Growth of InGaN Nanorings via Metal Organic Chemical Vapor Deposition

by

Zohair Zaidi

A Thesis Presented in Partial Fulfillment of the Requirements for the Degree Master of Science

Approved August 2012 by the Graduate Supervisory Committee:

Subhash Mahajan, Chair
Michael O'Connell
Stephen Krause

ARIZONA STATE UNIVERSITY

December 2012
ABSTRACT

III-Nitride nanostructures have been an active area of research recently due to their ability to tune their optoelectronic properties. Thus far work has been done on InGaN quantum dots, nanowires, nanopillars, amongst other structures, but this research reports the creation of a new type of InGaN nanostructure, nanorings. Hexagonal InGaN nanorings were formed using Metal Organic Chemical Vapor Deposition through droplet epitaxy. The nanorings were thoroughly analyzed using x-ray diffraction, photoluminescence, electron microscopy, electron diffraction, and atomic force microscopy. Nanorings with high indium incorporation were achieved with indium content up to 50% that was then controlled using the growth time, temperature, In/Ga ratio and III/N ratio. The analysis showed that the nanoring shape is able to incorporate more indium than other nanostructures, due to the relaxing mechanism involved in the formation of the nanoring. The ideal conditions were determined to be growth of 30 second droplets with a growth time of 1 minute 30 seconds at 770 C to achieve the most well developed rings with the highest indium concentration.
DEDICATION

I dedicate this thesis to firstly the Imam of my time, Imam Mahdi for whom I have dedicated my life and the pursuit of knowledge. Also to my parents, Syed Azhar Saeed Zaidi and Rubina Azhar who supported me and encouraged me towards success from the very moment I came into existence and finally to my grandfather Syed Muhammad Saeed Zaidi, because of whom I was put on the path of knowledge.
ACKNOWLEDGMENTS

I would first like to thank God for His support and Will in allowing me the opportunity to take part in seeing the beauty of His Creation. I would like to thank Dr. Subhash Mahajan for being a mentor and supporting me in this research. Without his constant motivation and encouragement, I would not have been able to complete this project. His support not only helped bring this research to fruition but also helped develop many skills in me that will be beneficial for years to come. I would also like to thank Dr. Michael O’Connell for supporting me and giving me motivation to look at research in a different light and always keep my eyes open at the smallest of things as often they bring new discoveries. And also to Dr. Stephen Krause for accepting to being on my committee and supporting me in this work.

I would also like to thank my wonderful research group who spent many hours to train and taught me all the tools necessary enable to perform this research: Heather McFelea, Rosa Diaz, Ilsu Han, Fanyu Meng, Reed Whittman.

The facilities and equipment at Arizona State University were excellent and provided everything I needed to characterize and develop the understanding of my results. Special thanks to Zhenquan Liu, Emmanuel Soignard, Karl Weiss. I gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science at Arizona State University.
For the optical characterization I am grateful to my colleague Leijun Yin for help with the PL equipment and to Dr. Cun-Zheng Ning for the fruitful discussions.

