METALORGANIC CHEMICAL VAPOR DEPOSITION OF INDIUM NITRIDE AND INDIUM GALLIUM NITRIDE THIN FILMS AND NANOSTRUCTURES FOR ELECTRONIC AND PHOTOVOLTAIC APPLICATIONS

By

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

METALORGANIC CHEMICAL VAPOR DEPOSITION OF INDIUM NITRITE AND INDIUM GALLIUM NITRITE THIN FILMS AND NANOSTRUCTURES FOR ELECTRONIC AND PHOTOVOLTAIC APPLICATIONS

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Single and multi-junction In$_x$Ga$_{1-x}$N solar cell devices were modeled in one dimension using MEDICI device simulation software to assess the potential of In$_x$Ga$_{1-x}$N-based solar cells. Cell efficiencies of 16 and 27.4%, under AM0 illumination were predicted for a single and a 5-junction In$_x$Ga$_{1-x}$N solar cell, respectively. Phase separation of In$_x$Ga$_{1-x}$N alloys is determined to have little to no negative effects on the solar cell efficiency.

In$_x$Ga$_{1-x}$N alloys were grown by MOCVD over the entire compositional range (0 ≤ $x$ ≤ 1) and phase separation was analyzed with respect to substrate material and growth temperature. A low deposition temperature of 530 °C was used to produce metastable In$_x$Ga$_{1-x}$N/c-Al$_2$O$_3$ thin films over the entire compositional range, which was demonstrated for the first time by MOCVD. The use of higher deposition temperature and closely lattice matched substrates resulted in phase separated films. Substrates with a larger lattice mismatch (c-Al$_2$O$_3$) introduce strain in In$_x$Ga$_{1-x}$N which helps to stabilize the film, however, at the expense of crystalline quality.

Growth of InN nanowires by MOCVD was controlled without the use of templates or catalysts by varying the inlet flow pattern, N/In ratio, growth temperature, and substrate material.
A VLS growth mechanism is proposed, however, a VS growth mechanism can be achieved at high N/In ratios. SEM and TEM analysis revealed a core-shell nanowire structure with a single crystal InN core and a poly-crystalline In$_2$O$_3$ shell. Nanowire growth occurs along the [0002] direction with diameters and lengths ranging from 100 to 300 nm and 10 to 40 μm, respectively for a 1 hr growth.

H-MOCVD growth of InN nano- and microrods occurred on different substrates and the nanorod structure was studied by TEM. The polarity of the substrate directly affected the nanorod tip shape and prismatic stacking faults are suggested as the cause for the flower-like growth habit. Variation of growth parameters, such as temperature, N/In ratio, and Cl/In ratio proved to be ineffective at changing the aspect ratio of the nanorods. Increased growth duration produces microrod size dimensions regardless of the chosen growth conditions.
CHAPTER 1
INTRODUCTION

1.1 Group III-Nitrides

The III-nitrides and their alloys exhibit direct band gap values ranging from infrared to ultraviolet wavelengths, which make them important for applications in electronic and optoelectronic devices. Gallium nitride (GaN) and its alloy with indium nitride (In$_x$Ga$_{1-x}$N) have become dominant materials for producing high brightness light emitting diodes (LEDs) and laser diodes (LDs) that emit light in the blue region of the visible spectrum. Research on III-nitrides has resulted in LEDs and LDs that emit light at visible, infrared (IR) and ultra-violet (UV) wavelengths. These optoelectronic devices can be used for CD and DVD media, high brightness displays, and solid state lighting, which has been projected to reach seven billion dollars by 2009.\textsuperscript{1} The wide band gap energy range also makes these materials candidates for absorber layers in solar cells since the absorption edge of these materials can be varied to optimize cell efficiency. III-nitride electronic devices are also more environmentally friendly because they do not contain toxic elements such as arsenic, which is used to fabricate other compound semiconductors.

1.1.1 The III-Nitride Crystal Structure

III-nitrides can exist as a cubic zincblende crystal structure, but it is thermodynamically more stable to exist in the hexagonal wurtzite crystal structure. The cubic and hexagonal phases differ only by the stacking sequence of close-packed III-N planes, and the energy difference between the two structures is small. Changing the sequence during growth produces defects such as stacking faults. The zincblende structure (space group F43m, number 216) has an ABCABC stacking sequence of (111) close packed planes (Figure 1-1). The wurtzite structure (space group P6$_3$mc, number 186) has an ABABAB stacking sequence with alternating layers of
close packed (0001) metal atoms (In, Ga, Al) and nitrogen pairs, where every other layer is directly aligned (Figure 1-2).²

The zincblende and wurtzite structures both contain polar axes and therefore lack inversion symmetry. The polarity type of grown films has been shown to significantly affect bulk and surface properties.³,⁴ The bonds in the <0001> direction (wurtzite) and <111> (zincblende) are cation-faced while the opposite direction is nitrogen-faced (Figure 1-3).⁵ As a general rule the term “termination”, such as N-terminated, is reserved for describing a surface property. For example the surface of an indium nitride film can be N-terminated by depositing one monolayer of nitrogen atoms, but the orientation of the crystal remains unchanged.⁶ GaN has been shown to be Ga-faced when deposited by MOCVD on sapphire substrates and N-faced when deposited by MBE or HVPE on sapphire substrates.⁷-¹⁰ Ga-faced GaN films usually have an atomically smooth surface while N-faced GaN films have a rough surface morphology.¹¹ The growth parameters such as substrate material, substrate surface treatment, and N/III ratio are important factors in controlling the polarity.⁶

1.1.2 Properties of InN and GaN

The properties of InN and GaN will be discussed in this section and AlN will be ignored since it is not the primary focus of this work. Some fundamental properties of wurtzite and zincblende InN and GaN are shown in Table 1.1. The lattice parameter of InₓGa₁₋ₓN can be found by using Vegard’s law as a function of the composition (x) (Eq. 1-1). The InₓGa₁₋ₓN film composition can be determined experimentally by techniques such as X-ray diffraction (XRD) and Rutherford Backscattering (RBS).

\[
a_{\text{In}, \text{Ga}_{1-x} \text{N}} = x a_{\text{InN}} + (1-x) a_{\text{GaN}} , \text{ similarly for c-axis}
\] (1-1)
Electrical properties. As grown InN and GaN typically have large background n-type carrier concentrations, which makes p-type doping of these materials difficult. GaN has been more heavily studied than InN and the GaN film quality has progressed such that the background carrier concentration is low (4 x 10^{16} cm^{-3}) with relatively high electron mobility (600 cm^{2}/V-s). With these advances p-type doping of GaN has been consistently reproduced for a number of years. It is known that the ability to dope semiconductors depends on the position of the valence and conduction band edges with respect to a common energy reference (i.e. the Fermi level stabilization energy, $E_{FS}$). For this reason it is assumed that InN would be easier to p-type dope than GaN because the position of the valence band edge is 1.1 eV closer to the $E_{FS}$. InN however still proves to be very difficult to p-type dope. Evidence has been recently presented for bulk p-type doping of InN with magnesium by isolating the effects of the n-type surface accumulation layer that occurs in InN structures. It is also believed that only a small fraction of Mg acceptors are ionized at room temperature, but these recent results are promising for the development of InN p-n junction devices. Theoretical mobilities and controlled doping ranges of InN and GaN are listed in Table 1-2. InN and GaN have been shown to have very high peak drift velocities at room temperature, higher than that of GaAs, and unlike GaAs the drift velocities were shown to be fairly insensitive to temperature (Figure 1-4).

1.1.3 Growth of InN and In_{x}Ga_{1-x}N

Indium Nitride Thin Films. InN was first demonstrated by Juza and Hahn in 1938 from a \(\text{InF}_6(\text{NH}_4)_3\) precursor and the resulting InN had a wurtzite crystal structure. In the following years, attempts at producing InN were made by several researchers. The resulting InN samples were typically powders or small crystals and were prepared by ammonization of indium containing molecules or thermal decomposition of more complex molecules containing indium and nitrogen. These early experiments revealed that indium containing molecules would not
react with inactive N$_2$ molecules, even at higher temperature$^{25}$ and that the equilibrium nitrogen vapor pressure was very high.$^{24}$ During the 1970s and 80s polycrystalline InN films were being deposited mainly by sputter deposition. Growth on silicon and sapphire substrates was done at temperatures ranging from room temperature to 600 °C with typical electron mobility of 250 ± 50 cm$^2$/V-s and carrier concentrations in the range of 5-8 x 10$^{18}$ cm$^{-3}$. Analysis of the optical properties of InN corresponded to a band gap energy value of 2.0 eV.$^{27-30}$ During this period Tansley and Foley extensively studied RF sputtering of InN and its properties$^{31-36}$ and they have grown films with the highest mobility and lowest intrinsic carrier concentration to date (2700 cm$^2$/V-s and $n = 5 \times 10^{16}$ cm$^{-3}$).$^{31}$ It has been shown that InN dissociates at temperature greater than 600 °C.$^{28}$

During the 1990s single crystal growth of InN became more prevalent, mostly by MOCVD and molecular beam epitaxy (MBE) growth techniques and subsequent films properties were dramatically improved. Single crystal InN by MOCVD on sapphire substrates was first grown by Matsuoka et al. using trimethyl indium (TMIn) and ammonia precursors.$^{37}$ At about the same time Wakahara et al. also demonstrated MOCVD single crystal InN on sapphire substrates by reacting TMIn with microwave activated nitrogen.$^{38,39}$ By 2002, single crystal InN films with low background carrier concentrations and high mobilities had been produced, 5.8 x 10$^{18}$ cm$^{-3}$ and 730 cm$^2$/V-s (for MOCVD)$^{40}$ and 3.49 x 10$^{17}$ cm$^{-3}$ and 2050 cm$^2$/V-s (for MBE)$^{41}$ These were significant improvements in InN film quality at the time because it was difficult to grow InN films by MOCVD and MBE with background carrier concentrations below 10$^{19}$ cm$^{-3}$ with mobility greater than 300 cm$^2$/V-s.

By 2002 many researchers started to question the fundamental band gap energy value of InN, because photoluminescence and absorbance data suggested that InN’s band gap energy was
closer to 0.7 eV,\textsuperscript{42-49} instead of the previously accepted value of 2.0 eV. Today, the value of the band gap energy of InN is still not agreed upon; although there is compelling evidence that the lower band gap energy value is correct. There have been several reviews and recent papers that try to reveal reasons for the discrepancies in the InN band gap energy value.\textsuperscript{50-55} The theories that receive the most attention for band gap energy modulation in InN are oxygen incorporation in the films, Moss-Burstein effect, trapping levels, and film stoichiometry. Indium oxide has a band gap energy of 3.2 eV, therefore it is assumed that oxynitrides are formed during growth and increase the band gap energy. The Moss-Burstein effect, which was first studied by Trainer and Rose,\textsuperscript{28} occurs when the Fermi level is pushed into the conduction band as the electron concentration increases above the Mott critical density and therefore the band gap energy is overestimated by optical absorption. The Mott critical density is reached when an electron gas cannot sustain itself due to reduced electron screening in order to form bound states.\textsuperscript{56} A source for under estimation in the InN band gap energy from PL measurements of InN films can be linked to deep level traps, with activation energies on the order of 0.6-0.7 eV. The defect level explanation is reinforced by the fact the highest mobility of InN to date (2700 cm\textsuperscript{2}/V-s)\textsuperscript{31} is much lower then the theoretically predicted maximum value of 4400 cm\textsuperscript{2}/V-s,\textsuperscript{57} suggesting a high concentration of compensated defects.\textsuperscript{58}

Non-stoichiometric films are potential causes for band gap energy variation in InN. In-rich film stoichiometry leads to the formation of deep level defects (0.7 eV) when indium aggregates form and these defects states can serve as potential photoluminescence peaks.\textsuperscript{59} A low band gap energy value of 0.7 eV can also be the result of Mie resonances from indium precipitates. It is well known that optical losses occur from resonant light scattering and absorption by dispersed metallic particles.\textsuperscript{60} MBE grown In-rich InN samples showed that bipolar absorption,
accompanied with transformation into heat occurred in indium clusters, as well as resonant light scattering due to plasmon excitations. Absorption from these indium precipitates makes it difficult to determine the true band gap energy value when using optical absorption measurements. Current evidence for the InN band gap energy values range from 0.6 to 2.3 eV, suggesting that a variety of factors are involved and that no singular source is responsible for the disparity in the InN band gap energy.

The band gap energy of In$_x$Ga$_{1-x}$N can be inferred from a linear interpolation of the compound band gap energy values and using the bowing parameter (b, determined experimentally), as seen in Eq. 1-2. Recent results by Davydov et al. have shown the In$_x$Ga$_{1-x}$N bowing parameter to be 2.5 eV, while other researchers have presented evidence for a bowing parameter that is a function of composition, as represented by Eq. 1-3.

\[
E_g(x) = xE_g(\text{InN}) + (1-x)E_g(\text{GaN}) - bx(1-x) \quad (1-2)
\]

\[
b(x) = (1-x)[11.4 - 19.4x] \text{ eV} \quad (1-3)
\]

There are several growth challenges that make it difficult to produce high quality single crystal InN films by MOCVD. Of the III-nitrides, InN is by far the most difficult to grow due to its high equilibrium nitrogen vapor pressure (Figure 1-5). The high equilibrium vapor pressure of InN limits the deposition temperature to less than 650 °C to prevent film decomposition. The source materials typically used in MOCVD growth of InN are TMIn and NH$_3$. At these lower deposition temperatures, the extent of ammonia decomposition is very low, less than 0.1% at 500 °C. Due to this lack of reactive nitrogen, indium droplets can form on the surface, therefore the inlet N/In ratio must be kept sufficiently high (~50,000) to avoid formation of indium droplets.
High inlet N/In ratios are only required for growth at temperature \( \leq 600 \, ^\circ\text{C} \) since ammonia decomposition occurs readily at higher temperature \( (\geq 650 \, ^\circ\text{C}) \). The extent of decomposition of ammonia, however, significantly increases the \( \text{H}_2 \) partial pressure, which has been shown to retard the InN growth rate.\(^{66}\) This is also the reason that a nitrogen carrier gas is preferred over a hydrogen carrier gas. Other nitrogen sources such as hydrazine (\( \text{N}_2\text{H}_4 \)) have been suggested from the results of equilibrium calculations for the growth of III-nitrides.\(^{67}\) The analysis showed that the growth rate of InN could be increased without the formation of indium droplets if hydrazine was used. From a practical standpoint ammonia is still used most frequently in MOCVD growth of InN due to the explosive nature of hydrazine.

With these growth challenges, there is a narrow temperature window (400 – 650 \(^\circ\text{C}\)) for successful growth of InN by MOCVD. For conventional MOCVD the growth temperature is the most important parameter for controlling film properties such as crystalline quality, growth rate, surface morphology and carrier concentration.\(^{68}\) Modified MOCVD deposition techniques, such as plasma or laser assisted MOCVD are starting to gain popularity due to the ability to produce more reactive nitrogen at low growth temperatures, thus avoiding some of the pitfalls of conventional MOCVD.

High quality growth of InN is also hindered by the fact that there are no substrates that are appropriately matched for lattice constant and thermal expansion coefficient. Sapphire substrates (c-\( \text{Al}_2\text{O}_3 \)) are most frequently used for growth of InN even though there is a large lattice mismatch, 26%. A-, C-, and R-plane sapphire substrates were used for selected growths in this work and the different crystal orientations of sapphire are shown in Figure 1-6.\(^5\) Silicon substrates are becoming more popular due to their lower cost and potential for future device integration.\(^{69}\) Compared to sapphire, silicon substrates have a much lower lattice mismatch (8%
for Si(111)) with InN, but the resulting InN films are usually polycrystalline due to an amorphous SiNx layer that forms at the Si surface during the initiation of growth.\textsuperscript{70} Typical substrates used for growth of InN and their corresponding lattice mismatches and thermal expansion coefficient difference are shown in Table 1-3.

A large lattice mismatch and difference in thermal expansion coefficient can lead to a large number of structural defects. To reduce the number of defects in the heteroepitaxial InN, substrate nitridation (for c-Al\textsubscript{2}O\textsubscript{3}) and buffer layers are used to improve film quality. Buffer layers are a two step growth method that is commonly used in heteroepitaxy, which consists of a low temperature nucleation layer followed by the main epitaxial layer. The buffer layer serves to change the nucleation process to promote lateral growth of the subsequent film. For sapphire substrates initial nitridation as well as buffer layers are used to improve crystal quality. Substrate nitridation forms AlN nuclei on the c-Al\textsubscript{2}O\textsubscript{3} surface, and the lattice mismatch is reduced from 26\% to 14\% for InN/AlN.\textsuperscript{70-72} Complementary to nitridation, InN,\textsuperscript{73,74} GaN,\textsuperscript{75,76} and AlN\textsuperscript{77} buffer layers are used to improve InN film quality on sapphire substrates. InN films with the lowest background carrier concentration and highest electron mobility to date were grown by MBE (3.49 x 10\textsuperscript{17} cm\textsuperscript{-3} and 2,050 cm\textsuperscript{2}/V-s) using a GaN buffer layer on sapphire.\textsuperscript{41} The best MOCVD results to date are a carrier concentration and electron mobility of 5.8 x 10\textsuperscript{18} cm\textsuperscript{-3} and 900 cm\textsuperscript{2}/V-s, respectively, which were grown on c-sapphire substrates at atmospheric pressure.\textsuperscript{78} Similar to sapphire substrates, the crystalline quality of InN on Si substrates has also been improved by the use of buffer layers.\textsuperscript{69,77,79,80}

\textbf{Indium Nitride Nanostructures.} Since Iijima discovered carbon nanotubes,\textsuperscript{81} there has been a large interest in developing one-dimensional (1D) structures, such as nanowires, nanorods, nanotubes, and nanobelts from other materials. Nanostructures are unique because
dimensionality and size confinement affects electrical, optical, and structural properties. Contrary to nano-films, the additional confinement dimension of nanowires allows carrier confinement along a specific conducting path. III-nitride nanowires have potential applications in low power field-effect transistors (FETs), LEDs, solar cells, terahertz emitters and detectors. These types of nanostructures are synthesized by a variety of physical and chemical methods. The first InN nanowires were demonstrated by Dingman et al. by decomposition of azido-indium precursors. The nanowires had lengths ranging from 100-1000 nm with an average diameter of 20 nm and the growth was attributed to a precursor solution-liquid-solid (SLS) mechanism. The growth of InN nanowires and nanorods has been reported by a number of researchers.

Similar to Dingman et al., other researchers have used solvothermal methods to grow single crystal InN nanostructures at relatively low temperature (300 °C). InN nanowires have been synthesized over a wide range of temperature, and as high as 700 °C. Other investigators have synthesized InN nanowires at 420 °C, 450 °C, 440-525 °C, 500 °C, 550 °C, 600 °C, 550-700 °C, and 600-730 °C.

A variety of precursors have been used for InN nanowire growth. Single source precursors are less common and most InN nanowire synthesis uses separate indium and nitrogen precursors. Solid sources are typically used for the indium precursor, while nitrogen precursors are gas sources. Indium precursors are pure indium metal, trimethyl indium, indium oxide powder, or a combination of both indium and indium oxide. The nitrogen source is typically NH₃ but activated N₂ has also been used.

Most InN nanowire growth processes occur via vapor-solid (VS) or vapor-liquid-solid (VLS) mechanisms. As previously mentioned InN nanowire growth via SLS mechanism has
been done, however the majority of synthesis does not proceed through this route. The VLS mechanism uses a metal particle that acts as a catalytically active site that promotes growth of the nanowire. The metal catalyst forms a liquid alloy with indium, where by gas phase reactions occur with the liquid metal alloy to form a solid nanowire. The liquid alloy attracts indium vapor which leads to solid precipitation once the alloys reaches a super saturation point. A metal catalyst such as Au or Ni have been used to create a VLS mechanism for growth and it has also been suggested that indium acts as a catalyst (unintentionally) when no catalyst other catalyst is used. When no metal droplet is present at the end of the nanowire it is assumed that the reaction proceeded through a VS mechanism. Figure 1-7 shows a schematic of the VLS mechanism, as well as experimental pictures of nanowires with and without metal droplets at the end.

InN nanowires have been grown on several different substrates, Si/SiO2, Si(100), Al2O3(0001), polycrystalline AlN and GaN, or no intentional substrate at all. In the case of growth without an intentional substrate, nanowire samples are scratched from reactor walls or precursor crucibles and subsequently characterized.

The diameter of InN nanowires range from 10 to 500 nm with lengths on the order of 1 to 100 microns and the growth rate varies significantly depending on the type of deposition technique used. Nanowire properties, such as band gap energy, also vary depending on the type of growth method used. The band gap values range from 0.7 to 0.9 eV, 1.1 eV, and 1.7 to 1.9 eV, and some researchers have even reported low (0.8 eV) and high (1.9 eV) band gap energy values for InN nanowires grown by the same method. Lan et al. produced InN nanorods on Si(100) substrates using a gold catalyst where the diameter of the nanorod influenced the band gap energy. No conclusions were
presented for the difference in the band gap energy with respect to nanorod diameter. Surface electron accumulation and the Moss-Burstein effect are likely possibilities for this band gap energy variation. Vaddiraju et al. suggested the higher band gap energy values of InN nanowires are from oxygen incorporation into the nanowires, since samples often contain mixtures of In$_2$O$_3$ and InN.

Zhang et al. and Yin et al. have demonstrated single step growth methods that produce core-shell nanowire structures, InN core-In$_2$O$_3$ shell and InN core-InP shell, respectively. Core-shell structures offer the ability to study how interfacial states affect nanowire properties and progress for developing future radial heterostructure nanowire devices. Qian et al. has grown GaN-based radial core-shell LED heterostructures that emit light over wavelengths from 365 to 600 nm with high quantum efficiencies.

For InN nanowire device technology to progress several growth challenges must be overcome. As in the case of InN films some fundamental properties of InN nanostructures, such as the band gap energy, need to be studied. A variety of InN nanowire synthesis processes have been reviewed in this section, but it is important that deposition techniques be implemented with current technologies. It is also important that InN nanostructures be reproducible and the deposition be precisely controlled to make progress towards more complex devices. The ability to p-type dope InN nanostructures will also be important for future device applications.

**Indium Gallium Nitride Thin Films.** The first In$_x$Ga$_{1-x}$N alloys were grown by Osamura et al. and optical absorption measurements were given to reveal the relationship between band gap energy and alloy composition and theoretical bowing parameter of 1.05 eV was determined. Osamura et al. later noticed that In$_x$Ga$_{1-x}$N alloys phase separated after annealing in an argon atmosphere at 700 °C. Nagatomo et al. grew In$_x$Ga$_{1-x}$N alloys by
MOCVD on sapphire substrates with $0 \leq x \leq 0.42$ at 500 °C, while Yoshimoto et al.\textsuperscript{110} produced single crystal $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys on sapphire substrates with $0 \leq x \leq 0.22$ at 800 °C. The higher temperature growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ sufficiently improved the quality to allow for PL to be observed for the first time from an $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy.

The primary focus of $\text{In}_x\text{Ga}_{1-x}\text{N}$ research has been for Ga-rich solutions that are important for applications in light emitting diodes (LEDs). Shuji Nakamura pioneered the development of visible LEDs in the early 1990s, especially high brightness blue LEDs based on III-nitride heterstructures.\textsuperscript{111} Adding small amounts of indium to GaN became the optimal material for active layers in LEDs. $\text{In}_x\text{Ga}_{1-x}\text{N}$ active regions are usually highly defective due to a large number of threading dislocations, yet the LEDs remain highly efficient.\textsuperscript{112} Other III-V compound semiconductors have a much more sensitive relationship between extended defect density and device performance. Blue, green, amber, and UV LEDs have been demonstrated using $\text{In}_x\text{Ga}_{1-x}\text{N}$ active regions in either double heterostructure or quantum well structures.\textsuperscript{113} The indium composition of these active layers are usually less than 10%, with the exception of some quantum well structures where the indium content can be as high as 45%. Considerably less studies of In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have been made because AlGaAs and AlGaInP LEDs cover this wavelength range. LED devices typically use very thin layers of $\text{In}_x\text{Ga}_{1-x}\text{N}$, as small as 25 Å, and the indium content not usually greater than 50%. The InN band gap energy controversy, which started in 2002, has increased the interest in In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys as a result of device applications now possible with the smaller band gap energy of InN such as full spectrum solar cells\textsuperscript{14} and terahertz emitters and detectors.\textsuperscript{114} Most of the recent research on In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ has been focused on understanding the fundamental properties of the alloys,
such as structural, electrical properties, and optical properties as well as improving film quality.\textsuperscript{115-122}

There are several growth challenges that must be overcome for successful growth of In\textsubscript{x}Ga\textsubscript{1-x}N alloys. Perhaps most challenging is phase separation occurs in the alloy due to an 11\% lattice mismatch between InN and GaN. Ho and Stringfellow analyzed the solid phase miscibility gap in the In\textsubscript{x}Ga\textsubscript{1-x}N system and determined the maximum equilibrium incorporation of In into GaN (or Ga into InN) is less than 6\% at a typical deposition temperature of 800 °C.\textsuperscript{123} The binodal and spinodal curves were calculated using a modified valence-force-field (VFF) model (Figure 1-8) to estimate the interaction energy assuming the solid solution behaves as a regular solution. It can be seen that In\textsubscript{x}Ga\textsubscript{1-x}N alloys are theoretically unstable or metastable over a large compositional range at typical growth temperatures (Figure 1-8). The critical temperature at which complete miscibility exists was calculated to be 1250 °C, which is greater than the melting temperature of InN. Karpov performed a similar calculation to predict phase separation of In\textsubscript{x}Ga\textsubscript{1-x}N alloys and showed that the miscibility gap could be reduced by introducing compressive lattice strain (compared to unstrained films, Figure 1-9).\textsuperscript{124} Karpov’s results have been experimentally confirmed as evidence for the observation of single phase In\textsubscript{x}Ga\textsubscript{1-x}N with up to 30\% In incorporation at deposition temperature of 700-800 °C, for In\textsubscript{x}Ga\textsubscript{1-x}N heterostructures or quantum dots.\textsuperscript{125-129} Phase separation can be identified by TEM analysis or by observing peak shouldering or separation from XRD measurements (Figure 1-10).

More recently researchers have shown that single phase metastable In\textsubscript{x}Ga\textsubscript{1-x}N can be grown over the entire compositional range by MBE when a low temperature is used.\textsuperscript{47,130} Compositional modulation also occurs in In\textsubscript{x}Ga\textsubscript{1-x}N films where nano-domains of In-rich or Ga-rich sections can be formed.\textsuperscript{118,120,131,132} This non-uniform distribution has been shown to
The vapor pressure difference between InN and GaN (Figure 1-5) is another problem that affects high quality growth of In$_x$Ga$_{1-x}$N alloys. At lower deposition temperature indium incorporation can be increased, however, higher crystalline quality is achieved at higher deposition temperature. Figure 1-11 shows how indium incorporation is affected by deposition temperature when using TMIn and TEGa$^{12}$ The distribution coefficient of In between the vapor and solid phases is considerably greater than unity at 800 °C because of the large difference in decomposition pressure at elevated temperature along with near equilibrium conditions at the growth interface at this higher temperature. At the lower temperature of 500 °C the distribution coefficient is close to unity suggesting non-equilibrium (reaction limited) conditions are expected. It is also evident that at 800 °C, control of the composition becomes difficult for intermediate compositions given the rapid change in solid composition with that in the vapor.

Choosing the optimal N/III inlet ratio is directly affected by the specified deposition temperature. Ammonia decomposition efficiency will determine the actual N/III ratio, however it is very difficult to know the exact NH$_3$ decomposition efficiency since the value relies heavily on the reactor design as well as temperature. For this reason the inlet flow ratio of NH$_3$/(TMIn+TEGa) is commonly listed as the N/III ratio for MOCVD growth. In this work, a N/III ratio of 50,000 is frequently used; however the actual N/In ratio at the substrate surface will be lower, depending on the deposition temperature used. For simplicity the N/III ratio mentioned in this work represents the NH$_3$/(TMIn+TEGa) molar flow ratio into the reactor. When the deposition temperature is low (≤ 600 °C) the inlet N/III ratio must be high enough to maintain sufficient levels of active nitrogen and avoid In droplet formation. As the temperature
is increased above 650 °C the N/III ratio must be appropriately decreased so the excess hydrogen partial pressure doesn’t inhibit In incorporation into the film. Growth of In$_x$Ga$_{1-x}$N alloys (especially for In-rich compositions) is fairly difficult due to the narrow growth regimes of InN coupled with phase separation and vapor pressure differences that occur with the addition of gallium to InN.

**Indium Gallium Nitride Nanostructures.** Growth of In$_x$Ga$_{1-x}$N nanostructures offers the promise for improving the efficiency of III-nitride based LEDs. The main loss of efficiency in III-nitride LEDs is through non-radiative recombination due to threading dislocations formed during GaN and In$_x$Ga$_{1-x}$N film growth. Nanowire or nanorod growth is a way to practically eliminate threading dislocations and significantly reduce the non-radiative recombination centers. In$_x$Ga$_{1-x}$N nanostructures have been studied far less than InN nanostructures; there are only a few reports for In$_x$Ga$_{1-x}$N nanostructured growth.

The first In$_x$Ga$_{1-x}$N nanostructures were produced by Kim *et al.* using hydride vapor phase epitaxy at a low temperature of 510 °C. These In$_x$Ga$_{1-x}$N nanorods on sapphire (0001) substrates were approximately 50 nm in diameter, 10 μm in length, and oriented in the c-axis (also known as “well aligned”). All the In$_x$Ga$_{1-x}$N nanorods were Ga-rich alloys with maximum indium composition of 20%.

Chen *et al.* produced In$_x$Ga$_{1-x}$N nanorings/nanodots and ordered In$_x$Ga$_{1-x}$N nanolines/nanodots, respectively, by using selective area nitride growth on patterned SiO$_2$ masks on GaN substrates. These In$_x$Ga$_{1-x}$N nanostructures, approximately 80 nm in diameter (or across) were also Ga-rich showing PL emissions at 420 nm (2.95 eV) and 450-500 nm (2.76 – 2.48 eV).
Cai et al.\textsuperscript{135} was the first to demonstrate In-rich In\textsubscript{x}Ga\textsubscript{1-x}N nanostructure growth. In\textsubscript{x}Ga\textsubscript{1-x}N straight and helical nanowires were grown in a tube furnace using elemental Ga and In which were evaporated in an NH\textsubscript{3}/Ar flow and deposited on a Au covered Si(100) substrate. This method is similar to that has been used to produce InN nanowires.\textsuperscript{92} These In\textsubscript{x}Ga\textsubscript{1-x}N nanostructures also show a high In-content core (30-60\%) and low In-content shell (4-10\%) with either a hexagonal or cubic structure. Possible mechanisms for the helical growth structure was attributed to lateral displacement of the Au catalyst compared to the nanowire central axis or differing growth rates between the core and shell of the nanowire. The core-shell structure was believed to occur due to phase separation of the In\textsubscript{x}Ga\textsubscript{1-x}N alloy.

Growth of In\textsubscript{x}Ga\textsubscript{1-x}N nanostructures involves the difficulties related to In\textsubscript{x}Ga\textsubscript{1-x}N film growth such as compositional control and phase separation as well as reproducibility and controlled synthesis related to nanowire growth. As previously mentioned growth synthesis can be precisely controlled using patterning of SiO\textsubscript{2} masks, however, future device specifications may not always allow for patterning schemes to take place.

1.2 Photovoltaics

Photovoltaics (PV) is the field of study where electricity is directly produced from solar radiation (sunlight). The photovoltaic effect was first discovered by Edmund Baquerel in 1839 when he observed the effect of light on silver coated platinum electrodes that were immersed in an electrolyte.\textsuperscript{140} By the 1950s developments in the silicon electronics industry made it possible to fabricate silicon p-n junctions, which served as the first solar cell devices.\textsuperscript{141} During the 1950s and 60s silicon solar cell technology was developed for space and satellite applications where delivery of fuel was difficult. Interest in solar cells peaked again in the western world in the 1970s due to the oil-dependent energy crisis. During this time other cheaper solar cell technologies were explored, such as polycrystalline Si, amorphous Si, thin film, and organic
The 1990s was a time where the need was recognized for renewable energy sources and alternatives to fossil fuels, promptly significant growth in solar cell research and technology occurred at this time. By the late 1990s the photovoltaics industry was growing by 15-25% per year, and for the first time solar cell power generation became competitive with remote low power applications (rural electrification, navigation, and telecommunications). The photovoltaics industry was growing by 15-25% per year, and for the first time solar cell power generation became competitive with remote low power applications (rural electrification, navigation, and telecommunications). 

Today solar cell technology and its implementation is of global interest and some countries such as Germany and Japan are leading the way. By 2003 the solar electricity industry provided employment for over 35,000 people worldwide (European Photovoltaic Industry Association, Brussels, Belgium, EPIA Roadmap, 2004, http://www.epia.org/documents/Roadmap_EPIA.pdf, accessed April 2007). From 2004 to 2005 the PV industry doubled and annual sales have surpassed $10 billion, which is drawing significant capital investment. U.S. implementation of solar cell modules has increased in recent years, however, the U.S. has been losing market share to other countries in Europe as well as Japan. The loss in market share is directly related to the lack of U.S. growth in grid connected systems, which has grown significantly (worldwide) in recent years. One third of the 90 Megawatts (MW) that were installed in the U.S. in 2004 came from California alone. The progress of U.S. photovoltaic module implementation in recent years can be seen in Figure 1-12, and a comparison to world wide markets can be seen in Figure 1-13.

Over 95% of current solar cell technologies in use are silicon based (Figure 1-14). There are however a variety of technologies and materials being actively researched to produce more cost effective solar cells. Some of the new technologies being pursued are solar concentration systems that focus light onto solar cell absorbers, thin film organic and inorganic
materials to reduce materials cost and processing time and multi-junction solar cells to absorb more of the solar spectrum’s light.

The highest efficiency solar cells to date are based on III-V materials, specifically GaInP/GaInAs/Ge tandem cells that achieve efficiencies of 39%.\textsuperscript{146} In\textsubscript{x}Ga\textsubscript{1-x}N alloys are currently only proposed as a potential material for high efficiency solar cells.

