</td>
<td>10 (c)</td>
<td></td>
</tr>
<tr>
<td>Nakamura [39]</td>
<td>&gt;&gt;</td>
<td>780 °C</td>
<td>~ 50</td>
<td>0.92</td>
<td>0.24</td>
<td>24</td>
<td>2</td>
<td>7 (c)</td>
<td></td>
</tr>
<tr>
<td>Nakamura [39]</td>
<td>&gt;&gt;</td>
<td>830 °C</td>
<td>~ 50</td>
<td>0.92</td>
<td>0.14</td>
<td>24</td>
<td>2</td>
<td>7 (c)</td>
<td></td>
</tr>
</tbody>
</table>
Matsuoka et al. [43,44] were the first to grow InGaN at an elevated temperature (800 °C) using a high indium source flow rate. Prior to their contribution, experiments were carried out at ~ 500 °C, due to the low InN stability, high equilibrium vapor pressure of N₂ over InN and high indium evaporation at increased temperatures. However, the crystalline quality of the films grown at 500 °C was not good and photoluminescence was not observed. The authors used a vertical cold-wall reactor operating at 76 torr. TMIn, TEGa and ammonia were the source gases with N₂ being the carrier gas. The NH₃ flowrate is fixed at 20 slm. Inlet configuration details are not given, and we assume that metalorganics and ammonia are fed together in the reactor. At temperatures lower than 700 °C and V/III ratios less than 15,000, they report indium droplets on the surface. The growth rate does not vary significantly with temperature and lies in the 33 - 66 Å/min range. The authors report a decrease in indium incorporation efficiency with increasing temperature. Their main findings are included in Table 5-III.
Keller et al. [45,46] were the first to explicitly report on the effect of growth rate on indium incorporation. They deposited InGaN films at the 650 – 800 °C temperature range using TMGa, TMIn and ammonia with nitrogen carrier gas. A horizontal reactor operating at atmospheric pressure was used. Growth rates range between 18 and 150 Å/min. The results are presented in terms of the relative indium segregation coefficient:

\[
k_{\text{In}} = \frac{x_{\text{In}}^f f_{\text{TMGa}}}{(1-x_{\text{In}}^f)f_{\text{TMIn}}},
\]

where \( f_{\text{TMGa}} \) and \( f_{\text{TMIn}} \) are the inlet molar flow rates of TMGa and TMIn respectively. The authors report an increase of \( k_{\text{In}} \) with increasing growth rate at a given temperature. The growth rate is increased by increasing \( f_{\text{TMGa}} \) and \( f_{\text{TMIn}} \). However, adjusting a number of parameters (pressure, flow rate, carrier gas, III molar flow rate) can give rise to growth rate variations, and their effect on \( k_{\text{In}} \) could provide insight in the underlying chemistry. As an example, it would be valuable to know, if any increase in the growth rate, independent of the reason causing it, can lead to higher indium incorporation efficiency. The authors also studied the morphology of the InGaN layers, as it relates to \( f_{\text{TMIn}} \). At low flow rates, InGaN layers are mirror-like at all temperatures. Exceeding a critical TMIn flow rate at a given temperature gives rise to indium droplets on the surface and the morphology of the layers degrades. The maximum TMIn flow rate where mirror-like layers are grown decreases with decreasing temperature. The authors relate this behavior to a deficiency of active nitrogen species on the surface caused by the less efficient ammonia decomposition at lower temperatures.

Van der Stricht et al. [47,48] used the close-spaced reactor presented earlier (Figure 3-1) to deposit GaN and InGaN films. For InGaN growth, the reactor is operated at nearly atmospheric pressure (700 torr), using a high rotation rate (800 rpm). Ammonia, TMGa and TMIn are used in \( N_2 \) carrier gas. Typical experimental results are included in Table 5-III.
Increasing the temperature in the 780 – 830 °C range leads to improved PL characteristics, but lowers the indium content of the grown layers.

5.3.2 InGaN simulation approach

InGaN growth is the most intriguing of all group III-nitrides, mainly because of the limited success researchers have in trying to grow high-indium content device-quality material, and also the growth rate dependence of indium incorporation efficiency, a dependence unique among ternary III-V compound semiconductors. In analyzing InGaN growth, the following considerations are made:

- In contrast to AlN, GaN and other compound semiconductors, InN has a very low dissociation temperature. The thermal stability of InN single crystal films was recently studied for the first time [49]. The authors annealed single crystalline InN films at various temperatures. The films were grown at low temperature by microwave-excited OMVPE. By observing the RHEED patterns, they conclude that InN single crystal film is stable up to 500 °C. During annealing at temperatures above 550 °C, the InN film decomposes, nitrogen desorbs and an indium residue is left on the surface. XPS study of the In(3d) and N(1s) peaks reveals that while their ratio is similar that for the as-grown films for samples annealed at 500 °C, the N(1s) peak begins to decrease at 550 °C and disappears completely at 600 °C. The intensity of the In(3d)-related peaks does not change. These results indicate that InN is thermally unstable at the typical conditions of OMCVD growth (650 – 850 °C).

- The vapor pressure of N₂ necessary for InN stability is very high. A recent study, [35], summarized the existing experimental data on this issue, pointing out that the range of uncertainty covers several orders of magnitude. All studies agree, however, that bulk InN
decomposes at temperatures as low as 600 °C, and that N₂ pressures higher that 35kbar are necessary to suppress decomposition of InN at 700 °C.

- Indium has a high vapor pressure under typical nitride OMCVD conditions, and can desorb from the surface. As a reference, the indium vapor pressure is 2 torr at 800 °C, while gallium vapor pressure is 0.1 torr. The thermal desorption of indium from GaAs has been studied [50] by monitoring temperature programmed desorption of indium. The authors observed first-order desorption and calculated the Arrhenius parameters, which were found to be very similar to those for vaporization of pure metallic indium. In particular, the desorption energy they obtain, 53.5 kcal/mole, is nearly equal to the enthalpy of vaporization of pure metallic In, 55.3 kcal/mole. This result is consistent with desorption of In from small two-dimensional islands on the GaAs surface, with dissociation from the island being the rate limiting step. In that case, their results can be also applicable to InGaN growth.

- OMCVD of the binary InN appears to be very difficult to realize, based on the very limited number of published experimental studies. InN has been deposited on GaAs(111) and GaP(111) by microwave-excited OMCVD using TMIn and N₂ at 500 °C and 1.3 Torr. Growth rates of 50 Å/min were achieved. InN deposition was also realized on Si(100) substrates, using TMIn and NH₃ at low temperature (~ 400 °C) using a 308-nm UV laser to assist growth [51]. When the temperature was raised above 550 °C, dissociation and desorption of In- and N- containing species occurred and no InN film was formed. It can be therefore concluded that InN can not be grown by conventional OMCVD at the growth conditions where InGaN growth is carried out. This inability cannot be attributed to inefficient NH₃ decomposition, because GaN growth using NH₃ can be routinely performed in
this temperature range, as was described in the previous chapter. The instability of InN and/or inability of the NH$_3$ presence to suppress InN decomposition may be responsible.

- In contrast to AlN, GaN and other compound semiconductors, the carrier gas choice, specifically the use of hydrogen, has a profound effect on indium incorporation when InGaN is grown. As was discussed in the previous chapter, the effect of changing the carrier gas in OMCVD is manifested through changes in the gas flow pattern and mass-transfer parameters as well as shifts in the homogeneous precursor decomposition kinetics. Most of the work on nitride growth reported in the literature to date uses hydrogen as the carrier gas. However, in the work involving indium-related nitrides, nitrogen becomes the predominantly used carrier gas. Piner et al. [52] first reported on the effect of H$_2$ on the indium incorporation in OMCVD of InGaN. In the growth temperature range of 650 – 750 °C, a consistent reduction in the InN percent is observed with increasing amounts of hydrogen. Adding 20 sccm H$_2$ to 10 slm carrier gas mixture (N$_2$:NH$_3$ = 1:1) decreases the indium content from 40% to 30% at 710 °C and from 28% to 15% at 730 °C. The dependence of indium composition on ammonia flowrate was also investigated. Varying the ammonia flowrate between 1 and 5 slm (while keeping the total flowrate constant by using N$_2$ make-up gas) does not appreciably change the InN content of the films in the 700 – 800 °C range. The authors concluded that less than 0.1% of ammonia decomposes under those conditions, since higher decomposition rates would liberate hydrogen and, consequently, lower In content.