And above all, I am always grateful to my family for their support and encouragement that drove me to complete my academic degree and succeed in this research. And finally to my wonderful friends who supported me till the very end.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>PREFACE</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1 INTRODUCTION TO NANOMATERIALS</td>
<td>1</td>
</tr>
<tr>
<td>History of Nanotechnology</td>
<td>1</td>
</tr>
<tr>
<td>Unique Properties of Nanostructures</td>
<td>3</td>
</tr>
<tr>
<td>2 III-NITRIDE MATERIAL SYSTEM</td>
<td>8</td>
</tr>
<tr>
<td>Band structure of III-N</td>
<td>8</td>
</tr>
<tr>
<td>Challenges of Growing InGaN Material</td>
<td>12</td>
</tr>
<tr>
<td>3 MOCVD GROWTH OF INGAN MATERIAL</td>
<td>17</td>
</tr>
<tr>
<td>Introduction to MOCVD</td>
<td>17</td>
</tr>
<tr>
<td>MOCVD Growth Preparation</td>
<td>19</td>
</tr>
<tr>
<td>4 CHARACTERIZATION TECHNIQUES</td>
<td>23</td>
</tr>
<tr>
<td>Atomic Force Microscopy</td>
<td>23</td>
</tr>
<tr>
<td>X-ray Diffraction</td>
<td>24</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>26</td>
</tr>
<tr>
<td>5 GROWTH OF INGAN NANORINGS</td>
<td>28</td>
</tr>
<tr>
<td>Results &amp; Discussion</td>
<td>28</td>
</tr>
<tr>
<td>Conclusion</td>
<td>59</td>
</tr>
<tr>
<td>References</td>
<td>61</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Physical properties of AlN, GaN, InN</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Lattice constants for GaN, InN, Sapphire</td>
<td>12</td>
</tr>
</tbody>
</table>
1. Chart showing increasing trend of investments in nanotechnology................................................................. 1
2. Illustration as the material size decreases smaller and smaller, the surface-to-volume ratio increases exponentially. ............ 3
3. Results of absorption in nanotechnology based solar cells…… 4
4. Density of States are shown for 3D, 2D, 1D, and 0D nanostructure cases............................................................. 6
5. III-Nitride alloys spans the entire visible spectrum allowing for potential optoelectronic devices. .................................. 7
6. Band structure of GaN indicating it having a direct band gap due to the alignment of the minima of the conduction and maxima of the valence bands. ........................................ 9
7. Band structure of InN similarly showing its direct band gap..... 9
8. InGaN wurtzite crystal structure indicating ABAB stacking .... 10
9. Gibbs free energy curve minima indicating the positions of where spinodal decomposition begins to occur in InGaN .... 14
10. Spinodal decomposition occurs across most of the GaN-InN alloy except below 7% and above 95%............................... 15
11. Stranski-Krastanow mechanism of growth indicated by first monolayer by monolayer growth occurs until a critical point of
stress is reached in the material where formation of quantum dots becomes more favorable than thin layers.

12. Mechanism of how atomic force microscopy works using a cantilever with atomic size tip that allows for interaction with the sample and data is collected via various detectors.

13. Incident laser beam hits the sample then is focused via lenses and the excited wavelengths are finally detected using a silicon based photo-detector.

14. Electrons first start off in ground state, then upon incident excitation electrons move to the conduction band from where they eventually decay back down to the lower energy band and release a photon equal to the energy difference of the two bands.

15. In-Ga droplets with 16% indium.

16. In-Ga droplets with 63.06% indium with increased diameter.

17. In the absence of a nucleation layer droplets aren’t able to wet the rough sapphire substrate and thus no In-Ga droplets are visible.

18. The formation of InGaN nanoparticles after 30 seconds. At this point the particles appear to be completely filled with no holes present.
19. After 1 minute of growth, majority of the nanoparticles have been converted into nanorings ........................................ 30
20. After 1 minute 30 seconds of growth the samples have became hexagonal nanorings with a clearly visible hole in their center. ................................................................. 31
21. After 2 minutes of growth the nanorings begin to fill up again causing their hole to disappear................................. 31
22. InGaN nanorings at 670 C .................................................... 33
23. InGaN nanorings at 770 C .................................................... 33
24. InGaN nanorings at 880 C .................................................... 34
25. InGa droplets grown using 40/1 TMIn/TMGa ratio .......... 35
26. InGa droplets grown using 20/1 TMIn/TMGa ratio .......... 36
27. InGa droplets grown using 13/1 TMIn/TMGa ratio with the droplets being much more mobile then the other cases ...... 37
28. InGaN nanorings grown using 10/1 TMIn/TMGa ratio .......... 38
29. InGaN nanorings grown using 13/1 TMIn/TMGa ratio .......... 39
30. InGaN nanorings grown using 15/1 TMIn/TMGa ratio .......... 39
31. InGaN nanorings grown using 20/1 TMIn/TMGa ratio .......... 40
32. InGaN nanorings grown using 23/1 TMIn/TMGa ratio .......... 40
33. InGaN nanorings grown using 30/1 TMIn/TMGa ratio .......... 41
34. InGaN nanorings grown using 500 sccm NH3 ................. 42
35. InGaN nanorings grown using 1000 sccm NH3 .................. 42
36. InGaN nanorings grown using 1500 sccm NH3 .................. 43
37. InGaN nanoring grown at 880 °C for 1 minute .................. 46
38. InGaN nanoring grown at 880 °C for 1:30 minute .............. 46
39. InGaN nanoring grown at 770 °C ................................. 47
40. InGaN nanoring grown at 670 °C ................................. 47
41. InGaN nanoring grown at 670 °C, with InGaN peak at 33.15° . 49
42. InGaN nanoring grown at 770 °C, with InGaN peak at 32.93° 50
43. InGaN nanoring grown at 870 °C, with InGaN peak at 33.15° 50
44. InGaN nanoring grown at 300 mbar pressure ................... 51
45. InGaN nanoring grown at 600 mbar pressure ................... 52
46. InGaN droplets grown at 300 mbar and nanorings at 600 mbar.. 53