1.2.1 Fundamental Physics of Solar Cell Devices

For light energy to be converted into electricity a solar cell first absorbs incident photons. If the energy of the photon is greater than the electronic band gap energy of the semiconductor then the energy of the photon is transferred to the semiconductor which generates electron-hole pairs. A built in electric field created by a p-n junction is used to separate the electron-hole pair, and the electrons and holes are collected via external metal contacts of the solar cell device. A schematic of a p-n junction solar cell device, including light absorption and generation of electron-hole pairs, is shown in Figure 1-15.\textsuperscript{147} The p-n junction can be formed by like semiconductor materials (homojunctions) or unlike materials (heterojunctions). Light absorption in the solar cell device depends on the absorption coefficient (α), which is an inherent property of the chosen semiconductor material.

Solar radiation, the raw material for photovoltaic energy conversion, is emitted by the sun over a range of wavelengths from ultraviolet to infrared. The power density at the surface of the sun is 62 MW/m\textsuperscript{2} and the solar flux is reduced to 1335 W/m\textsuperscript{2} at the earth’s atmosphere, mostly due to the reduced angular range of the sun.\textsuperscript{141} The power density available on the surface of earth is reduced to approximately 900 W/m\textsuperscript{2} due to atmospheric absorption of light. The extraterrestrial and terrestrial solar spectrums are shown in Figure 1-16. The atmospheric absorption due to water molecules occurs primarily at 900, 1100, 1400, and 1900 nm and for
CO₂ molecules at 1800 and 2600 nm (Figure 1-16). The atmospheric absorption is quantified by using an air mass factor, \( n_{\text{AirMass}} \), which is defined as

\[
n_{\text{AirMass}} = \frac{\text{optical path length to Sun}}{\text{optical path length if Sun directly overhead}} = \text{cosec} (\gamma_s)
\]  

(1-4)

where \( \gamma_s \) is the angle of elevation of the sun. From this definition the extraterrestrial solar spectrum corresponds to Air Mass 0 or AM0. The AM0 spectrum can also be modeled by assuming black body radiation at 5760K. The standard terrestrial solar spectrum is AM1.5, however, actual solar irradiances varies depending on the season, daily variation of the sun's position, orientation of the earth, and cloud conditions. Average global solar irradiances vary from below 100 to over 300 W/m², where the higher values are usually found at inland desert areas (Figure 1-17). The black disks located on the map represent the area needed to meet today’s total global energy supply, producing 18 terawatts of electricity (TWe), assuming a modest conversion efficiency of 8% (Figure 1-17).

A solar cell device can be considered a forward biased diode whose current flows in the opposite direction of the built-in bias. The rectifying behavior of solar cell devices is needed to separate the carriers that are generated. A solar cells output power is determined by the open circuit voltage \( (V_{oc}) \), short circuit current \( (I_{sc}) \), and fill factor (FF). Figure 1-18a shows the I-V characteristics for a solar cell under dark and illuminated conditions and Figure 1-18b shows the maximum power rectangle formed by the I-V characteristics where the boxed area is proportional to the power output of the cell. The maximum power, \( P_{\text{max}} \), is the area of the maximum power rectangle or the product of maximum power current \( (I_{mp}) \) and maximum power voltage \( (V_{mp}) \), \( P_{\text{max}} = I_{mp} \times V_{mp} \). The intersection of \( I_{mp} \) and \( V_{mp} \) is the maximum power operating point. The FF describes the squareness of the I-V characteristics and is always less than one.
Equations for the fill factor and efficiency ($\eta$) of a solar cell device is given by Eqs. 1-5 and 1-6, respectively.

$$FF \equiv \frac{P_{max}}{I_{sc}V_{oc}} = \frac{I_{mp}V_{mp}}{I_{sc}V_{oc}}$$

$$\eta \equiv \frac{P_{max}}{P_{in}} = \frac{I_{mp}V_{mp}}{P_{in}} = \frac{FF \cdot I_{sc}V_{oc}}{P_{in}}$$

Quantities such as FF, $\eta$, $I_{sc}$, and $V_{oc}$ are the main parameters used to characterize a solar cell device, but these quantities are dependent on the semiconductor structural quality and electronic properties. Two objectives for obtaining an efficient solar cell involve minimizing recombination of generated electron-hole pairs and maximizing the absorption of photons.

### 1.2.2 Why In$_x$Ga$_{1-x}$N?

With the discovery of a lower band gap energy of InN,$^{42-49}$ the wavelength range of In$_x$Ga$_{1-x}$N now spans from infrared (0.7 eV) to ultraviolet (3.4 eV). This wavelength range covers virtually the entire solar spectrum and creates the opportunity for In$_x$Ga$_{1-x}$N based high efficiency solar cells (Figure 1-19). To exploit the ability of In$_x$Ga$_{1-x}$N to absorb light at multiple wavelengths it has been proposed to fabricate multi-junction tandem solar cells using different compositions of In$_x$Ga$_{1-x}$N (Wladek Walukiewicz, 2002, Full Solar Spectrum Photovoltaic Material Identified, www.lbl.gov/msd/Pis/Walukiewicz/02/02_8_Full_Solar_Spectrum.html, accessed April 2007). Typically most high efficiency tandem solar cells are based on monolithic In-Ga-As-P-based layers grown on germanium substrates.$^{145}$ When compared to these systems, In$_x$Ga$_{1-x}$N-based devices have has the ability to be grown on inexpensive silicon substrates and use fewer and less toxic elements, which make fabrication more flexible and cost effective.

InN has been shown to have a high absorption coefficient, $\sim 10^5$ cm$^{-1}$ (this work), which means only thin absorber layers are needed to absorb the majority of incoming photons. Thinner
films mean reduced manufacture time and higher throughput, therefore reducing final solar cell costs. Another benefit of In\textsubscript{x}Ga\textsubscript{1-x}N alloys is that they are radiation hard, which is beneficial for space PV because it is difficult to replace solar cells in space, so long device lifetimes are important.\textsuperscript{14}

1.2.3 Current Progress of InN and In\textsubscript{x}Ga\textsubscript{1-x}N Solar Cells

Indium nitride (InN) as a possible photovoltaic (PV) material is a relatively new idea that was first suggested by Yamamoto \textit{et al.} in 1994.\textsuperscript{149} At that time it was suggested that InN be used as the top cell in a 2-junction tandem solar cell since the band gap energy of InN (1.95 eV) was close to the optimum value for AM0 illumination. Throughout the 1990s little attention was given to InN as a PV material, instead research efforts focused on single crystal growth of InN on different substrates using mostly MOCVD and MBE growth techniques.\textsuperscript{68} Later Malakhov\textsuperscript{150} proposed a InN/Si heterojunction for a high performance and cost effective solar cell (again considering a InN band gap energy value of \(\sim\) 2.0 eV).

Modeling In\textsubscript{x}Ga\textsubscript{1-x}N tandem solar cell structures has recently been done by Hamzaoui \textit{et al.}\textsuperscript{151} Simulations were done for two, three, four, five, and six In\textsubscript{x}Ga\textsubscript{1-x}N junction tandem solar cells. The efficiency ranged from 27\%, for a two junction cell, to 40\% for a six junction cell. A maximum theoretical efficiency greater than 50\% could be achieved using the In\textsubscript{x}Ga\textsubscript{1-x}N ternary alloy to produce a multi-junction solar cell (using optimum band gaps under concentration).\textsuperscript{152} In\textsubscript{x}Ga\textsubscript{1-x}N heterojunctions on p-Si and p-Ge substrates were simulated by Neff \textit{et al.} for In compositions ranging from 0.4 to 1.0.\textsuperscript{153} Best calculated cell efficiencies under AM1.5 illumination were 18 and 27\% for In\textsubscript{x}Ga\textsubscript{1-x}N on p-Ge and p-Si, respectively. Pure InN heterostructures showed a reduced efficiency of 2.5\%.

Although the majority of single crystal InN growth has occurred on sapphire substrates,\textsuperscript{68} growth on other substrates such as silicon or germanium is preferred for PV applications. Silicon
substrates are desired for their low cost and large area capabilities. Initially single crystal growth on Si substrates was not possible due to an amorphous SiNx layer forming during growth, however, more recent MBE results have produced single crystal InN and In$_x$Ga$_{1-x}$N films on Si(111) substrates by performing brief silicon substrate nitridation for 3 min. These recent MBE results also demonstrated rectifying characteristics of n-InN/p-Si (on most samples). Earlier CVD of n-Ga$_x$In$_{1-x}$N/p-Si films also showed rectifying behavior.

Germanium substrates provide adequate lattice matching to InN (11.3\% for InN(0001)/Ge(111)) and also can be used to fabricate vertical conduction PV device designs, which lead to higher efficiencies than top-connected cells. Trybus et al. has recently produced single crystal InN on Ge(111) substrates using MBE, and also assessed some aspects of InN/Ge based PV. I-V tests of their n-InN/p-Ge showed only ohmic behavior. In their assessment it is pointed out that without p-type doping of InN the traditional tandem solar cell structure must be redesigned, specifically involving the tunnel junctions. Tunnel junctions are degenerately doped semiconductors that serve as interconnects between the absorber layers of the solar cells as well as collection areas for minority carriers. In efforts to bypass the need for p-InN, Trybus et al. suggests using a layer of epitaxial Al between the Ge substrate and InN layer as a sub-cell interconnect and collecting junction. The Al layer also prevents an In-Ge eutectic from forming at the interface.

Another problem that hinders the progress of InN-based PV is the high background n-type doping. The high intrinsic electron concentration is one of the main issues that makes p-type doping more difficult. InN has displayed strong band bending at the surface and heterointerfaces, which coupled with the high n-type background makes it more difficult to form rectifying solid-state junctions. Very recently Jones et al. has presented evidence for p-type
doping of InN using Mg acceptors. It was shown from capacitance-voltage measurements that Mg-doped InN contains a bulk p-type region that is electrically suppressed by a thin surface inversion n-type layer. The surface accumulation layer is believed to be caused by donor-like surface defects and chemical or physical treatments have been shown to be ineffective at removing this layer. Initial p-type doping results are promising for eventual progress towards InN based devices. With these present device limitations of InN only one reference can be found where In$_x$Ga$_{1-x}$N solar cell devices have been tested. Two types of devices were tested, p-i-n solar cells with i-In$_{0.07}$Ga$_{0.93}$N layers (using n,p-GaN capping layers) and a quantum well device with In$_{0.4}$Ga$_{0.6}$N layers as the wells. The internal quantum efficiency (IQE) results for the two p-i-n cells and the quantum well device are listed in Table 1-4. The IQE is the ratio of the number of collected carriers to the number of photons that enter the cell. The IQE is related to the collection efficiency but it takes into account losses associated to the limited thickness of the absorber layer. The low IQE for cell 2 was attributed to poor crystalline quality, implying a large number of defects. X-ray data for cell 1 showed that the indium composition in the i-layer ranged from 3-16% with a maximum intensity at 7%. Lower efficiency of the quantum well structure was due to incomplete adsorption of the light due to the low thickness of the wells (1 nm).

In summary, theoretical predictions have shown that In$_x$Ga$_{1-x}$N is a promising absorber material for high efficiency solar cells. Current progress includes growth on Si and Ge substrates which are beneficial for PV devices as well as progress towards p-type doping of InN. Challenges that must be addressed for developing In$_x$Ga$_{1-x}$N-based solar cells include successful p-type doping of In-rich In$_x$Ga$_{1-x}$N and understanding the alloy phase separation that occurs during growth and its effect on cell characteristics. These current device limitations have lead to
the demonstration of In\textsubscript{x}Ga\textsubscript{1-x}N-based solar cell devices with atypical structures, such as thin quantum wells.

### 1.3 Terahertz Applications for InN and In\textsubscript{x}Ga\textsubscript{1-x}N

Terahertz (THz = 10\textsuperscript{12} Hz) is a term used to describe waves with a spectrum ranging from 0.1 to 10 THz, or wavelengths from 3 mm to 30 \textmu m, respectively. A frequency of 1 THz is equivalent to wavelengths of 0.3 mm (300 \textmu m), wavenumber of 33 cm\textsuperscript{-1}, or energy of 4.14 meV. The THz frequency region is located between the infrared and millimeter wavelengths on the electromagnetic spectrum (Figure 1-20).\textsuperscript{164}

The THz frequency regime lies between the electronic and photonic domains and therefore a mixture of optical and electronic mechanisms is often used to generate THz emission.\textsuperscript{165} Semiconductor photonic devices, which are dominated by inter-band transitions are limited to the high end of the THz range (\textasciitilde 10s of THz), while today’s electronic devices can only reach frequencies up to a few hundred gigahertz, past which causes circuit failure.\textsuperscript{164} THz fields are not well-developed even though the region sits between the well developed (by comparison) regimes of photonics and microwave technology.\textsuperscript{166} In recent years, however, THz technology has made significant developments mostly due to the improvement and availability of femtosecond lasers.\textsuperscript{167}

THz frequency devices have applications in a variety of fields including astrophysics, plasma physics, spectroscopy, medical imaging (T-rays), biology, and communications.\textsuperscript{165} There is thus considerable motivation to improve the current THz technology, which has several disadvantages. Current photonic THz emitters are bulky and expensive or must be operated at cryogenic temperature, as in the case of quantum tunneling lasers.\textsuperscript{168} THz detectors are also bulky, expensive, and lack precision.\textsuperscript{164}
InN was established as an ideal material for high frequency terahertz devices once the theoretically predicted values of the peak electron velocity was shown to be higher than that of GaAs and GaN, under moderate electric fields.\textsuperscript{19,169} Other favorable electron transport properties of InN are large intervalley energy separation, large polar optical phonon energy and a small effective mass.\textsuperscript{18,19,170,171}

There has been little experimental work analyzing terahertz emission and detection of InN\textsuperscript{114,172} and no known work on In\textsubscript{x}Ga\textsubscript{1-x}N thin film alloys. A few researchers have investigated terahertz emission from In\textsubscript{x}Ga\textsubscript{1-x}N/GaN multi-quantum wells\textsuperscript{167,173-175} and more researchers have theoretically investigated THz frequency aspects of InN\textsuperscript{176-180} and III-nitride heterstructures.\textsuperscript{181-184}

Brazis \textit{et al.}\textsuperscript{184} performed Monte Carlo simulations of the third harmonic generation (THG) efficiency of GaAs, InP, InN, and GaN to compare to Si. Their results showed that the III-V semiconductors predicted THG efficiency exceeds experimental values for Si by two orders of magnitude. Cooling to liquid nitrogen temperature (77K) increased the THG efficiency. It was also noted that InP and InN showed superior maximum efficiencies for the materials examined. Shiktorov \textit{et al.}\textsuperscript{178} examined frequency multiplication by higher order odd harmonic generation with Monte Carlo simulations and confirmed that InN was a more ideal material than InP or GaAs.

InN n\textsuperscript{+}nn\textsuperscript{+} or n\textsuperscript{+}n\textsuperscript{+}nn\textsuperscript{+} structures have been modeled by Monte Carlo simulations.\textsuperscript{176,177,180} Optical phonon emission was shown to be the dominant scattering mechanism in a n\textsuperscript{+}nn\textsuperscript{+} structure and that a free carrier grating can be formed in the n-region.\textsuperscript{180} InN n\textsuperscript{+}n\textsuperscript{+}nn\textsuperscript{+} structures were predicted to emit 50 µW of microwave power in the 1.1 to 1.2 THz range when connected to an external circuit and operated at liquid nitrogen temperature.\textsuperscript{177} Starikov \textit{et al.}\textsuperscript{176} showed
that noise enhancement in \( n^+nn^+ \) structures of InN and Ga\(_x\)In\(_{1-x}\)As can predict the onset of instability.

O’Leary \textit{et al.}\textsuperscript{179} compared the THz emission of bulk InN vs. thin films by using Monte Carlo simulation. Bulk InN (10 \( \mu \)m) showed possible emission at 10 GHz while 100 nm thick InN had emission frequencies up to 2.5 THz. Korotyeyev \textit{et al.}\textsuperscript{183} also modeled the benefits of III-N heterostructures vs. bulk materials and attributed the benefit to electron pinning.

Promising experimental results for THz emission have been found for In\(_x\)Ga\(_{1-x}\)N/GaN heterostructures\textsuperscript{173,175} and it was shown that emission efficiency in In\(_x\)Ga\(_{1-x}\)N/GaN heterostructures is better than rectification processes in bulk crystals like ZnTe.\textsuperscript{167} Stanton \textit{et al.}\textsuperscript{174} presented evidence that acoustic phonons could be used to image surfaces and interfaces in nanostructures from experiments on In\(_x\)Ga\(_{1-x}\)N/GaN heterostructures.

The first THz emission from InN was demonstrated by Ascazubi \textit{et al.}\textsuperscript{114} by optical excitation of ultrashort radiation pulses from the surface of InN (at room temperature). The semiconductor was unbiased and excitation was generated by femtosecond Ti:sapphire laser pulses at 800 nm. THz radiation from InN was compared to that of optimized p-type InAs and showed radiation on the same order of magnitude. This is a promising result since the InN thin films contained high defect densities and carrier concentrations (10\textsuperscript{10} cm\textsuperscript{-2} and 10\textsuperscript{18} cm\textsuperscript{-3}, respectively), and also because InAs is currently one of the best THz semiconductor surface emitters.\textsuperscript{185} Optimized InN layers are believed to produce much higher THz emission since lower carrier concentrations will lead to less free carrier absorption. Meziani \textit{et al.}\textsuperscript{172} investigated THz emission from high quality InN epitaxial layers under a range of temperatures (2-300K) and magnetic fields up to 13 Tesla. Higher THz transmission was noticed for higher magnetic fields, which was confirmed by simulations, and helicon waves were considered an
important contribution to emission. It was shown that the carrier concentration and momentum scattering rate, thus the film quality, could be determined by using this contactless method of THz transmission.

Also, THz emission and detection by GaN HEMTs was recently reported by several investigators.185-187 These recent results suggest that $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys are promising materials for small size, room temperature and high performance THz emitters and detectors.

1.4 Statement of Thesis

Properties such as a high absorption coefficient, radiation hardness, and absorption over a wide range of wavelengths make $\text{In}_x\text{Ga}_{1-x}\text{N}$ an attractive photovoltaic material (Section 1.2.2). To better understand $\text{In}_x\text{Ga}_{1-x}\text{N}$’s potential as a PV absorber layer, $\text{In}_x\text{Ga}_{1-x}\text{N}$-based solar cell device simulations were performed using the MEDICI device simulation software package (Chapter 2). Optimized single junction and multi-junction $\text{In}_x\text{Ga}_{1-x}\text{N}$ solar cells were simulated and the potential effects of phase separation are assessed.

$\text{InN}$ and $\text{In}_x\text{Ga}_{1-x}\text{N}$ are materials that show a great deal of potential in applications such as high efficiency solar cells and terahertz electronic devices, and $\text{In}_x\text{Ga}_{1-x}\text{N}$ has already been proven to be a dominant material for LED applications. Although significant progress has been made in the field of $\text{In}_x\text{Ga}_{1-x}\text{N}$ based LEDs, the properties of $\text{InN}$ and $\text{In}$-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ are still not very well understood. It is for this reason that growth $\text{In}_x\text{Ga}_{1-x}\text{N}$ thin films have been grown over the entire compositional range ($0 \leq x \leq 1$), so that fundamental issues such as phase separation can be better understood. For the applications of solar cells, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy composition is very important for the design of high efficiency multi-junction solar cells. Understanding and optimizing growth conditions for different $\text{In}_x\text{Ga}_{1-x}\text{N}$ compositions is important for THz applications since THz emission is inversely proportional to doping concentration due to free carrier absorption, which is natively very high in nitrides. Phase
separation in In\textsubscript{x}Ga\textsubscript{1-x}N alloys might also prove interesting for THz applications because residual strain affects the internal bias and thus the emission efficiency. The growth of InN and In\textsubscript{x}Ga\textsubscript{1-x}N thin films is presented in Chapter 3.

The benefits of semiconductor nanostructures were discussed in Section 1.1.3, and these nanostructures offer unique abilities to understand the properties of InN that cannot be gleaned from bulk samples. InN and In\textsubscript{x}Ga\textsubscript{1-x}N nanostructures are specifically advantageous for PV and THz applications due to their large surface to volume ratio. For solar cells a larger surface area can result in greater collection efficiency and THz emission efficiency should increase with increased surface area since the emission mechanism results from interfacial interactions. The growth of InN nanostructures has been presented in the literature more frequently in recent years, however, growth is typically not highly controllable. There is a need for nanostructured growth to be incorporated with current growth techniques and process requirements, which is why controlled MOCVD or H-MOCVD growth of nanostructures is preferred. Growth of InN nanowires by MOCVD and InN nano- and micro-rods by H-MOCVD are presented in Chapter 4 and 5, respectively.

Chapter 6 contains an exploratory study of GaN nanostructures by MOCVD. This section is only discussed briefly since GaN nanostructures are not the primary focus of this work, however, this area is scientifically interesting. Recommendations for future work are presented in Chapter 7.
Figure 1-1. The III-nitride zincblende crystal structure along various directions. A) [100] (1 unit cell). B) [110] (2 unit cells). C) [111] (2 unit cells) (Ref 2).

Figure 1-2. The III-nitride wurtzite crystal structure along various directions. A) [0001]. B) [1120]. C) [1010] (Ref. 2).

Figure 1-3. Cation-faced (Ga) and nitrogen-faced polarity for the GaN wurtzite crystal structure (Ref. 5).
Figure 1-4. Velocity-field characteristics ($T = 300K, n = 10^{17} \text{ cm}^{-3}$) for wurtzite InN, GaN, AlN, and zincblende GaAs (Ref. 19).

Figure 1-5. Vapor pressure of $N_2$ in equilibrium with of InN, GaN, and AlN as a function of temperature (Ref. 63).
Figure 1-6. Rhombohedral structure and surface planes of sapphire (Ref 5).

Figure 1-7. Theoretical and experimental examples of nanowire growth mechanisms.  
A) Theoretical VLS growth mechanism (Ref. 107).  B) Experimental evidence for a VLS mechanism showing metal catalyst at tip of nanowire (Ref. 92).  
C) Experimental evidence for a VS mechanism, showing no metal droplet (Ref. 103).
Figure 1-8. Predicted binodal (solid) and spinodal (dashed) decomposition curves for In$_x$Ga$_{1-x}$N assuming regular solution mixing (Ref. 123).

Figure 1-9. The T-x phase diagrams of ternary In$_x$Ga$_{1-x}$N compounds. A) Relaxed In$_x$Ga$_{1-x}$N layers. B) Strained In$_x$Ga$_{1-x}$N layers with the interface orientation perpendicular to the hexagonal axis of the crystal (Ref. 124).
Figure 1-10. Several XRD spectra of phase separated In$_x$Ga$_{1-x}$N films at different temperatures (Ref. 12).

Figure 1-11. Compositional control of In$_x$Ga$_{1-x}$N with respect to growth temperature (Ref. 12).
Figure 1-12. U.S. photovoltaic module implementation from 1992-2003 (Ref. 144).

Figure 1-13. Comparison of world wide growth of PV production from 1990-2004 (Ref. 143).
Figure 1-14. Market shares of different photovoltaic materials as of 2001 (Ref. 145).

![Figure 1-14](image)

Figure 1-15. Schematic of light induced carrier generation in a generic solar cell (Ref. 147).

![Figure 1-15](image)

Figure 1-18. Current-voltage characteristics of a generic solar cell. A) under dark (solid line) and illuminated (dashed line) conditions. B) The resulting maximum power rectangle (under illumination) (Ref. 151).
Figure 1-19. Incident solar flux for AM0 (black) and AM1.5 (red) as well as the In$_x$Ga$_{1-x}$N band gap energy range (colored box).

Figure 1-20. Terahertz frequency range (shaded) of the electromagnetic spectrum, including molecular transitions (Ref. 168).
Table 1-1. Some fundamental properties of InN and GaN (Ref. 50\textsuperscript{a}, 188, 189\textsuperscript{b}, 190\textsuperscript{c}).

<table>
<thead>
<tr>
<th>Property</th>
<th>GaN (wurtzite)</th>
<th>InN (wurtzite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature band gap energy (eV)</td>
<td>3.39</td>
<td>0.6-2.1\textsuperscript{a}</td>
</tr>
<tr>
<td>Temperature coefficient (eV/K)</td>
<td>dE\textsubscript{g}/dT = -6.0 x 10\textsuperscript{-4}</td>
<td>dE\textsubscript{g}/dT = -1.8 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Lattice constants (Å)</td>
<td>a = 3.189</td>
<td>a = 3.5377\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>c = 5.185</td>
<td>c = 5.7037\textsuperscript{b}</td>
</tr>
<tr>
<td>Thermal expansion (K\textsuperscript{-1})</td>
<td>Δa/a = 5.59 x 10\textsuperscript{-6}</td>
<td>Δa/a = 4 x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td></td>
<td>Δc/c = 3.17 x 10\textsuperscript{-6}</td>
<td>Δc/c = 3 x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm-K)</td>
<td>1.3</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>2.67</td>
<td>2.9-3.05</td>
</tr>
<tr>
<td></td>
<td>GaN (zincblende)</td>
<td>InN (zincblende)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>GaN (zincblende)</th>
<th>InN (zincblende)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature band gap energy (eV)</td>
<td>3.2-3.3</td>
<td>0.6\textsuperscript{c}</td>
</tr>
<tr>
<td>Lattice constants (Å)</td>
<td>a = 4.52</td>
<td>a = 4.986\textsuperscript{c}</td>
</tr>
</tbody>
</table>

Table 1-2. Theoretical and experimental mobility and controlled doping ranges for InN and GaN.

<table>
<thead>
<tr>
<th>Property</th>
<th>InN</th>
<th>Ref.</th>
<th>GaN</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical maximum electron mobility (cm\textsuperscript{2}/V-s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300K</td>
<td>4,400</td>
<td>57</td>
<td>1,350</td>
<td>192</td>
</tr>
<tr>
<td>77K</td>
<td>30,000</td>
<td></td>
<td>19,200</td>
<td></td>
</tr>
<tr>
<td>Experimental maximum hole mobility (cm\textsuperscript{2}/V-s)</td>
<td>no available data</td>
<td>13</td>
<td></td>
<td>193</td>
</tr>
<tr>
<td>300K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Controlled doping range (cm\textsuperscript{3})</td>
<td>n-type (Si)</td>
<td>5x10\textsuperscript{16} to 5x10\textsuperscript{20}</td>
<td>10\textsuperscript{16} to 4x10\textsuperscript{20}</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>p-type (Mg)</td>
<td>no available data</td>
<td>10\textsuperscript{16} to 6x10\textsuperscript{18}</td>
<td></td>
</tr>
</tbody>
</table>
Table 1-3. Lattice and thermal expansion constants for InN substrates and buffer layers (Ref. 5, 196).

<table>
<thead>
<tr>
<th>Substrate material or buffer Layer</th>
<th>Space group symmetry</th>
<th>lattice parameters</th>
<th>Thermal expansion coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>GaN</td>
<td>P63mc</td>
<td>3.189</td>
<td>5.185</td>
</tr>
<tr>
<td>AlN</td>
<td>P63mc</td>
<td>3.112</td>
<td>4.982</td>
</tr>
<tr>
<td>c-Al2O3</td>
<td>R3c</td>
<td>4.759</td>
<td>12.991</td>
</tr>
<tr>
<td>Si (111)</td>
<td>Fd3m</td>
<td>5.430</td>
<td>-----</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>P63mc</td>
<td>3.080</td>
<td>15.117</td>
</tr>
<tr>
<td>GaAs</td>
<td>F43m</td>
<td>5.653</td>
<td>-----</td>
</tr>
<tr>
<td>InP</td>
<td>F43m</td>
<td>5.869</td>
<td>-----</td>
</tr>
<tr>
<td>GaP</td>
<td>F43m</td>
<td>5.451</td>
<td>-----</td>
</tr>
<tr>
<td>ZnO</td>
<td>P63mc</td>
<td>3.252</td>
<td>5.213</td>
</tr>
<tr>
<td>MgO</td>
<td>Fm3m</td>
<td>4.216</td>
<td>-----</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>Fd3m</td>
<td>8.083</td>
<td>-----</td>
</tr>
<tr>
<td>LiAlO2</td>
<td>P41212</td>
<td>5.169</td>
<td>6.268</td>
</tr>
<tr>
<td>LiGaO2</td>
<td>Pna21</td>
<td>5.406</td>
<td>5.013</td>
</tr>
</tbody>
</table>

Table 1-4. Internal quantum efficiency (IQE) of In_xGa_1-xN p-i-n and quantum well solar cells (Ref. 162).

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Type</th>
<th>In_xGa_1-xN (x)</th>
<th>IQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-i-n</td>
<td>0.07</td>
<td>19.0</td>
</tr>
<tr>
<td>2</td>
<td>p-i-n</td>
<td>0.40</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>quantum well</td>
<td>0.40</td>
<td>8.0</td>
</tr>
</tbody>
</table>
CHAPTER 2
INDIUM GALLIUM NITRIDE SOLAR CELL DEVICE SIMULATIONS

2.1 Introduction

In$_x$Ga$_{1-x}$N is an optimal material for absorber layers in solar cells because the InN-GaN alloy system covers a wide spectral range that spans the majority of wavelengths in the solar spectrum. In-rich In$_x$Ga$_{1-x}$N has a high absorption coefficient and has also been proven to be highly radiation resistant. A more detailed explanation of In$_x$Ga$_{1-x}$N’s material qualifications for PV applications is given in Section 1.2.2. Development of In$_x$Ga$_{1-x}$N based photovoltaics has been delayed by the difficulty in p-type doping of InN and In-rich In$_x$Ga$_{1-x}$N alloys. The recent results for Mg doped InN, however, are encouraging for eventual p-type doping of InN and thus In-rich In$_x$Ga$_{1-x}$N alloys.

In this chapter, single and multi-junction In$_x$Ga$_{1-x}$N solar cells are modeled using MEDICI device simulation software. The optimum cell parameters are determined for a single-junction In$_x$Ga$_{1-x}$N solar cell and multi-junction solar cells are simulated for two, three, four, and five junctions. The implications of phase separation and the effect on cell efficiencies are also discussed for both single and multi-junction In$_x$Ga$_{1-x}$N solar cells.

The intention of this simulation study is to estimate the efficiency of In$_x$Ga$_{1-x}$N solar cells by applying realistic limits (thickness, doping levels, band gap energy, etc) to the cell layers and to use the most recent material properties from the available literature. No p-n junction In$_x$Ga$_{1-x}$N solar cell has been demonstrated to date therefore it is not possible to match the predictions to real devices. Applying realistic cell parameters is currently the best method to measure the possible potential of In$_x$Ga$_{1-x}$N solar cells.
2.2 MEDICI Device Simulation Software

Medici is a 2-dimensional device simulator that models the electrical, thermal, and optical properties of semiconductor devices. The Taurus-Medici program is part of the Technology Computer-Aided Design (TCAD) software distributed by the Synopsys Corporation. Medici is frequently used to model MOS and BJT devices. A 2D non-uniform mesh grid is used that can model planar or nonplanar surface features. For each grid section Medici solves Poisson’s equations as well as the electron and hole continuity equations and predicts the two-dimensional distributions of potential and carrier concentrations at arbitrary bias conditions. The program can model several phenomenons such as recombination, photogeneration, impact ionization, band gap narrowing, band-to-band tunneling, mobility, and carrier lifetimes (Synopsis TCAD Medici user manual version 2001.4).

2.3 Identification of In\textsubscript{x}Ga\textsubscript{1-x}N Solar Cell Parameters

Material Properties. Table 2-1 lists the input parameter values for InN and GaN which are used in the Medici simulation. The appropriate references are listed for each input parameter and if no values are available in the literature then a realistic value was estimated or assumed (values in italics). For example, no definitive p-type doping has been demonstrated for InN; therefore no hole mobility values have been published. It can, however, be estimated because mobility (μ) of a semiconductor is inversely proportional to the effective mass (m*) (Eq. 2-1),197

\[ \mu = \frac{q\langle\tau\rangle}{m^*} \]

where \( \langle\tau\rangle \) is the average time between collisions and q is the unit of charge. The electron effective mass of GaN (0.22m\textsubscript{o}) \(^{198} \) is larger than the effective mass of InN (0.07m\textsubscript{o}), \(^{41} \) where m\textsubscript{o} is the electron rest mass (9.11 x 10\textsuperscript{-31} kg). Prior to the InN band gap controversy, theoretical calculations were performed that showed the hole effective mass of InN was approximately the
same or less than the values for GaN (for light hole and heavy holes).\textsuperscript{199} It has been suggested that the hole effective mass be revised (and decreased) due to the commonly accepted lower InN band gap energy value\textsuperscript{198}. From the available theoretical calculations it is safe to assume that the hole mobility of InN is the same or slightly greater than the value obtained experimentally for GaN (200 cm\textsuperscript{2}/V-s).\textsuperscript{200} For the simulations presented here a hole mobility of 200 cm\textsuperscript{2}/V-s was chosen for InN, although the real value is likely higher. A wide range of electron mobility data has been published for InN which ranges from 200 to 2700 cm\textsuperscript{2}/V-s depending on the type of deposition technique.\textsuperscript{31,41,42,58,201,202} High quality InN layers grown by MOCVD have electron mobilities close to 1000 cm\textsuperscript{2}/V-s, therefore this was the value used for the Medici simulations.