A number of possible mechanisms were considered in order to understand indium incorporation during InGaN growth. A thermodynamic analysis was presented by Kukitu et al. [53] where InGaN growth was assumed to occur through the following reactions:

$$\text{Ga(g) + NH}_3(\text{g}) \leftrightarrow \text{GaN(s)} + \frac{3}{2} \text{H}_2(\text{g})$$ [5-1]
In(g) + NH₃(g) ⇌ InN(s) + \frac{3}{2} H₂(g) \quad [5-2]

They concluded that growth, etching or regions of droplets would occur based on parameters such as V/III ratio and extent of ammonia decomposition. Assuming reaction [5-2] is in equilibrium at the interface yields the following mass action expression:

\[
\frac{a_{inN}P_{H₂}^{3/2}}{P_{in}^{eq}P_{NH₃}} = K_{inN}, \text{ or equivalently } P_{in}^{eq} = \frac{a_{inN}P_{H₂}^{3/2}}{K_{inN}P_{NH₃}},
\]

where the solid activities can be calculated using:

\[
a_{inN} = x_{inN}^s \exp \left( \frac{1 - x_{inN}^s}{Ω} \right) RT.
\]

Ω is the semi-empirical interaction parameter in a Delta Lattice Parameter model [17]. Similarly to the case of AlGaN, following Ho and Stringfellow [54] a modified Valence Force Field model can be used and Ωₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐ}_{170}
such drop-off is not observed experimentally. But perhaps the strongest argument against the assumption of growth under thermodynamic equilibrium is that according to reaction [5-2] \( \Delta G_{5:2}^{\text{RN}} = -23.75 \text{ kcal/mole at 700 } ^\circ\text{C, } \Delta G_{5:2}^{\text{RN}} = -21.34 \text{ kcal/mole at 800 } ^\circ\text{C} \) binary InN growth in the 700 – 800 °C range is predicted, contradicting all experimental observations.

We subsequently assumed that InN growth is simply dictated by a balance of indium evaporation and mass-transfer limited supply of In-containing precursors on the surface. This approach was abandoned too, because it predicts growth of InN under conditions where a number of experimental studies show no indium incorporation in InGaN or binary InN growth. Based upon the information presented above, we believe that InN growth, especially at temperatures of interest 650 – 800 °C, must depend on reaction kinetics and on the presence of Ga-containing species. A phenomenological model is proposed that involves trapping of InN by the growing GaN film. The InN growth rate is then determined by:

\[
[\text{InN growth rate}] = [\text{GaN growth rate}] \times \Theta_{\text{In}*}
\]

where \( \Theta_{\text{In}*} \) denoted the indium surface coverage, and the GaN growth rate is determined by the kinetic mechanism presented in the previous chapter. The indium surface coverage is determined by a balance between the supply of In-precursors from the gas-phase, desorption of In*, and indium loss according to reaction [5-3]. Similar trapping mechanisms are used to explain dopant incorporation in silicon (e.g. boron) in excess of the solubility limit or autodoping in silicon epitaxy by CVD [55]. While a mechanism as simple as reaction [5-3] cannot capture the growth process in its multi-faceted details, it can be used to gain more insight by comparing simulation predictions to available experimental data from a variety of operating conditions and reactor configurations.
5.3.3 Simulation results

Since the exact geometry of the reactors used in the InGaN experimental studies is not known, and a simple kinetic mechanism independent of transport phenomena was used to account for InN decomposition, the simulations presented below were carried in an axisymmetric vertical reactor similar to the one described by Matsuoka et al. [43].

![Graph showing simulation and experimental data for solid indium composition vs. relative inlet mole fraction as a function of temperature.]

Figure 5-6. Comparison of simulation (lines) and experimental [43] (points) data of solid indium composition vs. relative inlet mole fraction as a function of temperature.

Figure 5-6 presents comparison of experimental data from the group of Matsuoka et al., and simulation results for the temperature dependence of indium incorporation. Good agreement is observed. However, the solid indium mole fraction decreases at constant temperature and relative gaseous composition when the absolute amount of both TMGa and TMIn is halved. This indicates that the mechanism can capture the effect of growth rate on solid indium composition.
A better illustration is given in Figure 5-7 where the indium segregation coefficient is shown as a function of growth rate. Again, good agreement with experimental data from the group of Denbaars et al. is obtained.

Figure 5-7. Comparison of simulation (lines) and experimental [45] (points) data of indium segregation coefficient vs. growth rate.

Figure 5-8 shows comparison between simulations (dashed line) and experimental data from the group of Nakamura et al. for the temperature dependence of solid indium mole fraction at constant gaseous composition ($x_{\text{in}}^y = 0.9$). As discussed earlier, the group III inlet partial pressures are increased at higher temperatures in the experimental study although $x_{\text{in}}^y$ is kept constant (see Table 5-III). The corresponding increase in growth rate will lead to increased indium incorporation (see Fig. 5-7) in order to compensate for the increased indium desorption at high temperature (see Fig. 5-6).
Figure 5-8. Comparison of simulation (lines) and experimental [2] (points) data of solid indium composition as a function of temperature at fixed relative gaseous composition.

When the group III inlet partial pressures are adjusted in the simulations to give the reported growth rates, very good agreement (solid line) with this set of experimental data is also observed. These simulations also demonstrate how the important parameters in determining solid indium content ($T, x_{\text{In}}^c, \text{growth rate}$) can be manipulated to optimize the deposition process.

Revisiting the role of hydrogen in InGaN deposition, we should point out that any explanation of such role at this point would be speculation. Nevertheless, consider the following reaction:

$$\text{In(l)} + \text{NH}_3(\text{g}) \leftrightarrow \text{InN(s)} + \frac{3}{2} \text{H}_2(\text{g}) \quad [5-3]$$
with mass action expression:

\[
\frac{a_{\text{InN}} P_{\text{H}_2}^{3/2}}{P_{\text{NH}_3}} = K_{5-3}.
\]

As written, \( \Delta G^{\text{InN}}_{5-3} = 8.63 \text{ kcal/mole at } 700 \, ^\circ\text{C} \) and \( \Delta G^{\text{InN}}_{5-3} = 8.35 \text{ kcal/mole at } 800 \, ^\circ\text{C} \) indicating that at these temperature conditions formation of indium droplets on the surface is favored over InN deposition, as is experimentally observed. If however, InGaN is deposited and InN is grown via the “trapping mechanism”, reaction [5-3] may be used to determine the stability of the InN in the film and quantify the effect of hydrogen. \( K_{5-3} = 7.7 \) at 700 °C and 45.6 at 800 °C. Thus, if an InGaN film is being deposited at 700 °C with \( x_{\text{In}}^s = 0.3 \), then for the case \( P_{\text{NH}_3} = 0.25 \text{ atm}, P_{\text{H}_2} = 0.75 \) the equilibrium constant is 4.3 indicating that the alloy is stable. If ammonia decomposes and the partial pressures close to the substrate are \( P_{\text{NH}_3} = 0.01 \text{ atm} \) and \( P_{\text{H}_2} = 1.11 \), the equilibrium constant is 194 and InN would decompose. While simulations can be used to investigate various theories in a systematic manner, experimental studies that focus on the extent of ammonia decomposition and the presence of hydrogen at the growth interface are needed. In particular the difference, if any, between surface N-H* bonds arising from hydrogen and ammonia adsorption needs to be elucidated.

In summary, InN growth was investigated and a simple trapping mechanism was proposed for InN growth in InGaN ternary alloys. In agreement with multiple experimental observations, the indium content appears to be controlled by competition between desorption kinetics and incorporation, the latter being determined by the GaN growth rate since InN is not stable under typical growth conditions.
5.4 References


Chapter 6. Kinetic modeling of selective OMCVD growth of $\text{In}_x\text{Ga}_{1-x}\text{As/P}$

6.1 Introduction

Optoelectronic device integration is becoming increasingly important in the development of inexpensive components for optical communication and processing systems. Such integration, in addition to decreasing the cost, is expected to increase reliability resulting in a wider application of this technology. The ability to deposit a range of III-V compound semiconductor heterostructures on the same substrate is key to this integration. The organometallic chemical vapor deposition (OMCVD) process has been shown to be capable of yielding device quality III-V compound films with a high degree of control on the composition, doping and thickness uniformity [1-4]. Subsequent processing steps such as lithography and etching can be then used to define the structures in the two-dimensional growth plane in order to obtain the desired device. In an alternative approach, deposition is controlled so that growth takes place only in window openings in a dielectric material (typically SiO$_2$ or Si$_3$N$_4$) covering part of the substrate surface. In this case, with the right choice of operating parameters (low pressure, high temperature, high gas velocity) polycrystalline deposits on the masked surfaces can be completely avoided and selective epitaxy is achieved. Selective growth of GaAs was first demonstrated by Taush and Lapierre [5] over 30 years ago. The unique opportunities selective
epitaxy offers for device isolation and monolithic device integration onto the same substrate have pushed this technique to the forefront of various OMCVD growth implementations. Selective growth of GaAs, AlGaAs, InP, and InGaAs/P has been investigated; recent reviews on a variety of material systems and applications can be found in [6,7]. Selective epitaxy has been used in a range of applications such as single step growth of buried heterostructure lasers [8], quantum wire fabrication [9,10], fabrication of vertical multiple quantum (MQW) structures [11], integration of waveguides with lasers [12-14], photodetectors [15] and electroabsorption modulators [16,17].