47. InGaN droplet time increased to 1 minute ....................... 54
48. InGaN nanoring grown for 45 seconds ........................... 55
49. InGaN nanorings grown for 1 minute ............................ 55
50. InGaN nanorings grown for 1 minute 30 seconds .............. 56
51. InGaN nanoring grown for 2 minutes ............................ 56
52. InGaN nanoring grown for 5 minutes ............................ 57
Chapter 1 | INTRODUCTION TO NANOMATERIALS

In the past decade, nanotechnology has emerged as one of the greatest technological advancements in modern times. Increasing demands in energy and the concern for the environment has led to rapid development of the use of nanotechnology in devices and applications. In 2008, almost $60 billion worth of manufactured goods contained some type of nanotechnology, a 20-fold increase from 2006. The National Science Foundation estimates the nanotechnology industry will become a $1 trillion market by 2010. [11] With this growing commercial and social interest in nanotechnology, it has become imperative on scientists and researchers to create and discover new materials that can fulfill the needs of society.

Figure 1.1 Chart showing increasing trend of investments in nanotechnology in the U.S. and around the world
Initial research in nanotechnology was dependent on the development of tools and equipment through which nanomaterials could be properly grown and analyzed. In the 1980’s the scanning tunneling microscope was developed that allowed for direct interaction with nanomaterials that eventually led to fullerenes being discovered in 1986, shortly followed by nanotubes [12]. Nanotechnology research then really took off in 2000 when President Clinton created the National Nanotechnology Initiative with a funding of $422 million. NNI describes nanotechnology as “the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications.” [13] The two major struggles in nanotechnology have been precisely this: the understanding of why and how nanomaterials form and the ability to precisely control material at such a small scale. Often nanomaterials such as carbon nanotubes have existed in nature for much of man’s history but because of the lack of tools available we could not sense them or learn about their properties. As the history of science has shown, initially after a new material is found or developed, its full potential is not known for many years until all its properties have not been investigated and learned, as was the case with carbon nanotubes which remained undervalued until they were able to be separated years after their discovery. The research presented in this dissertation is precisely of that nature; a new form of InGaN based
nanostructure, InGaN nanorings that could potentially be used for technology in the future.

**Unique Properties of Nanostructures**

Nanomaterials bring several key advantages over their bulk counterparts that bring them such attention and technological application. In terms of energy, the density of states (DOS) of nanomaterials becomes quantized and discrete rather than continuous thereby giving them many unique electrical properties. As a result of this fundamental change, materials that have poor conductivity and electrical properties in the bulk can become extremely well conductors. The change in DOS depends upon the type of nanostructure. 0D nanostructures are like quantum dots which confine electrons in all three special dimensions causing the energy levels to become completely discrete, similar to atoms. 1D nanostructures are nanowires which confine electrons in two directions and allow flow in one direction. 2D nanostructures can be like graphene and nanofilms which confine electrons in one direction. Finally 3D nanostructures allow flow of electrons in all three spatial directions but are still in the nanosize range. Nanorings can be expected to fall somewhere in between 2D and 3D nanostructures depending on the inner and outer diameter of the rings as well as the height.
Another important feature of nanomaterials is the extremely high surface to volume ratio since nanomaterials consist of a finite number of atoms, majority of the atoms make up the surface of the material rather than the bulk. These atoms then have different bonding structure and coordination number. Because of this, surface effects come into play that cause a material to have significantly different properties such as with melting point.
and phase stability.

Figure 1.1 Illustration as the material size decreases smaller and smaller, the surface-to-volume ratio increases exponentially.