Optimization for the growth of InN thin films on c-Al\textsubscript{2}O\textsubscript{3} by MOCVD, can be found in Ref. 203. High quality single crystal InN films were grown on c-Al\textsubscript{2}O\textsubscript{3} substrates using substrate nitridation and a low temperature InN buffer layer, resulting in a XRD FWHM of 1339 arcsec.\textsuperscript{203} The absorption coefficient ($\alpha$) of this high quality InN film was measured (Figure 2-1). The absorption of InN ranges from $7 \times 10^4$ to $1.5 \times 10^5$ cm\textsuperscript{-1} in the incident energy range of 0.7 to 3.4 eV with an average value of $9 \times 10^4$ cm\textsuperscript{-1} (up to the band gap energy of GaN). The absorption dropped quickly to zero at an approximate band gap energy value of 0.65 eV (not shown in Figure 2-1). For the absorption measurements, an incandescent lamp inside a quartz tube was used as the illumination source and a diffraction grating was used to filter light into different spectral ranges. A Hitachi 330 spectrophotometer was used to detect the transmitted light. The absorption coefficient of GaN was measured by Muth \textit{et al.}\textsuperscript{204} with an average value of $1 \times 10^5$ cm\textsuperscript{-1}. For simplicity a common value for the absorption coefficient of $9.5 \times 10^4$ cm\textsuperscript{-1} was used for all In\textsubscript{x}Ga\textsubscript{1-x}N compositions.
The properties in Table 2-1 were varied as a linear function based on In$_x$Ga$_{1-x}$N composition, with the exception of the band gap energy. A variable band gap energy bowing parameter is used that has been determined by fitting data to several sets of In$_x$Ga$_{1-x}$N alloys. This bowing parameter is believed to be the most accurate because other bowing parameters are usually determined from limited composition ranges (i.e. either Ga-rich or In-rich compositions only). The equations determining the band gap energy and variable bowing parameter were previously shown (Eqs. 1-2 and 1-3).

**Illumination sources.** Terrestrial (AM1.5) and extraterrestrial (AM0) solar spectra were used as illumination sources for the In$_x$Ga$_{1-x}$N cells. The AM1.5 spectrum was simulated by using spectral irradiance values (as a function of wavelength) from the American Society for Testing and Materials reference spectrum (G-173-03). The AM0 spectrum was modeled by the Medici software by assuming black body radiation at a temperature of 5800K (Eq. 2-2).

\[
\Delta I = \left( \frac{R_S}{R_{SE}} \right)^2 \frac{2\pi h c^2}{\exp \left( \frac{hc}{kT} \right) - 1} \frac{\lambda^5}{\Delta \lambda}
\]

where $R_S$ is the radius of the sun ($7 \times 10^8$ m), $R_{SE}$ is the distance between the sun and the earth ($1.5 \times 10^{11}$ m), $T$ is the temperature of the black body, and $\lambda$ is the wavelength.

**Recombination Models.** The “CONSRH” and “AUGER” Medici recombination models are used to describe the recombination in the In$_x$Ga$_{1-x}$N layers. CONSRH refers to a concentration dependent Shockley-Read-Hall model, where the carrier concentration determines the carrier lifetimes and the probability for recombination and generation. The Shockley-Read-Hall model was developed in 1952 and used to describe the recombination and generation statistics for holes and electrons by using a distribution of trap states in the forbidden gap as well as kinetic transport models for electrons and holes. With the CONSRH model, Medici
determines a probability for recombination through trap states by predicting a distribution of trap states within the band gap. The AUGER model refers to Auger recombination, which is band to band recombination that occurs when two like carriers collide. When two electrons collide in the conduction band one carrier loses its energy and is recombined with a hole in the valence band, while the surviving carrier receives the energy released by recombination and becomes a higher energy electron. The excited electron subsequently loses its energy to lattice vibrations through collisions with the semiconductor lattice.\textsuperscript{197} Other than these two defect models, no specific defect levels or interface states were used in the simulation.

\textbf{2.4 Results}

\textbf{2.4.1 Single-Junction In}$_x$GaN\textsubscript{1-x} Cell Optimization

Cell parameters such as n-side thickness, p-side thickness, doping concentrations, and band gap energy were optimized to obtain the maximum efficiency of a single In$_x$Ga$_{1-x}$N p-n junction solar cell. The cell parameters were limited by design rules typically assigned to thin film single-junction solar cells. A fundamental design rule of thin film solar cells is that the thickness of the solar cell must be on the order of a few microns. The motivation for thin film solar cells is to obtain the best cell efficiency while keeping layers thin to reduce processing time and the cost of fabrication. Thin film silicon solar cell technologies are approximately 10 \( \mu \text{m} \) thick compared to the bulk cells which are 250 \( \mu \text{m} \) thick. When the cell layer thickness decreases light trapping techniques such as surface roughing and texturing are important to enhance absorption in the cell.\textsuperscript{208} This is done for Si solar cells because the absorption coefficient is low compared to other photovoltaic materials (Figure 2-2). More recently investigated photovoltaic materials such as CuInSe$_2$ (CIS) have a higher absorption coefficient over a broad range of wavelengths (Figure 2-2). Absorber layers fabricated with CIS then have lower thicknesses (\( \sim 2 \mu \text{m} \)).\textsuperscript{147} Since
In$_x$Ga$_{1-x}$N has a similar absorption coefficient the same maximum thickness design rule (approximately 2-3 $\mu$m thick absorber layers) was applied.

Typically p-n junction solar cells employ asymmetric doping between the p-type and n-type layers, which also differ in thickness. Generally the thickest layer ($\sim 2 \mu$m) is lowly doped ($10^{17}$ cm$^{-3}$) while the thinner layer is highly doped ($10^{20}$ cm$^{-3}$). It is also preferred that the thicker layer be p-type because of the lower mobility holes. Since minority carriers are collected instead of majority carriers, it is preferred to have higher mobility electrons traveling through the thickest part of the solar cell, thus requiring a thick p-type region. This is beneficial because a higher mobility means carriers are more likely to be collected before recombination can occur. The motivation for the asymmetric doping and thickness structure is to minimize the light absorption by free carriers while still producing a large depletion region to minimize diffusion lengths (available time for recombination) and increase charge carrier separation. Free carrier absorption reduces efficiency because this absorption does not generate electron hole pairs, but instead promotes carriers in the conduction and valence bands to higher energies, which is then lost in the form of heat.

It is assumed for In$_x$Ga$_{1-x}$N that p-type doping will be achieved though it is currently very difficult. For this work the acceptable p-type doping range is limited to $1 \times 10^{16}$ to $1 \times 10^{17}$ cm$^{-3}$. This doping range was chosen because similar controlled doping ranges have been exhibited for InP MOCVD. A comparison with InP must be made since no doping levels have been measured for p-type InN. InP is a III-V semiconductor with a band gap energy (1.34 eV) that is close to InN’s band gap energy (0.7-1.0 eV). The controllable n-type doping range of InN has been shown to be $1 \times 10^{18}$ to $1 \times 10^{20}$ cm$^{-3}$. From these doping characteristics it is ideal to use a low doped thick p-type In$_x$Ga$_{1-x}$N layer with a highly doped thin n-type In$_x$Ga$_{1-x}$N layer for
the structure of the solar cell (Figure 2-3). The anti-reflecting (AR) coating is used to prevent light reflection from the top surface of the semiconductor. Electrical connections to the cell are made by the back and front contacts, where the back contact could be metal contact to a p-type silicon substrate and the front contact is also a metal contact deposited in a finger arrangement to maximize light transmission. For the Medici simulation no exact substrate properties (such as those for Si) were included for the calculations, instead a generic contact resistance was used. The resistance for the back and top contacts are modeled by including a contact resistance of $2 \times 10^{-6}$ (Medici user manual version 2001.4) and $1 \times 10^{-4} \Omega \cdot \text{cm}^2$, respectively.

All single-junction simulations were p-In$_x$Ga$_{1-x}$N/n-In$_x$Ga$_{1-x}$N junctions and were modeled by 1D Medici simulations. Arbitrary doping and thickness conditions were initially set to determine the optimal band gap energy for the maximum single-junction cell efficiency. The thickness and doping level of the p- and n-type layers were then optimized, and then the band gap energy value was re-evaluated in an iterative process. When band gap energy values were varied during optimization the same band gap energy value was used for both p- and n-type layers. During all optimization steps only one variable (such as n-side thickness, p-side doping concentration, etc.) was varied while all other parameters remained fixed.

The initial absorber structure (Figure 2-4a) consisted of a homoepitaxial stack of a 300 nm n-type In$_x$Ga$_{1-x}$N layer with a doping concentration of $10^{19} \text{ cm}^{-3}$ and a 2 $\mu$m thick p-type In$_x$Ga$_{1-x}$N layer with a doping concentration of $10^{16} \text{ cm}^{-3}$. The efficiency calculations for the various steps of the optimization procedure are plotted in Figure 2-5. The efficiency of the initial structure was low with an efficiency of about 4%. As previously shown in Eq. 1-6 the efficiency is the maximum power produced by the solar cell divided by the inlet power (incident energy from the simulated solar spectrum). The dominant factor for the low efficiency of this cell is the
thickness of the highly doped n-type layer that gives strong free carrier absorption and recombination in this layer. The band gap energy of In$_x$Ga$_{1-x}$N for the initial structure was varied from 1.1 to 1.6 eV (Figure 2-5, represented by blue diamond symbols) and the maximum efficiency occurred at a band gap energy of 1.5 eV, which is close to the optimal ideal band gap energy of approximately 1.4 eV.$^{145}$

In the next stage of optimization, the thickness of the n-type layer was varied (at a constant band gap energy value of 1.5 eV). A reduction from 300 to 25 nm produced a significant increase in the efficiency due to reduced free carrier absorption and carrier scattering (square symbols in Figure 2-5). A further increase in efficiency is obtained when a linear graded carrier concentration in the n-type layer is used instead of a uniform doping profile (triangle symbols in Figure 2-5).

The p-side doping concentration was varied from $10^{16}$ cm$^{-3}$ to $10^{17}$ cm$^{-3}$ and the best cell efficiencies were obtained at a doping concentration $10^{17}$ cm$^{-3}$. The doping concentration of the p-type layer did not exceed $10^{17}$ cm$^{-3}$ due to the previously assumed design rules. Finally the absorption coefficient of In$_x$Ga$_{1-x}$N is sufficiently high that increasing the p-side thickness will not provide any significant improvement in efficiency, therefore the thickness of the p-side layer was decreased to determine the reduction in efficiency. When the p-side thickness is reduced from 2 to 1.5 to 1 μm the change in efficiency with respect to the 2 μm thickness is -0.21% (1.5 μm) and -0.62% (1 μm). For the purposes of this study a p-side thickness of 2 μm was used in order to obtain the maximum efficiencies possible, however it can clearly be seen that material processing times can be significantly reduced (for absorber layer growth) with only a minimal loss in efficiency. Also, adding thickness to the p-side layer will only increase the series resistance, leading to a decrease in voltage.
The maximum efficiency band gap energy was re-evaluated using the refined absorber layer structure (Figure 2-4b). A plot of the cell efficiency versus band gap energy for both AM0 and AM1.5 illumination is shown in Figure 2-6. The maximum calculated efficiency was obtained at a band gap energy of 1.44 eV for both AM0 and AM1.5 illumination. Plots of the cell power versus load and J-V curves for AM0 and AM1.5 are shown in Figures 2-7 and 2-8, respectively, and the cell characteristics (J_{sc}, V_{oc}, maximum power, FF, and collection η) are listed in Table 2-2. Both illumination conditions show similar values for the fill factor (86%) and the efficiency is slightly higher for the AM1.5 (16% compared to 15.3% for AM0). The highest collection efficiency is obtained for the intermediate band gap energy values tested and that the efficiency decreases for large or small band gap energy values (Figure 2-6). As the band gap energy increases the voltage of the solar cell will increase, however the solar flux decreases at these higher band gap energies (Figure 1-19). As the band gap energy of the solar cell increases all the light energy below the cell band gap energy cannot be collected. This creates a trade off between band gap energy and the available light energy for collection, which is why a maximum efficiency is obtained at a band gap energy value of 1.4-1.5 eV.

It is difficult to assess the validity of these simulations because no p-n In_{x}Ga_{1-x}N solar cells have been fabricated. The In_{x}Ga_{1-x}N simulations presented here were compared to copper indium gallium diselenide (CIGS) Medici simulations that use the properties that are measured for real CIGS solar cell devices, such as absorption coefficients, layer thicknesses, and doping concentrations. Comparing these two materials is ideal because both materials are thin film absorber structures with similar absorption coefficients. Both simulated solar cells were assigned a band gap energy of 1.24 eV and illuminated with AM0 light. At this band gap energy value the efficiency of the CIGS devices was 16% (FF = 73.8%) and the In_{x}Ga_{1-x}N cell had an
efficiency of 14.6% (FF = 83.8%). Current laboratory best efficiencies for CIGS are 19.5% while larger scale module efficiency range from 13 to 15%. The Medici solar simulator in conjunction with the recombination models used produces cell efficiencies in between the best laboratory cells and module efficiencies. The difference in FF was attributed to a CdS buffer layer and ZnO transparent conducting oxide (TCO) layer, which was not present in the InₓGa₁₋ₓN structure. No p-n InₓGa₁₋ₓN solar cells have been fabricated to date, however, this comparison was used to validate the model used for the Medici InₓGa₁₋ₓN simulations. As previously mentioned the InₓGa₁₋ₓN cell efficiencies could be improved by increasing the level of p-type doping which would provide similar or higher efficiency values as CIGS. However, the doping levels were capped at lower levels to represent anticipated near future InₓGa₁₋ₓN p-type doping capabilities. The same recombination models and contact resistances were used for the CIGS simulation for accuracy in the comparison.

2.4.2 Multi-Junction InₓGa₁₋ₓN Solar Cells

Multi-junction InₓGa₁₋ₓN solar cells were next simulated using the refined single-junction solar cell structure previously described as a starting point. Two, three, four, and five solar cell junctions were modeled. The p- and n-side thickness of each p-n junction remained fixed at 2 μm and 40 nm, respectively, for each absorber layer simulated. It was previously assumed that the achievable levels of p-type doping for InₓGa₁₋ₓN are much below degenerate doping levels. For this reason the solar cell junctions must be connected in a mechanical stack arrangement instead of monolithically using tunnel junctions. It is possible, however, that an alternative material system could be used for the tunnel junction. Each layer of the mechanical stack multi-junction cell is simulated separately thus requiring two connections per cell in the stack.

The efficiency of each multi-junction solar cell is simply the summation of each individual junction within the cell, with only the spectrum of the incident radiation changing, depending on
the characteristics of the cell above it. The same approach is used for determining the cell open
circuit voltage. A plot of the solar cell efficiency and open circuit voltage is shown in Figure 2-9
as a function junction number. The optimized p-n junction band gap energy values for each
multi-junction cell are shown in Table 2-4. The efficiency increases from 15.4% for a
single-junction cell to 27.4% for a five junction solar cell (Figure 2-9). These solar cell
efficiencies are slightly less than current III-V space solar cells produced by Spectrolab© based
on GaInP2/GaAs/Ge cells, which have efficiencies up to 28.3%, which use three cell junctions
(Spectrolab Inc, Ultra Triple Junction Space Solar Cell data sheets,

For these simulations conservative estimates were made for the structure of the p-n
junction absorber so it is not surprising that the efficiencies are lower. It was also assumed that
no light greater than the band gap energy of a specific junction was allowed to transmit to
subsequent junctions. Other researchers have simulated InxGa1-xN solar cells by applying a less
constrictive model to the cell parameters and have predicted efficiencies of 39% for a five
junction monolithic cell under AM1.5 illumination. Therefore, InxGa1-xN multi-junction solar
cell absorbers have been predicted to reach similar efficiencies as the current best cells in
production even after assigning a constrictive model to the simulations. There is also potential
for obtaining much higher efficiencies if InxGa1-xN absorber layers can be grown with superior
material properties.

2.4.3 Phase Separation in InxGa1-xN Solar Cells

2.4.3.1 Effect on single-junction cells

Since phase separation is known to occur in InxGa1-xN alloys it is important to assess how
solar cell characteristics might be affected. Upon initial inspection it is not clear how phase
separation will affect cell characteristics because there are several carrier dynamics to consider
when a solar cell is illuminated. For example, consider a uniform direct band gap energy semiconductor p-n junction that is connected to an external circuit. Electron-hole pairs are created when the p-n junction is illuminated with photon energy greater than the band gap energy of the semiconductor (Figure 2-10). When photons with energy much greater than the band gap energy are absorbed then electrons can be promoted high into the conduction band (Figure 2-10). The excess absorbed energy can be transferred to either of the two bands (or both), but typically the majority of the excess energy is transferred to the band with the smaller carrier effective mass.\(^{215}\) The p-type In\(_x\)Ga\(_{1-x}\)N region is the bulk of the solar cell absorber and the electrons have the smallest effective mass, therefore the majority of the energy is transferred to the conduction band (Figure 2-10). The energetic electron is called a hot electron because the electron temperature \((T_e)\) is higher than the semiconductor lattice temperature \((T_0)\). Typically this energetic electron loses its energy through a series of phonon scattering events within the semiconductor lattice, where the electron relaxes to the band edge with an electron temperature \(T_0\). The time constant \((\tau)\) for hot electron relaxation to the band edge is on the order of picoseconds\(^{216,217}\) while band to band recombination is on the order of microseconds.\(^{207}\)

Now consider an In\(_x\)Ga\(_{1-x}\)N p-n junction which contains phase segregated regions of In\(_y\)Ga\(_{1-y}\)N where \(x > y\). This structure forms an In-rich In\(_x\)Ga\(_{1-x}\)N matrix with Ga-rich precipitates (Figure 2-11). A representative band diagram is shown in Figure 2-12 for the matrix and precipitate in the p-type region of the p-n junction. A “type I” band offset applies to InN/GaN interface where the valence and conduction band edges of InN lie within the band edges of GaN.\(^{218}\) There is a greater band gap discontinuity in the conduction band \((\Delta E_c \sim 1.7 \text{ eV})\) than the valence band \((\Delta E_v \sim 1 \text{ eV})\), however there is still some debate about the exact offset values.\(^{42,122,219,220}\) Minority carriers (electrons) in the phase-separated structure that are
generated under illumination will be accelerated towards the n-type region, assuming that this region is within the depletion region of the junction. This type of phase-separated structure will be beneficial for the generation of hot carriers (compared to carriers generated in the matrix) since the band gap energy of the precipitates are greater than the matrix. If it is assumed that the hot carriers generated in the precipitates quickly relax to the band edges of the matrix before being collected by external contacts then the efficiency of the solar cell will simply take on the electrical characteristics of the matrix material. The efficiency of a phase-separated solar cell might be slightly reduced due to an increased transit time around the wider band gap energy regions, resulting in a higher probability of recombination. Regardless of a slight decrease in efficiency a single-junction phase-separated solar cell should closely model a uniform solar with the same band gap energy and doping characteristics as the matrix material in the phase-separated solar cell. This predicted result is based on the assumption that all hot carriers are relaxed before being collected.

If it is assumed that hot carriers are allowed to remain hot and this energy can be collected without relaxing to the band edge of the matrix then the efficiency of a phase-separated solar cell can be increased compared to a uniform single-junction solar cell. For this situation a device structure was assumed to contain an In-rich In$_x$Ga$_{1-x}$N matrix with a band gap energy of 1.0 eV and precipitate phase with a band gap energy of 2.0 eV. The overall thickness of the cell was approximately 2 μm and the same doping profiles were used as the previously optimized single-junction cell. The precipitate volume fractions were varied from 0.1 to 0.25 for the phase-separated In$_x$Ga$_{1-x}$N solar cells, assuming a uniform distribution of precipitates. The matrix and precipitate band gap energy values were assigned because experimental compositions (from XRD) corresponding to these band gap energies were seen for phase-separated In$_x$Ga$_{1-x}$N
thin film samples. No experimental evidence has been determined for the volume fraction of the precipitates therefore these values were assumed. For these simulations hot carriers were allowed to remain hot and be collected at their hot energy and it was assumed that no increased recombination occurred due to increased transit time around the wide band gap energy precipitates. It was also assumed that hot carriers were only contributed from the wider band gap energy phase-separated regions. As expected the maximum efficiency occurred at the highest volume fraction of precipitates because more hot carriers were produced and the cell characteristics are shown in Table 2-3. Illumination from both AM0 and AM1.5 produced efficiencies of 19% for a precipitate volume fraction of 0.25. This is an impressive result for a single-junction solar cell since the efficiency increased 3% compared to a uniform structure, however this result assumes that the hot carriers do not relax from their elevated state.

In certain cases it is safe to assume that some carriers can remain hot because the energy bands are capable of sustaining the extra energy. For example in semiconductors majority carriers can relax back to the band edge while minority carriers remain hot.\(^{221}\) This situation can be appropriately applied to the 2 \(\mu\)m p-type In\(_x\)Ga\(_{1-x}\)N absorber layer, where the majority of light absorption takes place. As previously mentioned, the majority of energy is transferred to the band with the smaller effective mass which is the conduction band and the electrons are also the minority carriers in the p-type region. These conditions are ideal for maintaining hot electrons in the solar cell. However, even if the minority carrier electrons can remain hot significant phonon scattering will likely occur at the metal contact and cause the hot electrons to relax to the band edge. Other researchers have suggested wide band gap energy semiconductors with very narrow band widths (\(\approx kT_e\)) as contacts, which would allow for isentropic cooling of hot electrons.\(^{222}\) The voltage for this type of cell would be determined by the summation of the free energy
difference between each hot electron hole pair. This is an attractive approach, however, not practical for real devices due to the assumptions that must be made for the isentropic contacts.

Another potential increase in cell efficiency that can be applied to phase-separated solar cells is the generation of more electron hole pairs through impact ionization. Impact ionization occurs when an electron is accelerated to the point where it collides with an atom in the lattice and the energy transfer frees a bound electron, creating an electron hole pair.\textsuperscript{197} When high electric fields are present impact ionization leads to carrier multiplication (avalanching) that can cause semiconductor devices to fail (breakdown). This effect would be beneficial for solar cells because the increased carrier generation would lead to an increased current. An impact ionization model from the Medici simulation program was applied to the same phase-separated solar cell structure used for modeling the hot electrons. The results revealed that there was little to no change in the device efficiency due to impact ionization. Since impact ionization occurs most frequently at high electric fields it is likely that the built in bias in the solar cell device is too low to accelerate carriers enough to ionize atoms in the lattice.

\textbf{2.4.3.2 Effect on multi-junction solar cells}

A phase-separated solar cell structure could potentially have negative effects on the efficiency of a multi-junction absorber structure. A lower efficiency is possible as a result of the reduced absorption of light in the precipitate regions of bottom cells because high energy wavelengths will have already been absorbed. This will essentially create optically transparent regions which will not produce carriers. Efficiency reduction due to phase separation will become more pronounced when the number of junctions is increased because the band gap energy values are precisely tuned for certain wavelengths. If these light wavelengths are absorbed before reaching the appropriately designed cell then inactive areas (dead volumes) are produced in the cell.
To show how a two junction solar cell can be unaffected by phase separation consider a top absorber layer with a matrix band gap energy of 1.8 eV (with a higher band gap energy precipitate phase) and a bottom absorber layer with a matrix band gap energy of 1.0 eV. As long as the precipitate band gap energy in the bottom cell has a band gap energy below 1.8 eV then the cell characteristics will be unaffected. The negative effects of phase separation in multi-junction solar cells can be avoided by making cell layers sufficiently thick to compensate for any inactive area in the absorber layers. Previous single-junction results show that there is no significant change in absorber efficiency when the p-side thickness is reduced from 2.0 to 1.0 μm. This indicates that the majority of the absorption takes place in the first μm of the p-type layer and that the additional micron just assures that all of the light is absorbed. If it is assumed that 30% (by volume) of a phase-separated solar cell is made up of wide band gap energy (optically inactive) areas, then absorption will be limited to 70% of the solar cell material. If a 2 μm absorber layer thickness is used then there will be approximately 1.4 μm of active area. This thickness should be sufficient for absorbing the majority of incident light on the solar cell and the only expected reduction in efficiency is attributed to increased recombination, due to longer transit times for carriers around the inactive regions.

Wider band gap energy junction layers are important for obtaining high efficiency multi-junction solar cells. For example the largest band gap energy of the five junction solar cell previously simulated was 2.6 eV. To achieve these wider band gap energies more gallium must be incorporated into In$_x$Ga$_{1-x}$N. When the alloy composition becomes Ga-rich then it is likely that In-rich segregated phases will form, which will have a smaller band gap energy then the Ga-rich matrix. These smaller band gap energy precipitates will trap carriers, leading to more recombination and a reduction in collection efficiency (Figure 2-13). Recombination in the
narrow gap precipitate region can lead to light emission which can be re-absorbed by junctions further down the cell. However, not all recombination will lead to the production of light and this is not an efficient way to collect the light energy because the solar cell takes high energy light and converts it to a reduced amount of lower energy light. Therefore phase separation in the form of smaller band gap energy precipitates in a wide band gap energy matrix will lead to a reduced efficiency. It is important to mention that the probability of phase separation is reduced as the In composition decreases far below 50%, therefore the negative effects of phase separation for a multi-junction solar cell is limited to a small compositional range ($0.5 \leq x \leq 0.3$).

## 2.5 Conclusions

In this solar cell modeling approach, conservative cell properties were assigned to absorber layers to anticipate efficiency of In$_x$Ga$_{1-x}$N-based solar cells. The main assumption of this model is that low p-type doping capabilities will be achieved for In-rich In$_x$Ga$_{1-x}$N. Single-junction simulations revealed that the optimal band gap energy for both AM0 and AM1.5 illumination conditions is 1.44 eV, yielding an efficiency of 15.3% and 16%, respectively. The structure for the refined single-junction was a 40 nm n-type layer with a graded carrier concentration of $1 \times 10^{18}$ to $1 \times 10^{20}$ cm$^{-3}$ on top of a 2 μm thick p-type layer with a uniform carrier concentration of $1 \times 10^{17}$ cm$^{-3}$. Multi-junction solar cells that were connected in a mechanical stack arrangement were simulated using the same structure as the refined single-junction solar cell. The maximum efficiency (27.4%) was obtained for a five junction In$_x$Ga$_{1-x}$N solar cell, which is comparable to current III-V solar cells based on Ga$_x$In$_{1-x}$P/GaAs/Ge. Comparing the conservative efficiency estimates with other simulation approaches shows that the predicted efficiency for a five junction In$_x$Ga$_{1-x}$N cell can range from 27-39%. The impressive upper limit can only be achieved if material growth of In$_x$Ga$_{1-x}$N progresses to achieve the optimum properties required for these cells. If the lower of the two cell efficiencies is only possible, as
assumed in this simulation, then the efficiency is still close to the best solar cells currently available.

The effect of phase separation which occurs in In\textsubscript{x}Ga\textsubscript{1-x}N was also assessed to determine the positive or negative effects on cell efficiency. For a single-junction solar cell, phase separation could theoretically have a positive effect through the efficient generation of hot electrons, however, it is mostly likely that phase separation will have a negligible effect on single-junction cell efficiency. The refined In\textsubscript{x}Ga\textsubscript{1-x}N absorber structure presented here was shown to be ideal for sustaining hot electrons. Even if the hot electrons do not relax, phonon scattering at metal contacts would prevent the extra energy from being collected. Methods for collecting hot electrons have been suggested by other researchers, however, these methods are not practical. If an absorber layer phase separates, then the solar cell will take on the efficiency characteristics of the lowest band gap energy material, which is assumed to be the majority component or matrix material in an In-rich In\textsubscript{x}Ga\textsubscript{1-x}N alloy. The possibility of impact ionization was also considered for phase-separated solar cells, however, no increase in efficiency was produced most likely due to the lack of a high electric field in the semiconductor depletion region.

Single-junction solar cells are predicted to practically unaffected by phase separation unless the gallium composition becomes greater than 50%, leading to the formation In-rich In\textsubscript{x}Ga\textsubscript{1-x}N precipitates. These smaller band gap energy precipitates will likely form carrier wells where recombination will occur. Typically higher gallium contents are required for the top absorber layers in multi-junction cells which require a wide band gap energy. For this reason it is believed that phase separation could reduce the efficiency of top junctions in multi-junction
cell when gallium rich In$_x$Ga$_{1-x}$N alloys make up the matrix phase, however, only in a small compositional range.

Figure 2-1. Absorption coefficient of an InN thin film grown by MOCVD (Ref. 203).

Figure 2-2. Absorption coefficient as a function of wavelength for several photovoltaic semiconductors (Ref. 140).
Figure 2-3. Proposed single-junction In$_x$Ga$_{1-x}$N solar cell which has been modeled by Medici.

Figure 2-4. Solar cell structures used in single-junction solar cell simulation. A) Initial structure used as a starting point for the simulations. B) Absorber structure after refinement of cell parameters.
Figure 2-5. Single-junction absorber optimization steps.

Figure 2-6. Simulated solar cell efficiency vs. band gap energy of the refined In$_x$Ga$_{1-x}$N cell structure for AM0 and AM1.5 illumination.
Figure 2-7. Power vs. load plots for the refined solar cell structure for AM0 and AM1.5 illumination.

Figure 2-8. Current density vs. voltage curves for the refined solar cell structure under AM0 and AM1.5 illumination.
Figure 2-9. The efficiency and open circuit voltage as a function of junction number for multi-junction In$_x$Ga$_{1-x}$N solar cells.

Figure 2-10. Energy band diagram showing the generation of electron-hole pairs and hot carriers from incident light energy, adapted from Ref. 197.

Figure 2-11. Phase-separated In$_x$Ga$_{1-x}$N p-n junction showing Ga-rich In$_x$Ga$_{1-x}$N precipitates (green circles) in an In-rich In$_x$Ga$_{1-x}$N matrix (yellow bulk).
Figure 2-12. Corresponding band diagram from the p-type region in Figure 2-11 showing the In-rich In$_{x}$Ga$_{1-x}$N matrix and the Ga-rich precipitate (ppt).

Figure 2-13. Band diagram showing trapping of carriers and recombination in narrow band gap energy precipitates (ppt) in the wider band gap energy Ga-rich In$_{x}$Ga$_{1-x}$N matrix.

Table 2-1. The GaN and InN material parameters used in the Medici simulations. Estimated parameters in italics (Ref. 42$^a$, 47$^b$, 200$^c$, 219$^d$, 220$^e$, 223$^f$, 224$^g$, 225$h$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Band gap energy (eV)</th>
<th>Electron affinity (eV)</th>
<th>Dielectric constant</th>
<th>Valence band density of states ($N_v$, cm$^{-3}$)</th>
<th>Conduction band density of states ($N_c$, cm$^{-3}$)</th>
<th>Electron mobility (cm$^2$/V-s)</th>
<th>Hole mobility (cm$^2$/V-s)</th>
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<tr>
<td>GaN</td>
<td>3.46$^c$</td>
<td>4.1$^d$</td>
<td>8.9$^b$</td>
<td>4.62 x 10$^{19}$ g</td>
<td>2.23 x 10$^{18}$ g</td>
<td>1000$^b$</td>
<td>200$^c$</td>
</tr>
<tr>
<td>InN</td>
<td>0.70$^a$</td>
<td>5.8$^I$</td>
<td>15.3$^b$</td>
<td>5.20 x 10$^{19}$ g</td>
<td>9.15 x 10$^{17}$ g</td>
<td>1000</td>
<td>200</td>
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Table 2-2. Cell parameters for optimized cell structure with optimum band gap energy.

<table>
<thead>
<tr>
<th>Band gap (eV)</th>
<th>Illumination</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>Max Power (mW/cm$^2$)</th>
<th>Incident Power (mW/cm$^2$)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
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<tr>
<td>1.44</td>
<td>AM0</td>
<td>-24.95</td>
<td>0.918</td>
<td>19.72</td>
<td>128</td>
<td>86.09</td>
<td>15.36</td>
</tr>
<tr>
<td>1.44</td>
<td>AM1.5</td>
<td>-20.11</td>
<td>0.912</td>
<td>15.77</td>
<td>98</td>
<td>86.01</td>
<td>16.03</td>
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Table 2-3. Cell characteristics for simulations allowing hot carrier collection in phase-separated \( \text{In}_x\text{Ga}_{1-x}\text{N} \) solar cells.

<table>
<thead>
<tr>
<th>Matrix/Precipitate band gap energy (eV)</th>
<th>Precipitate volume fraction</th>
<th>Illumination</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( V_{oc} ) (V)</th>
<th>Max Power (mW/cm(^2))</th>
<th>Incident Power (mW/cm(^2))</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
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<td>1.0 / 2.0</td>
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<td>AM0</td>
<td>-39.16</td>
<td>0.593</td>
<td>18.93</td>
<td>128</td>
<td>81.53</td>
<td>14.75</td>
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<td>AM1.5</td>
<td>-30.20</td>
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<td>14.64</td>
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<td>AM0</td>
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</tr>
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<td>-30.22</td>
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<td>AM1.5</td>
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<td>18.69</td>
<td>98</td>
<td>83.97</td>
<td>19.00</td>
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Table 2-4. Characteristics of individual layers and overall cell for simulated multi-junction \( \text{In}_x\text{Ga}_{1-x}\text{N} \) solar cells.

<table>
<thead>
<tr>
<th>Junction number</th>
<th>Optimized band gap energy (eV)</th>
<th>Individual absorber ( V_{oc} ) (V)</th>
<th>Individual cell max power (mW/cm(^2))</th>
<th>AM0 Input power (mW/cm(^2))</th>
<th>Overall Voc (V)</th>
<th>Overall efficiency (%)</th>
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<tr>
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CHAPTER 3
GROWTH OF INDIUM NITRIDE AND INDIUM GALLIUM NITRIDE THIN FILMS BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION

3.1 Introduction

InN and In$_x$Ga$_{1-x}$N are less studied materials when compared to semiconductors such as Si or GaAs. Ga-rich In$_x$Ga$_{1-x}$N (0 ≤ x ≤ 0.3) alloys have become dominant materials as active layers in visible LEDs even though the mechanisms for light emission are not completely understood. InN and In-rich In$_x$Ga$_{1-x}$N have been studied far less than Ga-rich In$_x$Ga$_{1-x}$N primarily due to the few new device applications in the ~ 2 eV band gap energy range and the inability to grow high quality single crystal InN. More recently single crystal InN has been consistently reproduced by MBE and MOCVD growth techniques. Available high quality InN epitaxial layers have made it possible to investigate the properties of InN in greater detail. The band gap energy controversy has sparked more interest in InN and In-rich In$_x$Ga$_{1-x}$N films because it created new applications for these materials. These new applications include terahertz emitters and detectors as well as high efficiency solar cells.

Before these new applications can be exploited it would be helpful if the fundamental properties such as relationships between growth conditions and the resulting phase separation, film composition, doping level, and crystalline quality were established. In this chapter In$_x$Ga$_{1-x}$N phase separation will be discussed with respect to substrate material, buffer layer, growth temperature, and inlet composition (film composition).