Growth rate enhancement across the substrate window is a major feature of selective epitaxy. In OMCVD growth on a patterned substrate the growth rate is higher than that on an unmasked substrate, the enhancement being greater the smaller the ratio of the opening width to the dielectric film width is [6]. It is also observed that the growth rate is substantially higher at the edges than in the center of the window opening. Growth rate enhancements (GRE = growth rate at the substrate edge/growth rate away from the mask) as high as 6 have been reported during epitaxy of GaAs at typical OMCVD conditions (650 °C, 76 Torr) using a large masked area [18]. These growth rate differences along the substrate surface result in thickness non-uniformities which can be detrimental to device performance and need to be understood. A great deal of effort has been devoted to this issue, with some researchers proposing adsorption and surface diffusion along the mask as the main cause of the effect [10,19,20], while others have claimed it is the result of desorption from the masked areas and lateral gas-phase diffusion [21,22]. Since under typical OMCVD conditions the growth rate is determined by the arrival of group III species, the additional supply of this species would enhance the semiconductor growth rate.

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A basic understanding of the lateral thickness variations is established with the carefully designed experiments by Kayser [23], Colas et al. [24] and Gibbon et al. [25]. Kayser compared the growth rate on two circular openings (500 μm in diameter) in a mask, one of which was surrounded by a narrow (10 μm width) ring-shaped opening positioned 20 μm away from the opening. Since the migration length on the semiconductor surface is of the order of 1 μm, this opening would act as a trap for species migrating on the mask surface and would therefore reduce the growth rate in the main circular area. Although a GRE of 3 was measured, the presence of the ring did not cause any measurable effect on the growth rate indicating that surface diffusion from the masked area does not play an important role in selective OMCVD. The adsorbed species re-evaporate rather than migrate. Accumulation of the precursors over the mask and lateral diffusion in the gas-phase must account for the observed growth rate enhancement. Colas et al. [24] observed that the presence of a large masked area is felt, in terms of GRE, over distances greater than 500 μm further indicating that different areas of the substrate “communicate” via the gas-phase. Gibbon et al. [25] improved on Kayser’s idea by selectively growing InP and InGaAs on a substrate where deep trenches were etched near the masked regions. If lateral gas-phase diffusion is the supply mechanism of excess precursor, the 4-μm width of the trench will not alter the gas-phase concentrations and corresponding growth rate enhancement. On the contrary, the presence of the 55-μm deep trench will have a major effect on the growth rate if surface diffusion is important. The measured film thickness excess was the same along the trench direction and a perpendicular direction without a trench, thus confirming that gas-phase diffusion is the predominant mechanism of lateral precursor supply.
In addition to growth rate enhancement, substantial compositional deviation close to the mask/substrate interface can occur in selective growth of ternary alloys such as InGaAs [10,18,20,23], or InGaP [18,21] and quaternary alloy InGaAsP [16,26]. Compound semiconductor alloys offer the possibility to tune the energy bandgap of the material grown depending on composition. As an example, for InGaAs the bandgap can vary from 0.36 eV (InAs) to 1.43 eV (GaAs). When grown lattice-matched to InP (In_{0.53}Ga_{0.47}As), InGaAs has an energy bandgap of ~ 0.9 eV (1.38 μm), which makes it useful for detectors for the state-of-the-art fiber-optics systems operating in the 1.3-1.5 μm wavelength range [27]. To realize optoelectronic components close control of the composition has to be achieved, since variations affect directly lattice-matching (with all the associated problems caused by strain when lattice-mismatch occurs), as well as the energy bandgap of the material.

![Graph](image)

**Figure 6-1.** Indium mole fraction $x_{\text{in}}$ of In$_{x}$Ga$_{1-x}$As selectively grown on InP using a 10 x 20 mm$^2$ mask. After [18]. The line has been added for visual aid. Bandgap vs. composition data are taken from [28].
Figure 6-1 is taken from an extensive study of selective growth of InGaAs and InGaP [18]. A large masked area approach was chosen and the indium mole fraction ($x_{\text{In}}$) in the epitaxial film as a function of distance away from the mask-substrate interface was reported. Solid indium composition enrichment close to the interface is very significant and extends beyond 100 μm from the mask. Both GaAs and InAs growth rates are increased close to the mask; the extent is different among the two materials. The corresponding shift in bandgap is also shown in the figure insert. Indium enrichment close to the interface is larger in InGaAs than InGaP deposition. Since a large masked area was used, polycrystalline deposits on the mask away from the interface could not be avoided. Nevertheless, subsequent experiments using 0.2 mm wide masked stripes where no deposits on the mask were observed, yielded similar results [29]. In addition, the effect of the group III metalorganic precursor was studied and reduced indium enrichment was observed when the precursor combination TEGa/TMIn was used relative to TMGa/TMIn. Scholz and coworkers also studied the same effect by substituting the conventional indium precursor TMIn with a novel, more stable compound, namely dimethylaminopropyl-dimethyl-indium (DADI) [30,31]. They reported a less pronounced indium incorporation enhancement using DADI/TEGa relative to TMIn/TEGa.

Although these thickness and composition changes are largely undesired in many applications of selective growth, they can be exploited to fabricate novel device structures. Joyner et al. [11] fabricated multiquantum well (MQW) InGaAs(P)/InP material systems in the same plane with a single growth by designing the SiO$_2$ mask shape and exploiting the resulting quantum-size effect (thicker QW’s close to the mask) and bandgap shift (indium rich QW’s close to the mask). Large energy bandgap shifts (136 meV) were achieved that allow the deposition of lasers, modulators, and low-loss waveguides in a single plane. In addition to lateral dimensional
control, Colas et al. [24] proposed that selective epitaxy can be used to gain control over longitudinal thickness variations of the semiconductor structures. By changing the shape of the mask along its length, the extent of growth rate increase can be controlled and waveguides of tapered thickness can be fabricated. The same authors demonstrated the feasibility of this proposal by fabricating low loss optical waveguide tapers by selective OMCVD of InGaAsP/InP [32]. Their method was recently implemented by Takiguchi et al. [33] who fabricated a MQW laser diode monolithically integrated to a tapered thickness waveguide lens.

As can be seen in Figure 6-2, significant gains in cost, light beam spread angle, and optical fiber connection loss are realized. These examples demonstrate the potential of selective area growth
to become an important technology for the fabrication of tailored optoelectronic devices. However, a quantitative understanding of the growth mechanisms is essential to fully achieve its potential.

A qualitative explanation of the In enrichment in selective growth seems to be agreed upon by many researchers. It is pointed out that In-containing reactive fragments have a higher “effective” diffusion coefficient that Ga-containing ones [29]. This occurs because TMIn decomposes at lower temperatures than TMGa [1]. Additionally TMIn decomposition yields metallic In which is a comparatively smaller molecule than the smallest Ga-containing fragment, GaCH₃, hence with a higher diffusion coefficient. Following this argument many researchers have claimed that since indium growth species diffuse faster than gallium ones, and gas phase diffusion is responsible for the lateral growth rate enhancement, epitaxial films should be In-rich close to the interface [7,11,18,26]. Consistent with this assumption is the observed decrease in In enrichment when TEGa replaces TMGa given the lower chemical stability of triethyl-gallium. To explain the different In enrichment in InGaAs and InGaP the influence of the group V hydride (AsH₃ and PH₃) on the metalorganic group III precursors was invoked [7]. Eckel et al. [30] also attributed the In incorporation enhancement to the lower decomposition temperature of In- relative to Ga-containing precursors. However, they proposed that the lower temperature onset of decomposition leads to In fragments with higher reactivity, rather than higher diffusivity, with the same net result, namely increased In incorporation. While a clear understanding of the fundamental mechanisms of In enrichment from experimental studies has yet to emerge, modeling efforts of selective area epitaxy have not elucidated these mechanisms either, as will be presented in the following section.
The objective of this chapter is to present a mathematical model of selective area epitaxy and investigate the origins of compositional variations in the growth of ternary alloys. Models of increasing complexity are used in a hierarchical approach. Stagnant-layer models illustrate the relative effects of variations in diffusivity and reactivity, two-dimensional reactor-scale parametric simulations identify the relative importance of mass transport, gas-phase and surface reactions and three-dimensional simulations are used to interpret experimental data.