Nanomaterials have had applications ranging from semiconductors, optoelectronics, medicine, automotive, and aerospace. The size effect of nanomaterials can be seen in numerous examples such as with photovoltaic cells. For instance, photovoltaic cells performance previously had been limited due to bulk silicon’s inability to absorb large portion of the solar spectrum. But simply by adding silicon nanoparticles to the films, it caused an almost 60% improvement in absorbing in the UV spectrum [37]. In another research the size effects of nanoparticles and the effect of the shape of nanostructures can be shown in the figures below:
Figure 1.2 Results of absorption in nanotechnology based solar cells shows how the optical and electrical properties of nanostructures depend upon the size and shape of the nanostructure and provide improvement over traditional thin-films. [2]

History of III-Nitride Materials

Size factor is only one part of the story, as important is the material selection. Much of the initial research in nanomaterials focused on silicon and GaAs as those materials were readily being used in semiconductor technology. However the most recent family of semiconductor materials to be investigated was the III-Nitride family, consisting of AlN, GaN, and InN. Earliest work on III-nitride material was done in the 1950s when Juza and Hahn produced small needles and platelets of GaN for the first time revealing many of its structural properties at the time [14]. Soon after in
the 1960s Maruska and Tietjen were able to grow n-type GaN film on sapphire. [15] However, unintentional doping and defects in the material hindered progress for a couple decades until finally twenty years later in the 1980s Akasaki and Amano were able to grow the p-type counterpart, making GaN finally suitable for device application [16]. Research into the developing III-Nitride based applications began in the early 90’s and really took off with the work of Nakamura with the development of blue and green-based GaN LED’s which made full color LED displays possible [17]. Development of InN took much longer due to the difficulty in growing InN. Juza and Rabenua attempted to synthesize it in the 1950’s but failed due to the inability of getting a direct reaction between an indium compound and ammonia [18]. It wasn’t until 1972 when Hovel and Cuomo were able to grow InN and measure its characteristics and analyze its structure [19]. Initially the band gap of InN was measured to be 1.7 eV by Trainor and Rose [20], 1.95 eV by Osamura [21], and 2.07 eV by Puychevrier and Minoret [22]. Then years later a huge number of articles appeared in which they clearly proved that the true band gap of InN in fact lies around ~0.7 eV and the previous results were incorrectly obtained due to oxygen contamination and Moss-Burstein shift [23]. With this newly discovered band gap value, the ternary alloy between 3.4 eV GaN and 0.7 eV InN became quite attractive all of a sudden due to its ability of spanning the entire visible spectrum into the UV, opening a wide range of potential optoelectronic applications.
Chapter 2 | III-NITRIDE MATERIAL SYSTEM

Optical Properties

As mentioned previously, the key advantage of III-Nitride alloys, specifically the alloy between GaN and InN, is their ability to span the entire visible spectrum. As seen from the figure below, GaN has a band gap of 3.4 eV and InN of 0.7 eV, covering colors from UV to IR. When making the alloy between GaN and InN, the resulting band gap has to be adjusted for a bowing factor due to the inclusion of curvature.

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

Figure 2.1 III-Nitride alloys spans the entire visible spectrum allowing for potential optoelectronic devices. [4]

The bowing parameter, \( b \) in the above equation, has been subject to lot of discussion in recent years with values ranging from 1.2 eV to 3.2 eV depending on the amount of strain and composition of the alloy [24]. A more close approximate to the bowing factor can be taken as
2.77/(1+1.007x) where x is the amount of indium incorporated in the alloy. This will later be used in the results & discussion section to analyze photoluminescence results and calculate band gap.

**Band Gap**

Another key property, which makes the III-nitride family of alloys ideal for optoelectronic applications, is their direct band gap. In semiconductor materials, there exists a finite gap between the lowest conduction band, or unoccupied electron levels and the highest valence band, or the occupied electron levels. If the lowest and highest point between these two occurs at the same k-value then it is known as a direct band gap material, otherwise it is indirect. The advantage of a direct band gap material, like InGaN, is that an electron can make the transition from the valence to conduction band or vice versa without losing any additional energy to a change in momentum. Therefore, electronic transitions in a direct band gap material like InGaN are optically active and result in the emission of a photon or light whereas in an indirect band gap material like silicon they only release energy and no photons.
Figure 2.2 Band structure of GaN indicating it having a direct band gap due to the alignment of the minima of the conduction and maxima of the valence bands. [5]