Currently high quality Ga-rich In$_x$Ga$_{1-x}$N alloys are grown at high temperature (800 °C) for LED applications and In-rich In$_x$Ga$_{1-x}$N is being grown for the fundamental study of In-rich In$_x$Ga$_{1-x}$N alloy properties. A current summary of In$_x$Ga$_{1-x}$N alloy growth progress is reviewed in Section 1.1.3. It has been shown experimentally that approximately 30% indium can be incorporated into GaN at temperature above 700 °C. Low temperature growth by MBE has
demonstrated metastable In$_x$Ga$_{1-x}$N over the entire compositional range. No results have been published for In$_x$Ga$_{1-x}$N over the entire compositional range by MOCVD. Also, no analysis has specifically examined In$_x$Ga$_{1-x}$N growth parameters as they relate to phase separation. In general most literature work merely states that phase separation was noticed and no correlation to the growth conditions is made. This work aims to understand how changes in deposition temperature, substrate material, and, substrate pretreatments (including buffer layers) affect In$_x$Ga$_{1-x}$N phase separation.

3.2 Experimental Procedure

3.2.1 Substrate Preparation

InN and In$_x$Ga$_{1-x}$N thin films were typically deposited on c-Al$_2$O$_3$ substrates, however, a-Al$_2$O$_3$, GaN/c-Al$_2$O$_3$, Si (100), and Si (111) substrates were also included in selected runs. The GaN/c-Al$_2$O$_3$ substrates used in this study were obtained from Uniroyal Optoelectronics GaN (5 μm) grown by MOCVD on c-Al$_2$O$_3$. No chemicals were used to clean the GaN/c-Al$_2$O$_3$ surface and the substrates were cleaned with a high pressure nitrogen gun to remove any particles from the surface before loading. The sapphire and silicon substrates were cleaned in boiling trichloroethylene (TCE), acetone, and methanol each for 5 min to remove organic material. A high pressure nitrogen gun was used to quickly dry the substrates after removal from the methanol cleaning step.

3.2.2 The MOCVD Deposition Technique

Metal organic sources used in MOCVD are typically liquids, finely crushed solids, or dissolved in a solvent and are contained in stainless steel bubblers. The pressure and temperature of the bubblers is adjusted to control the partial pressure of the precursor species inside the bubbler. Adjusting the total pressure and flow rate of the carrier gas controls the transport to the reactor. This dilute stream of metal organic vapor and carrier gas is then mixed with the other
source materials, typically hydrides, and delivered to a substrate placed on a heated susceptor.
The susceptor is commonly heated by RF induction, radiative (lamp), or resistance heating. The
gaseous sources undergo complex homogeneous and heterogeneous reactions in the hot region at
and near the heated substrate to produce film growth.226,227

MOCVD reaction chambers are typically made of stainless steel or quartz and the shape of
the reactor is designed to produce laminar flow over the susceptor. Most MOCVD systems
operate at low pressure (50-200 Torr) because it reduces closed streamline flows which decrease
dead volumes or vortices. This type of growth technique is popular for III-V materials and is
typically used to grow epitaxial single crystal films, however, polycrystalline and amorphous
films can also be grown.226,227

**Reaction Chemistry for MOCVD GaN and InN.** The formation of GaN or InN on the
substrate surface from the reaction between the group III (TEGa or TMIn) and group V (NH₃)
sources. The overall reactions are given by Eqs. 3-1 and 3-2.

\[
(C_2H_5)_3Ga (g) + NH_3 (g) \rightarrow GaN (s) + 3C_2H_6 (g) \tag{3-1}
\]

\[
(CH_3)_3In (g) + NH_3 (g) \rightarrow InN (s) + 3CH_4 (g) \tag{3-2}
\]

A general reaction for GaN or InN is represented by

\[
R_3M + NH_3 \rightarrow MN (s) + 3RH (g) \tag{3-3}
\]

Where M = Ga or In, R = CH₃ or C₂H₅.228,229

This expression does not reflect the actual reaction pathways because the details are not very
well established and the available information suggests the reactions are complex. Jacko and
Price were the first to study the pyrolysis of TMIn and suggested the following mechanism.230

\[
In(CH_3)_3 \rightarrow In(CH_3)_2 + CH_3• \tag{3-4}
\]

\[
In(CH_3)_2 \rightarrow In(CH_3) + CH_3• \tag{3-5}
\]
In(CH₃) → In + CH₃•  \hspace{1cm} (3-6)

DenBaars et al.\textsuperscript{231} later studied the decomposition of trimethyl gallium in the growth of epitaxial GaAs and concluded the same mechanism as Jacko and Price. More recently the decomposition of TMIn was studied by in-situ Raman spectroscopy.\textsuperscript{232} The results of this study suggest several reaction intermediates appear during the decomposition of TMIn,

\begin{align*}
n\text{MMIn} & \leftrightarrow (\text{MMIn})_n \hspace{1cm} (3-7) \\
2\text{DMIn} & \leftrightarrow (\text{DMIn})_2 \hspace{1cm} (3-8) \\
\text{DMIn} + \text{MMIn} & \leftrightarrow \text{DMIn-MMIn} \hspace{1cm} (3-9) \\
\text{DMIn-MMIn} & \leftrightarrow \text{CH₃InCH₂} + \text{HInCH₃} \hspace{1cm} (3-10) \\
\text{TMIn} + \text{MMIn} & \leftrightarrow (\text{DMIn})_2 \hspace{1cm} (3-11)
\end{align*}

where MMIn is monomethyl indium and DMIn is dimethyl indium. The most energetically favorable intermediate was calculated to be (DMIn)\textsubscript{2} followed by the slightly less favorable production of DMIn-MMIn.

The decomposition of ammonia at high growth temperature is assumed to take place on the substrate surface or reactor walls to yield atomic nitrogen or a nitrogen containing radical. Thermodynamically it is known that NH\textsubscript{3} decomposes completely into N\textsubscript{2} an H\textsubscript{2} at temperatures above 300 °C. When temperature is below 650 °C and no catalyst is used, NH\textsubscript{3} decomposition is slow and strongly depends on growth conditions and reactor design.\textsuperscript{233} It is also believed that the removal of the first hydrogen bond is the rate limiting step in ammonia decomposition.\textsuperscript{228}

\[ \text{NH}_3 \ (g) \rightarrow \text{NH}_3-x \ (g) + x\text{H} \ (g) \hspace{1cm} (3-12) \]

From the reaction in Eq. 3-12 a possible growth mechanism for InN and GaN at a solid gas interface is,

\[ \text{M(CH}_3\text{) (s/g)} + \text{NH (s/g)} \rightarrow \text{M-N (s)} + \text{CH}_4 \hspace{1cm} (3-13) \]
where \( M = \text{Ga or In} \).

MOCVD growth is not an equilibrium process, therefore thermodynamics can only determine the overall driving force for the reaction and reactor kinetics or transport rates define the rate at which film growth will proceed. Thus the reaction pathways and rate constants, along with the flow velocities and temperature gradients near the substrate are very important. A schematic of the precursors at the solid-gas interface and boundary layer regions for the reaction of trimethyl gallium (TMGa) and ammonia to form GaN (Figure 3-1). A similar diagram is expected for TMIn and NH\(_3\) sources to form InN at the solid-gas interface. TMGa must diffuse through the boundary layer, possibly pyrolize, and then adsorb on to the substrate surface where the adsorbed Ga-containing molecule or atom reacts with ammonia that also diffused through the boundary layer with possible reactions (Figure 3-1). The growth rate of these MOCVD reactions is controlled by the reaction rate at low temperature and diffusion of the group III source though the boundary layer at higher temperatures where the reaction rates become high, since NH\(_3\) is usually in great excess. Adduct formation such as Ga(CH\(_3\))\(_2\)-NH\(_2\) can also be important for high temperature growth (Figure 3-1). The growth kinetics and the growth mechanisms that occur at the solid gas interface are not very well understood, however, this has not prevented empirical growth studies.\(^{228}\)

3.2.3 The MOCVD Reactor

MOCVD experiments were performed in a horizontal, low pressure (100 Torr), cold-walled quartz reactor with RF-inductive heating of a tilted graphite susceptor. This MOCVD system was originally designed by Nippon Sanso for low temperature GaAs growth, but has subsequently been modified for InN, GaN, or In\(_x\)Ga\(_{1-x}\)N growth.\(^{203,234}\) Solid trimethyl indium (TMIn, 99.9995%, Rhom and Haas Electronic Materials), liquid triethyl gallium (TEGa,
99.9995%, Rhom and Haas Electronic Materials), and ammonia (NH₃, 99.9999%, Air Products) are used as precursors with a nitrogen carrier gas (UF Microfabritech building LN₂ boil off).

The MOCVD reactor schematic and a photo are shown in Figure 3-2. Samples are loaded onto a quartz wafer tray and placed in a load-lock which is evacuated and purged 8 to 10 times to minimize oxygen contamination from reaching the reactor. A mechanical fork is used to load the wafer tray onto the susceptor before starting the reaction. During the experiment N₂ is delivered to the metal organic precursor bubbler, which is then combined with a dilution N₂ stream and the pure NH₃ stream, just before entering the quartz chamber. The metal organic precursor temperature is controlled by NESLAB RTE (Thermo Electron Corporation) refrigerated bath/circulators. In these studies, the susceptor temperature was in the range of 450-850 °C and the quartz wall was maintained at a constant 25 °C with cooling water. Downstream waste gases are pumped by a dry vacuum pump (BOC Edwards XDS 10) and removed through the Microfabritech exhaust system.

The growth parameters such as susceptor growth temperature, N/III ratio, substrate nitridation time and temperature, buffer layer material thickness, total flow rate and reactor pressure are chosen depending on the desired epitaxial layer properties. The N/III ratio is the inlet molar ratio of NH₃/TMIn (or NH₃/TEGa) and the N/III ratio is controlled by adjusting the flow rates of nitrogen through the TMIn (TEGa) bubbler and independently by the ammonia flow rate. Growth temperatures is controlled by a PID temperature controller (Gultan West 2070) that uses a quartz insulated thermocouple to measure the susceptor temperature and adjust the power of a Lepal T-15 RF generator. The thermocouple is located inside the center of the graphite susceptor, via a drilled hole in the susceptor.
3.2.4 In-Situ Sapphire Substrate Surface Treatment and Buffer Layers

In-situ pretreatments such as nitridation of sapphire substrates or the addition of a low temperature (LT) InN buffer layers are used for the growth of InN and In\textsubscript{x}Ga\textsubscript{1-x}N thin films. Nitridation of sapphire substrates is applied to grade the lattice mismatch between the III-nitride main layer and the sapphire substrate by forming an AlN nucleation layer.\textsuperscript{70} LT InN buffer layers have also been shown to improve subsequent film quality compared to samples without buffer layers.\textsuperscript{73,74} Aspects of substrate nitridation and buffer layers are discussed in greater detail in Section 1.1.3.

Sapphire substrates were nitridated under an ammonia flow (1600 sccm, 4 SLM N\textsubscript{2} dilution) at high temperature (850 °C) for duration of 15 min prior to growth. After nitridation the reactor was allowed to cool (in a low pressure N\textsubscript{2} atmosphere) to the appropriate growth temperature selected for buffer layer growth or the main layer growth. LT InN buffer layers were only used for some In\textsubscript{x}Ga\textsubscript{1-x}N samples because the primary focus of this study was not to produce high crystalline quality but to understand how phase separation is related to growth conditions. When used, LT InN buffer layers were grown for 15 min at a temperature of 450 °C and a N/III ratio of 50,000. MOCVD optimization of InN deposition temperature, N/III ratio, buffer layer temperature/duration, and substrate nitridation temperature/duration has been done elsewhere.\textsuperscript{203,234}

3.3 Results

3.3.1 Indium Nitride

3.3.1.1 Growth on silicon substrates

Silicon is widely used in the semiconductor industry and the integration of nitride-based devices with Si IC technology is a driver for using Si substrates. Si (111) substrates have a lattice mismatch of -8% with InN, which is less than nitridated Al\textsubscript{2}O\textsubscript{3} (AlN, 13%) and GaN
(11%), while Si (100) has a lattice mismatch of 35% with InN. InN thin films were grown on p-Si (100) and n-Si (111) substrates at 530 °C and an inlet N/III ratio of 50,000. Surface pretreatment conditions such as nitridation and the use of an InN buffer layer were varied to refine the growth conditions of InN on silicon substrates.

Growth of InN directly on silicon substrates can lead to growth of incomplete films or polycrystalline films with very small and broad XRD peak intensities. Standard TCE, acetone, and methanol chemical cleaning steps were used to clean the Si substrates prior to growth. Direct growth on Si (111) substrates without the use of a LT InN buffer layer or substrate nitridation forms an incomplete film of InN ($T_g = 530 \degree C$ and N/III = 50,000, Figure 3-3). When a LT InN buffer layer is used a continuous film is formed (SEM, Figure 3-4), however the resulting films is polycrystalline, as seen from the appearance of the (002), (101), and (102) reflections in the XRD pattern (Figure 3-5). InN is believed to be polycrystalline when grown directly on silicon substrates due to an amorphous SiNx layer that forms during the initial stage of growth from the exposure of Si to NH$_3$. InN is believed to be polycrystalline when grown directly on silicon substrates due to an amorphous SiNx layer that forms during the initial stage of growth from the exposure of Si to NH$_3$. The formation of SiNx can be suppressed by growing a protective non-nitride heterostructured buffer layer, such as GaAs followed by subsequent growth of InN, yielding a continuous and smooth surface morphology.

Intentional substrate nitridation to form a crystalline $\beta$-Si$_3$N$_4$ layer by reacting NH$_3$ with the silicon substrate at high temperature has also been tested. When brief substrate nitridation is used ($\leq 15$ min), however, it is likely that a silicon oxynitride (SiO$_x$N$_{1-x}$) forms instead of a pure $\beta$-Si$_3$N$_4$. This result has been shown by Kryliouk et al. using identical deposition equipment and substrate nitridation conditions. The formation of a silicon oxynitride intermediate layer has been shown to be an ideal method for producing single crystal GaN on silicon substrates. A TEM image of GaN/Si (111) shows a thin amorphous structure for the
silicon oxynitride layer (Figure 3-6). Details about the growth and characterization of the SiO_xN_{1-x} intermediate layer can be found elsewhere.\textsuperscript{234,238} This result encourages performing silicon substrate nitridation followed by growth of a LT InN buffer layer to grow single crystal InN on Si (111) and (100). The same sapphire nitridation step (850 °C, 1600 sccm NH_3 for 15 min) was applied to silicon substrates (as described for sapphire in Section 3.2.4), and InN was grown for 1 hr at 530 °C (N/III = 50,000). XRD patterns of InN on Si (111) and Si (100) are shown in Figure 3-7. Comparing the patterns for InN/Si (111) (Figures 3-5 and 3-7) it can be seen that the use of substrate nitridation produces a highly textured InN film with a preferred growth orientation in the [0001] direction and the InN (101) reflection can no longer be detected. When substrate nitridation and a LT InN buffer layer are used for InN growth on Si (100) only the InN (002) reflection is detected and no polycrystalline peaks appear. The Si (200) substrate peak occurs at a 2θ value which is close to the polycrystalline InN (101) peak, which can cause the polycrystalline InN peak to go unnoticed. Adding a slight tilt (3 or 4°) in the omega angle (normal to the film surface) during an XRD scan will cause the single crystal silicon peak to be undetected while the less crystalline InN remains unchanged. With the Si substrate peak removed, no polycrystalline InN (101) peak is detected (Figure 3-7). For the nitridated Si substrates, there is little difference in the magnitude of the peak intensities of the (002) reflection for InN/Si (111) and InN/Si (100) even though there is a large difference in lattice mismatch with respect to InN. The XRD peak intensity is strongly dependent upon the specimen interaction volume (film thickness and surface area) and the crystallinity of the film. The growth rate of InN/Si (100) was determined to be ~ 80 nm/hr from cross-sectional SEM (Figure 3-8) and a similar growth rate was found for InN/Si (111). Therefore the film thickness can be ignored as contributing factor to any difference in InN (002) peak intensity. Films were typically grown on
cut 10 x 10 mm² substrates, which eliminates any sample size affect on the XRD peak intensity. This result suggests that the oxynitride layer has more influence over the film crystallinity than the silicon substrate orientation. The intermediate SiOₓN₁₋ₓ layer was previously determined to have an amorphous structure,²³⁴ which may account for the small InN (002) peak intensities when grown on Si.

Even with the use of substrate nitridation the InN (002) peak intensities are relatively small compared to InN/c-Al₂O₃, grown under otherwise identical conditions and therefore the crystalline quality of InN/Si could be significantly improved. The growth rate of InN/c-Al₂O₃ is ~ 100 nm/hr and was previously determined for the same deposition equipment used in this study.²⁰³ Since InN has a similar growth rate and similar sample sizes (10 x 10 mm²) were tested, then the difference in InN (002) peak intensity can be attributed to a difference in crystalline quality. InN/Si was grown for two hr to account for any growth rate difference for c-Al₂O₃ and Si substrates, which again yielded a much larger peak for InN/c-Al₂O₃.

For this reason, InN thin films were grown on Si (111) substrates by using a hydride-MOCVD growth technique. In this technique, HCl reacts with the metal organic species (TMIn) to form volatile InCl, which then reacts with NH₃ to form InN. A more detailed description of the H-MOCVD deposition technique is given in Section 5.2.2. This technique is beneficial for growth because the presence of HCl cleans residual SiOₓ on the Si surface and takes advantage of the small lattice mismatch (~8%) between InN (002) and Si (111). The oxynitride cannot form because HCl reacts with SiOₓ to form volatile SiH₄Cl₄₋ₓ and H₂O. Other benefits of the H-MOCVD technique include the ability to grow InN at low N/III ratios due to preferential etching of In droplets by HCl.²³⁴ H-MOCVD growth of InN also allows for high growth rate of
InN without sacrificing growth quality, which would occur if a conventional MOCVD used a similar high concentration of reactants.

Thus InN growth on Si was attempted in a different reactor by H-MOCVD as described below. After standard chemical cleaning, the Si surface was cleaned in-situ (prior to growth) by annealing in a H₂ atmosphere for 10 min at 850 °C. The reactor was allowed to cool in a H₂ atmosphere to the buffer layer growth temperature of 450 °C. HCl gas was allowed to flow into the reactor for 2 min prior to buffer layer growth (450 °C) with no other source materials flowing to provide secondary cleaning of the silicon substrate. A LT InN buffer layer was grown (in N₂ carrier) for 15 min (N/In = 2,500 and 450 °C) followed by InN growth at 560 °C (N/In = 2,500) for 2 hr. When grown on Si (111) in the H-MOCVD system, InN is highly textured in the (002) direction and with a large and narrow peak intensity signifying increased crystalline quality compared to InN/Si (111) grown by conventional MOCVD (XRD, Figure 3-9). H-MOCVD InN/Si (111) grows in a columnar structure with a very rough surface where grain sizes range from 150 to 500 nm (SEM, Figure 3-10). It is suggested that the columnar structure is made up of vertical InN (002) columns since the XRD results show a highly textured film in the [0002] direction.

Another benefit of H-MOCVD besides increased crystalline quality is that the growth rate of InN (750 nm/hr) is an order of magnitude higher compared to traditional MOCVD (78 nm/hr). It must be noted that a significantly higher TMIn flow rate is used in the H-MOCVD (0.67 sccm) compared to conventional MOCVD (0.03 sccm). It is difficult to scale up a conventional MOCVD system to achieve this high growth rate because it would require an extremely large NH₃ flow rate (35 SLM) to maintain the required inlet N/III ratio of 50,000 for preventing indium droplet formation. The addition of HCl using the H-MOCVD system allows for a
moderate NH₃ flow rates of 1.7 SLM to be used. The results of energy dispersive spectroscopy (EDS) and Auger electron spectroscopy (AES) analysis confirmed that no chlorine was detected in the film (within the available detection limits, ~ 0.5-1 atomic %, Figure 3-11).

Growth of InN on Si substrates is desired for several reasons including the reduced cost of silicon, large area substrates, and future device integration. Substrate nitridation and the formation of a SiOₓN₁₋ₓ intermediate layer is shown to be critical to form highly textured InN (002) when grown on Si (111) and Si (100) by MOCVD. The amorphous SiOₓN₁₋ₓ layer, however, affects the ability to form high quality InN. H-MOCVD proves to be an ideal technique for growth of InN/Si (111) because the addition of HCl prevents the oxynitride from forming and the lattice mismatch remains at -8%. The low lattice mismatch produces a highly textured InN (002) film and a higher growth rate was possible with H-MOCVD at a low N/III ratio without the formation of indium droplets. This is a huge advantage compared to traditional MOCVD where InN is typically growth at N/III ratios of 50,000.

3.3.1.2 Film stability and aging

Long term film stability is important for future device integration of InN based materials. If InN is not stable in oxygen containing environments such as air then fabrication steps such as annealing of electrical contacts becomes more difficult. It has been suggested that oxygen is incorporated into InN films after air exposure at room temperature, for example sputtered InN films have been shown to incorporate oxygen into the grain boundaries of InN and form crystalline In₂O₃ phases at room temperature. This room temperature annealing process was determined over a period of months to years. To independently verify this room temperature annealing process, InN thin films were grown on a-,c-, and r-orientations of Al₂O₃ as well as Si (100) and Si (111) by MOCVD. For all orientations of Al₂O₃ and Si substrates, substrate nitridation and a LT InN buffer layer were used. Post growth characterization was done by XRD.
and then the samples were stored in air for a period of 12 to 15 months. After aging (i.e., room temperature annealing) in air the same samples were analyzed again by XRD (Figure 3-12). There is no evidence of In$_2$O$_3$ crystalline phase formation when InN samples (on c-Al$_2$O$_3$ or Si (100) substrates) are aged in air for periods exceeding one year (Figure 3-12). It is important to mention that amorphous oxide phases are undetectable by XRD. This analysis does not support the claim by Butcher and Tansley$^{50}$ that crystalline indium oxide phases can form in InN after room temperature aging. However, sputtered films were used in the reference case and MOCVD grown InN was used for this work. It is possible that grain boundaries play a role for oxygen incorporation into InN films. Sputtered films are polycrystalline which lead to a large number of grain boundaries and impurity diffusion occurs more rapidly through grain boundaries compared to the bulk for single crystal films.$^{239}$ No differences in In$_2$O$_3$ formation were noticed for single crystal InN (InN/c-Al$_2$O$_3$) and polycrystalline InN (InN/Si (100)), which differ by the amount of grain boundary densities and area available for oxide growth and oxygen transport. From this analysis it remains unclear how crystalline oxide phases could form in InN at room temperature.

From the results above, formation of crystalline indium oxides does not occur at room temperature to an extent detectable by XRD, at higher temperature, however, crystalline oxide phases are more likely to form. Yodo et al.$^{240}$ found that crystalline In$_2$O$_3$ (222) forms in InN upon annealing at 500 °C for 5 min in a N$_2$ atmosphere (1 atm). These MBE InN samples were deposited at 500 °C for a much greater time than the annealing time and no In$_2$O$_3$ XRD peak was evident in the as grown film. SIMS analysis determined a 1% residual oxygen concentration in the as-grown film. These MBE samples were deposited under In-rich conditions and therefore In-droplets formed on the surface. It was concluded that the indium droplets reacted with
oxygen to form amorphous indium oxides upon air exposure and these phases will crystallize after annealing at elevated temperature.

For comparison InN/c-Al2O3 substrates were grown by MOCVD using substrate nitridation and a LT InN buffer layer and then exposed to air. These samples were then aged for 6 months to ensure that sufficient time was given for oxygen to diffuse into the film. A high N/In ratio (50,000) was used for growth therefore no In droplets were present on the surface. After aging, InN was annealed in a low pressure (100 Torr) N2 atmosphere for 20 min at 500 °C, 15 min at 525 °C and 10 min at 550 °C. The as-grown samples are compared to the annealed samples (Figure 3-13). The In2O3 (222) peak occurs at $2\theta = 30.6^\circ$ and it is clear (Figure 3-13) that no crystalline indium oxide is formed when InN is annealed up to 550 °C in a low pressure N2 atmosphere. For all three annealing conditions the InN (002) peak intensity is increased when the same XRD setup was used, suggesting that the film crystallinity was improved. A slight narrowing ($\Delta$FWHM = -144 arcsec) of the InN (002) peak was found for annealed samples compared to the as-grown sample. From this analysis it can be determined that annealing in low pressure N2 atmospheres can prevent the formation of indium oxide crystalline phases in InN (without In droplets), even after exposure to air. These results also suggest that the growth of stoichiometric InN films is important for preventing the formation crystalline In2O3.

### 3.3.2 Indium Gallium Nitride

#### 3.3.2.1 Metastable In$_x$Ga$_{1-x}$N alloys over the entire range ($0 \leq x \leq 1$)

In$_x$Ga$_{1-x}$N alloys were grown on c-Al2O3 substrates without an InN buffer layer at 530 °C at varying composition over the entire compositional range ($0 \leq x \leq 1$). Each film has approximate thickness of 100 nm, based on previous growth rate analysis. typically a fixed deposition temperature is not used for growth over the entire compositional range because higher Ga compositions achieve better crystallinity at higher temperature. Low deposition temperature,
however, has been used to grow metastable In$_x$Ga$_{1-x}$N alloys by MBE over the entire compositional range. These metastable films have only been grown by MBE techniques and currently no evidence has been published for metastable In$_x$Ga$_{1-x}$N films grown over the entire compositional range by MOCVD.

In this work a low temperature approach was used to suppress phase separation. The In$_x$Ga$_{1-x}$N film composition was controlled by varying the inlet group III flux (TEGa or TMIn flow rate). The inlet flow ratio, TMIn/(TMIn + TEGa) or simplified as In/(In+Ga), is the molar ratio of the TMIn molar flow to the total inlet group III molar flow. The ammonia flow rate was adjusted to maintain a constant N/III ratio of 50,000 for each experiment. XRD patterns of pure InN, pure GaN, and seven different compositions of In$_x$Ga$_{1-x}$N are shown in Figure 3-14. The pure InN (002) reflection located at $2\theta = 31.4^\circ$ shifts to the right (towards the GaN (002) peak) as the flow ratio is changed to lower values (more Ga-rich) (Figure 3-14). Also, it is important to notice that there is no second reflection in the pattern that would suggest microscopic phase separation. These results are consistent with the hypothesis that a low growth temperature will suppress phase separation. This is the first time single phase deposition of In$_x$Ga$_{1-x}$N has been demonstrated over the entire compositional range using MOCVD. It is also evident that the low growth temperature significantly affects the crystalline quality, since high crystalline quality for GaN usually occurs at temperatures at or above 850 °C.

A table of inlet flow ratio and the corresponding film composition ($x$) as determined by XRD for each run, is shown in Table 3-1. Bragg’s law (Eq. 3-14) is used to determine the distance between atomic planes, d-spacing, by using the experimental 2$\theta$ values recorded for the In$_x$Ga$_{1-x}$N (002) peak at each flow ratio.

\[ n\lambda = 2d \sin(\theta) \]  

(3-14)
In the equation for Bragg’s law, \( n \) is an integer and \( \lambda \) is the wavelength of the incident X-rays (Cu\( K_a = 1.54056 \) Å). Using the d-spacing value calculated from Bragg’s law and the corresponding crystal plane indices, the a and c lattice parameters can be determined (Eq. 3-15). Simplifications of Eq. 3-15 are shown for \( \text{In}_x\text{Ga}_{1-x}\text{N} \) (002) and \( \text{In}_x\text{Ga}_{1-x}\text{N} \) (101) (Eqs. 3-16 and 3-17, respectively). The relationship between cubic indices and hexagonal indices are given in Eq. 3-18.

For hexagonal structures:  
\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \frac{l^2}{c^2} \]  
(3-15)

\( \text{In}_x\text{Ga}_{1-x}\text{N} \) (002):  
\[ \frac{1}{d^2} = \frac{l^2}{c^2} = \frac{4}{c^2} \quad \text{or} \quad c = \frac{2}{d} = \frac{4 \sin \theta}{n \lambda} \]  
(3-16)

\( \text{In}_x\text{Ga}_{1-x}\text{N} \) (101):  
\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2}{a^2} \right) + \frac{l^2}{c^2} \]  
(3-17)

Cubic \((h k l) \leftrightarrow \) Hexagonal \((h k i l)\), where \( i = -(h + k) \)  
(3-18)

The \( \text{In}_x\text{Ga}_{1-x}\text{N} \) composition approximately follows a linear dependence with a slope of one for all compositions tested (Figure 3-15). The compositional dependence shows a negative deviation \((x_{\text{film}} < x_{\text{inlet}})\) for \( \text{In}/(\text{In}+\text{Ga}) > 0.5 \) and a positive deviation \((x_{\text{film}} > x_{\text{inlet}})\) for \( \text{In}/(\text{In}+\text{Ga}) < 0.5 \). A similar linear dependence on composition has been shown by Matsuoka et al. for Ga-rich \( \text{In}_x\text{Ga}_{1-x}\text{N} \) alloys grown by MOCVD (Figure 1-11).\(^{12}\) The positive and negative compositional deviations can be explained by the suppression of InN decomposition by GaN coverage and surface site blocking by methyl radicals, respectively. It is know that InN is reaction limited at the low deposition temperature used (530 °C) due to decreased NH\(_3\) decomposition efficiency.\(^{241,242}\) Talaleav et al. studied kinetic effects limiting the growth rate of III-V compounds by MOCVD and concluded that the blocking of group III species by methyl radicals was a dominant mechanism for reducing the growth rate.\(^{243}\) In this case of \( \text{In}_x\text{Ga}_{1-x}\text{N} \) growth at
low temperature (530 °C), the addition of TEGa (for In/(In+Ga) > 0.5) is believed to reduce the growth rate of InN due to site blocking by Ga atoms and methyl radicals. This leads to a negative deviation from the linear relationship between composition and inlet flow ratio. As the inlet flow ratio becomes greater than 0.5 it is believed that surface coverage by GaN suppresses thermal decomposition of InN, which increases the solid indium composition in the film. The suppression of InN decomposition produces a positive deviation from the linear dependence of composition to the inlet flow ratio.

3.3.2.2 Effect of growth temperature on stability of In$_{0.8}$Ga$_{0.2}$N

To understand the temperature dependence on phase separation, In$_x$Ga$_{1-x}$N alloys were grown at a constant flow ratio (In/(In+Ga) = 0.8) and deposition temperature was varied in the range from 530 to 850 °C in 30 °C intervals. Films were grown on c-Al$_2$O$_3$ substrates without an InN buffer layer with an approximate thicknesses of 300 nm, as estimated by previous growth rate analysis. A constant N/III ratio of 50,000 was maintained at each growth temperature. A value of In/(In+Ga) = 0.8 was chosen for this study because phase separation is typically not seen with films grown at this inlet In fraction. As the indium inlet fraction decreases below 0.8 phase separation is more likely to occur. The results given in the previous section suggests that phase separation is suppressed when using a low growth temperature and it is postulated that phase separation would be more likely to occur at higher deposition temperature. At higher deposition temperatures Ga is more likely to incorporate into the solid solution due to the increased thermal decomposition of InN. This result has been verified experimentally (Figure 1-11) for a deposition temperature of 800 °C. Increasing the deposition temperature will change the In$_x$Ga$_{1-x}$N composition for the same In-rich flow condition used to grow stable In$_{0.8}$Ga$_{0.2}$N (at 530 °C). It is believed that higher deposition temperature will lead to phase separation since the Ga content will increase (at a constant inlet flow ratio), and the In$_x$Ga$_{1-x}$N
solid solution will approach unstable compositions \((x > 0.3)\). The inlet flow value of 0.8 was chosen as a base line to analyze the effect of temperature on phase separation, since it has been demonstrated to be stable at \(T_g = 530 \, ^\circ\text{C}\).

The majority of incident solar energy lies in the band gap energy range of 0.7 to 2.0 eV, therefore for solar cell device applications In-rich \(\text{In}_x\text{Ga}_{1-x}\text{N}\) compositions are desired. Generally it is desired to fabricate semiconductor layers with low defect density and high crystalline quality for electronic applications. High quality materials make it easier to control the device performance, and for solar cells the efficiency of a high quality device increases efficiency due to the more efficient collection of generated carriers. One way to increase \(\text{In}_x\text{Ga}_{1-x}\text{N}\) film quality is to increase the deposition temperature. This increases atom surface mobility and allows for atoms to find a lower free energy adsorption site leading to less defects and a higher degree of crystallinity. There is a trade off for increasing the \(\text{In}_x\text{Ga}_{1-x}\text{N}\) deposition temperature to achieve better crystallinity because higher temperature leads to more rapid InN decomposition. For this reason it is important to study the effects of crystalline quality of In-rich \(\text{In}_x\text{Ga}_{1-x}\text{N}\) alloys at elevated temperatures to predict the appropriate deposition temperature and the occurrence of phase separation.

\(\text{In}_x\text{Ga}_{1-x}\text{N}\) thin films were grown on nitridated c-\(\text{Al}_2\text{O}_3\) substrates without the addition of a LT InN buffer layer. It is possible for an InN buffer layer to influence phase separation by creating more lattice matched nucleation sites for InN deposition compared to GaN, therefore the buffer layer was omitted. Substrate nitridation occurred at 850 °C for 15 min as previously described in Section 3.2.4.

Several \(\text{In}_x\text{Ga}_{1-x}\text{N}\) thin films were grown with a constant inlet flow ratio of \(\text{In}/(\text{Ga}+\text{In}) = 0.8\) at 530, 560, 590, 620, 650, 680, 710, 740, and 770 °C and characterized by
XRD (Figure 3-16). InN (530 °C) and GaN (850 °C) samples grown with the same sequence are included as a reference (Figure 3-16). At first glance these XRD patterns seem complex, however, the peaks can be systemically separated to understand the phase separation that occurs at different growth temperatures. It is noted that InN thin films that are grown on c-Al$_2$O$_3$ substrates without the use of LT InN buffer layers typically produce polycrystalline films, due to the large lattice mismatch between the substrate and thin film. Reflections from other orientations such as InN (100) and InN (101) can occur at $2\theta = 28.99^\circ$ and $33.18^\circ$, respectively. Examining the XRD pattern for pure InN (Figure 3-16), a peak is evident at $2\theta = 33.2^\circ$, consistent with a small amount of InN (101). A similar result is noticed for In$_x$Ga$_{1-x}$N grown at 530 °C, where In$_x$Ga$_{1-x}$N (100), In$_x$Ga$_{1-x}$N (002), and In$_x$Ga$_{1-x}$N (101) peaks are observed at $2\theta = 29.89^\circ$, $31.87^\circ$ and $33.93^\circ$, respectively (Figure 3-16). The peak intensity ratios indicate that the film is highly textured In$_x$Ga$_{1-x}$N (002). It is important to acknowledge the presence of polycrystalline peaks, especially In$_x$Ga$_{1-x}$N (101) peaks, because they can be misinterpreted as Ga-rich In$_x$Ga$_{1-x}$N (002) since the range of possible $2\theta$ values for the solid solution contains the reflections of the other planes.