6.2 Mathematical modeling efforts

Process models can be used to provide valuable insight in the relationships between process parameters and observed growth phenomena. The earliest models for selective area Si and Ge deposition attributed the growth rate enhancement entirely to either gas-phase diffusion [34], or surface diffusion [35]. Coronell and Jensen [36] used a single-species coupled volume and surface diffusion model to investigate OMCVD of GaAs over patterned substrates. An isothermal stagnant layer 100-μm high above the substrate was considered, while neglecting forced convection and gas-phase reactions. The flux to the surface (substrate or mask) is obtained as an impingement rate (calculated from the kinetic theory of gases) multiplied by a corresponding sticking coefficient. The effects of various parameters (sticking coefficient, desorption time, surface diffusion length, pressure) on growth rate enhancement were analyzed by means of a parametric modeling study. Good agreement was obtained with experimental data from [37] for the GRE dependence on mask/substrate width ratio. They also demonstrated that direct gas-phase diffusion is the predominant mechanism of lateral excess material supply.
Yamaguchi and Okamoto [38,39] analyzed the surface concentration of the reactant species on the mask by a one-dimensional surface diffusion model. Comparison to experimental data for selective growth of GaAs from TMGa and AsH\textsubscript{3} at atmospheric pressure allowed the estimation of the surface migration lengths. The lengths were 0.45 μm and 0.07 μm at 610 °C on SiO\textsubscript{2} and W masks, respectively. These estimates of sub-micron surface diffusion lengths on common masking materials further supported the aforementioned conclusions on dominant gas-phase diffusion.

With the origins of growth rate enhancement in binary systems established, modeling efforts focused on the compositional variations in selective growth of ternary systems. Gibbon et al. [25] expanded the stagnant layer approach of [36] by including a second group III precursor for In. By neglecting the minimal contributions of surface diffusion, they limited the number of unknown quantities and observed that a single fitting parameter (D/k) can be used to describe selective epitaxy behavior. The symbol D [in m\textsuperscript{2}/sec] represents the diffusion coefficient of the group III precursor in the carrier gas, while k [in sec\textsuperscript{-1}] represents the rate constant of the surface adsorption of the precursor. By adjusting D/k for TMGa and TMIn, they obtained excellent agreement with experimental data of growth rate and indium composition profiles in the open areas as well as the dependence on mask/substrate width ratio. (D/k)\textsubscript{In} was 14% of (D/k)\textsubscript{Ga} and since TMGa and TMIn have comparable diffusion coefficients, the increased In incorporation close to the substrate was attributed to the apparent higher surface reaction rate of In species. Scholz et al. [31] used the same analysis to find that (D/k)\textsubscript{In} was 11% of (D/k)\textsubscript{Ga} with the TMIn/TEGa precursor combination and increased to 43% of (D/k)\textsubscript{Ga} when DADI/TEGa were used.
More recently, Fujii and Ekawa [40,41] argued that different adsorption rates for Ga and In species cannot be assumed because they are inconsistent with results from metalorganic molecular beam epitaxy (MOMBE). Furthermore, different adsorption rates would lead to Ga(As/P) growth rates that are much lower than those of In(As/P) in planar conventional MOVPE, contradicting all experimental findings. They proposed a different stagnant layer model with multiple adjustable parameters (such as escaping probability of desorbed source species from the mask, sticking coefficients on mask and substrate, vapor-phase mean free path etc.), which also excludes surface diffusion. By using five independent parameters, they succeeded in fitting experimental data of growth rate and indium composition at different pressures and concluded that the origin of compositional modulation is in the mask region. Korgel and Hicks [42] similarly argued that since under typical OMCVD conditions the growth rate is not kinetically limited, the assumption of different surface kinetics of Ga and In is not applicable to actual OMCVD processes. They proceeded to reinstate surface diffusion as the mechanism for the growth rate enhancement and introduced a new parameter, the “capture probability”, in a stagnant layer model. This parameter is an estimate of the probability that an organometallic molecule adsorbed on the mask diffuses to the window and incorporates in the growing film. The authors obtained very good agreement with the experimental data of [37] on the GRE dependence on mask/window width and claimed that, in contrast to earlier models, only one fitting parameter can be used to describe selective growth. This “capture probability” however, is an empirical parameter with vague physical meaning and depends on masking material, organometallic precursor, and reactor conditions. Of note is the authors’ disregard of overwhelming experimental evidence on the insignificant role of surface diffusion. Similarly, their choice of experimental data of GRE vs. mask width used for comparison needs to be
addressed. Since the growth rate enhancement is measured on the mask/substrate interface, simple models using either volume diffusion [25,36] or surface diffusion can give good agreement. On the other hand, experimental data of the growth rate or In composition profile on the substrate exhibit large "communication distances" (over 100 µm) observed in selective growth that cannot be accounted for by surface diffusion. In light of the abundance of experimental data on growth rate and \( x_{\text{In}} \) profiles available [16,18,20,24,25,29], the authors' choice of 10 year old data on GRE vs. mask width raises concerns about the validity of their model.

All the modeling efforts summarized above treat only a boundary layer close to a symmetrically patterned substrate. Gas-phase reactions are neglected, as are convection and thermal gradient effects. Clearly, such models cannot be used to correlate process parameters (temperature, pressure, feed rate, reactor geometry etc.) to growth characteristics. These models have at least two adjustable parameters, namely the height of the boundary layer and the conditions specified at that upper bound. Normalized growth rates are reported to eliminate these parameters and the height or the flux at the top boundary is adjusted to match experimental data, or the height is increased until self-consistent results on the substrate are obtained. While some insight into the observed variations is gained, the need to extract fitting parameters from experimental data limits the use of these models in elucidating the origins of the variations and in designing precursors/reactors that control them. In addition, distinctly different models can give consistent predictions with the same experimental data and even when the same model is used, the fitting parameters cannot be estimated uniquely ((\( D/k \))_{TMI} = 30 at 640 °C in [31] and (\( D/k \))_{TMI} = 15 at 650 °C in [25]).
6.3 Stagnant layer simulations

Similarly to [36], we assume that an isothermal stagnant boundary layer exists very close to the substrate (height: 100-200 \( \mu \text{m} \)) where the deposition rate is mass-transport-limited and can be predicted by the diffusion of the group III precursors. In this case, the fluid flow equations of momentum and mass conservation presented in Chapter 2, need not be solved since a simple Laplace equation describes the physical phenomena. Although film theory and simple boundary layer models are actually inappropriate for typical OMCVD reactors [43] due to the low Reynolds numbers encountered, they are useful as long as one keeps in mind what exactly they stand for: a simple method for investigating different assumptions and obtaining trends.

The computational domain is shown in Figure 6-3. A two-dimensional model is used, assuming large aspect ratio. Periodically arranged stripes allow the definition of symmetry boundary conditions. The topography of the mask and emerging film is not accounted for, i.e., the growing crystal and the dielectric mask are considered to be level with each other at all times – the simulation of species transport within the trench and prediction of the growth profile evaluation are outside the scope of this study. Models based on direct simulation Monte Carlo (DSMC) calculations [44,45] have been used to address these issues. Equal uniform concentrations of TMGa and TMIn are set at a height of 100 \( \mu \text{m} \) above the surface. The mask/substrate ratio is unity and the lateral dimension is simulated along 200 \( \mu \text{m} \). Based on the experimental evidence and parametric modeling efforts presented above, surface diffusion on the mask and, consequently, sticking of the reactants on the mask can be neglected. The surface adsorption rate constant \( (k) \) [cm/sec] is evaluated as a sticking coefficient multiplying the impingement rate calculated from the kinetic theory of gases:
where \( s \) is the dimensionless sticking coefficient, \( R \text{ [g cm}^2\text{/sec}^2\text{/mole/K]} \) is the ideal gas constant, \( T \text{ [K]} \) is the temperature, and \( M_w \text{ [g/mole]} \) is the organometallic precursor molecular weight. By equaling the surface adsorption rate to the diffusive flux of reactants on the substrate, the growth is assumed to be limited by mass transport, as is observed under typical OMCVD conditions.

\[
k = s \frac{R T}{2 \pi M_w}
\]

Figure 6-3. Computational domain for stagnant layer model of selective growth. \( C \text{ [cm}^3\text{/sec]} \) is the precursor concentration, \( D_g \text{ [cm}^2\text{/sec]} \) is the gas-phase diffusion coefficient, and \( k \text{ [cm/sec]} \) is the surface adsorption rate constant.