Figure 2.3 Band structure of InN similarly showing its direct band gap. [6]
**Crystal Structure**

Depending on the conditions, III-nitride materials can crystallize into either wurtzite hexagonal or zincblende cubic crystal structures. The difference between the two crystal structures lies within the nature of the stacking of the atoms. The wurtzite structure has a stacking of ABABAB in which four cations encapsulate the anion whereas the zincblende structure has a stacking of ABCABC. In the zincblende structure the tetrahedral bonds between the III atoms and nitrogen is rotated by 60° whereas they are aligned in the wurtzite structure. The wurtzite structure in the III-nitride material gives it unique properties in terms of polarization and piezoelectric effects not found in other materials in the larger III-V family [7].
Figure 2.4 InGaN wurtzite crystal structure indicating ABAB stacking [7]

Table 2.1 Physical properties of AlN, GaN, InN [7]

<table>
<thead>
<tr>
<th>Property</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal expansion coefficient (300K)</td>
<td>4.2</td>
<td>5.59</td>
<td>5.7</td>
</tr>
<tr>
<td>$a \times 10^{-6}$ K$^{-1}$</td>
<td>5.3</td>
<td>3.17</td>
<td>3.7</td>
</tr>
<tr>
<td>$c \times 10^{-6}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>&gt;3000</td>
<td>&gt;2500</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>Cohesive energy per bond (eV)</td>
<td>2.88</td>
<td>2.24</td>
<td>1.93</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>1.89</td>
<td>1.94</td>
<td>2.15</td>
</tr>
<tr>
<td>Thermal conductivity $\kappa$ (W/cm-K)</td>
<td>2.0</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Bulk modulus (GPa) (300K)</td>
<td>210</td>
<td>210 ± 10</td>
<td>140</td>
</tr>
<tr>
<td>Refractive index, $n$</td>
<td>2.2</td>
<td>2.35</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Challenges of Growing InGaN Material

Several major challenges exist with respect to III-nitride materials and in particular GaN/InN that makes it difficult to grow. The first major challenge is the lack of a lattice-matched substrate for growing the material. A good substrate for semiconductor growth should have a lattice and coefficient of thermal expansion value similar to the material being grown and should be economical. GaN has a lattice constant of 3.19 and InN a constant of 3.54, with the alloy lattice constant varying in between. The most economical substrate used for this material system is sapphire, which has a lattice constant of 4.78. As a result, there is a 15-25% lattice mismatch between
InGaN and the sapphire substrate, resulting in a very high dislocation density to emerge. SiC on the other hand has a mismatch of only about 3% but is more expensive (10x cost) and GaN/InN wets poorly on the surface requiring additional treatment of the surface prior to growth [35]. More recently, GaN substrates have been created with would allow virtually a mismatch free growth of InGaN and have shown to produce extremely high quality material [35]. However with costs in the thousands for a single wafer, these do not seem to be a feasible solution in until production costs can be brought down. Therefore the best solution thus far has been to use sapphire with the combination of several techniques such as a GaN buffer layer to help reduce the mismatch. Ideally, an alternative substrate would be desired because if one is able to reduce the defect density by one order of magnitude, then the threshold current can be greatly reduced and a greater output in power and reliability can be achieved.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>3.192</td>
</tr>
<tr>
<td>InN</td>
<td>3.536</td>
</tr>
<tr>
<td>Sapphire</td>
<td>4.785</td>
</tr>
</tbody>
</table>

Table 2.2 Lattice constants for GaN, InN, and Sapphire
**Phase Separation**

One of the main problems faced when growing InGaN alloys is phase separation that occurs with high indium incorporation. The main reason for this separation is due to the dichotomy that exists between the necessity of high temperatures for ammonia dissociation and the weak InN bond that becomes unstable at higher temperatures [25]. For growing GaN, the decomposition temperature is around 1040-1060 °C which also results in reducing the amount of nitrogen evaporation. On the other hand, InN decomposes at temperatures around 500-650 °C, causing it difficult for nitrogen to evaporate due to the high overpressure of nitrogen [26]. Thus the higher the temperature the growth is performed at, the higher quality of InGaN material is obtained, however with the trade-off that indium incorporation reduces as the temperature increases.