The most important region to analyze lies between the InN (002), $2\theta = 31.4^\circ$ and the GaN (002), $2\theta = 34.6^\circ$ vertical lines (Figure 3-16). This is the entire range where In$_x$Ga$_{1-x}$N (002) peaks are expected. The peaks to the right of GaN (002) correspond to the c-Al$_2$O$_3$ substrate and are labeled as such. The XRD peaks close to the InN (002) reflection at $2\theta = 31.4^\circ$ are In-rich In$_x$Ga$_{1-x}$N (002) phase while the peaks closer to the GaN (002) $2\theta$ values (34.6°) are either Ga-rich In$_x$Ga$_{1-x}$N (002) or In-rich In$_x$Ga$_{1-x}$N (101) peaks. To clarify, it is possible that In$_x$Ga$_{1-x}$N (100) reflections can also appear close to the $2\theta$ value of InN (002), $2\theta = 31.4^\circ$, if the
Ga content is sufficiently high. These (100) reflections are not likely to be confused with (002) reflections because the intensity ratio is significantly higher for the (002) reflection.

In$_x$Ga$_{1-x}$N thin films grown at 530 °C do not show microscopic phase separation (Figure 3-16), which is consistent with the results discussed in Section 3.3.1. When the deposition temperature is increased, peak splitting occurs which is direct evidence for phase separation in the film. Separate In$_x$Ga$_{1-x}$N (002) peaks at different values of 2θ (composition) are resolved for deposition temperature in the range 560 to 620 °C. In the temperature range from 650 to 680 °C the XRD peaks broaden, making it more difficult to resolve individual peaks. At deposition temperature of 710 °C or above, specific peaks are again easier to resolve and phase separation occurs with two very different compositions. Table 3-2 lists the peak positions and corresponding In$_x$Ga$_{1-x}$N composition(s) (as determined by XRD) for each deposition temperature.

It is difficult to compare the effect of deposition temperature on film crystalline quality when XRD data is plotted on a logarithmic scale (Figure 3-16). For this reason the magnitude of the In$_x$Ga$_{1-x}$N (002) peak intensity was plotted for each deposition temperature (Figure 3-17). Each experiment used the exact same flow conditions and the sapphire substrates were the same size, therefore an increase in the XRD peak intensity can be attributed to an increase in film crystallinity or structural quality. It is also possible that higher temperatures could increase the growth rate and produce higher XRD peak intensities due to thickness changes. Adachi et al. found that the MOCVD InN growth rate increased over the temperature range of 500-620 °C when the TMIn supply was constant.246 The growth rate, however, cannot be the only contributing factor the XRD peak intensity since InN film decomposition also occurs in this same temperature range.
The stable In$_x$Ga$_{1-x}$N film grown at 530 °C has a low XRD peak intensity (Figure 3-17). The crystallinity increases significantly when the deposition temperature is increased to 560 °C, which is attributed to a reduction in strain since the film becomes phase separated and slight increase in growth rate. It is also possible that the higher temperature increases surface atom mobility leading to better crystallinity. No significant decomposition occurs at 560 °C and other researchers grow pure InN by MOCVD at this temperature.\textsuperscript{74,247,248}

Since many factors contribute to the XRD peak intensity, the FWHM of the In$_x$Ga$_{1-x}$N (002) peaks are plotted as a function of deposition temperature for 530, 560, 590, and 620 °C (Figure 3-18). Phase separation is noticed for the three highest temperatures (Figure 3-18) and the FWHM was measured for each of the In$_x$Ga$_{1-x}$N (002) phase separated peaks. The data points for the phase separated temperatures represents the average FWHM, while the extremes of the error bars represents the FWHM of each phase separated In$_x$Ga$_{1-x}$N (002) peak. The highest FWHM (3672 arcsec) is noticed for the In$_x$Ga$_{1-x}$N film deposited at 530 °C (Figure 3-18). The FWHM reaches a minimum value of 936 and 1440, for the two highest intensity (dominant) phase separated peaks at a deposition temperature of 560 °C. The values for the FWHM increases for deposition temperature of 590 and 620 °C, and the value for the FWHM, however, is still lower than the metastable In$_x$Ga$_{1-x}$N (530 °C). These results suggest that the crystalline quality of the phase separated In$_x$Ga$_{1-x}$N films are better than the metastable In$_x$Ga$_{1-x}$N film grown at 530 °C. The results indicate a deposition temperature of 560 °C should be used to obtain the best crystalline quality at the inlet flow ratio tested (In/(In+Ga) = 0.8). If phase separation cannot be tolerated, the low deposition temperature of 530 °C must be used.

A decrease in crystallinity is seen at 590 °C (compared to 560 °C) possibly due to increased decomposition of InN, or a higher growth that leads to 3D island growth instead of the
more desirable 2D growth (from a structural quality perspective). It has been shown by other researchers that InN film quality degrades at temperatures ~ 600 °C. Similar film degradation (InN decomposition and 3D growth) mechanisms can be used to describe the decreased crystalline quality at 620 °C.

At deposition temperature > 650 °C the decomposition rate of InN becomes rapid, even though ammonia also decomposes rapidly in this temperature regime, thus reducing the InₓGa₁₋ₓN (002) peak intensity (Figure 3-17). Highly efficient decomposition of NH₃ leads to an increase of partial pressure of hydrogen at the higher deposition temperature (> 650 °C), which retards the growth rate of InN. Therefore when using an inlet flow ratio of In/(In+Ga) = 0.8 the deposition temperature must remain near 530 °C to produce stable InₓGa₁₋ₓN films. At a growth temperature of 560 °C the InₓGa₁₋ₓN film becomes phase separated, however, the crystalline quality increases for the phase separated regions. The intermediate temperature range 650 to 710 °C produces very small InₓGa₁₋ₓN peak intensities which are slightly above the background XRD intensity. The small intensities are most likely due to InN decomposition as well as a low GaN growth rate at these temperatures. Higher growth rate (and higher quality) GaN is achieved at deposition temperature of 850 to 1150 °C.

Polycrystalline In-rich InₓGa₁₋ₓN (101) peaks occur at 2θ = 33.85° for low deposition temperatures (< 650 °C) (Figure 3-16). When the deposition temperature is increased to 710 °C or above, a Ga-rich InₓGa₁₋ₓN (002) phase starts to form in the region where In-rich InₓGa₁₋ₓN (101) peaks would be expected. This result can be seen from the magnitude of InₓGa₁₋ₓN (101) peak intensities for each deposition temperature (Figure 3-19). There is an increase in peak intensity (in the region of 2θ = 33.8°) from T = 710 to 740 °C, and this is attributed to the formation of Ga-rich InₓGa₁₋ₓN (002) phases since In-rich InₓGa₁₋ₓN phases are less likely to
occur at these temperatures. Even though In-rich In$_x$Ga$_{1-x}$N (101) and Ga-rich In$_x$Ga$_{1-x}$N (002) XRD peaks can overlap, In-rich In$_x$Ga$_{1-x}$N (101) peaks are dominant at lower (< 650 °C) deposition temperatures and Ga-rich In$_x$Ga$_{1-x}$N (002) are dominant at higher (> 710 °C) deposition temperatures. This result can be attributed to the increase growth rate of GaN at higher deposition temperatures as well as the increased InN thermal decomposition. It is also not likely that the polycrystalline In-rich In$_x$Ga$_{1-x}$N (101) peak would be detected with a significant peak intensity when the In-rich In$_x$Ga$_{1-x}$N (002) peak intensity is also low, since the films are textured in the [002] direction.

At 740 °C the intensity of the Ga-rich In$_x$Ga$_{1-x}$N (002) phase increases, which is not surprising because GaN is more favorable at higher temperature. It is surprising, however, that the XRD intensity of the In-rich In$_x$Ga$_{1-x}$N (002) also increases at this temperature compared to 710 °C. It is not clear why the In-rich phase showed an increase in XRD intensity at a higher temperature, but it is possible that an increase in the GaN growth rate allows more surface coverage of InN and inhibits thermal decomposition. An increase in XRD intensity due to thickness is also not likely, especially for In-rich phases due to excess hydrogen partial pressure inhibiting the growth rate of InN. A 30 degree increase in temperature (770 °C) no longer shows the presence of an In-rich In$_x$Ga$_{1-x}$N (002) phase, only Ga-rich In$_x$Ga$_{1-x}$N (002) is present. This result is consistent with the work done by Matsuoka et al., who found that Ga-rich In$_x$Ga$_{1-x}$N alloys still form at high deposition temperature even when inlet flow conditions are In-rich.$^{12}$

To summarize, In$_x$Ga$_{1-x}$N films can have been grown in the temperature range 530-770 °C using a constant inlet flow ratio of TMIn/(TMIn + TEGa) = 0.8. Growth at 530 °C produces a stable In$_x$Ga$_{1-x}$N film, but as the temperature is increased phase separation occurs. At lower deposition temperature (560, 590, and 620 °C) the separate In$_x$Ga$_{1-x}$N phases have compositions
that lie in the In-rich regime. These deposition temperatures also show an increase in crystalline quality, attributed to a reduction in strain from phase separation, and the best quality was obtained at a deposition temperature of 560 °C. At T_g = 590 °C, two In_xGa_{1-x}N (002) phases can be resolved from the XRD data that correspond to In_{0.86}Ga_{0.14}N and In_{0.71}Ga_{0.29}N, and a similar result occurs at 560 and 620 °C. In the intermediate temperature range (650 to 710 °C) produces In_xGa_{1-x}N films with very broad XRD peaks and poor structural quality. At 740 °C, separate In_xGa_{1-x}N (002) phases are noticed with one phase In-rich (In_{0.86}Ga_{0.14}N) and the other Ga-rich (In_{0.27}Ga_{0.73}N) phase. The highest deposition temperature used, 770 °C, produced an In_xGa_{1-x}N film with no distinct In-rich peak, only a Ga-rich peak (In_{0.28}Ga_{0.72}N) with a broad shoulder to the left, which signifies phase separation with a lesser gallium content. Films deposited at 560 °C, had three distinct In_xGa_{1-x}N (002) compositional phases that could be resolved from XRD data, In_{0.85}Ga_{0.15}N, In_{0.7}Ga_{0.3}N and In_{0.4}Ga_{0.6}N. These phases are easily identified for T_g = 560 °C because this temperature produced the highest peak intensities of all the temperatures examined. It is possible that films deposited at other deposition temperature also had several In_xGa_{1-x}N (002) compositional phases present, however, these phases cannot be specifically identified due to XRD peak broadening and low intensities.

3.3.2.3 Effect of substrate on stability of In_xGa_{1-x}N alloys

An early prediction of the miscibility gap of In_xGa_{1-x}N by Ho and Stringfellow^{123} indicates the limit is ~ 6% Ga incorporation into InN or In incorporation into GaN, at typical growth temperature (800 °C). More recent analysis has shown that the introduction of compressive strain into In_xGa_{1-x}N alloy films reduces the miscibility gap (when coherently deposited on unstrained GaN).^{124} The amount of strain (compressive or tensile) in an epitaxial film is directly related to the lattice mismatch between the substrate or buffer layer and the film. To understand the substrate effect on the film stability, In_xGa_{1-x}N alloys were grown on a-Al_2O_3 and
GaN/c-Al$_2$O$_3$ substrates and compared to metastable In$_x$Ga$_{1-x}$N alloys grown on c-Al$_2$O$_3$. The same growth temperature was used for each substrate, $T_g = 530$ °C along with N/III = 50,000. Substrate nitridation and a LT InN buffer layer were used for each growth with overall film thicknesses of $\sim$ 100 nm.

A series of In$_x$Ga$_{1-x}$N films grown at 530 °C on the a-plane Al$_2$O$_3$ during which the inlet flow ratio (TMIn/(TMIn+TEGa) was varied from 0 to 1 were characterized by XRD (Figure 3-20). Immediately it can be seen that a-Al$_2$O$_3$ substrate (Figure 3-20) differs significantly from c-Al$_2$O$_3$ substrate (Figure 3-14) with respect to phase separation. The films grown on c-plane Al$_2$O$_3$ substrates are single phase films while the films grown on a-plane sapphire show obvious phase separation from XRD peak separation. Although, phase separation occurs most frequently in the compositional range of $0.3 < x < 0.7$, this is not the result seen for In$_x$Ga$_{1-x}$N grown on a-Al$_2$O$_3$ substrates. Phase separation occurs at inlet flow ratios of 0.7 and 0.6 but not at 0.5. Interestingly, values of flow ratio of 0.1 and 0.3 show phase separation, while the flow ratio of 0.2 does not show phase separation.

The lattice mismatch between a-Al$_2$O$_3$ and InN or GaN is -8.8% or 1.9%, respectively. This gives a lattice matched condition at In$_{0.8}$Ga$_{0.2}$N. In the case of InN/a-Al$_2$O$_3$ the reduced lattice mismatch is beneficial because the structural quality of InN is improved due to reduced strain in the heteroepitaxial film (compared to c-Al$_2$O$_3$). This prediction has been verified experimentally by growing InN on both a- and c-Al$_2$O$_3$ substrates during the same growth. Substrate nitridation was used as well as a LT InN buffer layer for the growth of InN on a- and c-Al$_2$O$_3$ (XRD, Figure 3-21). The FWHM of the InN (002) peak decreases from 1080 (c-Al$_2$O$_3$) to 864 arcsec (a-Al$_2$O$_3$) confirming that the structural quality of InN is improved when growth occurs on a-plane sapphire. The difference in crystalline quality for the a- and c-planes of
sapphire would be even larger if substrate nitridation was not used (due to improving the mismatch between InN and c-Al₂O₃). The a-plane of sapphire would seem to be the preferred substrate for growth of InₓGa₁₋ₓN alloys from a structural quality perspective due to a decreased lattice mismatch between the substrate and the film. From the experimental results, however, the lack of substrate induced strain shifts the binodal decomposition more towards ideal solution behavior, leading phase separation to occur over a wide range of compositions. Assuming a regular solution model predicts a large InₓGa₁₋ₓN alloy miscibility gap and a high critical temperature (1250 °C). These experimental results suggest that substrate selection is an important parameter when considering the effects of phase separation for specific InₓGa₁₋ₓN compositions. In the case of c-Al₂O₃ the lattice mismatch between the substrate and the alloy film is sufficiently high, ranging from 33 to 26% when x = 0 and 1, respectively. The large lattice mismatch produces elastic strain (compressive) which helps to suppress phase separation at the compositions tested (based on the results presented in Section 3.3.2.1). Therefore it is suggested that the elastic strain induced by the substrate stabilizes the InₓGa₁₋ₓN alloy film from phase separation.

Thermodynamic analysis of the InₓGa₁₋ₓN alloys system has shown that phase separation can be suppressed (miscibility gap reduction and also a lowering of the critical temperature) when compressive or tensile stress is included in the Hemholtz free energy calculation. The Hemholtz free energy (F, Eq. 3-19) of a system can be described by contributions from the macroscopic (Fₒ, Eq. 3-20) and microscopic (ΔF, Eq. 3-21) mixtures

\[
F = F_o + \Delta F \quad (3-19)
\]

\[
F_o(x,T) = (1-x)F_{GaN}(T) + xF_{InN}(T) \quad (3-20)
\]

\[
\Delta F(x,T) = \Delta U(x,T) - T\Delta S(x,T) \quad (3-21)
\]
\[ \Delta U(x,T) = \sum_{j=0}^{M} M j \varepsilon_j - M \left[ (1-x) \varepsilon_0 + x \varepsilon_j \right] \]  

(3-22)

where \( \Delta U \) is the mixing internal energy (identified with the mixing enthalpy of the alloy), \( \Delta S \) is the mixing entropy, \( M \) is the cluster number, \( \varepsilon \) is the cluster energy, and \( j \) is the cluster class index (when using a quasichemical approach to disorder and composition and a pseudopotential-plane-wave approximation for the total energy). The \( F_0 \) term can be calculated by determining the standard Hemholtz energy of \( \text{FGaN} \) and \( \text{FInN} \) using standard thermodynamic properties of binary compounds. The internal energy (Eq. 3-22) is a function of elastic energy (\( \varepsilon \)) and introducing strain into the system causes the elastic energy to decrease and therefore the excess free energy (\( \Delta F \)) decreases. Lowering the excess free energy reduces the critical temperature to overcome phase separation and reduces the miscibility gap (when assuming a uniform distribution of strain). The critical temperature is decreased by 120K (to 1130K) when -5% biaxial strain is included and the miscibility gap is reduced more for In-rich compositions due to a compositional dependent interaction parameter that produces asymmetry. Allowing the biaxial strain to be distributed inhomogeneously further reduces \( \Delta F \) so the values become negative over the entire compositional range (at \( T > 700 \text{K} \)). The significant lowering of \( \Delta F \) occurs because the strain energy is proportional to the square of the in-plane strain energy (biaxial strain). In this case the miscibility gap and the critical temperature are significantly reduced. These theoretical predictions suggest that a lack of substrate induced strain (due to the smaller lattice mismatch) favors a phase separation for \( \text{In}_x\text{Ga}_{1-x}\text{N} \) when deposited on \( \text{a-Al}_2\text{O}_3 \).

Although the strain from the substrate helps prevent phase separation, the crystalline quality is reduced due to the high level of strain in the alloyed film. An increase in \( \text{In}_x\text{Ga}_{1-x}\text{N} \) strain, as determined by a decrease in XRD FWHM of the \( \text{In}_x\text{Ga}_{1-x}\text{N} \) (002) peak, is in good agreement with the suppression of phase separation for \( \text{In}_x\text{Ga}_{1-x}\text{N/a-Al}_2\text{O}_3 \) (Figure 3-22). As the
flow ratio changes to include more Ga in the film (In/In+Ga = 0.9 and 0.8) the strain energy increases, which increases the In\textsubscript{x}Ga\textsubscript{1-x}N (002) FWHM, signifying a decreased crystalline quality (Figure 3-22). At a flow ratio of In/In+Ga = 0.7 the film strain cannot be stabilized by the substrate and phase separation occurs. Upon phase separation the FWHM decreases, suggesting an increase in crystalline quality. A similar trend can be seen for the remaining inlet flow ratios (Fig. 3-22), where the stable films (at In/In+Ga = 0.5 and 0.2) are less crystalline compared to the phase separated films where the strain has been relaxed (In/In+Ga = 0.7, 0.6, 0.4, 0.3, and 0.1).

Recently, Zheng et al.\textsuperscript{253} determined the Hemholtz energy of mixing for unstrained and strained 32-atom In\textsubscript{x}Ga\textsubscript{1-x}N clusters at 0K from ab-initio calculation by using the Vienna Ab-initio Simulation Package (VASP) within the frame work of density functional theory (DFT) and the local density approximation. The Hemholtz energy was calculated using Eq. 3-19. Strain was introduced into the structures by replacing the In\textsubscript{x}Ga\textsubscript{1-x}N equilibrium lattice parameter (a\textsubscript{o}) with the lattice parameter of InN (a\textsubscript{InN}) or GaN (a\textsubscript{GaN}). Substituting the lattice parameters for InN or GaN produces the maximum possible tensile (a\textsubscript{InN}) or compressive (a\textsubscript{GaN}) strain that the In\textsubscript{x}Ga\textsubscript{1-x}N system can endure. It is important to mention that it is not likely that these fully strained cases could be realized experimentally, however, the calculations add insight to the affect of tensile or compressive strain on the mixing free energy. The resulting Hemholtz energy was calculated for strained and unstrained In\textsubscript{x}Ga\textsubscript{1-x}N clusters as a function of InN mole fraction (Figure 3-23). When the In\textsubscript{x}Ga\textsubscript{1-x}N equilibrium lattice parameter is used the Hemholtz energy is positive over the entire compositional range and the area under the curve represents the spinodal decomposition region (where phase separation will occur, Figure 3-23a). Adding compressive and tensile strain to the system causes the Hemholtz energy to become negative over the entire
compositional range for both types of strain (Figure 3-23b). These results suggest that elastic strain plays a significant role in reducing the miscibility gap of In$_x$Ga$_{1-x}$N, therefore it is suggested that the lack of substrate induced strain from more closely lattice matched substrates (a-Al$_2$O$_3$) increases the probability of phase separation (at a given composition) compared to c-Al$_2$O$_3$.

A similar phase separation analysis can be applied to In$_x$Ga$_{1-x}$N alloys grown on GaN (5 μm)/c-Al$_2$O$_3$. In$_x$Ga$_{1-x}$N films were grown at 530 °C and a N/III ratio of 50,000 with a LT InN buffer layer for all inlet flow compositions and characterized by XRD (Figure 3-24). Analysis of the XRD peaks is much more difficult when GaN/c-Al$_2$O$_3$ substrates are used due to the large peak intensity of the 5 μm GaN layer. Nevertheless it can be seen that a narrow peak of phase separated InN (002) is detected for all inlet flow ratios ($2\theta = 31.4^\circ$). This peak is assumed to be phase separated InN which is formed during In$_x$Ga$_{1-x}$N growth. It is possible, however unlikely, that this peak is detected due to the presence of an InN buffer layer. InN buffer layers are deposited for 15 min at low temperature (450 °C) resulting in a 5-10 nm film (based on RBS analysis), which is polycrystalline or amorphous (from XRD). The XRD FWHM of the phase separated InN is 288 arcsec, which is lower than the value obtained for optimized InN thin films (574 arcsec) using a LT InN buffer layer and the same GaN substrates.\textsuperscript{203} It has shown previously in this work that a reduction in strain improves the crystalline quality of the as grown films (from the reduction in the XRD FWHM). Therefore, it is suggested that the phase separated InN regions have very little residual strain due to occurrence of strain relaxation after phase separating, which leads to a higher degree of crystallinity.

Phase separation is believed to be more favorable on the GaN substrates when a LT InN buffer layer is included because no phase separation occurs at similar (Ga-rich) compositions
when no LT InN buffer layer is used.\textsuperscript{254} It is postulated that the LT InN buffer layer promotes phase separation by providing nucleation sites for InN, which are more energetically favorable sites compared to a compressively strained bond with GaN (when considering a Ga-rich sample).

For the growth of stable (non-phase separated) In\textsubscript{x}Ga\textsubscript{1-x}N thin films an ideal substrate is one that has sufficient lattice mismatch to develop enough compressive or tensile (at a given composition) to lower the mixing free energy for In\textsubscript{x}Ga\textsubscript{1-x}N. This conclusion has been verified with the growth of In\textsubscript{x}Ga\textsubscript{1-x}N on c-Al\textsubscript{2}O\textsubscript{3} substrates by producing metastable films over the entire compositional range. Regardless of the composition the lattice mismatch between c-Al\textsubscript{2}O\textsubscript{3} and In\textsubscript{x}Ga\textsubscript{1-x}N is sufficiently high to produce compressive strain in the film, therefore phase separation can be suppressed. In contrast, In\textsubscript{x}Ga\textsubscript{1-x}N alloys were grown on the more closely lattice matched substrates of a-Al\textsubscript{2}O\textsubscript{3} and GaN/c-Al\textsubscript{2}O\textsubscript{3}. Phase separation proved to be much more favorable on these substrates since strain could not be sustained in the alloy films. It has also been shown that increase in growth temperature kinetically favors phase separation for In\textsubscript{x}Ga\textsubscript{1-x}N/c-Al\textsubscript{2}O\textsubscript{3} (from Section 3.3.2.2). The increased temperature gives atoms in the alloy film enough energy to find an energetically favorable site (i.e. a lower strained bond).

### 3.3.2.4 Determination of In\textsubscript{x}Ga\textsubscript{1-x}N growth rate and composition from RBS measurements

In\textsubscript{x}Ga\textsubscript{1-x}N thin films were grown at 530 °C (N/III = 50,000) on sapphire substrates with varying inlet flow ratio and subsequently analyzed by RBS to determine the relationship between inlet flow ratio and solid solution composition (x). The RBS data was also used to predict the film thickness based on inlet flow conditions. Inlet flow ratio values of In/(In+Ga) = 0.2, 0.35, 0.5, 0.65, 0.75, and 0.8 were used for this analysis and films that included substrate nitridation and a LT InN buffer layer. RBS measurements were performed by exposing samples to a mono-energetic beam of 2 MeV \textsuperscript{4}He\textsuperscript{+} ions, which were generated by a 2.5 MeV Van de Graaff accelerator. A silicon surface barrier detector was positioned at a backscattered angle of 165°.
with respect to the incident beam to collect the backscattered He ions. The energy of the backscattered He ions is dictated by depth and mass of the target material (In$_x$Ga$_{1-x}$N). Therefore RBS can determine the depth profile of individual elements in the solid, giving the thickness and composition of In$_x$Ga$_{1-x}$N samples. RBS analysis was done for the entire thickness of the films tested (≤ 500 nm), meaning that the depth channeling was stopped once the substrate material was detected.

The thickness and composition as determined by RBS for each inlet flow ratio are shown in Table 3-3. In$_x$Ga$_{1-x}$N films were grown for 2 hr and it was determined from RBS that the LT InN buffer layer has an approximate thickness of 5 to 7 nm, which was not included in the thickness measurement (Table 3-3). All growths were performed at the same temperature therefore the extent of NH$_3$ decomposition efficiency should be similar for each experiment. When the total group III inlet flow rate increases, the amount of ammonia is increased to maintain a constant N/III ratio prior to each run. Since all growth occurred at a constant temperature in a reaction limited regime and the group III species is the limiting reactant the growth rate should be plotted as a function of total group III flow. The experimental thicknesses as a function of total group III (TMIn + TEGa) flow rate is plotted (Figure 3-25), where the error in the group III flows is due to variation in the bubbler pressure during the experiment. It can be seen that the growth rate of In$_x$Ga$_{1-x}$N increases by increasing the group III flow rate. At this deposition temperature (530 °C) the reaction is kinetically limited, therefore a first order reaction is expected between the group III sources and the growth rate. A linear regression is fit to the data where the intercept occurs at $y = 0$ (Figure 3-25), showing the experimental relationship between the group III flow and In$_x$Ga$_{1-x}$N growth rate, where the slope of the trendline is analogous to the reaction rate constant.
The RBS compositional data was used to determine the solid solution alloy deviation from the gas phase inlet flow ratio. The difference between the inlet flow ratio and the RBS solid solution composition is plotted with a linear relationship between inlet flow ratio and composition (Figure 3-26). When the value of the inlet flow ratio decrease below 0.7 then the film composition starts to deviate for a linear relationship, where the solid solution compositions contain more In than expected from the inlet flow ratio. This deviation most likely occurs due to GaN surface coverage which suppresses InN thermal decomposition. The solid solution composition as determined from RBS data are compared to solid solution composition determined from XRD data (Table 3-4). The XRD data from the metastable In$_x$Ga$_{1-x}$N/c-Al$_2$O$_3$ film (Section 3.3.2.1) was used in this comparison. The XRD and RBS compositions match fairly closely for flow ratios of 0.1, 0.2, 0.8, and 0.9, which correspond to In$_x$Ga$_{1-x}$N compositions close to pure GaN and pure InN, respectively. The largest discrepancy is seen for flow ratios of 0.4, 0.5, and 0.6, for which RBS measurements always gave a higher value of $x$. The difference in this flow ratio region is believed to be due to the poor crystalline quality and thus any error in interpreting the spread of the XRD peaks for these flow ratios.

3.3.2.5 Terahertz emission from In$_x$Ga$_{1-x}$N alloys

As previously discussed in Section 1.3, InN has been shown to emit in the terahertz frequency range after optical excitation. There are many potential advantages for using In$_x$Ga$_{1-x}$N alloys for THz emitters and detectors including reduced size, operation at room temperature, better signal detection, and cheaper manufacturing costs. Some work has been done on THz emission from In$_x$Ga$_{1-x}$N/GaN heterstructures, however, there is no known evidence of THz emission from In$_x$Ga$_{1-x}$N thin films. In this section THz emission from In$_x$Ga$_{1-x}$N thin films with up to 30% gallium content is presented for the first time.
THz emission measurements were performed on In\textsubscript{x}Ga\textsubscript{1-x}N alloys given on c-Al\textsubscript{2}O\textsubscript{3} substrates at 530 °C (N/III = 50,000) that includes substrate nitridation and a LT InN buffer layer for preparation. The alloy composition was varied by changing the inlet flow ratio, In/(In+Ga), from 0.0 to 0.4. A time domain THz measurement system was used to test the THz emission from In\textsubscript{x}Ga\textsubscript{1-x}N thin films (Figure 3-27). THz emission from In\textsubscript{x}Ga\textsubscript{1-x}N thin films occurs by exposing the surface to titanium-sapphire (Ti:S) laser pulses with a duration of 130 fs at a wavelength of 800 nm. A 1 mm thick ZnTe <110> crystal is used to detect the THz radiation by electro-optic sampling.

The THz signal was measured from the surface of InN, In\textsubscript{0.9}Ga\textsubscript{0.1}N, In\textsubscript{0.8}Ga\textsubscript{0.2}N, In\textsubscript{0.7}Ga\textsubscript{0.2}N, and In\textsubscript{0.6}Ga\textsubscript{0.4}N samples grown on c-Al\textsubscript{2}O\textsubscript{3} (Figure 3-28). The sample with the largest signal, labeled as “InN surface” (Figure 3-28) is a 1 μm thick InN reference sample grown by MBE for comparison. The THz signal for the InN and In\textsubscript{x}Ga\textsubscript{1-x}N alloys grown by MOCVD are much smaller than the MBE reference InN, which is attributed to the difference in film thickness. The MOCVD samples have a thickness of approximately 50 to 70 nm, which prevents a significant portion of the pulsed laser energy from being absorbed.

The highest THz emission intensity was produced by In\textsubscript{0.8}Ga\textsubscript{0.2}N (Figure 3-29). It is not completely clear as to why the 80% indium composition registers the highest THz signal but very likely that it is due to thickness variations between the In\textsubscript{x}Ga\textsubscript{1-x}N samples. The thicknesses of the In\textsubscript{0.9}Ga\textsubscript{0.1}N, In\textsubscript{0.8}Ga\textsubscript{0.2}N, In\textsubscript{0.7}Ga\textsubscript{0.2}N, and In\textsubscript{0.6}Ga\textsubscript{0.4}N films are 65, 94, 62, and 48 nm, respectively. Sample thickness was determined from the group III inlet flow values and using the relationship to growth rate described in Section 3.3.2.4. Therefore it is certainly possible that the increased thickness of In\textsubscript{0.8}Ga\textsubscript{0.2}N allowed for more absorption of the laser and thus a
corresponding increase in signal intensity. Film thickness (48 nm) might also account for the low signal to noise ratio when In$_{0.6}$Ga$_{0.4}$N was tested (Figure 3-30).

An indirect indication of the fundamental band gap energy of InN can be gleaned from THz emission of In$_x$Ga$_{1-x}$N. The titanium-sapphire used to stimulate THz emission from the surface of the semiconductor samples has a wavelength of 800 nm or 1.55 eV. The band gap energy of tested materials must be below 1.55 eV or the sample becomes optically transparent to the laser. For the In$_x$Ga$_{1-x}$N samples described here, THz emission was detected for up to 30% Gallium incorporation, which implies that the band gap energy is below 1.55 eV. If the band gap energy of InN is assumed to be a value of 0.7 eV and a linear relationship is used for band gap energy changes with composition then In$_{0.7}$Ga$_{0.3}$N would have a band gap energy value of 1.51 eV. THz emission from In$_{0.7}$Ga$_{0.3}$N is significant evidence that the band gap energy of InN is below 1.0 eV (assuming a linear relationship between $E_{gInN}$ and $E_{gGaN}$). The increased band gap energy of In$_{0.6}$Ga$_{0.4}$N is another reason for why the alloy composition showed no THz emission. A band energy gap value of ~ 2.0 eV has been independently verified by photoluminescence measurements for In$_{0.6}$Ga$_{0.4}$N.

3.4 Conclusions

MOCVD growth of InN was performed on Si (100) and Si (111) substrates and it was shown that the use of nitridation as well as a LT InN buffer layer were critical to forming highly textured InN (002). Although highly textured growth occurred on silicon substrates by MOCVD, XRD results showed low peak intensities and broad peak widths. It was determined that the formation of a silicon oxynitride layer was the most influential parameter for the subsequent films quality. The H-MOCVD growth technique was used to grow InN on Si (111) substrates at a low N/III ratio without the formation of indium droplets. The presence of HCl also inhibited the formation of a silicon oxynitride layer and therefore direct growth of InN on Si
(111) could occur. XRD and SEM results confirm the growth of a highly textured InN (002) film with a growth rate 10X greater than MOCVD (0.75 μm/hr compared to 0.078 μm/hr). The group III flow was significantly increased using the H-MOCVD technique, however, no reduction in film quality occurred. Also, this type of group III flow scaling would not be possible using the previously described MOCVD technique (Section 3.2.3).

The stability of InN thin films with respect to the formation of crystalline oxide phases was assessed by aging samples at room temperature and low pressure annealing at higher temperature. No evidence was found for the formation of crystalline indium oxide phases at room temperature or after annealing at temperature up to 550 °C for short periods of time (10 to 20 min). Other researchers have found that crystalline indium oxide phases were formed after only 5 min anneals at 500 °C in a nitrogen atmosphere. This aging study showed that crystalline oxides are extremely unlikely to form at room temperature and that crystalline oxide formation can be avoided at higher temperature by annealing at low pressure.