The TMGa and TMIn concentrations are assumed to be independent of each other. The decomposition kinetics of both organometallic precursors is well understood [1]. The thermal
decomposition of TMGa starts at ~ 410 °C and takes place in stepwise first order reactions. One Ga-CH₃ bond is broken at each step, with the apparent activation energy being ~59 kcal/mole for the first methyl group, and ~35 kcal/mole for the second [46]. These activation energies measured for decomposition in toluene are essentially the same for the case of H₂ carrier gas (~58 kcal/mole) [47]. It has also been established that monomethyl-gallium (MMGa) is the most stable product of homogeneous TMGa decomposition [48]. The onset of homogeneous TMIn decomposition is significantly lower, ~290 °C [1]. Similarly to TMGa, TMIn decomposes with successive loss of methyl radicals. Contrary to TMGa however, TMIn is known to completely decompose in the gas-phase to indium atoms [49]. An overall first order rate constant for TMIn decomposition in H₂ ambient was measured by time-of-flight mass spectrometric studies [50] with an activation barrier of 42.6 kcal/mole. As discussed earlier, according to one theory the local In enrichment has been attributed to the difference of the diffusion coefficients of TMGa and TMIn reactive fragments. Table 6-I shows the diffusion coefficients of the organometallic precursors and their most stable decomposition products in H₂ carrier gas at atmospheric pressure and room temperature. They were calculated using the Chapman-Enskog equation as described in Chapter 2. The corresponding Lennard-Jones potential parameters are taken from [51] (TMGa) and [52] (TMIn) and are included in Table 6-I. The differences are not significant, and GaCH₃ is shown to actually have a slightly larger Dₜ than In. The simple stagnant layer model cannot accommodate gas-phase reactions because boundary conditions for the reaction products cannot be established a-priori on the imaginary top edge of the layer. Instead, we investigated the effects of surface reaction and gas-phase diffusion by keeping one phenomenon constant while varying the other.
Table 6-I. Binary gas-phase diffusion coefficients of main group III precursor species in H₂ at 1 atm and 300 K, and Lennard-Jones potential parameters used in their calculation.

<table>
<thead>
<tr>
<th>Species</th>
<th>( D_g ) [cm²/sec]</th>
<th>( \sigma ) [Å]</th>
<th>( \varepsilon/k ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(CH₃)₃ (TMGa)</td>
<td>0.359</td>
<td>5.47</td>
<td>378.2</td>
</tr>
<tr>
<td>GaCH₃</td>
<td>0.447</td>
<td>4.29</td>
<td>611.3</td>
</tr>
<tr>
<td>In(CH₃)₃ (TMIn)</td>
<td>0.319</td>
<td>5.76</td>
<td>494.0</td>
</tr>
<tr>
<td>In</td>
<td>0.418</td>
<td>3.99</td>
<td>1217.9</td>
</tr>
</tbody>
</table>

The Galerkin finite element method was used to solve the governing equation. Biquadratic basis functions were employed. The mesh was refined close to the substrate, where the largest variations in concentration occurred. The simulations were performed at a temperature of 650 °C and a total reactor pressure of 76 Torr. Simulations at two limiting cases were performed as shown in Table 6-II. In case A, Ga- and In-species have equal surface adsorption rates and dissimilar diffusion coefficients. Conversely, in case B, Ga- and In-species have dissimilar surface adsorption rates but the same diffusion coefficients.

Table 6-II. Input parameters at the two limiting cases of stagnant layer calculations

<table>
<thead>
<tr>
<th></th>
<th>( D_g ) [cm²/sec] at 300 K, 1 atm</th>
<th>Sticking coefficient (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga-species</td>
<td>In-species</td>
</tr>
<tr>
<td>Case A</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>Case B</td>
<td>0.40</td>
<td>0.40</td>
</tr>
</tbody>
</table>

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Equal mole fractions of $1.2 \times 10^{-5}$ are assumed for both species at the top boundary. Results for Case A are shown in Figure 6-4. Figs 6-4(a) and 6-4(b) depict the Ga- and In-species mole fraction profiles just above the substrate, and the corresponding In composition of the growing film, respectively.

As expected, because of the no-growth masked area there is a lateral concentration gradient. In- and Ga-species profiles are very similar and since the growth rate is limited by diffusion and In is assigned a higher diffusion coefficient, the resulting film is indium rich. Contrary to experimental observations however, the In-composition profile is almost constant along the substrate and decreases close to the mask/substrate interface. These calculations
indicate that for equal surface reaction rates, the species with the higher diffusion coefficient is, on the average, incorporated more in the epitaxial film, due to faster diffusion in the vertical direction. However, the lateral variation of film composition reflects the lateral gradient in the gas phase. Again for equal reaction rates, the species with the higher \( D_g \) has a more level composition profile, due to fast diffusion, and ends up incorporated less in the vicinity of the mask-substrate interface. Therefore, assumptions of increased indium incorporation due to faster diffusing indium fragments cannot be supported. Increasing the In-species sticking coefficient to 1.0 while assigning equal diffusion coefficients results in the concentration and In-composition profiles shown in Figure 6-5.

Figure 6-5. Simulations results for Case B. (a): Ga- and In-species mole fractions in the gas-phase just above the substrate. (b): \( x_{\text{in}} \) in the growing film.
In-species now have a much steeper profile due to the faster reaction, and the resulting film is In-rich close to the interface. Due to the large mask/substrate ratio (1:1), significant In-enrichment is observed and the unperturbed composition away from the interface is not achieved within the 100 μm of substrate used in the calculations. From these calculations we can conclude, that while diffusion coefficient differences have negligible effects on the In incorporation with a reverse trend than seen experimentally, surface reaction differences can lead to significant In-enrichment close to the interface.

From a dimensionless analysis of the equations of the stagnant layer, a single dimensionless parameter combination arises that uniquely describes the solution, the surface Damköhler number:

\[ Da = \frac{k L}{D_g} = \frac{s L}{D_g} \sqrt{\frac{R T}{2 \pi M_w}} \]

where \( L \) is a characteristic length scale. The \( Da \) number provides a measure of relative importance of reaction and diffusion. If \( Da \) is large, the deposition is mass-transfer-limited; if \( Da \) is small, the deposition is limited by surface kinetics. Under typical OMCVD conditions, \( Da \) is large for both group III precursors. Hence, the specific value of \( Da \) is not important, since the solid composition is determined by the relative diffusion coefficients and inlet concentrations. During selective growth, however, the magnitude of \( Da \) is important and the species with the higher \( Da \) is preferentially incorporated closer to the mask/substrate interface. Control of the surface reactivity of the organometallic precursors can lead to precise control of the compositional non-uniformities.
6.4 Reactor-scale parametric studies

To investigate the origins of surface reactivity variations and correlate ternary alloy composition to process parameters, a chemical reaction mechanism in a vertical reactor was simulated. The two-dimensional axisymmetric rotating disk reactor has been extensively used in modeling studies [43,53] as a realistic representation of an actual reactor. Velocity and temperature profiles were obtained using the finite element method following the techniques described in Chapter 2. The dilute approximation was invoked and H₂ was used as the carrier gas. Operating conditions typical of InGa(As/P) deposition were chosen as follows: flowrate $F = 10$ slm H₂, substrate temperature $T_s = 923$ K, inlet temperature $T_o = 300$ K, reactor pressure $P = 76$ torr, substrate radius $r_s = 3.5$ cm, mask radius $r_m = 1.5$ cm, and inlet mole fractions $x_{TMMGa} = x_{TMn} = 1.2 \times 10^{-5}$. A circular masked area was assumed in the center of the substrate. The finite element mesh was refined close to the susceptor in the axial direction and on either side of the mask/substrate interface in the radial direction, as shown in Figure 6-6.
Flow streamlines and the temperature distribution in the reactor are also illustrated in Figure 6-6. A laminar flow field is established. The recirculation present is caused by the shape of the reactor inlet and can be eliminated by reshaping the walls.

The velocity and temperature distributions are then combined with a model of chemical reaction mechanism and species mass transport, as outlined in Chapter 2. Mole fraction distributions in the reactor and surface deposition rates are computed. Table 6-III illustrates the kinetic mechanism used in the simulations. The mechanism consists of six gas-phase species participating in three gas-phase and four surface reactions. The mechanism accounts only for the group III precursor chemistry since the growth is controlled by their arrival at the surface, group V precursors being in considerable excess.
Table 6-III. Gas-phase and surface reaction mechanism for deposition of InGa(As/P).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate = $k_0 \times \exp(-E_a/RT)$</th>
<th>$k_0$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[G1] $\text{Ga(CH}_3\text{)}_3$ → $\text{GaCH}_3 + 2 \text{CH}_3$</td>
<td>3.5$\times$10$^{15}$</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td>[G2] $\text{In(CH}_3\text{)}_3$ → $\text{In} + 3 \text{CH}_3$</td>
<td>1.0$\times$10$^{15}$</td>
<td>42.6</td>
<td></td>
</tr>
<tr>
<td>[G3] $\text{CH}_3 + \text{CH}_3$ → $\text{C}_2\text{H}_6$</td>
<td>2.0$\times$10$^{13}$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[S1] $\text{Ga(CH}_3\text{)}_3 + S$ → $[\text{GaAs/P}]_s + 3 \text{CH}_3 + S$</td>
<td>$s = 0.1$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[S2] $\text{In(CH}_3\text{)}_3 : + S$ → $[\text{InAs/P}]_s + 3 \text{CH}_3 + S$</td>
<td>$s = 0.1$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[S3] $\text{GaCH}_3 + S$ → $[\text{GaAs/P}]_s + \text{CH}_3 + S$</td>
<td>$s = 1.0$</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>[S4] $\text{In} + S$ → $[\text{InAs/P}]_s + S$</td>
<td>$s = 1.0$</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