Another significant factor is the immense size difference that exists between In and Ga atoms. Indium atoms are 155 pm where as gallium atoms are 130 pm, causing an inherent strain to emerge within an InGaN alloy that increases with increasing incorporation of indium [27]. Once strain increases and reaches a certain point, the way the alloy relaxes is through undergoing phase separation, which results in Indium rich regions within the ternary alloy. The issue can be looked at in terms of thermodynamics, which shows that a miscibility gap exists between the majority of the phase diagram between GaN and InN.
Figure 2.6 Gibbs free energy curve minima indicating the positions of where spinodal decomposition begins to occur in InGaN [8].

Inside the spinodal curve region is where spontaneous segregation occurs, indicating majority of InGaN is thermodynamically unstable. These factors make it a significant challenge to grow high quality InGaN nanostructures with high amount of indium incorporation. However in many technological applications such as with LEDs and lasers the presence of indium rich regions can be beneficial and contribute to strong optoelectronic properties in these devices [28].
Figure 2.7 Spinodal decomposition occurs across most of the GaN-InN alloy except below 7% and above 95%. [9]
III-Nitride materials are usually grown using either Metal Organic Chemical Vapor Deposition (MOCVD) or Molecular Beam Epitaxy (MBE), each with its benefits and consequences. In this research MOCVD was chosen as the growth method due to its faster growth rates, high temperature growths, and high quality samples. MOCVD growth first began in the 1960’s by Manasevit with growth of GaN and AlN using metal organic sources [29] and later mastered by Amano in 1986 who grew p-type GaN [30]. Compared to other growth methods, MOCVD is quite complex in nature and not completely understood. The method works by beginning with metal oxide precursors that are released into the reaction chamber in the form of gases and caused to react at the surface of substrate by controlling growth parameters such as temperature, pressure, and flow rates of the involved species. MOCVD growth is governed by both thermodynamics and kinetics. Thermodynamics determines the stable resulting composition of the material at a given temperature and pressure, while kinetics determines the rate at which reactions occur. Three such growth regions exist in typical MOCVD growths: kinetics limited, diffusion controlled, and thermodynamics limited.

In the thermodynamics limited region in particular, it is important to understand the stable phases that exist for each pressure and temperature. The way that can be determined is through the use of Gibbs
free energy. Gibbs free energy essentially requires that at a constant temperature and pressure, the resulting composition should result in such a way to minimize the energy. Then if any change should occur with either pressure or temperature, then the Gibbs energy should either decrease or remain unchanged.

Different types of precursors can be chosen with different operating temperatures based on the temperature they undergo pyrolysis. For instance, Trimethylgallium (TMGa) and triethylgallim (TEGa) are common precursors used as a gallium source. The reason why TMGa is chosen for this work is due to its low molecular weight and high vapor pressure that result in extremely high growth rates as compared to TEGa [31]. Similarly, trimethylindium (TMI) is chosen as the indium source. Both precursors are kept in carefully temperature-controlled bubblers due to the relationship between the precursor temperature and flow rate. The molar flow rate of each metal organic source (MO) can be calculated as follows:

\[
F_M = \frac{P_{\text{tot}} F_V}{RT} \quad [\text{Eq 2}]
\]

\(F_M\) is the molar flow rate of the MO source, \(P_{\text{tot}}\) is the total pressure measured immediately after the bubbler input, and \(F_V\) is the volume flow rate. From using the ideal gas law and substituting for the vapor pressure of the MO source [32], the final molar flow rate can be described as:

\[
F_M = 4.46 \times 10^{-5} \text{ mol/cm} \times \frac{P_{\text{MO}} F_V}{P_{\text{tot}}} \times F_{V, \text{tot}} \quad [\text{Eq 3}]
\]
Thus at -10 °C for TMGa, the flow rate of TMGa was calculated to be 24.58 µmol/min and 30.37 µmol/min for TMIn at 25 °C. The mass deposited per minute can be then calculated to be 0.002823 g/min for TMGa and 0.004857 g/min for TMIn. TMIn material deposition was kept at almost double the amount of TMGa due to the low sticking coefficient of indium and the difficulties of getting it incorporated in InGaN.