Growth of In$_x$Ga$_{1-x}$N alloys was performed at low temperature over the entire compositional range and growth occurred on a-Al$_2$O$_3$, c-Al$_2$O$_3$, and GaN/c-Al$_2$O$_3$ substrates. Microscopic single phase metastable In$_x$Ga$_{1-x}$N over the entire compositional range ($0 \leq x \leq 1$) was grown by MOCVD for the first time, using a low deposition temperature. Single phase In$_x$Ga$_{1-x}$N can be grown, however, the crystalline quality suffers due to the low deposition temperature of 530 °C.

The stability of In$_x$Ga$_{1-x}$N alloys is also affected by the chosen substrate when grown at low temperature. Phase separation is more likely to occur in In$_x$Ga$_{1-x}$N when more closely lattice matched substrates are used because less substrate induced strain can be introduced into the film. Compressive or tensile strain has been shown to decrease the miscibility gap and reduce the
critical temperature to overcome phase separation.\textsuperscript{252,253} Using a substrate with a large lattice mismatch (c-Al\textsubscript{2}O\textsubscript{3}) over the entire compositional range, builds a enough compressive strain into the film to suppress phase separation between InN and GaN. When substrates such as GaN/c-Al\textsubscript{2}O\textsubscript{3} or α-Al\textsubscript{2}O\textsubscript{3} are used, the probability of phase separation increases because less substrate induced strain is produce (due to the lower lattice mismatch with In\textsubscript{x}Ga\textsubscript{1-x}N).

In\textsubscript{x}Ga\textsubscript{1-x}N/c-Al\textsubscript{2}O\textsubscript{3} stability was assessed with respect to growth at higher deposition temperature when using a constant inlet flow ratio. The inlet flow conditions were set for an approximate composition of In\textsubscript{0.8}Ga\textsubscript{0.2}N, when grown at 530 °C. Phase separation was seen in all the films grown above 530 °C and the compositional difference between the phase separated regions became more pronounced as the temperature increased. The composition of the In-rich phase separated region remained fairly constant with increased temperature until thermal decomposition of InN became dominant. The composition of the phase separated region with a higher Ga-content was shifted toward GaN as the deposition temperature increased. It was concluded that avoiding phase separation of In-rich In\textsubscript{x}Ga\textsubscript{1-x}N alloys becomes increasingly difficult at higher deposition temperatures (T\textsubscript{g} > 530 °C). Once phase separation occurs the crystalline quality of the phase separated regions is increased.

Terahertz emission frequencies were shown for In\textsubscript{x}Ga\textsubscript{1-x}N/c-Al\textsubscript{2}O\textsubscript{3} samples at compositions of 0.7 ≤ x ≤ 1. Emission signals were weak for these samples mostly due to their thickness (50 to 90 nm) and no signal was detected for alloys with a 40% indium composition because these samples were believed to be optically transparent to the stimulating laser light. These results show promise for In\textsubscript{x}Ga\textsubscript{1-x}N thin films as candidates for THz emitter and detector applications, especially since current technologies can be drastically improved.
Figure 3-1. Solid-gas interfacial region for the reaction of TMGa and NH$_3$ to form GaN. Showing boundary layer diffusion, pyrolysis of reactant species, absorption, desorption, adduct formation, and surface reactions (Ref. 228).
Figure 3-2. The MOCVD reactor. A) A photo of the MOCVD reactor. B) The process reactor schematic.

Figure 3-3. Scanning electron microscope image of direct InN growth on Si (111) with no in-situ surface pretreatments. Resulting in incomplete film growth.
Figure 3-4. Scanning electron microscope image of InN grown on Si (111) using substrate nitridation followed by a LT InN buffer layer. Resulting in a continuous film.

Figure 3-5. An XRD pattern of a polycrystalline InN thin film grown on Si (111) using a LT InN buffer layer.
Figure 3-6. A TEM image of the SiO$_x$N$_{1-x}$ intermediate layer used to produce high quality single crystal GaN (Ref. 237).

Figure 3-7. X-ray diffraction patterns of InN grown on Si (111) and Si (100) substrates using substrate nitridation followed by a LT InN buffer layer. Intentional substrate nitridation at high temperature (850 °C) was used to form SiO$_x$N$_{1-x}$ intermediate layer. Data plotted on a logarithmic scale.
Figure 3-8. Cross-sectional SEM image of InN/Si (100) grown by MOCVD showing a growth rate of 78 nm/hr.

Figure 3-9. An XRD spectrum of InN/Si (111) grown by H-MOCVD.
Figure 3-10. Scanning electron microscope images of InN/Si (111) grown by H-MOCVD.

Figure 3-11. Energy dispersive spectroscopy and AES analysis showing no evidence of chlorine contamination in InN/Si (111) by H-MOCVD.
Figure 3-12. Comparison of XRD patterns between aged and as-grown samples of InN on silicon and sapphire substrates. Blue line–as-grown, Red line–aged.

Figure 3-13. X-ray diffraction patterns for InN/c-Al2O3 annealed in a N2 (100 Torr) atmosphere at 500 °C (20 min), 525 °C (15 min), and 550 °C (10 min). Blue line–as-grown, Red line–annealed.
Figure 3-14. A series of XRD patterns for In$_x$Ga$_{1-x}$N alloys grown at low temperature (530 °C) on c-Al$_2$O$_3$ substrates. Substrate nitridation followed by a LT InN buffer layer (N/III = 50,000) were used in each experiment.
Figure 3-15. Experimental In$_x$Ga$_{1-x}$N compositions vs. inlet flow ratio (blue line). Also plotted is a theoretical direct relationship between composition and flow ratio with a slope of 1 (red line).

Figure 3-16. X-ray diffraction patterns of In$_x$Ga$_{1-x}$N thin films grown on c-Al$_2$O$_3$ substrates at constant inlet flow ratio (In/(In+Ga) = 0.8) at temperature ranging from 530 to 770 °C (blue lines). Pure InN (530 °C) and pure GaN (850 °C) standards are plotted (red).
Figure 3-17. Magnitude of In$_x$Ga$_{1-x}$N (002) peak intensity vs. deposition temperature at a constant inlet flow ratio of In/(In+Ga) = 0.8.

Figure 3-18. Film crystalline quality as determined by XRD FWHM of the In$_x$Ga$_{1-x}$N (002) peak.
Figure 3-19. Magnitude of In-rich In$_x$Ga$_{1-x}$N (101) and Ga-rich In$_x$Ga$_{1-x}$N (002) peak intensity vs. deposition temperature at a constant inlet flow ratio of In/(In+Ga) = 0.8.

Figure 3-20. A series of XRD patterns for In$_x$Ga$_{1-x}$N alloys grown at low temperature (530 °C) on a-Al$_2$O$_3$ substrates. Substrate nitridation followed by a LT InN buffer layer (N/III = 50,000) were used in each experiment.
Figure 3-21. Comparison of XRD spectra for InN grown on a-Al$_2$O$_3$ (blue) and c-Al$_2$O$_3$ (red) substrates.

Figure 3-22. X-ray diffraction FWHM In$_x$Ga$_{1-x}$N/a-Al$_2$O$_3$ at different values of inlet flow ratio and the corresponding film stability.
Figure 3-23. Helmholtz free energy of mixing of In$_x$Ga$_{1-x}$N as a function of InN mole fraction. 
A) Equilibrium lattice parameter (unstrained bonds). B) Complete tensile or compressive atom bond straining (Ref. 253).

Figure 3-24. X-ray diffraction patterns for In$_x$Ga$_{1-x}$N alloys grown at different inlet flow ratios on LT InN/GaN/c-Al$_2$O$_3$. 

Figure 3-25. Growth rate of In$_x$Ga$_{1-x}$N/c-Al$_2$O$_3$ alloys as a function of total inlet group III flow (sccm). Films were deposited at 530 °C (N/III = 50,000).

Figure 3-26. Composition deviation of In$_x$Ga$_{1-x}$N/c-Al$_2$O$_3$ measured by RBS as a function of inlet flow ratio.
Figure 3-27. Time domain THz measurement system used to analyze In$_x$Ga$_{1-x}$N thin films (Diagram used with permission from Dr. Ingrid Wilke, Rensselaer Polytechnic Institute, Center for Terahertz Research, Troy, NY).

Figure 3-28. Terahertz signal measured from the surface of pure InN and In$_x$Ga$_{1-x}$N thin films.
Figure 3-29. The emitted THz frequency range and corresponding amplitude for InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys.

Figure 3-30. Poor THz signal to noise ratio for thin (48 nm) $\text{In}_{0.6}\text{Ga}_{0.4}\text{N}$.
Table 3-1. Flow ratios and corresponding In$_x$Ga$_{1-x}$N compositions for metastable In$_x$Ga$_{1-x}$N/c-Al$_2$O$_3$ grown at low temperature (530 °C). Composition determined by XRD measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>In$<em>x$Ga$</em>{1-x}$N (0002) $2\theta$ (°)</th>
<th>Composition (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure InN</td>
<td>31.4</td>
<td>1.00</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.9</td>
<td>31.8</td>
<td>0.85</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.8</td>
<td>32.1</td>
<td>0.75</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.6</td>
<td>32.8</td>
<td>0.52</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.5</td>
<td>33.2</td>
<td>0.41</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.4</td>
<td>33.1</td>
<td>0.45</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.2</td>
<td>33.6</td>
<td>0.30</td>
</tr>
<tr>
<td>In/(In+Ga) = 0.1</td>
<td>34.0</td>
<td>0.17</td>
</tr>
<tr>
<td>Pure GaN</td>
<td>34.6</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 3-2. The In$_x$Ga$_{1-x}$N (002) composition(s) for each deposition temperature ranging from 530 to 770 °C when grown at a constant inlet flow ratio of In/(In+Ga) = 0.8. Multiple In$_x$Ga$_{1-x}$N compositions are listed for phase separated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD peak separation (phase separation)</th>
<th>$2\theta$ (°)</th>
<th>Composition (x) by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 530 °C, InN (002)</td>
<td>n/a</td>
<td>31.4</td>
<td>1.00</td>
</tr>
<tr>
<td>T = 530 °C, In$<em>x$Ga$</em>{1-x}$N (002)</td>
<td>n/a</td>
<td>31.87</td>
<td>0.78</td>
</tr>
<tr>
<td>peak 1</td>
<td>31.65</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>peak 2</td>
<td>32.11</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>peak 3</td>
<td>33.05</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>T = 560 °C, In$<em>x$Ga$</em>{1-x}$N (002)</td>
<td>peak 1</td>
<td>31.65</td>
<td>0.86</td>
</tr>
<tr>
<td>peak 2</td>
<td>32.09</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>peak 3</td>
<td>33.05</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>T = 590 °C, In$<em>x$Ga$</em>{1-x}$N</td>
<td>peak 1</td>
<td>31.55</td>
<td>0.88</td>
</tr>
<tr>
<td>peak 2</td>
<td>32.05</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>T = 650 °C, In$<em>x$Ga$</em>{1-x}$N (002)</td>
<td>n/a</td>
<td>31.89</td>
<td>0.77</td>
</tr>
<tr>
<td>T = 680 °C, In$<em>x$Ga$</em>{1-x}$N (002)</td>
<td>n/a</td>
<td>31.65</td>
<td>0.85</td>
</tr>
<tr>
<td>T = 710 °C, In$<em>x$Ga$</em>{1-x}$N</td>
<td>peak 1</td>
<td>31.65</td>
<td>0.85</td>
</tr>
<tr>
<td>peak 2</td>
<td>33.51</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>T = 740 °C, In$<em>x$Ga$</em>{1-x}$N</td>
<td>peak 1</td>
<td>31.63</td>
<td>0.86</td>
</tr>
<tr>
<td>peak 2</td>
<td>33.51</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>T = 770 °C, In$<em>x$Ga$</em>{1-x}$N (002)</td>
<td>n/a</td>
<td>33.47</td>
<td>0.28</td>
</tr>
<tr>
<td>T = 850 °C, GaN (002)</td>
<td>n/a</td>
<td>34.6</td>
<td>0.00</td>
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</table>
Table 3-3. Thickness and compositional data obtained from RBS measurements for \( \text{In}_x\text{Ga}_{1-x}\text{N}/\text{c-Al}_2\text{O}_3 \) grown for 2 hr.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Growth temperature (°C)</th>
<th>Inlet flow ratio: In/(In+Ga)</th>
<th>Measured composition (by RBS)</th>
<th>Measured thickness (by RBS, in nm)</th>
<th>Calculated thickness based on inlet flows (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>850</td>
<td>0.00</td>
<td>0.00</td>
<td>490</td>
<td>--------------</td>
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<tr>
<td>136</td>
<td>530</td>
<td>0.20</td>
<td>0.32</td>
<td>70</td>
<td>101</td>
</tr>
<tr>
<td>137</td>
<td>530</td>
<td>0.35</td>
<td>0.49</td>
<td>90</td>
<td>102</td>
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<tr>
<td>135</td>
<td>530</td>
<td>0.49</td>
<td>0.59</td>
<td>110</td>
<td>107</td>
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<tr>
<td>138</td>
<td>530</td>
<td>0.64</td>
<td>0.68</td>
<td>110</td>
<td>108</td>
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<tr>
<td>133</td>
<td>530</td>
<td>0.75</td>
<td>0.70</td>
<td>90</td>
<td>99</td>
</tr>
<tr>
<td>134</td>
<td>530</td>
<td>0.80</td>
<td>0.78</td>
<td>125</td>
<td>123</td>
</tr>
<tr>
<td>131</td>
<td>530</td>
<td>1.00</td>
<td>1.00</td>
<td>70</td>
<td>--------------</td>
</tr>
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</table>

Table 3-4. Comparison of \( \text{In}_x\text{Ga}_{1-x}\text{N} \) film compositions as determined by XRD and RBS.

<table>
<thead>
<tr>
<th>Inlet flow ratio: In/(In+Ga)</th>
<th>((x)) in ( \text{In}<em>x\text{Ga}</em>{1-x}\text{N} ) by XRD</th>
<th>((x)) in ( \text{In}<em>x\text{Ga}</em>{1-x}\text{N} ) by RBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.85</td>
<td>0.91</td>
</tr>
<tr>
<td>0.8</td>
<td>0.75</td>
<td>0.78</td>
</tr>
<tr>
<td>0.6</td>
<td>0.52</td>
<td>0.65</td>
</tr>
<tr>
<td>0.5</td>
<td>0.41</td>
<td>0.59</td>
</tr>
<tr>
<td>0.4</td>
<td>0.45</td>
<td>0.52</td>
</tr>
<tr>
<td>0.2</td>
<td>0.30</td>
<td>0.32</td>
</tr>
<tr>
<td>0.1</td>
<td>0.17</td>
<td>0.16</td>
</tr>
</tbody>
</table>
CHAPTER 4
GROWTH OF INDIUM NITRIDE AND INDIUM GALLIUM NITRIDE NANOWIRES BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION

4.1 Introduction

Growth of one-dimensional semiconductor nanostructures, such as nanowires is of interest to better understand how dimensionality and size confinement affect semiconductor properties. From a device point of view nanostructures offer the benefit small feature size in two dimensions and thus a specific conduction pathway. III-nitride nanowires have applications in low-power and high-density field-effect transistors (FETs), solar cells, and terahertz emitters and detectors. For these device applications to be integrated with current technologies, controlled synthesis of III-nitride nanostructures must take place. The majority of the III-nitride nanowire literature (reviewed in Section 1.1.3) involves uncontrolled nanowire synthesis that would be difficult to scale to production levels. Simple uncontrolled nanowire growth is beneficial for initial analysis of semiconductor properties, however, controlled growth on a substrate is preferred for future device integration.

In this chapter, results of controlled InN nanowire growth using a traditional MOCVD reactor will be presented. The effects of selected growth parameters such as N/In ratio, relative flow velocity, annealing conditions, in-situ surface pretreatments, and type of substrate are specifically investigated. Substrate nitridation and low temperature InN buffer layers were selectively used as in-situ surface treatments on Si (100) substrates. Growth on GaN/c-Al₂O₃ substrates also occurred but substrate nitridation and LT InN buffer layer were not used. The surface treatments and chosen substrate directly affect the nucleation density of the nanowires on the substrate surface and the nanowire dimensions. Other growth parameters such as post growth annealing, the N/III ratio, and relative flow velocity are used to control the morphology and core-shell structure of the nanowires.
4.2 Experimental Procedure

Nanowires were synthesized in a Nippon Sanso quartz MOCVD reactor that uses RF inductive heating of a tilted graphite susceptor. The MOCVD reactor is described in greater detail in Section 3.2.3. The quartz inlet tube in the MOCVD reactor was modified for nanowire growth. For standard III-nitride film growth a horizontal quartz inlet tube is used where source gases are delivered in front of the tilted susceptor (Figure 4-1). This tilted susceptor design with laminar flow horizontal to the substrate surface allows enhanced mass transfer rate from boundary layer thinning along the susceptor length to compensate for reactant depletion. The boundary layer thinning is a result of the inverse velocity caused by the decreasing cross sectional area. InN nanowires, however, were grown using a “vertical” flow quartz inlet tube where source gases are delivered above the susceptor, directly over the wafer tray (Figure 4-2). A similar vertical inlet tube design was used to concentrate reactants over the susceptor to improve the growth rate of InN. It was noticed experimentally that incomplete films and nanostructures were formed on the edges of the wafer tray when this vertical inlet tube was used. Therefore this previous vertical inlet tube was slightly modified to produce incomplete films (i.e. nanostructures) over the entire wafer tray. The corresponding dimensions of the respective horizontal and vertical inlet tubes are shown in Figure 4-3.

In this study InN nanowires were grown on p-Si (100) and GaN/c-Al2O3 substrates. Silicon substrates were selected because of their low cost and potential for future device integration. GaN substrates were used to analyze any differences in growth with respect to silicon substrates, therefore adding insight to the nanowire growth mechanism. Silicon substrates were degreased in warm trichloroethylene (TCE), acetone and methanol each for 5 min and then blow dry with a static free nitrogen gun. For GaN/c-Al2O3 substrates no chemical cleaning was performed and a nitrogen gun was used to ensure that the surface was free
of particulates before loading. For Si, substrate nitridation and LT InN buffer layers were selectively included in growth experiments to understand how these surface pretreatments affects the nanowire nucleation and growth. As previously mentioned, no substrate nitridation or LT InN buffer layers were used for InN nanowire growth on GaN/c-Al₂O₃ substrates. The same LT InN buffer layer and substrate nitridation procedures were used for InN nanowire growth that which were described in greater detail in Section 3.2.4 (InN film growth).

4.3 Results

4.3.1 Proposed Mechanism for MOCVD Nanowire Growth

Nanowire growth commonly occurs via vapor-liquid-solid (VLS) growth mechanism and this mechanism is described in greater detail in Section 1.1.3. The VLS growth mechanism was first suggested by Wagner and Ellis in the 1960s to account for the growth of mm-sized silicon “whiskers” in the presence of Au particles. Confirmation of the VLS mechanism was made by Wu and Yang using real time TEM imaging of Ge nanowires grown in the presence of Au catalyst particles. In this mechanism, anisotropic crystal growth is promoted by the presence of a liquid-solid interface. A liquid metal layer resides at the growing tip of the nanowire, significantly enhancing the growth rate of the tip through a reduction in the activation of the growth process. A schematic of a typical VLS mechanism was previously given (Figure 1-7a), where a semiconductor nanowire is grown via gold catalyst-assisted growth.

A vapor-liquid-solid (VLS) growth mechanism is proposed for the growth of InN nanowires by MOCVD. For InN nanowires grown by MOCVD, the VLS mechanism is different than the process described above because the metal catalyst, indium, is self-seeded and consumed by the formation of InN. This differs from a seeded VLS mechanism that uses a separate metal catalyst that does not incorporate into the growing rod. In traditional inert catalyzed VLS, the size of the semiconductor nanowire is determined by the diameter of the
catalyst droplet, which is determined by the catalyst amount and surface tension. For MOCVD InN nanowires, the size of the initial indium droplet formed on the substrate surface does not determine the diameter of the nanowire, but the number density of nanowires formed. InN nanowire nucleation occurs at the solid-liquid interface and then carries an In droplet with it. The diameter of this droplet determines the diameter of the subsequent InN nanowire growth. This growth mechanism can be better understood schematically (Figure 4-4). The formation of indium droplets on the surface of the substrate and the indium droplets can differ in size (as shown by an increase in droplet size from left to right, Figure 4-4a). Larger indium droplets are formed by droplet coalescence in the near inlet region where the TMIn is concentrated. This concentrated region occurs primarily in the substrate zone directly under the inlet tube. This region is referred to as the deposition “hot spot” (Figure 4-5). In the “hot spot” region (orange colored region, Figure 4-5) large indium droplets are likely to form, while the light blue region represents regions where smaller indium droplets are nucleated, presumably due to the In depletion by the droplet formation in the “hot spot” region. The surface contact area of this initial indium droplet determines the resulting density of the nanowire patches (the larger the area the greater number of nanowires, Figure 4-4b). Each nanowire growing from the primary droplet contains a smaller nucleation droplet on the tip of the nanowire which acts as a catalyst for continued growth of the nanowire (Figure 4-4c).

This growth relationship was experimentally verified by SEM (Figure 4-6). The left image (Figure 4-6) represents a single nanowire growth, which occurs outside the “hot spot” deposition region (light blue region, Figure 4-5). A single nanowire is formed because the initial or primary indium droplet size was too small to produce more nanowires from the same droplet. The center image of Figure 4-6 shows a nanowire patch of a few nanowires which corresponds to the center
schematic in Figure 4-4. This type of nucleation and growth would be found in the transition region from low to high concentration of TMIn (from light blue to orange, Figure 4-5). The nanowire density increases due to an increase in indium droplet size on the surface of the substrate as the position of the substrate becomes closer to the inlet tube and higher TMIn concentration. Nanowire patches with a high density of nanowire nucleation are found in this “hot spot” region (far right image, Figure 4-6).

Previous experiments showed that InN thin films can be grown without the formation of In droplets on the film surface by using inlet N/In molar ratio greater than 50,000 (at a deposition temperature of 530 °C). InN nanowire growth occurred at the same deposition temperature (530 °C) and N/In ratio (50,000) when using the vertical inlet tube and In droplets formed at nanowire tips. Thus it is suggested from these experimental observations that the apparent N/In ratio at the substrate surface is less when the vertical inlet tube is used compared to the horizontal inlet tube design as evidenced by the formation of In droplets. It is believed that a decrease in residence time of source materials in the region of the susceptor is responsible for the discrepancy between inlet N/In ratio and apparent N/In ratio at the substrate surface. The average velocity and Reynolds number for the vertical inlet and the quartz reactor were calculated using Eqs. 4-1 and 4-3, respectively, and these values are listed in Table 4-1.

\[
\frac{\dot{V}}{A} = \frac{\dot{V}}{\pi r^2}, \text{ where } \dot{V} \text{ is the volumetric flow rate} \tag{4-1}
\]

\[
\rho = \frac{M_w P}{RT} \tag{4-2}
\]

\[
\text{Re} = \frac{\rho < v > D}{\mu}, \tag{4-3}
\]
where D is the pipe diameter and \( \mu \) is the dynamic viscosity. Although the horizontal inlet has the same outlet velocity as the vertical inlet, the gas exiting the horizontal inlet expands in the larger dimensions of the quartz reactor. This expansion occurs to fully developed flow in a length of one diameter. For the vertical inlet, the velocity at the outlet of the tube is assumed fully developed and the flow regime is an impinging jet. The average flow velocity at the outlet of each tube is two orders of magnitude higher than the average velocity of flow in the horizontal inlet (Table 4-1). Furthermore, the boundary layer that develops in an impinging jet flow scheme of this design is thinner than that developed in the boundary layer over a tilted horizontal plate. These conditions give shorter reactant residence time and less time at temperature thus gas phase reactions such as \( \text{NH}_3 \) decomposition and adduct formation should occur to a lesser extent. TMIn decomposes quickly at this temperature and is therefore less likely affected by the difference in boundary layer thickness. These combined effects create a lower effective N/In ratio when the vertical inlet tube is used and leads to the formation of indium droplets, which nucleate nanowire growth.

The formation of indium droplets is not the only requirement for successful growth of InN nanowires. The choice of substrate material significantly affects the ability to form InN nanowires. Previous experiments using the horizontal inlet showed that the InN film growth with reduced N/In ratios in the range of 6,000 to 50,000 showed no indication of nanowire formation when grown on Si (100) or LT GaN/c-Al\(_2\)O\(_3\) substrates.\(^{203}\) Substrate selection should affect the In metal wetting of the substrate, which directly affects the ability of the nanorods to form. InN nanowires were successfully grown on p-Si (100) substrates when using the vertical inlet tube, however, the same growth conditions (\( T_g = 530 \, ^\circ\text{C} \), N/In = 50,000) were unsuccessful when applied to GaN/c-Al\(_2\)O\(_3\) substrates. The same growth conditions yield different results.
when applied to p-Si (100) substrates (successful nanowire growth) and on GaN/c-Al$_2$O$_3$ substrates (no nanowire growth) (Figure 4-7). For GaN/c-Al$_2$O$_3$ substrates, crooked nanowires formed across the substrate surface and no nanowire growth occurred in the vertical direction, leading to the formation of an incomplete film. Indium wetting is known to be difficult on Si substrates which is one reason that InN film growth is challenging on silicon,\textsuperscript{257} however the lack of wetting is beneficial for nanowire growth because it creates an indium droplet which acts as a nucleation site for growth. For growth on GaN/c-Al$_2$O$_3$ substrates, indium forms a continuous wetting layer across the surface instead of droplets. It has been shown elsewhere that In-rich conditions on GaN substrates produce a monolayer of In bonded to a GaN bilayer.\textsuperscript{258} The wetting promotes 2D growth along the surface instead of 1D growth vertically (Figure 4-7).

4.3.2 Nanowire Morphology Dependence on Growth Parameters

4.3.2.1 Growth on p-Si (100) substrates

As previously mentioned, vertical (1D) growth of InN nanowires on GaN/c-Al$_2$O$_3$ substrates is more difficult than on Si (100) substrates due to the difference in surface tension of indium on the substrate surface. The lack of wetting across the silicon surface is favorable for 1D growth. For growth on silicon substrates it is important to mention the possible formation of an In-Si eutectic phase. Silicon and indium exhibit a nearly degenerate, simple eutectic phase diagram with a eutectic temperature of 156.6 °C (Figure 4-8). It is noted that at the growth temperature of 530 °C the solubility of Si is limited (< 1%). InN nanowire growth on p-Si (100) at higher deposition temperature was briefly explored, specifically at temperature greater than 650 °C. Deposition temperature in the range of 550 to 730 °C was used by other researchers to grow InN nanowires,\textsuperscript{96,104} since it was believed that higher temperatures would improve NH$_3$ decomposition efficiency. Increased NH$_3$ decomposition would increase the N/In ratio and reduce the relative amount of indium. Thermal decomposition proved to be dominant at these
temperatures and no InN nanowires were successfully grown, therefore all InN nanowires discussed in this work were grown at 530 °C. The growth conditions such as substrate nitridation, inclusion of a LT InN buffer layer, post growth annealing, inlet N/In ratio, and group V or group III preference at the beginning of growth were investigated to understand the effects on nanowire structure and morphology. Group V or group III preference simply means that either NH₃ or TMIn was allowed to flow into the reactor for several seconds prior to the other source material at the start of growth.

InN nanowires were grown on p-Si (100) substrates using the vertical inlet tube previously described (SEM, Figure 4-9). Substrate nitridation followed by a LT InN buffer layer were used as surface pretreatments before the nanowire growth. These are the same pretreatments used to grow continuous InN/Si thin films with the horizontal inlet arrangement. For comparison, a SEM image of an InN film grown at these conditions with the horizontal inlet is provided (Figure 4-10). The diameter of the InN nanowires ranged from 100 to 300 nm (see Figure 4-9a for a typical nanowire) with an average diameter of 200 nm and lengths ranged from 10 to 25 μm for 1 hr growth. The In metal droplet is clearly seen at the tip of the nanowire (Figure 4-9b), consistent with a VLS growth mechanism. The use of a LT InN buffer layer allows a high density of uniform nucleation sites to form, which promotes a high density nanowire growth on the substrate (Figure 4-9c and 4-9d). A continuous InN film is not formed by the LT InN buffer layer therefore the wetting of In on silicon (or lack there of) does not significantly change allowing for 1D growth to remain favorable.

Post growth annealing in a low pressure (100 Torr) NH₃ atmosphere was employed to determine the effect on the indium droplet at the tip of the nanowire. Annealing was done in-situ immediately after growth at 530 °C without exposing the nanowires to air. The ammonia flow
was kept at a constant flow of 1600 sccm (4 SLM N₂ dilution) for a duration up to 15 min. Ammonia reacts with the residual indium in the droplet to form a sharpened InN nanowire (SEM, Figure 4-11).

Morphological differences are clearly seen between InN grown with the horizontal versus the vertical inlet (at the same growth conditions), therefore InN nanowire growth conditions were varied to understand the effect of using substrate nitridation or a LT InN buffer layer prior to InN growth. The growth conditions and the morphological changes produced by variation in buffer layer and nitridation pretreatments, as well as group III or V source preference are summarized in Table 4-2. For simplicity the experimental run numbers (68 through 71) will be used to discuss the growth results as they pertain to substrate pretreatments used in this study. SEM images (Figures 4-12 through 4-15) are also referenced in Table 4-2 for the corresponding growth conditions. It is noted that the magnification of the images varies in these figures and the images were taken from a similar position in the “hot spot” of the flow pattern. Run 68 reproduced the InN nanowire results previously mentioned (Figure 4-9) that used both substrate nitridation followed by a LT InN buffer layer, except this run included post growth NH₃ annealing for 10 min. Similar results are obtained that show dense InN nanowires with fairly uniform diameters ranging from 100 to 300 nm (Figure 4-12). When the LT InN buffer is not used (run 69) the nanowire patch nucleation density is significantly reduced (Figure 4-13). The resulting nanowires also show a larger range of nanowire diameters (100 to 700 nm) within the same patch, however, the overall size of the nanowire patch remains nearly constant. Little variation in the nanowire patch size suggests that the nucleation processes are similar. The growth of nanowires in run 70 is done without the aid of substrate nitridation or a LT InN buffer layer. In this case the NH₃ was allowed to flow into the reactor for 10 sec prior to the initiation
of the TMIn flow and thus growth. This step is used to ensure that indium does not interact with
the substrate without the presence of NH$_3$ and no significant nitridation of the substrate is
believed to occur in 10 sec at the lower deposition temperature (based on the comparison
between substrates which were intentionally nitridated at 850 °C for 15 min). The growth results
from run 70 show a uniform nucleation distribution across the substrate surface, yet the nanowire
patches differ in size and hence the number of nanowires (Figure 4-14). The nanowire diameter
within a single patch range form 100 nm to 1 μm. No buffer layer or nitridation is used for run
71 and in contrast to run 70, TMIn was allowed to flow into the reactor without NH$_3$ present for
30 sec (Figure 4-15). In this case the nucleation sites are less ordered and the excess indium at
the beginning of the reaction leads to significant branching within the nanowire patches. The
branching leads to a larger number of smaller nanowires with respect to length and diameter.

The density of nucleation sites and nanowire size (diameter and length) can be modified by
using particular silicon substrate pretreatments before growth. The use of a LT InN buffer layer
produces densely nucleated nanowires that grow together and resulting in a “field” of nanowires.
Substrate nitridation only leads to sparse nucleation sites and a larger range of nanowire
diameters. When no surface treatment is performed prior to growth the nucleation size is less
controlled therefore there is a large variation in nanowire patch sizes. Branching occurs when
indium droplets are deposited on the surface in the absence of ammonia and the nucleation
patches vary in size and number of nanowires.

The nucleation of liquid In on the surface is clearly important to the density and size of the
patches, which are related to the density and size (length and diameter) of the nanowires. The
base growth conditions selected for this study lie on the boundary of forming InN directly and
forming In droplets. Thus NH$_3$ serves to shift this boundary at this conditions (these experiments
occur slightly within the 2-phase region). Nucleation of In droplets can occur initially only or continuously. If it is only initially and the surface properties are uniform, then a single size type distribution would be expected. If it is continuous, then the size would be greater for the early nucleation and smaller for the later ones. At higher nucleation density it is possible for secondary nucleation occur (droplet coalescence) to give size variation leading to a nanowires with a high extent of liquid fractions. Thus run 68 may be extremely high nucleation density or complete wetting (favorable InN coverage), while run 69 appears to have uniform nuclei (suggestion nucleation initially then once liquid In forms it catalyzes the NH₃ decomposition. Run 70 gives poorer surface conditions for nucleation (due to the low temperature nitridation) and run 71 gives higher nuclei density consistent with favorable In nucleation

4.3.2.2 Growth on GaN/c-Al₂O₃ substrates

The growth of InN nanowires also occurred on GaN/c-Al₂O₃ substrates, however the growth conditions had to be modified compared to those of the previous section. As previously shown the increased In wetting on the GaN surface causes InN nanowires to grow along the surface of the substrate instead of vertically (Figure 4-7). This result occurs when NH₃ is allowed to flow into the reactor slightly before TMIn. A similar result showing nanowire growth along the surface of the substrate (little to no vertical nanowire growth) is seen when TMIn is introduced into the reactor prior to NH₃ (Figure. 4-16). In this case, however, some small nanowires were found on the edges of the incomplete film regions on the GaN substrate, suggesting that the introduction of TMIn first is beneficial for forming nanowires.

To induce nanowire formation in the vertical direction the GaN substrate was preheated to 850 °C for 1 min prior to growth (4 SLM N₂ atmosphere, 100 Torr) to activate the surface of GaN. This process creates nitrogen vacancies in the surface of the film which change the metal wetting properties on the surface. Once the reactor cooled to the deposition temperature (530 °C)
TMIn was introduced into the reactor in the absence of NH$_3$ for 20 sec. Activation of the GaN surface proved critical to the formation of nanowires (Figure 4-17). Small pits in the GaN surface are clearly noticed (Figure 4-17), which were not seen in other attempts to grown InN nanowires on GaN (without the preheating step). Previously modeling work has shown that In can form a single monolayer in the top layer of GaN and even penetrate into the second monolayer.$^{259}$ Chen et al. verified the theoretical results from STM measurements and also determined that strain due to the occupation of indium in the first two monolayers caused pits to form in the GaN surface.$^{260}$ It is believed that the pit formation is the main mechanism that allows for the formation of InN nanowires on GaN substrates because the In metal wetting on the substrate is reduced, making droplet formation more likely. InN nanowires grown on GaN/c-Al$_2$O$_3$ substrates shows similar nanowire diameter and length as nanowires grown on Si substrates, 200-400 nm and 10-20 $\mu$m, respectively.