Only the most stable products of the homogeneous decomposition of TMGa and TMIn, GaCH$_3$ and In, respectively, have been considered. Release of the first methyl radical is the limiting step in TMGa decomposition and the corresponding rate constant [46] is assigned to the overall TMGa decomposition, reaction [G1]. The apparent first-order reaction rate measured in [50] is used for TMIn pyrolysis, reaction [G2]. The methyl recombination rate is taken from [51]. Secondary radical reactions such as H· production by methyl attack on H$_2$ and subsequent recombination reactions do not affect the growth rate, and are neglected in this study. These reactions, along with secondary surface reactions involving atomic hydrogen and methyl radicals, have to be included if an accurate prediction of all species concentrations is to be achieved. We have ignored them within the scope of our study, given the abundance of such
complete reaction models for conventional planar OMCVD epitaxy in the literature [2]. Under
typical operating conditions used in selective area epitaxy, the growth is limited by mass transfer
to the substrate. In fact, the chemisorption reactions [S1]-[S4] reflect this behavior by directly
contributing to growth. A nominal sticking coefficient of 0.1 corresponding to a chemisorption
barrier of ~ 4 kcal/mole is assumed for the saturated precursors TMGa and TMIn that are bulky,
less reactive molecules. The GaCH₃ and In reactive intermediates have unity sticking
coefficients. Complete selectivity was assumed. While indium desorption from the surface [54]
can decrease the deposition rate, this reaction becomes significant at temperatures higher than
750 °C, [52]; it is therefore ignored in this study.

The omission of the group V precursors (AsH₃, PH₃) from the kinetic mechanism needs
to be addressed. Selective growth of InₓGa₁₋ₓAs₁₋ₚP₀₋ₚ showed no y-composition variations as a
function of mask width, resulting in a constant As to P ratio [25]. While relative surface reaction
rates were earlier shown to be important in selective epitaxy, surface reactions of these
precursors can be neglected since no compositional variations are observed in the group V
sublattice. The presence of AsH₃ and PH₃ is known to influence the homogeneous
decomposition kinetics of the group III organometallic precursors [1,55]. These effects may be
important in selective growth and are also ignored in this study as a first approximation.
Although the proposed kinetic mechanism is simple, it captures the key features in ternary alloy
growth under mass-transfer-limited conditions and has no adjustable parameters.

The operating conditions reported earlier are used as the base-case computation. On an
unmasked substrate, these conditions lead to uniform growth rates of ~ 0.5 μm/hr and xIn ~ 0.55.
Concentration profiles for the four main gas-phase species are shown in Figure 6-7.
As the figure reveals, there is a significant difference in the TMGa and TMIn profiles. The TMIn concentration close to the substrate is almost zero, having decomposed to In. TMGa is present in significant amounts as can be easily seen by the strong influence of the masked region on the mole fraction contours. Both precursors exhibit increased concentrations close to the cold reactor wall. This increase is the result of thermal diffusion that drives the heavier organometallic precursors away from the heated region in the reactor. The concentration profiles
for both pyrolysis products exhibit a significant increase over the masked area and a concentration gradient is established in the gas phase. The absolute amount of In present close to the substrate is larger than GaCH\textsubscript{3} due to the faster TMIn decomposition. Henceforth, results of a parametric study investigating effects of inlet concentrations, mask/substrate ratio, gas-phase diffusion, homogeneous kinetics, and surface reactivity on composition modulation of ternary In\textsubscript{x}Ga\textsubscript{1-x}(As/P) are discussed. Simulation results are presented in the form of the solid indium composition as a function of the distance away from the mask/substrate interface, similarly to the experimental results in [18] that were presented in Figure 6-1.

6.4.1 Effect of inlet TMGa/TMIn ratio

The relative inlet concentrations of TMGa and TMIn have no impact on the In enrichment close to the mask. An increase or decrease of the TMGa/TMIn ratio leads to a corresponding shift in the solid composition as expected under mass-transport-limited conditions. The composition profile on the substrate, however, remains virtually unchanged as illustrated in Figure 6-8. X\textsubscript{In} increases close to the mask and qualitative agreement is obtained with the experimental data on the shape of the X\textsubscript{In} vs. distance curve, and the distance over which In enrichment is observed (~300 \textmu m). Quantitative comparison would be meaningless at this point, since the horizontal reactor where the experiments were carried out exhibits different behavior (e.g. flow pattern, mask pattern, depletion effects) from the simulated vertical reactor. It should be noted that while gas flow effects are typically not observed in selective epitaxy [25], when a large masked area was used in [18], the growth rate enhancement exhibited dependence on flow direction.
Figure 6-8. In mole fraction $x_{\text{In}}$ of In$_x$Ga$_{1-x}$V as a function of distance (d) from the mask edge. Inlet mole fractions are as noted, all other parameters are similar to Figure 6-7.

For equal mole fractions in the inlet, the unperturbed alloy composition away from the mask edge (d > 500 μm) is slightly In-rich due to the higher diffusion coefficient of the main In-species (atomic In) relative to the main Ga-species (TMGa). Indium-rich alloy over a 50 μm distance is obtained even for a 2:1 TMGa to TMIn ratio, demonstrating the severity of $x_{\text{In}}$ modulation by selective growth.

6.4.2 Effect of substrate/mask ratio

The ratio of the exposed window area to the total substrate area is an important parameter in practical applications of selective area epitaxy. The effect of the mask coverage on the indium composition is shown in Figure 6-9.
While the mask/window ratio alters the indium enrichment close to the mask, it does not have a significant impact and does not change the overall profile. Even for a very small masked area, significant In enrichment occurs, indicating that mask dimensions play but a secondary role in determining $x_{\text{In}}$. The effect of the mask coverage on the growth rate enhancement is also shown in Figure 6-9. The well-known “loading effect” of increasing growth rate enhancement with increasing mask area reported on all experimental and theoretical studies of selective growth is exhibited. Thus, while the mask/window ratio determines the growth rate close to the opening, it has only a minor impact on the relative rates of InV and GaV deposition that govern $x_{\text{In}}$. 
6.4.3 Effect of gas-phase diffusion

The effects of gas-phase diffusion differences on solid composition is illustrated in Figure 6-10. Volume diffusion coefficients for the In bearing species (TMIn and In) are artificially doubled and comparison with results for the base case is shown.

Since the growth is mass-transport-limited, the increase in the relative rates of In- and Ga-species diffusion leads to an increase of the solid In composition in the unperturbed deposition area away from the mask. Close to the mask, this significant increase in In-species diffusion coefficients leads to a decreased In enrichment, in agreement with the qualitative conclusions reached earlier from the stagnant-layer model. It is thus established that, in contrast
to theories describing selective epitaxy, high gas-phase diffusion coefficients cannot account for the indium enrichment observed; furthermore, the opposite effect on $x_{\text{In}}$ is predicted.

### 6.4.4 Effect of surface adsorption rate

The influence of surface reactivity on $x_{\text{In}}$ was investigated by comparing base case results with simulations where the sticking coefficients for both TMGa and TMIn were increased from 0.1 to 1.0. The results are shown in Figure 6-11 along with the respective growth rate profiles of GaV and InV for both cases, ($V = \text{As or P}$).

![Graphs showing In mole fraction $x_{\text{In}}$ and growth rates as a function of distance from the mask edge for TMGa and TMIn sticking coefficients: $0.1$ and $1.0$.](image)

Figure 6-11. In mole fraction $x_{\text{In}}$ of In$_x$Ga$_{1-x}$V and GaV, InV growth rates as a function of distance ($d$) from the mask edge for sticking coefficients of TMGa, TMIn.

Surface reactivity is the main parameter controlling the In-enrichment close to the mask. When all precursors contribute to growth with unity sticking coefficient, the $x_{\text{In}}$ vs. $d$ profile
remains almost flat over the entire deposition area and a small Ga enrichment close to the mask is predicted. This slight increase in $x_{Ga}$ (or equivalent decrease in $x_{In}$) can be understood in terms of the relative Da numbers as discussed earlier. For equal reaction rates, Ga-species with a higher Da due to lower diffusion coefficients will be incorporated more near the interface.

While both TMGa and TMIn sticking coefficients were increased, a significant increase of the relative Ga composition is predicted. This effect can be understood by comparing the InV and GaV growth profiles also shown in Figure 6-11. Increasing $s_{TMi}$ to 1.0 has no effect on InV growth, indicating that TMIn is decomposed prior to reaching the surface and InV growth occurs entirely through the In reactive intermediate. On the contrary, increasing $s_{TMGa}$ to 1.0 leads to a significant increase of GaV growth close to the mask, indicating that GaV growth proceeds primarily through TMGa surface adsorption and reaction. The higher surface reactivity of In relative to TMGa leads to higher “effective” Da number for In relative to Ga and the corresponding increase in $x_{In}$ close to the mask.