**MOCVD Growth Preparation**

Several potential issues exists with MOCVD growths that have to be taken into consideration when setting up the experiment including unwanted reactant mixing, pyrolysis occurring away from the substrate, reactant diffusion, and inability of the species to be accepted by the substrate due to thermodynamic or kinetic reasons [36]. The reactor that was used for the experiment was an Aixtron 200-RF horizontal reactor that is a commercial reactor used in industry for epitaxial growths. In this reactor, both the III and V precursors have their own separate inlets that ensure mixing doesn’t occur until they reach the reaction chamber. The wafer rests on a rotating satellite that allows for uniformity of the sample. The reactor uses a RF heating source that is connected to a graphite susceptor to allow for good heat conduction to the wafer. The reactor growths can be done in either hydrogen or nitrogen environments depending on the requirements. Finally, the precursors and gas pressures are controlled via computer using the reactor’s proprietary CACE software, which allows for automated as well as manual opening and closing of
valves. A sample recipe that is used as a base for majority of the samples grown in this research is presented in the Appendix.

For the InGaN nanoring growths 2” sapphire wafer (0001 orientation) were used. Sapphire wafers are relatively more stable than other wafers and don’t require any additional cleaning or purification prior to use in the reactor. Once the wafer is loaded, the initial step of the growth process involves hydrogen desorption, which involves introducing hydrogen at around 1190 C to remove all contaminants from the surface of the wafer. After desorption, the surface undergoes nitradation, which is the flow of pure nitrogen gas into the reactor chamber, at 560 C to remove any vacancies.

Once the initial preparation steps are done, the first growth step would be to grow a GaN buffer layer. This is done by introducing ammonia and TMGa into the system at 560 C. The reason a buffer layer is necessary is because if InGaN was grown directly on the sapphire substrate, the lattice mismatch would be so great to cause extremely poor quality material to be grown.

**Nanostructure Growth**

Nanostructures have been grown in several different ways including Volmer-Weber, Frank van der Merwe, and Stranski-Krastanow (SK) growth methods that allow for the formation of 3D nanostructures [33]. The
SK method has been the most common method of growing III-V nanostructures that is dependent on several factors including thickness of growth layers, amount of surface stress, and lattice mismatch. It works by growing material monolayer by monolayer until a critical thickness is reached in which the stress between the layers reaches a point where the material must form into a nanostructure to relax the strain. In this case droplet epitaxy was utilized which has several advantages over the other approaches. First, since the nanostructures are grown at the sites of the droplets, great uniformity and coverage of a sample can be achieved. Second, by controlling the diameter of the initial droplets, the final size of the nanostructures can be tailored. Third, since the growth process does not depend on the strain, as is common when growing traditional quantum dots, they are relatively stress free.

![Figure 3.1 Stranski-Krastanow mechanism of growth indicated by first monolayer-by-monolayer growth occurs until a critical point of stress is reached in the material where formation of quantum dots becomes more favorable then thin layers.](image)
Droplets form on the surface of a substrate when it is energetically favorable to reduce the interface energy that exists between the deposited atoms and the surface of the substrate, causing the atoms to migrate and bond together in the form of droplets. In these experiments the droplets were formed by introducing TMIn and TMGa at the same time at temperatures ranging from 350 C to 880 C and different pressures and flow rates to control the size and density of the droplets. The deposition rate of TMIn was kept almost twice as that of TMGa due to the extremely low sticking coefficient of indium atoms.

Once the In-Ga droplets were deposited, the next step was to transform them into nanorings. At varying temperatures, ammonia was then introduced into the system for various times ranging from 30 seconds to 5 minutes causing the droplets to crystallize and either crystallize into nanorings or other forms of nanostructures.
Chapter 4 | Characterization Techniques

Atomic Force Microscope

Binning et. al invented the Atomic Force Microscope (AFM) in the late 1980’s when the need for atomic level microscopy grew greatly. The AFM combined the techniques of scanning tunneling microscope (STM) and profilometer, using an extremely small tip it can profile and image the surface of almost any material, opening the door of imaging to a wide range of materials. The AFM has a cantilever with a Si or Si₃N₄ tip, which is on the order of a couple nanometers. The tip is then used to “feel” the surface of the material by bringing it close to the surface of the material, causing the tip to deflect due to the forces that result from the interaction of the tip and the surface. Then forces such as van Der Waals and capillary forces are measured through using special sensors. The accuracy of measuring the deflection of the tip is further enhanced by capturing the reflection of a laser in a series of photodiodes. Piezoelectric actuators enable the tip to be moved accurately in any direction, allowing for accurate 3D images of the samples.
Figure 4.1 Mechanism of how atomic force microscopy works using a cantilever with atomic size tip that allows for interaction with the sample and data is collected via various detectors. [10]