The inlet flow velocity was studied to determine the effects of the effective N/In ratio on the resulting morphology of the nanowires. For this study the nitrogen carrier gas and the ammonia flow rates were reduced by half and the TMIn flow was adjusted to maintain a constant inlet N/In ratio of 50,000. The ammonia flow was reduced from 1600 to 800 sccm and the N$_2$ carrier gas was reduced from 4000 to 2000 sccm. The reduced flow velocity out of the vertical inlet tube slightly increases the residence time of NH$_3$, which increases decomposition efficiency, therefore increasing the effective N/In ratio. The increase in the effective N/In ratio reduces the diameter of the nanowires (averaging 150 nm) and increases their length up to 40 $\mu$m for 1 hr growth (Figure 4-18). Interestingly the nanowires also exhibit very sharp tips without having to employ post growth annealing. An increase in growth rate and reduction in nanowire diameter is expected with an increase in the effective N/In ratio. Most of the nanowire growth
occurs in an In-rich regime, therefore increasing the amount of active nitrogen decreases the size of the catalyst droplet at the end of the nanowire, thus making the nanowire diameter smaller. Since active nitrogen is the limiting reactant then the growth rate will increase if the relative N/In ratio is increased.

To produce more stoichiometric growth conditions, close to single phase InN (i.e. less evidence of excess indium after growth), the inlet N/In ratio was set to 73,000, while the inlet carrier gas flow and NH$_3$ flow were also cut by half. With these conditions the overall increase in the N/In ratio was too high and no nanowires were produced (only film), and it was determined that there needed to be some In-rich step to initiate nanowire growth. A two step growth method was used in which nanowires were nucleated at a N/In ratio of 50,000 (at reduced flow velocity) for 5 min and then the inlet N/In was increased to 73,000 for the duration of the 1 hr growth. For this two step growth no indium droplet is apparent at the tip of the nanowire (Figure 4-19). The roughness of the nanowire walls is also an indication that growth did not occur via a VLS mechanism. Once the indium droplet is consumed from the initial nucleation step the reaction is believed to progress via solid-vapor mechanism. The nanowire diameters average 150 nm and the lengths are significantly shorter (< 10 μm) than the nanowires grown by VLS for the same growth duration, due to the higher N/In ratio and different growth mechanism.

### 4.3.3 InN Nanowire Composition and Structure

The InN nanowire composition and structure were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), and transmission electron microscopy (TEM). Characterization by these techniques indicates the nanowires exist as a core-shell structure which contains a single crystal InN core with a polycrystalline In$_2$O$_3$ shell (regardless of the substrate) (Figure 4-21). XRD results confirm the InN core–In$_2$O$_3$ shell structure (Figure 4-21). A single crystal InN (002) reflection exist along
with In$_2$O$_3$ (222) and In$_2$O$_3$ (400) polycrystalline reflections, at $2\theta = 31.4$, 30.6, and 35.45$^{\circ}$, respectively. Further confirmation of the composition of the core-shell structure was obtained from EDS (Figure 4-22). The electron beam was focused on a single core-shell nanowire where oxygen, nitrogen, and indium are detected as well as a silicon peak from the underlying substrate. The crystalline quality of the core-shell was analyzed using TEM and single crystal InN core and the transition to the polycrystalline In$_2$O$_3$ shell can be clearly distinguished (Figure 4-23). Selected area diffraction patterns (SADP) were taken of the InN core (Figure 4-24). The single diffraction spots reinforces that the InN core is single crystal and the pattern indicates that [00.2] is the preferred growth direction.

Evidence of the core-shell structure requires that the proposed VLS growth mechanism must account for the inclusion of oxygen. Two likely sources of oxygen are native oxides from the substrate and residual oxygen in the reaction chamber, or a combination of both sources. Oxygen from the native oxides on the substrate is possible especially when silicon substrates are used. This hypothesis was tested by comparing InN–In$_2$O$_3$ core-shell nanowires grown on native oxide Si, buffered oxide etched Si and GaN/c-Al$_2$O$_3$ substrates at the same growth conditions. XRD, SEM, and EDS analysis revealed that there was no significant difference in the oxygen content of the nanowires when grown on these different substrates. However, these characterization techniques have an oxygen sensitivity limits ~ 1%. Nevertheless this result suggests that residual oxygen from the reaction chamber (or an air leak) is also a source for oxygen contamination. This is possible since the nanowire growth experiments are carried out at low pressure, 100 Torr. The Gibbs energy of reaction ($\Delta G_i$) at nanowire growth conditions for the formation of InN and In$_2$O$_3$ are given in Eqs. 4-4 and 4-5, respectively.\textsuperscript{261}
\[
\text{In} + \text{NH}_3 \rightarrow \text{InN} + \frac{3}{2}\text{H}_2 \quad G_f = -86 \text{ KJ/mol} \quad (4-4)
\]
\[
2\text{In} + \frac{3}{2}\text{O}_2 \rightarrow \text{In}_2\text{O}_3 \quad G_f = -669.5 \text{ KJ/mol} \quad (4-5)
\]

It is clear that the formation of indium oxide is more favorable due to the larger negative Gibbs free energy value. However there is a significantly larger amount of ammonia in the reaction chamber than residual oxygen and NH\textsubscript{3} decomposition forms H\textsubscript{2} or H\textsubscript{2}O which will help reduce oxygen. Therefore it is likely that the oxide layer forms upon cooling when NH\textsubscript{3} is kinetically limited for reducing the oxide. During cooling the ammonia decomposition reduces to essentially zero\textsuperscript{242} and the reaction between indium and oxygen is still thermodynamically favorable, especially when there is excess indium metal on the outside of the nanowire.

Excess indium can be eliminated from the nanowire tip and walls of the nanowire by using a two step nucleation and growth method that adjusts the inlet N/In ratio, as described in the previous section. The elimination of the excess indium makes it less favorable for oxygen to form on the outside of the nanowire, and no oxygen signal is detected by EDS for nanowires grown at these conditions (Figure 4-25). In this case, InN nanowires were grown on a GaN/c-Al\textsubscript{2}O\textsubscript{3} substrate to minimize oxygen incorporation from the substrate (compared to Si).

From this analysis it is believed that the indium oxide layer forms on the outside of the nanowire during cooling and that the primary source of oxygen is residual oxygen in the reaction chamber (e.g. carrier gas, small leak, desorption). It is important to mention that oxygen from the substrate could also play a role, however, it is believed to be less significant.

### 4.3.4 Transport Properties of InN–In\textsubscript{2}O\textsubscript{3} Core-Shell Nanowires

Single InN–In\textsubscript{2}O\textsubscript{3} core-shell nanowires devices were fabricated and the contact resistivity and sheet resistivity of the nanowires were measured using a transmission line model (TLM). The TLM method is often used to describe current transport in lateral contacts of semiconductors.\textsuperscript{262,263} InN–In\textsubscript{2}O\textsubscript{3} core-shell nanowires were grown on nitridated Si (100)
substrates at 530 °C for 1 hr and then annealed in NH₃ for 15 min in-situ immediately after
growth. The core-shell nanowires were removed from the silicon substrate by sonication and
then transferred to an insulating substrate. A shadow mask was used to evaporate Ti/Al/Pt/Au
(20/80/40/80 nm) ohmic contacts. Metal was deposited in the openings of the shadow mask
(50 x 50 μm² or 115 x 115 μm²) leaving 10 μm gaps between metal contacts to provide electrical
contacts to the nanowires (Figure 4-26).

To determine contact and sheet resistivity, the total resistance of several InN-In₂O₃ core-
shell nanowires was measured from I-V measurements (Figure 4-27 and Eq. 4-6). The total
measured resistance (Rₜ) for a circular wire is given by Eq. 4-7.²⁶⁴

\[ V = I R_T \]  \hspace{1cm} (4-6)

\[ R_T = 2R_c + \left( \frac{\rho_s}{\pi} \right) \left( \frac{L}{r^2} \right) \]  \hspace{1cm} (4-7)

Rₖ is the total contact resistance, ρₛ is the sheet resistivity of the InN – In₂O₃ wire, L is the length
of the wire, and r is the radius. The total measured resistance from I-V data for 4 samples was
plotted versus L/r² (Figure 4-28). The nanowire dimensions were determined by SEM (Figure
4-29). A linear relationship was fit to the experimental data from Figure 4-28. It can be seen
from Eq. 4-7 that the slope of the trendline in Figure 4-28 is equal to ρₛ/π, while the y-intercept is
equal to 2Rₖ. Therefore the sheet and contact (ρₖ) resistivity are calculated from Eqs. 4-8 and
4-9.²⁶⁵

\[ \rho_s = \pi \cdot \text{slope} \]  \hspace{1cm} (4-8)

\[ \rho_c = \frac{2r^3 \pi^2 R_c^2}{\rho_s} \]  \hspace{1cm} (4-9)

From the experimental data presented, the sheet resistivity and contact resistivity for a single
InN–In₂O₃ nanowire is 1.5 x 10⁻³ Ω-cm and 1.16 x 10⁻⁵ Ω-cm². The value for contact resistivity
is only an approximation because small changes in the slope of the linear fit of the TLM method can significantly change the magnitude of $\rho_c$.

The sheet resistivity of the InN–In$_2$O$_3$ core shell nanowires presented here were compared to InN nanowires grown by ammonization of indium metal on gold patterned silicon substrates at 500 °C in a tube furnace. InN nanowires grown by this method produced a sheet and contact resistivity of $4 \times 10^{-4}$ Ω-cm and $1.09 \times 10^{-7}$ Ω-cm$^2$, respectively. The sheet resistivity of the InN–In$_2$O$_3$ core-shell nanowires is one order of magnitude higher than the referenced InN nanowires. The oxide shell is believed to be responsible for the increase in resistivity because it reduces the available cross sectional area for current transport. It is believed that the oxide shell does not have a more significant impact on the sheet resistivity because the InN core is very conductive. Increased conductivity in the InN core could be due to an In-rich InN layer between the nitride and the oxide or potential silicon doping of the InN. As previously mentioned silicon and indium form a eutectic phase at 156.6 °C. Even though silicon is an amphoteric dopant in many III-V compound semiconductors, Si has been shown to be an n-type dopant in InN. TLM data also suggests that contact resistivity of the InN–In$_2$O$_3$ core-shell nanowires is two orders of magnitude higher than the referenced InN nanowires. It was previously mentioned that experimental errors could significantly affect these value so verifying the two order of magnitude difference in contact resistivity is not possible. It is safe to assume, however, that the addition of an oxide shell on the nanowire would increase the contact resistivity.

4.3.5 Single InN–In$_2$O$_3$ Core-Shell Nanowire for H$_2$ Gas Sensing

Using nanowires for gas sensing devices has proved to be advantageous due to their large surface to volume ratio, low power consumption, selectivity at room temperature, and low weight. Development of selective nanowire H$_2$ gas sensors is important for use with proton-exchange membrane (PEM) and solid oxide fuel cells (SOFCs), which are proposed for
use in space and future transportation applications. The mechanism for gas detection involves the removal or addition of atoms on the surface of the nanowire, which changes the conductivity of the nanowire. Oxygen molecules will absorb onto the In$_2$O$_3$ shell surface of the InN–In$_2$O$_3$ core-shell nanowire after air exposure. Once H$_2$ is introduced into the system a reduction of the absorbed oxygen surface states will occur, leading to a drop in the nanowire resistance due to a creation of surface donor sites (oxygen vacancies).

To test the capability of InN–In$_2$O$_3$ core shell nanowires for selective H$_2$ gas sensing, single wires devices were fabricated by the same method as described in Section 4.3.4. Single InN – In$_2$O$_3$ core shell nanowires were wire bonded before testing (Figure 4-31). The I-V characteristics for time dependent current response under N$_2$ and 500 ppm H$_2$ (in N$_2$) ambients of the single wire device were determined (Figure 4-32). The I-V characteristics are identical for both ambients, which indicates that there is no selective response to H$_2$ (Figure 4-32a). This result is confirmed with time dependent current measurements (Figure 4-32b) that show no signal response when the nanowire is exposed to hydrogen. The H$_2$ sensitivity of a gas sensor can be increased by adding a catalytic metal coating or by doping the sensor material with a transition metal. A catalyst such as Pt will functionalize the surface of the nanowire and promote the dissociation of H$_2$.

For this reason individual core-shell nanowires were sputter coated with Pt clusters in an attempt to improve the H$_2$ signal response from the nanowires. Core-shell nanowires were coated with 3 and 10 Å of Pt and the corresponding I-V characteristics and time dependent response to 500 ppm of H$_2$ were measured (Figures 4-33 and 4-34, respectively). It can be seen from the I-V characteristics (Figure 4-33) that the bare and 3 Å Pt coated nanowire show similar conductivity, but the 10 Å Pt coated nanowire shows an order of magnitude increase in the
conductivity. The increase in conductivity after the 10 Å coating is most likely due to the formation of a continuous Pt film instead of Pt clusters. This possibility is reinforced when the 10 Å Pt coated core-shell nanowire registers a significantly higher current response to the introduction of 500 ppm H₂ (in N₂) compared to the 3 Å Pt coating (Figure 4-34b). The 3 Å coating does increase the signal response to H₂ compared to the bare core-shell nanowire (Figure 4-34a), however, the signal only changes 1.3 µA (0.5% change). The signal response for the bare or 3 Å coated nanowire is too low for these InN–In₂O₃ core-shell nanowires to be effective for detecting H₂. One possible reason that the InN–In₂O₃ core shell nanowires were not able to selectively detect hydrogen is because the wires were intrinsically too conductive. This causes the depletion effect to be too small thus causing a low sensitivity.

4.4 Conclusions

Controlled growth of InN nanowires was successfully demonstrated using a standard MOCVD reactor by changing the flow pattern with a modified inlet tube. The modified vertical flow regime reduced the residence time of NH₃ over the hot susceptor, thus reducing decomposition and decreasing the effective N/In ratio. A lower N/In ratio leads to excess indium and the stability of In droplets. Poor wetting of the substrate surface by liquid indium proved to be critical to the formation of nanowires. The excess indium acts as a catalyst site and remains at the tip of the nanowire to promote subsequent growth. It is important to mention that lowering the N/In ratio while using the horizontal inlet tube does not lead to nanowire formation.

Nanowires were grown on Si (100) substrates and the morphology of the nanowires was sensitive to the growth conditions. The use of nitridation followed by growth of a LT InN buffer layer produces dense fields of uniform diameter nanowires that completely cover the substrate. Growth without a LT InN buffer leads to less dense growth, which forms patches of InN nanowires. Nanowire length, diameter, and degree of branching changed with the use of
substrate nitridation and/or initial exposure to only TMIn or NH₃ source materials for a
determined length of time prior to the start of growth. Post-growth NH₃ annealing was shown to
sharpen the tip of the nanowire and eliminate the amount of indium metal at the tip of the
nanowire. The dimensions of the nanowires depend on the growth conditions applied, but the
InN nanowires have average diameters in the range of 100 to 400 nm with lengths ranging from
10 to 25 μm. It was also found that a reduction in flow velocity increased the relative N/In ratio
during growth, which leads to reduced nanowire diameter (~ 150 nm) and increased length, up to
40 μm for a 1 hr growth.

Characterization of the nanowires revealed that an InN–In₂O₃ core-shell structure was
formed during growth. The InN core was found to be single crystal with the preferred growth in
the [002] direction while the In₂O₃ shell is polycrystalline. Potential sources of oxygen are from
the substrate surface (especially in the case of Si) as well as residual oxygen in the reaction
chamber (e.g. inlet gas source, air leak). It is believed that the oxide shell is formed during
cooling when NH₃ can no longer reduce residual oxygen species at lower temperatures (due to
decreased thermal decomposition efficiency).

GaN/c-Al₂O₃ substrates required that the growth conditions used for Si substrates be
modified to reduce the amount of indium wetting on the GaN surface. It was also found that
using a two-step growth method of nucleation at a lower N/In ratio followed by growth at a
higher N/In ratio eliminated the indium droplet form the tip of the nanowire. The growth method
is believed to change from a VLS to a VS growth mechanism when the excess indium from the
nucleation step is consumed, producing a rough surface morphology with no indium droplet tip.
These nanowires also were much shorter (5 μm), which is additional evidence for a solid-vapor
growth mechanism. The lack of excess indium on the surface of the nanowires also eliminated
the oxide shell from forming on the nanowire. The surface morphology of the nanowires grown by the VS mechanism shows a similar surface morphology to InN thin films grown by MOCVD (using the horizontal inlet). This is further confirmation that a VS mechanism occurs at higher N/In ratios.

Single nanowire transport measurements were done using the transmission line method (TLM), which showed that the core-shell nanowires were highly conductive and that the oxide shell increased the contact resistance. The nanowires were believed to be highly conductive due to n-type silicon doping or a possible In-metal rich layer between the oxide shell and the nitride core. This high conductivity also proved to be detrimental for using these nanowires as single nanowire gas sensing devices. It is believed a reduce field effect led to a small change upon exposure to dilute H₂ (in N₂) gas, which was not significant enough for the required device applications. Nanowires without the presence of the oxide shell were unable to be tested due to the difficulty in testing nanowires with lengths below 10 μm.

Figure 4-1. Schematic of the standard horizontal inlet tube and its position with respect to the graphite susceptor. Stream lines are shown for the expected flow pattern.
Figure 4-2. Schematic of the vertical quartz inlet tube and its relative position with respect to the graphite susceptor. Stream lines are shown to demonstrate the expected flow pattern.

Figure 4-3. Inlet tube dimensions for film and nanostructured growth. A) horizontal (film) inlet tube. B) vertical (nanostructure) inlet tube.
Figure 4-4. Schematic of the VLS mechanism for InN nanowire growth by MOCVD. 
A) Primary nucleation of indium droplets with varying sizes on the substrate surface. 
B) Initial nanowire formation plus secondary formation of nanowire In metal catalyst. 
C) Nanowire density as a function of primary indium droplet size.

Figure 4-5. Overhead view of vertical inlet tube showing the hot spot deposition zone (orange) and the region where small In metal primary nucleation is likely to form (light blue).
Figure 4-6. Experimental verification of the proposed nanowire density variation due to initial indium droplet nucleation size. Upon close inspection the metal indium droplet can be seen at the tip of each nanowire.

Figure 4-7. Effect of In metal wetting for InN nanowire growth on Si (100) and GaN substrates. Successful nanowire growth on silicon substrates (poor In metal wetting leading to droplet formation) and unsuccessful growth on GaN/c-Al₂O₃ substrates (complete In metal wetting, no droplet formation).
Figure 4-8. Indium-Silicon binary phase diagram (obtained from the Center for Research in Computational Thermochemistry website using the compound and solution “Fact” database, http://www.crct.polymtl.ca/fact/documentation/, retrieved March 2007, site authored by Christopher W. Bale).

Figure 4-9. Scanning electron microscope images of InN nanowires grown on p-Si (100) substrates using nitridation followed by a LT InN buffer pretreatment. A) Single InN nanowire with 250 nm diameter. B) Single InN nanowire showing indium droplet at tip. C and D) High density of nanowires growing together and covering the substrate.
Figure 4-10. Scanning electron microscope image of a continuous polycrystalline InN thin film grown with the horizontal inlet arrangement on p-Si (100). Substrate nitridation followed by a LT InN buffer layer pretreatment was used for this experiment.

Figure 4-11. Effect of post growth annealing on InN nanowire tip morphology. A) No anneal showing indium droplet. B) Sharpened InN nanowire tip after 15 min NH₃ anneal (T = 530 °C, 1600 sccm, 100 Torr).
Figure 4-12. Scanning electron microscope images of InN nanowires (experiment number 68) showing uniform dense coverage of the substrate. Growth conditions are summarized in Table 4-2.

Figure 4-13. Scanning electron microscope images of InN nanowires (experiment number 69) showing less dense substrate coverage with uniform patches of nanowires. Growth conditions are summarized in Table 4-2.
Figure 4-14. Scanning electron images of InN nanowires (experiment number 70) showing uniform coverage of the substrate with nanowire patches that vary in size and nanowire density per patch. Individual nanowires vary in diameter and length. Growth conditions are summarized in Table 4.2.
Figure 4-15. Scanning electron microscope images of InN nanowires (experiment number 71) showing less ordered nanowire growth with significant nanowire branching. Growth conditions are summarized in Table 4.2.

Figure 4-16. Scanning electron microscope image of unsuccessful InN nanowire growth on GaN/c-Al₂O₃ substrate. TMIn was allowed to flow into the reactor in the absence of NH₃ for 20 sec.
Figure 4-17. Successful growth of InN nanowires on GaN/c-Al₂O₃ substrates by activating the surface of GaN. Surface activation occurred at 850 °C (in N₂ atmosphere) for 1 min before growth at 530 °C. Post growth NH₃ annealing was done for 15 min at 530 °C for this experiment.

Figure 4-18. Scanning electron microscope image of InN nanowires grown on GaN/c-Al₂O₃ substrate at reduced inlet flow velocities. No post-growth NH₃ anneal was used.
Figure 4-19. Scanning electron microscope images of InN nanowires grown on GaN/c-Al$_2$O$_3$ using two-step nucleation and growth approach. Nucleation and growth used a N/In of 50,000 and 73,000, respectively. N/In ratios are for reduced flow rate conditions, NH$_3$ = 800 sccm, and N$_2$ carrier = 2000 sccm.
Figure 4-20. Scanning electron microscope images depicting the InN core-In$_2$O$_3$ shell structure seen from broken nanowires.
Figure 4-21. X-ray diffraction spectra of InN core-shell nanowires on Si (100) substrate indicating single crystal InN and polycrystalline In$_2$O$_3$ phases.

Figure 4-22. Energy dispersive spectroscopy spot analysis on the outside of a core-shell nanowires where indium, nitrogen, and oxygen are detected as well as silicon from the underlying substrate.
Figure 4-23. Transmission electron microscope images of a single InN-In$_2$O$_3$ core-shell nanowire. The core and shell can be clearly identified and are labeled appropriately.
Figure 4-24. Selected area diffraction patterns of the InN core of an InN-In$_2$O$_3$ core-shell nanowire. The patterns indicate the core is single crystal and that growth occurs on the [00.2] direction.

Figure 4-25. Energy dispersive spectroscopy showing no oxygen detected for nanowires grown at high inlet N/In ratios and reduced flow velocities. No In droplet at the nanowire tip was evident (Figure 4-18).
Figure 4-26. Scanning electron microscope image of single InN–In$_2$O$_3$ core-shell nanowire contacted by Ti/Al/Pt/Au pads for electrical measurements.

Figure 4-27. Current-voltage measurements for several InN–In$_2$O$_3$ core-shell nanowires, used for determining the total resistance ($R_T$) of each wire.
Figure 4-28. The total measured resistance versus $l/r^2$ for InN–In$_2$O$_3$ nanowires.

Figure 4-29. Scanning electron microscope images and dimensions of single InN–In$_2$O$_3$ core-shell nanowires used in the contact and sheet resistivity calculations.
Figure 4-30. Optical micrograph of a single InN–In$_2$O$_3$ core-shell nanowire after wire bonding.

Figure 4-31. Current-voltage characteristics and time dependent response of InN–In$_2$O$_3$ single wire device under N$_2$ and 500 ppm H$_2$ (in N$_2$) ambients. A) Current-Voltage characteristics. B) Time dependent response.
Figure 4-32. Current-voltage characteristics of single InN–In$_2$O$_3$ core-shell nanowires before and after coating with 3 or 10 Å of Pt.

Figure 4-33. Time dependent current response of a single InN–In$_2$O$_3$ core-shell nanowires in a 500 ppm H$_2$ ambient with different thicknesses of Pt. A) Bare and 3 Å Pt coated core-shell nanowire. B) 10 Å Pt coated core-shell nanowire.
Table 4-1. Flow velocities and Reynolds number at the outlet of the vertical inlet and inside the quartz reactor tube (Ref. 203).

<table>
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<tr>
<th></th>
<th>Vertical inlet</th>
<th>Quartz reactor</th>
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<tbody>
<tr>
<td>Carrier gas, N₂</td>
<td>4000 sccm</td>
<td>4000 sccm</td>
</tr>
<tr>
<td>Ammonia flow</td>
<td>1600 sccm</td>
<td>1600 sccm</td>
</tr>
<tr>
<td>Total flow</td>
<td>5600 sccm</td>
<td>5600 sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>100 Torr</td>
<td>100 Torr</td>
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<tr>
<td>Pipe diameter</td>
<td>0.386 cm</td>
<td>8.5 cm</td>
</tr>
<tr>
<td>Kinematic viscosity, n</td>
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<td>$1.116 \times 10^{-6}$ m$^2$/s</td>
</tr>
<tr>
<td>Average velocity, $\langle v \rangle$</td>
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<td>0.0164 m/s</td>
</tr>
<tr>
<td>Reynolds number</td>
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<td>12.5</td>
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</table>
Table 4-2. The InN nanowire growth conditions for samples with varying substrate/surface pretreatments and the resulting morphology information.

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<th>69</th>
<th>70</th>
<th>71</th>
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</thead>
<tbody>
<tr>
<td>InN buffer layer (duration / temperature)</td>
<td>15 min / 450 °C</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Nitridation (duration / temperature)</td>
<td>15 min / 850 °C</td>
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<td>none</td>
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<tr>
<td>Source valve opened first (duration)</td>
<td>NH₃ (5 sec)</td>
<td>NH₃ (5 sec)</td>
<td>NH₃ (10 sec)</td>
<td>TMIn (30 sec)</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>530 °C</td>
<td>530 °C</td>
<td>530 °C</td>
<td>530 °C</td>
</tr>
<tr>
<td>Inlet V/III ratio</td>
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<td>50,000</td>
<td>50,000</td>
<td>50,000</td>
</tr>
<tr>
<td>Post growth annealing (Duration / temperature)</td>
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<td>10 min / 530 °C</td>
<td>10 min / 530 °C</td>
<td>10 min / 530 °C</td>
</tr>
<tr>
<td>Reference figure</td>
<td>Figure 4-10</td>
<td>Figure 4-11</td>
<td>Figure 4-12</td>
<td>Figure 4-13</td>
</tr>
<tr>
<td>Separation between nanowire patches</td>
<td>~ 0</td>
<td>20 - 100 μm</td>
<td>0 - 10 μm</td>
<td>0 - 20 μm</td>
</tr>
<tr>
<td>Nanowire patch size variation</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Nanowire diameter range</td>
<td>100 - 300 nm</td>
<td>100 - 700 nm</td>
<td>100 - 1000 nm</td>
<td>60 - 400 nm</td>
</tr>
<tr>
<td>Nanowire length range*</td>
<td>10 - 25 μm</td>
<td>10 - 25 μm</td>
<td>8 - 20 μm</td>
<td>1 - 20 μm</td>
</tr>
</tbody>
</table>

*based on 1 hr growth
CHAPTER 5
GROWTH AND CHARACTERIZATION OF INDIUM NITRIDE NANO- AND MICRORODS
BY HYDRIDE-METAL ORGANIC CHEMICAL VAPOR DEPOSITION

5.1 Introduction

As discussed in Chapter 4, the growth of InN nanowires can be achieved by MOCVD, however the inlet N/In ratio must be precisely controlled during growth because indium droplet formation is sensitive to this growth parameter. The presence of indium metal also leads to the formation of indium oxide, which may not be desired for particular applications such as III-nitride heterostructure nanorods. Therefore there is a motivation to produce InN nanostructures without excess indium that can react to form oxides.

In this chapter the growth of InN nano- and microrods were grown by H-MOCVD on GaN/c-Al₂O₃, c-Al₂O₃, and silicon substrates. The effect of growth parameters, such as Cl/In ratio and temperature were specifically investigated and the resulting nanostructures were characterized to investigate the nanorod structural and optical properties.

5.2 Experimental Procedure

5.2.1 Substrate Preparation

Silicon substrates were cleaned in warm TCE, acetone, and methanol each for 5 min and blown dry with a nitrogen gun before loading. Sapphire substrates were only cleaned in warm methanol for 5 min and blown dry, while no chemical cleaning was done for GaN/c-Al₂O₃ substrates. A nitrogen gun was used to remove any particulates from the GaN substrate surface before loading.

5.2.2 The H-MOCVD Reactor and Deposition Technique

The H-MOCVD growth technique is similar to conventional MOCVD because metal organic sources are used, yet the H-MOCVD reactor has the ability include HCl in the source gas stream. The addition of HCl forms metal chlorides by reacting with the metal organic species
and the chlorides subsequently react with the group V species (NH$_3$). In traditional MOCVD, metal organic molecules react directly with ammonia. For this reason the technique has been dubbed hydride or “H-” MOCVD. When HCl is not used the reactor can be operated as a standard MOCVD reactor.

This H-MOCVD technique is beneficial because the MOCVD design offers the ability to do precise source switching, which is not possible with standard HVPE growth techniques that use liquid metal sources, due to metal chloride outgassing. Similar to HVPE growth, the H-MOCVD technique has been shown to produce high growth rates of high quality GaN (20 μm/hr)$^{270}$ InN nanorods have also been demonstrated by this growth technique and the nanostructures have been shown to be beneficial for selective gas detection devices.$^{271}$ H-MOCVD is also beneficial because the polarity of the grown films can be controlled. When HCl is used N-faced films are grown (producing a rough surface) and Ga-faced films are grown (resulting in a smooth surface) when conventional MOCVD mode is used (on c-Al$_2$O$_3$ substrates). It was also mentioned in Chapter 3 that the use of HCl allows InN films to be grown at low N/In ratios without the formation of indium droplets on the surface.

The H-MOCVD operates at atmospheric pressure and is a hot walled reactor that uses six individually controlled heating elements to control the temperature of the quartz reactor tube. Quartz starts to become less rigid when the temperature is above the 1000 °C, therefore the maximum reactor temperature is limited to 1000 °C. A load lock is used to minimize oxygen contamination from reaching the reactor and the substrates are loaded into the growth zone on a tilted quartz susceptor with a magnetic load arm. Waste gases pass through Novapure S407 scrubber media for removal of unreacted ammonia and then vented to the atmosphere. TMIn, TMGa, NH$_3$, and 10% HCl (in nitrogen) are used as source materials and N$_2$, H$_2$ or 4% H$_2$ (in
nitrogen) can be used as a carrier gas. The H-MOCVD reactor uses a triply concentric inlet tube to deliver the source gases (Figure 5-1). The overall reaction and decomposition mechanisms are shown below in Eq. 5-1 through 5-3 and 5-4 through 5-6, respectively.

\[
\begin{align*}
\text{In(CH}_3\text{)}_3\text{(g)} + \text{HCl (g)} & \rightarrow \text{InCl(g)} + 3\text{CH}_4\text{ (g)} + \text{C}_2\text{H}_6\text{(g)} \quad (5-1) \\
\text{InCl(g)} + \text{NH}_3\text{(g)} & \rightarrow \text{InN(s)} + \text{HCl(g)} + \text{H}_2\text{(g)} \quad (5-2) \\
\text{In(CH}_3\text{)}_3\text{(g)} + \text{NH}_3\text{(g)} & \rightarrow \text{InN(s)} + 3\text{CH}_4\text{(g)} \quad (5-3) \\
\text{InN(s)} & \rightarrow \text{In (l)} + \frac{1}{2} \text{N}_2\text{(g)} \quad (5-4) \\
\text{In(l)} + \text{HCl} & \rightarrow \text{InCl} + \frac{1}{2} \text{H}_2 \quad (5-5) \\
\text{InN(s)} + \text{HCl(g)} & \rightarrow \text{InCl(g)} + \frac{1}{2} \text{H}_2\text{(g)} + \frac{1}{2} \text{N}_2\text{(g)} \quad (5-6)
\end{align*}
\]

TMIn flows out of the smallest diameter tube at the center of the inlet where it reacts with HCl to form InCl (Eq. 5-1). The InCl leaves the inlet tube and reacts with NH3 to form InN in the hot substrate zone (Eq. 5-2). It is possible for InCl3 to form along with of InCl, however InCl3 has been determined to be thermodynamically unfavorable (compared to InCl) when the temperature is greater than 450K.\textsuperscript{272} The overall reaction for MOCVD mode (i.e. no HCl flow) is shown in Eq. 5-3. Decomposition reactions can also occur, such as thermal decomposition of InN at the growth temperature (Eq. 5-4) or etching of InN by HCl (Eq. 5-6). Complex chemical equilibrium calculations of the In-C-H-Cl-N system show that In droplets are preferentially etched (Eq. 5-5) before InN (Eq. 5-6) at typical InN growth temperatures (500-600 °C).\textsuperscript{234} Reactions in an H\textsubscript{2} ambient were not considered since InN is typically grown in a nitrogen carrier gas.

5.3 Results

5.3.1 Characterization of InN Nanorods Grown on Different Substrates

InN nanorods were grown by H-MOCVD on a-, c-, and r-plane orientations of Al\textsubscript{2}O\textsubscript{3} as well as Si (111) and GaN (0001) substrates. InN nanorods were grown at a deposition
temperature of 600 °C, N/In ratio of 250, and a Cl/In ratio of 4.0. Growth on different substrates was investigated to understand how the polarity of the chosen substrate affects the structural properties of the nanorods. After growth InN nanorods were “shaved” from the surface of the surface and placed onto lacey carbon grids for analysis by TEM.