It should be emphasized that, since growth under mass-transport-limited conditions is simulated, variations in surface adsorption rates should not change the unperturbed indium composition of the film away from the mask. This is demonstrated in Figure 6-11 where the same $x_{In}$ is reached at $d > 300 \ \mu m$ independent of the surface reaction rates. It is thus established, that kinetic limitations can be invoked to describe composition variations in selective growth under mass-transport-limited conditions, in contrast to the claims by Korgel and Hicks [42]. Furthermore, differences in surface reaction rates can explain the observed In enrichment without leading to dissimilar InV and GaV growth rates on unmasked substrates as argued by Fujii and Ekawa [40].
6.4.5 Effect of homogeneous precursor decomposition

The results presented above suggest that controlling the effective surface adsorption rates of In and Ga species can be used to modulate the solid composition in ternary alloys. Such control can potentially lead to the realization of many advanced optoelectronic devices that take advantage of the lateral In enrichment, as well as eliminate the enrichment when it is detrimental to device operation.

![Graph](image)

Activation energy for TMGa, TMIn decomposition:

- : Base case
- : \(E_{\text{TMGa}} : + 10 \text{ kcal/mole}\)
- : \(E_{\text{TMIn}} : - 5 \text{ kcal/mole}\)

Figure 6-12. In mole fraction \(x_{\text{In}}\) of \(\text{In}_x\text{Ga}_{1-x}\text{V}\) as a function of distance \((d)\) from the mask edge for different values of the homogeneous pyrolysis barriers for TMGa and TMIn decomposition.

Differences in the homogeneous decomposition kinetics of TMGa and TMIn cause the variations in the effective adsorption rates of Ga and In species. This is illustrated in Figure 6-12 where \(x_{\text{In}}\) vs. \(d\) profiles are shown as a function of the activation barriers for organometallic...
precursor decomposition. A decrease in the TMGa decomposition barrier or an increase in the TMIn barrier leads to a decrease in the In enrichment in the film. These predictions are consistent with experimental observations of the In enrichment dependence on organometallic precursor selection. Caneau et al. [29] reported reduced In enrichment when TMGa is replaced by the less stable TEGa as the Ga precursor. Qualitatively, this substitution corresponds to a decrease in the decomposition barrier for the Ga precursor. Reduced In enrichment is predicted by the simulations in that case, as seen in Figure 6-12. Scholz and coworkers [30,31] similarly reported reduced In enrichment when TMIn is replaced by the more stable DADI as the In precursor. This substitution corresponds to an increase in the decomposition barrier of the In precursor and qualitative agreement is obtained with the theoretical predictions. It should be also noted that gas-phase kinetics do not affect the solid In composition at distances higher than ~ 500 µm from the mask/substrate interface, in accordance with the mass-transport-limited deposition regime.

The parametric study presented above suggests that differences in the homogeneous decomposition kinetics of the organometallic precursors lead to differences in the effective surface reaction rates of Ga and In species, and cause the compositional modulation observed in selective area epitaxy of InGaAs/P. Optoelectronic devices with either substantial or negligible composition modulation can be fabricated by the appropriate choice of organometallic precursors. While the amount of PH₃ or AsH₃ used does not affect the deposition rate, the presence of the group V precursors alters the decomposition kinetics of the group III precursors. PH₃ is known to lower the decomposition temperature of TMIn. This additional pathway would have no effect on xₐ since TMIn would completely decompose even in the absence of PH₃ as shown earlier. However, the PH₃ fragments may induce additional TMGa decomposition, thus
lowering the extent of In enrichment. An accurate description of the joint decomposition kinetics of group III and V precursors can be used to quantitatively explain the different levels of In-enrichment shown by InGaAs and InGaP.

6.5 **Comparison of model predictions with experiments**

In order to assess the validity of the kinetic model to predict the effects of ternary alloy deposition on masked substrates, a comparison was made between the experimental results published by Caneau *et al.* [18] and the model predictions. In their experiments, a $2 \times 2$ cm$^2$ square area of SiO$_2$ was deposited in the center of each 5 cm wafer and selective growth of GaAs, InP, GaP, InAs, InGaAs and InGaP was performed.

![Figure 6-13](image.png)

Figure 6-13. Computational domain (finite element mesh) for simulating the horizontal experimental reactor used in [18].
The experiments were conducted in a horizontal reactor at 76 torr, 650 °C and with a H$_2$ carrier flow rate ensuring thickness and composition uniformity over an unmasked wafer. The presence of the large masked area gave rise to growth rate variations along both axial and lateral directions on the substrate. Thus, symmetry arguments that typically lead to two-dimensional simulations along the midplane of horizontal OMCVD reactors cannot be invoked. Three-dimensional calculations of fluid flow, heat and mass transfer were performed. A realistic description of the experimental reactor was obtained [56], and a finite element mesh that includes the fluid flow domain as well as the quartz reactor walls and graphite susceptor participating in the thermal environment was constructed. The mesh is depicted in Figure 6-13. The susceptor is tilted to ensure growth rate uniformity along the axial direction. Simulations of fluid flow and heat transfer including thermal radiation were performed following the method described in Chapter 2. The operating conditions used in the experiments were used in the calculations. Temperature distribution and flow profiles are shown in Figure 6-14. Natural convection to stagnant ambient air at room temperature was the heat transfer boundary condition on all reactor walls. Room temperature was also assigned at the reactor inlet.
A laminar flow profile is predicted without any buoyancy-driven recirculations. The same kinetic mechanism without any adjustable parameters presented earlier in Table 6-III is used in the simulations of individual species transport. Since the reactor is symmetric along the centerline (see Figure 6-13) only half of the computational domain is used in the mass-transfer calculations. This allows additional mesh refinement close to the substrate in the vertical direction and close to the mask/substrate interface in the lateral direction. The refinement can be seen in the finite element mesh in Figure 6-13. The need to calculate radiation exchange factors in the reactor enclosure requires calculation in the entire computational domain for fluid flow and heat transfer.

Concentration profiles of the group III precursor species along the reactor length are shown in Figure 6-15. Mole fractions over the open substrate area 1 cm away from the
mask/substrate interface are shown. Similarly to the concentration profiles presented earlier in the vertical reactor, reactant depletion close to the substrate due to surface reaction is exhibited by TMGa, GaCH₃, and In. TMIn decomposes completely in the gas phase and is absent from the deposition region.

![Diagram of concentration profiles](image)

Figure 6-15. Mole fraction profiles of TMGa, TMIn, GaCH₃, and indium along the reactor length in a horizontal OMCVD reactor. Inlet mole fractions: $x_{\text{TMGa}} = x_{\text{TMIn}} = 1.2 \times 10^{-5}$. Profiles are shown over the open substrate area at a distance of 1 cm from the dielectric mask.

Mole fraction profiles along the reactor length at the reactor centerline are shown in Figure 6-16. The reactor centerline runs over the middle of the square masked area. The
presence of the no-growth dielectric surface is reflected in the profiles of TMGa, GaCH₃, and In when compared to the corresponding profiles over the open area in Figure 6-15.

Figure 6-16. Mole fraction profiles of TMGa, TMIn, GaCH₃, and indium at the centerline along the reactor length. Inlet mole fractions: \( x_{\text{TMGa}} = x_{\text{TMIn}} = 1.2 \times 10^{-5} \). Profiles are shown over the center of the square dielectric mask.

In an actual OMCVD environment deposition of group III precursors at the reactor walls lowers the growth rate relative to the maximum rate predicted based on the inlet concentrations. Since relative effects of growth rate enhancement and In-enrichment are investigated, the inlet...
mole fractions of TMGa and TMIn in the calculations are adjusted to give growth rates and \( x_{\text{In}} \) over unmasked substrates equal to those measured experimentally. In addition, this adjustment nicely compensates for the mismatch between the actual wafer geometry (circular) and the one conveniently selected in the simulations (square).

Figure 6-17 shows the growth rate enhancement versus distance from the mask edge curves for GaAs deposition measured in the directions shown in the sketch. Experimental observations and model predictions are compared.

![Figure 6-17](image)

Figure 6-17. Predicted growth rate enhancement for GaAs as a function of the distance from the mask edge (lines). Experimental data (points) are from [18]. Results are shown along different directions as shown in the sketch.

The differences between the GRE vs. d curves are due to the lack of depletion over the mask (i.e. no-growth area) which results in a gas phase richer in growth species downstream of the mask that it would have been had it passed over an unmasked surface.
The $2 \times 2 \text{ cm}^2$ masked area being large, its effect is strong as evidenced by the much larger GRE in the flow direction downstream of the large pocket of excess growth species over the mask. The excellent agreement between experimental data and theoretical predictions offers validity to the proposed model. Gas phase diffusion along the lateral and longitudinal concentration gradients caused by the mask presence can account for GRE observed over distances $> 1000 \ \mu\text{m}$ as well as the directional dependence of this GRE. Clearly, surface diffusion taking place over a few mm from the mask edge cannot explain the experimental observations. It should be pointed out that identical GRE vs. d curves along the different directions are experimentally measured regardless of whether GaAs or InP is grown [18]. This observation further justifies our use of a simple kinetic model to describe the deposition process.

![Graph](image)

**Figure 6-18.** Predicted GaAs growth rate vs. distance curves in the axial direction at different distances form the mask as shown in the sketch.
The mechanism of growth rate enhancement in selective growth is illustrated from a different point of view in Figure 6-18. GaAs growth rate predictions along the substrate parallel to the mask are presented. In the open area 1 cm away from the mask (red line), nearly uniform deposition is predicted with a slightly decreasing growth rate trend caused by axial depletion of growth nutrients. The growth rate exhibits a similar trend before reaching the mask at the mask interface level (green line). The build up of excess material over the mask gives rise to a continuous growth rate increase in the axial direction close to the interface. When the precursors clear the masked area, the growth rate drops again but at a higher value than the respective growth rate 1 cm away.

Figure 6-19. In mole fraction $x_{\text{In}}$ of $\text{In}_{x}\text{Ga}_{1-x}\text{V}$ as a function of distance (d) from the mask edge. Experimental data (points) from [18] for $x_{\text{In}}$ of $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ grown with two different $\text{AsH}_3$ levels are included.

Inlet $\text{AsH}_3$ mole fraction: $\square = 5\times10^{-3}$, $\circ = 2.5\times10^{-3}$
The results presented above address the selective deposition of binary compounds and the corresponding enhancement in growth rate. Comparison between experimental data and model predictions for the In-enrichment close to the mask edge is shown in Figure 6-19. Data and simulation results along the direction represented by the green line in Figure 6-17 are reported. Nearly quantitative agreement with experimental data is obtained for the modulation of solid indium composition from a reactor-scale simulation.

6.6 Conclusion

A hierarchical modeling approach of selective area epitaxy was undertaken to identify the origins of growth rate enhancement and indium composition enrichment in the case of ternary InGa(As/P) growth. Simulations using the stagnant layer approach used in all the modeling studies reported in the literature reveal that surface reaction rate differences give rise to the compositional modulation. Gas phase diffusion differences are shown to have no significant influence. A realistic fluid flow description in a vertical axisymmetric reactor was coupled with a simple kinetic mechanism for InGaV deposition. This mechanism captures the salient features of homogeneous precursor decomposition and has no adjustable parameters. In contrast to the modeling efforts reported to date, growth rate and $x_{\text{In}}$ predictions can be compared to experimental data rather than computed from modeling parameters that are extracted through fitting to the data.

Differences in homogeneous decomposition kinetics of In and Ga precursors give rise to different "effective" surface reaction rates that lead to the observed In-enrichment. The proposed model is in agreement with various old and recent reports on the dependence of In-enrichment on operating parameters. Simulations show that, while the alloy deposition is limited by mass
transport, differences in kinetic parameters are responsible for the composition variations in selective growth. Thus, the usefulness of reaction-transport models in elucidating the relative roles of different deposition pathways and gaining insight to the deposition process is demonstrated. Tailoring of decomposition kinetics by precursor choice can be exploited to control selective area epitaxy and realize its capabilities for advanced optoelectronic devices.

Growth rate enhancement and In-enrichment model predictions are in excellent agreement with experimental data on lateral and axial dependence obtained in a horizontal reactor with a large masked area. In contrast to a recent report [42], the axial dependence of GRE re-establishes gas-phase diffusion as the predominant mechanism of excess material supply. The good agreement of model predictions and experimental data supports the use of our model for the simulation of selective growth by OMCVD.
6.7 References


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[56] R. Bhat (private communication).
Chapter 7. Summary and recommendations for future work

The main objective of this thesis has been accomplished – improved understanding of the complex interactions of transport phenomena and chemical kinetics in OMCVD growth of the AlGaInN compound semiconductor material system. In addition, selective area epitaxy of InGa(As/P) was studied and the origins of growth rate and alloy composition modulation were elucidated. Moreover, we demonstrated the capability of the systematic OMCVD modeling strategy followed in this thesis in identifying the relative roles of different transport processes and reaction deposition pathways to the overall growth performance in various reactor geometries.

OMCVD of AlGaInN involves complex chemistry and flow phenomena, which determine the quality of the deposited layers. Reproducible incorporation of significant concentrations of Al and In have proven difficult to achieve. The enormous technological importance of this material system in realizing solid state blue and green LEDs and LDs has spurred increasing research efforts. Nevertheless, an understanding of the dominant reaction pathways and their interaction with fluid dynamics to give different results on different reactor geometries had not emerged.

We described coupled finite element simulations of fluid flow, heat and mass transfer with emphasis on constructing kinetic mechanisms that incorporate all the chemistry information known by experimental studies and quantum chemistry calculations. Values of unknown
reaction parameters are resolved by incorporating the model in detailed transport phenomena simulations of realistic reactor geometries and comparing with experimental data.

A kinetic mechanism for GaN deposition was proposed. The model involves fast reaction between TMGa and NH₃ to form a Lewis type acid-base adduct which can dissociate or decompose at higher temperatures. The decomposition fragments can subsequently react to form dimer or trimer complexes in the gas phase containing multiple gallium-nitrogen bonds. Reaction rate parameters were obtained from quantum chemistry calculations in the literature and analysis of experimental data. The reaction mechanism was shown to be consistent with individual experimental observations, flow-tube decomposition studies, and growth rate temperature and pressure dependence in a horizontal OMCVD reactor as well as growth rate data in a close-spaced OMCVD reactor. The growth rate appears to be limited by GaN formation at low temperatures, mass transport at intermediate temperatures and GaN decomposition at temperatures higher than 1000 °C. Dimer and trimer formation can lead to an additional pathway of Ga supply to the surface at low temperatures and high pressures.

A mechanism for AlN growth was also proposed. Formation of dimers and trimers in the gas-phase was identified as the major pathway for decreased growth efficiency with decreasing pressure. An additional pathway involving nucleation and growth of oligomers from dimers and trimers, and ultimately particle formation, is consistent with decreased growth efficiency with increasing temperature. The kinetic model is consistent with experimental observations of temperature and pressure dependence of AlN growth rate in a horizontal hot-wall reactor and growth rate data for AlGaN in a close-spaced reactor.

A simple trapping mechanism was proposed for InN growth in InGaN ternary alloys. In agreement with multiple experimental observations, the indium content appears to be controlled
by competition between desorption kinetics and incorporation, the latter being determined by the GaN growth rate since InN is not stable under typical growth conditions.

A hierarchical modeling approach of selective area epitaxy was undertaken to identify the origins of growth rate enhancement and indium composition enrichment in the case of ternary InGa(As/P) growth. Simulations using the stagnant layer approach used in all the modeling studies reported in the literature reveal that surface reaction rate differences give rise to the compositional modulation. Gas phase diffusion differences are shown to have no significant influence. A realistic fluid flow description in a vertical axisymmetric reactor was coupled with a simple kinetic mechanism for InGaAs/P deposition. Differences in homogeneous decomposition kinetics of In and Ga precursors give rise to different “effective” surface reaction rates that lead to the observed In-enrichment. The proposed model is in agreement with various old and recent reports on the dependence of In-enrichment on operating parameters. Simulations show that, while the alloy deposition is limited by mass transport, differences in kinetic parameters are responsible for the composition variations in selective growth. Thus, the usefulness of reaction-transport models in elucidating the relative roles of different deposition pathways and gaining insight to the deposition process is demonstrated. Growth rate enhancement and In-enrichment model predictions are in excellent agreement with experimental data on lateral and axial dependence obtained in a horizontal reactor with a large masked area.

7.1 Recommendations for future work

Several issues needing further attention were revealed in the studies described in this thesis. Knowledge of the extent of catalytic ammonia decomposition close to the substrate
surface in nitride deposition would lead to better control of the “nitrogen” environment in the reactor. Thus, the issue of decreasing growth rate as a function of temperature at typical operating conditions would be addressed. Furthermore, direct spectroscopic evidence on the nature of gaseous species present in the reactor is required to improve upon the postulated mechanism presented in this thesis. This in turn, would lead to more accurate reaction-transport models that can be applied towards reactor optimization. Additional information, through experiments or quantum-chemistry calculations, on the probable interactions among Ga and Al adduct-derived species is necessary for an improved understanding of AlGaN deposition. Furthermore, the numerical description of particle nucleation and growth though homogeneous reactions is a very challenging task, which has not yet been fully solved in CVD reactors.