Growth on a-, c-, and r-Al$_2$O$_3$ substrates yield single crystal InN nanorods, however they differ by shape and faceting. Some of the nanorods are orientated in the c-axis however many nanorods grow in flower-like arrangement which results in randomly oriented growth directions of the nanorods (Figure 5-2). The most noticeable difference between InN nanorods grown on a-, c-, and r-Al$_2$O$_3$ is the different morphologies of the nanorod tips. Growth on a- and c-Al$_2$O$_3$ produces hexagonal cross sectioned tips (Figure 5-3), which are atomically flat while growth on non-polar r-Al$_2$O$_3$ generates faceted pencil-like tips (Figure 5-4). The lack of diffraction contrast in the TEM images indicates a high level of structural perfection in the nanorods. When the nanorod is separated from the substrate surface the bottom edge is rectangular and is not atomically flat. This helps determine the growth direction of the nanorods (Figure 5-3 and 5-4). The tip facets form at a 30° angle to the long facets on the side of the nanorod (Figure 5-4). When the nanorod is separated from the substrate a rectangular end is formed (TEM, Figure 5-5). The pencil-like tip of InN nanorods grown on r-plane Al$_2$O$_3$ are not atomically sharp, an approximately 20 nm plateau in the c-axis is found at the nanorod tip (Figure 5-6). Plane bending occurs in the tip of the sharpened nanorod (Figure 5-7). InN nanorods grown on Si (111) substrates have a similar tip shape as nanorods grown on r-Al$_2$O$_3$ while nanorods grown on GaN/c-Al$_2$O$_3$ show a similar morphology to nanorods grown on a-,c-Al$_2$O$_3$. Nanorods grown on Si (111) substrate show slightly asymmetric tips compared to r-Al$_2$O$_3$ (Figure 5-8). InN nanorods grown on all five different substrates show some sort of atomic roughness along the
long side facets of the nanorod (Figure 5-9). Some nanorod specimens exhibit atomic
smoothness along one of the side facets, however roughness is usually observed.

Convergence beam electron diffraction (CBED) was done on an InN nanorod grown on
a-Al\textsubscript{2}O\textsubscript{3}. The CBED analysis revealed that the atomically flat facets at the top end of the
nanorod form at 60\textdegree angles with respect to the c-axis (Figure 5-10). Occasionally the diameter of
InN nanorods grown on a-Al\textsubscript{2}O\textsubscript{3} varies along the length, shown by the v-shaped notch in region
II of Figure 5-10a. CBED patterns of region II (Figure 5-10c) shows the presence of two crystals
which are rotated 60\textdegree from each other. This 60\textdegree rotation corresponds to the [0\overline{1}11] direction
which has the same displacement vector as prismatic stacking faults (PSFs) which commonly
occur in InN films grown on sapphire substrates\textsuperscript{273}. It is possible that these PSFs are responsible
for the flower-like growth structure seen for these InN nanorods. The InN nanorod is grown
with nitrogen polarity, which is consistent with previous results (Figure 5-11).\textsuperscript{272}

Electron energy loss spectroscopy (EELS) was used to verify composition of the InN
nanorods. The majority of InN nanorods show a pure In and N composition however oxygen is
occasionally detected due to a small oxide layer on the outside of the InN nanorods. The oxygen
detection usually occurs when Al\textsubscript{2}O\textsubscript{3} substrates are used. EELS spectra are shown for InN
nanorods for grown on c-Al\textsubscript{2}O\textsubscript{3}, with and without the presence of a thin oxide layer (Figure
5-12). The amorphous oxide layer seldom forms, however, when formed it is very thin
compared to the size of the nanowire (Figure 5-13). Residual oxygen in the reactor is a potential
source of oxygen contamination that occasionally leads to the formation of a thin amorphous
surface oxide. This is the most likely source of oxygen contamination since the experiments are
carried out at atmospheric pressure. It is also possible that a small oxide layer could form after
the rods are exposed to air, however, not likely since the oxide layer is seldom detected.
InN nanorods were measured by photoluminescence (PL) and optical properties of the nanorods differ slightly depending on the substrate used for growth. The position of the PL peaks for all nanorods tested fell in the range of 0.9-0.95 eV (Figure 5-14), which corresponds to a carrier concentration of the mid 10¹⁹ (based on the Moss-Burstein effect and a true band gap energy of 0.7 eV). These PL results are slightly lower than energy values obtained previously (1.08 eV).²⁷² The properties of these nanorods are consistent with bulk InN because the nanorod diameters are typically greater than 100 nm. The crystalline quality and the diameter of the nanorod are expected to affect PL intensity as well as position of the peak. Larger sized diameter nanorods are expected to yield a stronger intensity and a lower PL energy because there is less electron accumulation at the surface. A surface electron accumulation layer typically forms in InN and is expected to over estimate the band gap energy of InN due to the Moss-Burstein effect.¹⁶,¹⁷,¹⁵⁸,¹⁵⁹,¹⁶⁰ A larger diameter nanorod will have a lower concentration of electron accumulated at the surface and therefore produce a larger intensity. InN nanorods grown on Si (111) substrates, which have the largest diameter (~ 600 nm) of samples tested, produces the strongest peak intensity and lowest peak energy (Figure 5-14).

5.3.2 Growth of InN Nano- and Microrods to Increase Aspect Ratio.

Previous growth of InN nanorods by H-MOCVD has shown that typical diameters of InN nanorods range from 100 to 300 nm and lengths of about 1 μm for a 1 hr growth.²⁷² Therefore the typical lengths to width (aspect) ratios range from 10:1 to 3.3:1. Single rod device fabrication of individual nanorods is cumbersome when the lengths are less than 10 microns. When increasing the length of the nanorod it is desired that the diameter remains in the nanometer range so the properties of the nanostructure remains significantly different than bulk materials. For this reason growth parameters such as deposition temperature, Cl/In ratio, and
N/In ratio were varied in an effort to increase the aspect ratio of InN nanorods grown by H-MOCVD. The Cl/In ratio is the ratio of inlet molar flows of HCl and TMIn.

InN nanorods with the dimensions previously mentioned were grown at 600 °C, N/In ratio of 250 and a Cl/In ratio of 4.0 for 1 hr. The growth duration was increased to 90 min and the microrods (no longer nanometer sized) aspect ratio remained consistent with an average aspect ratio of 7:1 (Figure 5-15). The growth temperature was increased to 650 °C and the Cl/In ratio was increased to 4.5, the N/In ratio (250) remained constant and nanorods were grown for 90 min. The density of the microrods was slightly reduced and the lengths ranged from 10 to 30 μm, but the diameter also ranged from roughly 1 to 5 μm, resulting in no change in the overall aspect ratio. The Cl/In ratio was again increased to 5.0 without changing the growth temperature, N/In ratio, or growth duration (650 °C, 250, 90 min, respectively). Again the nanorods exhibited a similar aspect ratio and only the density of the nanorods on the substrate was reduced (Figure 5-16). The growth temperature was increased to 700 °C and the N/In ratio was reduced to 200 while the Cl/In ratio remained at 5.0 for a 90 min growth. At these growth conditions etching becomes dominant and the microrods are almost completely etched (Figure 5-17). Post growth HCl etching was done to see if the InN microrods could be controllably etched to reduce the diameter to a nanometer range. Post growth etching (1.1 sccm HCl, T\text{anneal} = 550 °C, 30 min) of InN microrods (T_g = 650 °C, N/In = 250, Cl/In = 4.5) revealed that non-uniform etch pits formed on the microrod surface (Figure 5-18).

From this study it is shown that the length of H-MOCVD InN nanorods can only be increased at the expense of increasing the diameter, which usually proceeds into the microrod range. A random sampling of InN microrod lengths and diameters are given for a variety of growth conditions (Table 5-1). From this sample set it can be seen that the aspect ratio never
exceeds 10:1 and that the average aspect ratio is 8:1. Post growth etching reveals that even though the nanorods have been shown to uniformly grow in the growth-etch transition region it is not possible to uniformly etch the microrods.

5.3.3 Transport Properties of InN Microrods

Single InN microrod devices were fabricated and the contact resistivity and sheet resistivity of the microrods were determined by using a transmission line model. This is a similar method that was used to test the transport properties of InN–In$_2$O$_3$ core-shell nanowires (Section 4.3.4). InN microrods were grown on Si (111) substrates at 650 °C for 90 min at a N/In ratio = 250 and Cl/In = 4.5. The InN microrods were removed from the silicon substrate by sonication and then transferred to an insulating substrate. A shadow mask was used to evaporate Ti/Al/Pt/Au (20/80/40/80 nm) ohmic contacts. Metal was deposited in the openings of the shadow mask (50 x 50 μm$^2$ or 115 x 115 μm$^2$) leaving 10 μm gaps between metal contacts. The total measured resistance ($R_T$) for a hexagonal wire (Eq. 5-7$^{264}$ was determined from I-V measurements (Figure 5-19) using Eq. 5-8.

\[
R_T = 2R_c + \left(\frac{2\rho_s}{3\sqrt{3}}\right)\left(\frac{L}{a^2}\right) \tag{5-7}
\]

\[
V = IR_T \tag{5-8}
\]

\[
\rho_s = \frac{3\sqrt{3} \cdot \text{slope}}{2} \tag{5-9}
\]

\[
\rho_c = \frac{27}{\sqrt{3}} \left(\frac{a^3 R_c^2}{\rho_s}\right) \tag{5-10}
\]

The total measured resistance from I-V data was plotted versus microrod length/a$^2$, where a is the distance from the center of the microrod to the facet edge (Figure 5-20). The microrods and their corresponding dimensions were determined by SEM (Figure 5-21). A linear fit was assigned to the data (Figure 5-20) where the y-intercept corresponds to half the contact resistance ($R_c$) and the relationship between the slope of the line and sheet resistivity is shown in Eq. 5-9. Once the
sheet resistivity and contact resistance are determined the contact resistivity can be calculated (Eq. 5-10).

The sheet and contact resistivity for InN microrods was determined to be $2 \times 10^{-2}$ and $4 \times 10^{-6} \, \Omega \cdot \text{cm}$, respectively. When compared to the transport measurements done for InN–In$_2$O$_3$ in Chapter 4, the InN microrods have a higher sheet resistivity and a lower contact resistivity. It is not useful to compare the contact resistivity of the microrods to the nanowires because small changes in the slope of the linear fit could significantly change these values. It is likely that the InN microrods have a higher sheet resistivity because the core-shell nanowires are so conductive (thus giving a lower sheet resistivity). It was already suggested that the core-shell nanowires high conductivity was at fault for the lack of response in H$_2$ gas detection, so it is likely that the high quality InN microrods have a lower carrier concentration. InN nanorods have proven to be successful at selectively detecting H$_2$,\textsuperscript{271} which is more confirmation that core-shell nanowires are too conductive.

5.4 Conclusions

The growth of InN nanorods on different substrates (a-, c-, r-Al$_2$O$_3$, Si (111), and GaN/c-Al$_2$O$_3$) by H-MOCVD reveals different nanorod tip structures based on the polarity of the substrate. When InN nanorods are grown on polar substrates such as a-, c-Al$_2$O$_3$ the nanorod tips are flat while growth on non-polar r-Al$_2$O$_3$ yields sharp nanorod tips. Growth on silicon substrates also produce pointed nanorod tips, except the tips are asymmetric. When sharpened tips are noticed atomic plane bending occurs and a 20 nm plateau forms at the top of the nanorod tip. CBED analysis revealed that prismatic stacking faults may be responsible for the flower-like growth habit of the InN nanorods. TEM analysis of the side faceting of the nanorods shows atomic roughness and occasionally a thin oxide layer can be detected, however, the nanorods are usually oxide free.
By varying the growth conditions of InN nanorods it was determined that the aspect ratio of the nanorods cannot be increased above 10:1, regardless of the growth conditions. Therefore the nanorods will eventually become microrods with increased growth duration. It was also shown that in-situ etching did not preferentially etch InN in one growth direction. Instead etch pits were formed over the surface of the microrod.

Transport measurements were done for single InN microrods by using the transmission line method and it was shown that the sheet resistivity of the InN microrods was higher than the core-shell nanowires discussed in Chapter 4. This added further confirmation that the core-shell nanowires were too conductive for use as single wire gas sensing devices.

![Figure 5-1. Diagram of the H-MOCVD concentric inlet tube showing the arrangement of source material flows and typical temperatures used experimentally for the source and deposition zones.](image)

![Figure 5-2. A SEM image of the growth habits of InN nanorods illustrating flower-like growth and c-axis orientation (Ref. 272).](image)
Figure 5-3. Low resolution TEM image of an InN nanorod grown on a-Al$_2$O$_3$ substrate showing flat hexagonal cross section. Also, representative of growth on c-Al$_2$O$_3$.

Figure 5-4. Low resolution TEM image of an InN nanorod grown on r-Al$_2$O$_3$ substrate. The pencil-like tip as well as faceting angle between tip and edge of the nanorod are shown.

Figure 5-5. High resolution TEM image of the rectangular shape which is seen at the end of the nanorod when it is shaved from the substrate surface.
Figure 5-6. Low resolution and high resolution TEM images of the InN nanorod tip grown on r-Al$_2$O$_3$. The flat 20 nm plateau and side facet of the InN nanorod can be seen.

Figure 5-7. High resolution TEM images showing plane bending in the tip of an InN nanorod grown on r-Al$_2$O$_3$. 
Figure 5-8. Low resolution TEM images of InN nanorods grown on Si (111) substrate showing asymmetric pencil tip.

Figure 5-9. High resolution TEM images of side facet roughness occurring for most nanorods grown by H-MOCVD regardless of the substrate.
Figure 5-10. Low resolution TEM image and CBED patterns of an InN nanorod grown on a-Al₂O₃. A) Low resolution image of a single InN nanorod. B-D) Convergence beam electron diffraction images for labeled nanorod regions I-III, respectively.

Figure 5-11. Experimental and calculated CBED images indicating nitrogen polarity.
Figure 5-12. Electron energy loss spectra with and without the detection of oxygen. A) No oxygen detection. B) Nanowire where thin oxide layer is detected.

Figure 5-13. High resolution TEM image showing thin amorphous oxide layer that sometimes forms on the outside of the InN nanorods.
Figure 5-14. Photoluminescence spectra of InN nanorods grown on different substrates. A) Normalized linear scale. B) logarithmic scales.

Figure 5-15. Scanning electron microscope images of InN microrods grown on Si (111) substrate for 90 min using Cl/In = 4.0, N/In = 250, and T_g = 600 °C.
Figure 5-16. Scanning electron microscope images of InN microrods grown on Si (111) substrate for 90 min using Cl/In = 5.0, N/In = 250, and $T_g = 650 \degree C$.

Figure 5-17. A SEM image of InN microrods grown on Si (111) substrate for 90 min using Cl/In = 5.0, N/In = 200, and $T_g = 700 \degree C$.

Figure 5-18. Scanning electron microscope image of InN microrods grown on Si (111) substrate after post growth in-situ HCl gas etching.
Figure 5-19. Current-voltage measurements for several InN microrods, used for determining the total measured resistance ($R_T$) of each rod.

Figure 5-20. Total measured resistance vs. length/$a^2$ for InN microrods.
Figure 5-21. Scanning electron microscope images and dimensions of InN microrods used for TLM analysis.

Table 5-1. A random sampling of InN nanorod/microrod lengths and diameters for a variety of growth conditions.

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<th>Cl/III</th>
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<th>Length ($\mu$m)</th>
<th>Diameter ($\mu$m)</th>
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CHAPTER 6
EXPLORATORY STUDY OF GALLIUM NITRIDE NANO- AND MICROSTRUCTURED GROWTH BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION

6.1 Introduction

GaN nanostructures have gained attention for fundamental understanding of how dimensionality affects the electrical and optical properties, but also for nanodevice applications. Device applications involve nano-sized UV optoelectronics, high speed FETs, and high temperature microelectronics.\textsuperscript{274-277} GaN nanostructures have been grown by a variety of methods including catalytic CVD (typically using Ni or Au catalyst), thermal CVD, MBE and pulsed laser deposition (also using catalysts).\textsuperscript{86,278-282} Most CVD processes use pure gallium metal, GaN powder, Ga\textsubscript{2}O\textsubscript{3} oxide powder, or some combination of the three.

As in the case of InN nanowires, it is beneficial to controllable grow GaN nanostructures on substrates by MOCVD, since this growth technique is commonly used in industry. Also, III-nitride alloy growth can be more easily controlled compared to the majority of growth methods described above.

In this chapter the growth of GaN nanostructures by using a traditional MOCVD reactor is discussed. Growth parameters such as inlet N/Ga ratio, deposition temperature, and substrate material were investigated with regards to the GaN structure.

6.2 Experimental Procedure

For the growth of GaN nanotubes and nanowires a vertical inlet tube was used in the MOCVD reactor. Detailed descriptions of the MOCVD growth technique and vertical inlet tube setup are presented in Chapter 3 and 4, respectively. For MOCVD growth of GaN nanowires and nanotubes, triethyl gallium (TEGa) and ammonia (NH\textsubscript{3}) were used as precursors. The deposition temperature was varied from 560 to 850 °C and the N/Ga ratio ranged from 3,000 to 30,000. Growth occurred on Si (100), c-Al\textsubscript{2}O\textsubscript{3}, and GaN (5 μm)/c-Al\textsubscript{2}O\textsubscript{3} substrates. Silicon
substrates were degreased in warm trichloroethylene (TCE), acetone and methanol each for 5 min and then blow dry with a static free nitrogen gun. Sapphire substrates were only cleaned in methanol for 5 min and then blown dry. No chemical cleaning was done for GaN/c-Al2O3 substrates and a nitrogen gun was used to ensure that the surface was free of particulates before loading. Substrate nitridation at 850 °C for 15 min (1600 sccm NH3 in 4 SLM N2 dilution) was done for all samples and no low temperature buffer layers were used.

6.3 Results

As in the case of InN nanowire growth by MOCVD, GaN nanowire growth occurs by a VLS mechanism. Once the inlet N/Ga ratio is increased beyond a certain threshold value, GaN nanowire growth proceeds by a vapor-solid (VS) mechanism. This is a similar result seen for InN nanowires (see Section 4.3.2.2). GaN thin film growth optimization previously occurred and the ideal growth conditions for silicon substrate included substrate nitridation and LT GaN buffer layer at 560 °C (N/Ga = 3,000) for 15 min followed by HT GaN at 850 °C (N/Ga = 3,000).234 These previous growth optimizations were made using the standard horizontal inlet tube (Figure 4-1). For comparison a SEM image of a GaN film grown at ideal conditions using the horizontal inlet tube is compared to GaN grown by the vertical inlet tube (Figure 6-1). Both GaN films were grown on c-Al2O3 substrates. When the vertical inlet was used, no LT GaN buffer layer was used after substrate nitridation and prior to growth. GaN thin films have previously been grown on c-Al2O3 substrates without a LT buffer (using the horizontal inlet) and the morphology did not significantly change as in this instance. It is clear that the morphology of the two structures is different (Figure 6-1). The horizontal inlet grown GaN shows a relatively smooth surface compared to the extremely rough surface produced by the vertical inlet, (tilted SEM image, Figure 6-1c). At 850 °C it is assumed that Ga droplets do not form since ammonia decomposition is rapid at these temperatures. Therefore the vertical
island growth is believed to be due to significant increase in the growth rate by the concentration of reactants directly over the susceptor and wafer tray. Triangular tips on the ends of the GaN are an indication that cubic phases might also be present (Figure 6-1d). XRD verified that cubic and hexagonal phases are present in the GaN film grown on Si (100) with the vertical inlet (Figure 4-2). It is difficult to distinguish between the hexagonal (0002) and cubic (111) phases of GaN because the 2θ values overlap. It is likely that both of these phases coexist, since lower intensity polycrystalline peaks are detected for both cubic and hexagonal phases. The polycrystalline peaks can be positively identified because the peaks occur at different 2θ values. The SEM images in Figure 6-1 are representative for GaN grown with the vertical inlet on Si (100), c-Al2O3, and GaN/c-Al2O3, therefore the presence of cubic phases is expected at these conditions regardless of the substrate and this result was confirmed by XRD.

In order to produce more favorable conditions for GaN nanowire growth without the aid of catalysts the deposition temperature was reduced while maintaining a constant inlet N/Ga ratio of 3,000. At a deposition temperature of 750 °C the growth rate of GaN is reduced and films are formed on GaN/c-Al2O3 and c-Al2O3 that are less rough compared to growth at 850 °C with the vertical inlet (SEM, Figure 6-3). It is not completely clear why the GaN deposited on GaN/c-Al2O3 shows small voids or pits on the surface of the film. It is likely that Ga wetting of the surface increases strain in the first one or two monolayers on the surface, as in the case of In wetting on GaN which was previously described in Chapter 4. Evidence for the formation of Ga-droplets is verified by GaN growth on Si (100) substrates (at the same temperature). At 750 °C the GaN deposition is significantly different on Si (100), which is believed to be due to gallium wetting of the substrate surface, similar to the results presented in Chapter 4. On Si (100) substrates the GaN forms microwires with Ga droplets at the tip, (Figure 6-4a). Other
sections on the Si (100) substrate can be found where the GaN droplet has been consumed which reveals a tube structure (Figure 6-4b,c).

Decreasing the deposition temperature to 650 °C with a constant inlet N/Ga ratio of 3,000 reduces the effective N/Ga ratio because the decreased temperature reduces NH₃ decomposition efficiency. With these growth conditions the decrease in active nitrogen creates an excess of gallium metal which promotes microstructure growth via VLS mechanism. Figure 6-5 shows SEM images of GaN nanowires grown on GaN/c-Al₂O₃, c-Al₂O₃, and Si (100). The microtubes range from 1 to 3 μm thick where the diameter decreases as the tube get longer due to the consumption of the Ga metal droplet. Lengths range from 2 to 15 μm where the size of the remaining Ga droplet at the end of growth is inversely proportional to the length. EDS was done on the GaN microtube and only Ga and N were detected, which suggests that there is no significant carbon incorporation that is responsible for the formation of the tube structure (Figure 6-6). This EDS spectrum is representative for GaN microtubes grown at all growth conditions (i.e. 750 °C, 650 °C, etc.).

GaN was also deposited with the vertical inlet using an inlet N/Ga ratio of 3,000 at 600 °C and 560 °C. As expected the lower temperature further reduced the NH₃ decomposition and an increase in Ga metal at the tip of the microtubes is noticed (Figure 6-7). To determine the extent of nitride growth below the excess metal, the Ga droplets were selectively wet etched in a 10% HCl (90% water) by volume for 10 min. After etching the excess gallium is removed, which reveals a GaN nanotube structure (Figure 6-8). EDS was done after etching which confirmed that the nanotubes were composed of Ga and N (Figure 6-9).

The deposition temperature that provided the most uniform GaN microstructure for all three substrates tested was 650 °C. For this reason the inlet N/Ga ratio was increase at this
deposition temperature to see the morphological effect on the microwire structure. The highest inlet N/Ga ratio tested (20,000) produced mostly GaN thin films with occasional sites where 1D growth occurred (Figure 6-10). This result was consistent for all substrates tested (GaN/c-Al$_2$O$_3$, c-Al$_2$O$_3$, and Si (100)). The growth at this high N/Ga ratio forms small microrods that have grown by a VS mechanism instead of a VLS mechanism. At this high N/Ga ratio the group V (active N) species becomes the excess source material and the growth rate of the nanostructure is limited by the group III flux. The sparse microrods are approximately 1 μm in diameter and 2-3 μm in height. Lowering the N/Ga ratio by half to 10,000 (at T$_g$ = 650 °C) increases the number of 1D nucleation because TEGa increases possibility of metal rich nucleation sites (Figure 6-11). The density of 1D growth is increased when the inlet N/Ga ratio is reduced to 7,000 (Figure 6-12). For these growth conditions nanowires lengths range from 3-5 μm with diameters ranging from 100-200 nm. Reducing the N/Ga ratio below 7,000 at a deposition temperature 650 °C results in similar nanowire structures, however the samples with the greatest uniformity across the substrate were grown at this condition.

Frequently, small areas of curly GaN nanowires were found on substrates whose edges were placed outside of the primary deposition zone or “hot spot” of the vertical inlet tube. A schematic of the vertical inlet and the associated hot spot were previously discussed in Chapter 4 (Figure 4-5). Outside the “hot spot” curly GaN nanowires typically form (Figure 6-13). These nanowires are typically seen for deposition temperatures at or below 650 °C and they occur at the edges of the graphite susceptor. It is not completely clear why these curly GaN nanowires form but it is possible that the relative N/Ga ratio is significantly changed far away from the primary deposition zone. From a quality control point of view the region furthest from the vertical inlet tube is the most difficult region where growth can be control growth. These curly GaN
nanowires have lengths (uncurled) in the range of 10-20 μm and diameters of 100-300 nm. Producing the growth of these nanowires in the primary deposition zone proved to be very difficult and could not be reproducibly controlled.

GaN nanotubes were grown at 650 °C on c-Al₂O₃ to be fabricated into a gas sensing device for selective room temperature H₂ detection. The wire bonding step (Figure 6-13) proved to be detrimental to the device operation because the thin walled nanotubes were crushed upon contacting. This contacting method proved ineffective for making a successful Ohmic contact and therefore the device test could not be completed.

6.4 Conclusions

From this exploratory study it has been shown that GaN microstructures can be grown by traditional MOCVD by using vertical inlet tube to deliver the source materials. The most reproducible microstructures were produces at a deposition temperature of 650 °C and an inlet N/Ga ratio of 7,000. For these growth conditions the effect of the chosen substrate had little influence on the morphology of the microstructure. This was also the case for high temperature growth (850 °C) even though only island growth occurred (instead of micro or nanostructures). When a deposition temperature was between 650 and 750 °C the chosen substrate material had a greater effect on the microstructure, likely due to the wetting nature (surface tension) of gallium on the substrate.
Figure 6-1. Comparison of GaN/c-Al₂O₃ grown at similar growth conditions with the horizontal and vertical inlets. A) horizontal inlet showing smooth GaN film. B-D) vertical inlet showing extremely rough GaN surface morphology.

Figure 6-2. X-ray diffraction pattern of GaN grown with the vertical inlet on Si (100) substrates. Cubic and hexagonal phases are detected.
Figure 6-3. Scanning electron microscope images of GaN grown at 750 °C and an inlet N/Ga ratio of 3,000 on different substrates. A) c-Al₂O₃ substrate. B) GaN/c-Al₂O₃ substrates.

Figure 6-4. Scanning electron microscope images of GaN microtubes grown at 750 °C and an inlet N/Ga ratio of 3,000 on Si (100) substrates. A) Ga droplet at tip of microwire. B,C) Microtube structure of GaN.
Figure 6-5. Scanning electron microscope images of GaN grown using the vertical inlet at 650 °C and N/Ga ratio of 3,000 on different substrates. A) GaN/c-Al₂O₃ substrate. B) c-Al₂O₃ substrates. C,D) Si (100) substrate.
Figure 6-6. Representative EDS spectrum of single GaN microtube grown on Si (100) substrate.

Figure 6-7. Scanning electron microscope images of GaN grown with the vertical inlet at the lowest temperature tested (560-600 °C) showing excess of metal droplets on the surface of the nanotubes.
Figure 6-8. Scanning electron microscope images of GaN growth with the vertical inlet at 560 °C after a 10 min 10% HCl wet etch showing nanotube structure.

Figure 6-9. Energy dispersive spectrum of GaN nanotubes after HCl wet etching.
Figure 6-10. Scanning electron microscope images of GaN/Si (100) with the vertical inlet at 650 °C and N/Ga = 20,000.

Figure 6-11. A SEM images of GaN/Si (100) with the vertical inlet at 650 °C and N/Ga = 10,000.
Figure 6-12. Scanning electron microscope images of GaN/Si (100) with the vertical inlet at 650 °C and N/Ga = 7,000.
Figure 6-13. Scanning electron microscope images of curly GaN nanowires that form outside the primary deposition zone of the vertical inlet.

Figure 6-14. Wire bonding step of GaN nanotube H$_2$ gas sensing device where damage to the nanotubes occurred.
CHAPTER 7
FUTURE WORK AND RECOMMENDATIONS

7.1 Role of Oxygen in InN

Currently it is not well understood how oxygen incorporates into InN and the resulting
effect on electrical and optical properties. There are many debatable claims made about the role
of oxygen in InN and these claims are summarized in reviews, for example see Ref. 50. It has
been suggested that oxygen is a possible cause for increasing the band gap energy of InN\textsuperscript{44} and
that oxygen can contribute to n-type doping of InN\textsuperscript{283}. Oxygen is believed to exist in InN
samples in amorphous phases, which is why oxygen may not be detected from XRD
measurements. InN films presumed to contain amorphous oxygen form crystalline \( \text{In}_2\text{O}_3 \) phases
after annealing at 500 °C in a nitrogen atmosphere\textsuperscript{240}. Room temperature aging of InN films in
air for periods of months and even years has produced XRD peaks of crystalline \( \text{In}_2\text{O}_3 \)\textsuperscript{50}.

It is difficult to study the role of oxygen from current literature because much of the
evidence is contradictory. For example in this work we unsuccessfully tried to reproduce the
results of Hur \textit{et al.}\textsuperscript{284} in which InN films were annealed at 550 °C for 10 min under a high
vacuum (10\textsuperscript{-5} Torr) to form crystalline \( \text{In}_2\text{O}_3 \). We annealed single crystal InN/c-\( \text{Al}_2\text{O}_3 \) thin films
in a low pressure (100 Torr) nitrogen atmosphere (after being exposed to air for several months)
at 500, 525, 550 °C for a duration greater or equal to 10 min. XRD results showed that InN films
did start to decompose (due to the appearance of an indium peak) at \( T_{\text{anneal}} > 500 \) °C, however no
crystalline \( \text{In}_2\text{O}_3 \) peaks were produced.

Since current literature results are scattered and analysis has occurred on a variety of
different substrates and growth techniques it is suggested that oxygen incorporation into InN be
studied. Understanding the role of oxygen is important for improving film quality, identifying
the ideal deposition techniques and how aging in air will affect material quality. The air-surface
interface is also important for InN because it is believed that this interface affects the surface charge accumulation seen in InN. The surface charge accumulation layer is one of the hurdles that must be overcome for successful p-type doping of InN to occur.

7.2 Improving Crystalline Quality of In$_x$Ga$_{1-x}$N (1 $\leq x \leq$ 0.3) Alloys

Growth of In$_x$Ga$_{1-x}$N alloys is difficult due to the 11% lattice mismatch and resulting phase separation that occurs between InN and GaN. Differences in equilibrium nitrogen vapor pressures also make it difficult to incorporate indium at high growth temperatures (preferred for GaN) and crystalline quality must be sacrificed at low temperatures for indium rich alloys. In recent years Ga-rich alloys (up to 20-30% indium) have been produced with high structural qualities and good photoluminescence properties, mostly due to applications in visible LEDs (Technologies and Devices International, Inc. press release, TDI Demonstrates Novel InGaN Epitaxial Materials at the International Workshop on Nitride Semiconductors (IWNS) 2006, http://www.tdii.com/release_html_b1.html, accessed April 2007). In-rich In$_x$Ga$_{1-x}$N alloys have gained more attention in recent years however improvements in film quality and reproducibility must occur, especially in the compositional range where phase separation is most prevalent (0.7 $\leq x \leq$ 0.3). The relationship between growth temperature, alloy composition, and N/III ratio will be crucial for improving crystalline quality. Developing high quality In$_x$Ga$_{1-x}$N alloys over the entire compositional range is beneficial for a variety of applications such as high efficiency solar cells, terahertz electronics, communications, and optoelectronics.

7.3 P-Type Doping of InN and In-Rich In$_x$Ga$_{1-x}$N

InN and In-rich In$_x$Ga$_{1-x}$N based electronic and optoelectronic devices are severely limited by the inability to form p-n homojunctions, since InN and In-rich In$_x$Ga$_{1-x}$N alloys have not successfully been p-type doped. Some researchers are making progress in Mg doping of InN to make p-type films, but even slight evidence of p-type doping in the bulk is difficult to
achieve. It is suggested that Mg and Zn are used for p-type dopants since Mg is a successful p-type dopant in GaN and Zn has been successful for InP. Both of these elements should be tried independently and also together via co-doping. Mg acceptors are difficult to ionize in GaN since the activation energy is higher for the deep acceptor so annealing of InN doped films will become important. If possible a high pressure annealing chamber should be designed and built such that InN samples can be annealed at higher temperatures to prevent film decomposition.

7.4 Growth of In\textsubscript{x}Ga\textsubscript{1-x}N Alloys by H-MOVPE

As discussed in Chapter 5 the H-MOVPE technique offers the unique ability to be operated as a conventional MOVPE reactor or a HVPE reactor that uses metal organic sources instead of metal only precursor. H-MOVPE is beneficial because it has already been proven to be a valuable technique for high quality growth of InN on silicon substrates and has exceptionally high growth rates (compared to conventional MOVPE). Therefore it is suggested that In\textsubscript{x}Ga\textsubscript{1-x}N alloys are grown by H-MOVPE which can then be compared to the growth of In\textsubscript{x}Ga\textsubscript{1-x}N by MOVPE (presented in this work). Specifically it would be interesting to determine the effect on phase separation when H-MOVPE is used, since the deposition technique operates closer to equilibrium than MOVPE. On several occasions during this work the film thickness of MOVPE In\textsubscript{x}Ga\textsubscript{1-x}N limited the amount of characterization and analysis that could be done, such as PL and THz measurements. Once In\textsubscript{x}Ga\textsubscript{1-x}N growth is optimized for H-MOVPE a 1 \(\mu\)m thick film could be produce in one hr, which would take approximately 18 hr by MOVPE. Thick (1-3 \(\mu\)m) layer will also be required for future solar cell device applications which simply cannot be obtained by our MOVPE system.
LIST OF REFERENCES


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Tae Woong Kim’s doctoral dissertation. Advisor: Dr. Tim Anderson, Department of Chemical Engineering, University of Florida (2006)


BIOGRAPHICAL SKETCH

Josh Mangum was born in Greensboro, North Carolina on May 13th, 1981. He is the son of William and Cassandra Mangum and has an older brother, Matthew. In 1999, he graduated from Walter Hines Page High School, where his interest in chemistry first developed with the aid of a wonderful teacher, Mrs. Peggy Stevens. After High School, Josh attended North Carolina State University in Raleigh, NC to major in chemical engineering and he graduated with a bachelor of science in May 2003. Immediately after receiving his undergraduate degree in chemical engineering Josh moved to Gainesville, FL to pursue a PhD in chemical engineering at the University of Florida. Upon joining Dr. Tim Anderson’s research group, his research interests mainly involved crystal growth of nitride semiconductors (specifically InN, In_,Ga1-xN, and GaN). While at UF he was lucky enough to move in across the street from a beautiful graduate student, Kimberly Gray, who later became his fiancée, and the two were married shortly after the completion of Josh’s Ph.D.