**X-ray Diffraction**

X-ray Diffraction (XRD) is a technique that uses incident x-rays to determine the positions of planes of atoms based on the diffraction angle. Since x-rays wavelength is on the order of atoms, they can easily probe and determine the atomic structure of different inhomogeneous materials with relative ease. X-rays are first hit on a target species, in this case copper, after which x-rays with precise wavelength of 1.54 Å. The x-rays then interact with the electrons of the atoms in the material and are deflected away in an elastic or inelastic manner. The diffracted electrons are then collected and measured according to the relative angle of diffraction, which produces a plot used to determine the material composition, crystallinity, and phase information. In a θ-2θ scan, the
sample is scanned at a range of selected angles, which potentially correspond to the spacing that exists between the atoms present in the sample. A relationship was derived by Bragg that is as follows:

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

[Eq 4]

In this case \( \theta \) is the angle at which the x-ray is scattered, \( n \) the order of the diffraction, and \( d \) is the interplanar distance between planes of atoms. In the case of III-nitride materials, the (0002) reflection typically gleans the most information from the sample, which was used in this case. In the case of a ternary alloy like InGaN, the lattice spacings of the material is dependent on the relative compositions of indium and gallium within the alloy, with the final spacing being found between GaN and InN. Thus,

\[ X_{\text{InGaN}} = \frac{C_{\text{GaN}} - \frac{\lambda}{\sin \theta}}{C_{\text{GaN}} - C_{\text{InN}}} \]  

[Eq 5]

Vegard's law can be readily applied to get a close approximation of the expected peaks based on the composition of InGaN and using the lattice constants, \( c \), of GaN and InN.

Several unique features to InGaN can also be determined using XRD such as phase separation which was discussed earlier. If phase separation occurs, then broadening of peaks happens and peaks of different compositions of InGaN would be found.
Photoluminescence

Photoluminescence (PL) is a technique used to determine various electrical and band properties of a material through optical excitation. The technique works by having an incident laser hit the sample causing photons to be absorbed and electrons to be released based upon the band structure and excitation levels present in the material. When the material absorbs photons, two types of excitations can occur: radiative and non-radiative. Radiative excitations occur when photons with energy equivalent to the energy levels in the material are absorbed, causing electrons to have enough energy to jump to the next available energy state, and then release a photon upon relaxation. Non-radiative excitations do not result in the emission of a photon due to the presence of trap sites or defects that hinder a complete band-to-band relaxation from happening.

Figure 4.2 Incident laser beam hits the sample then is focused via lenses and the excited wavelengths are finally detected using a silicon-based photo-detector.
PL has the advantage of being an effective technique to find the band gap of a material and thereby indirectly determine the composition of the material, as was done in the case of InGaN samples.

Figure 4.3 Electrons first start off in ground state, then upon incident excitation electrons move to the conduction band from where they eventually decay back down to the lower energy band and release a photon equal to the energy difference of the two bands.
Chapter 5 | Results & Discussion

*InGa Droplets*

Initially the first step in achieving nanorings was to be able to control the density and composition of the In-Ga droplets. Since the droplets are the seeds for the nanorings, it was important to achieve indium rich droplets to achieve nanorings with high indium composition. It was verified in the initial study that indium tends to escape and is better incorporated at lower temperatures, where samples were grown at 350 °C, 570 °C, and 880 °C to get 84.6%, 63.06%, and 16% indium respectively. It was also found that at higher temperatures the density of the droplets tends to become sparser at higher temperatures. This is due to the higher energy available for indium-gallium atoms to migrate across the surface.

![Image of InGa droplets with 16% indium.](image)

**Figure 5.1** In-Ga droplets with 16% indium.
The second thing that was investigated was the role of the GaN nucleation layer in the growth of InGaN nanostructures. Due to the extreme disparity in lattice constant between InGaN and the sapphire substrate, which increases with increasing indium content, it became evident a GaN nucleation layer would be necessary to reduce the amount of stress between the two.

Figure 5.2 In-Ga droplets with 63.06% indium with increased diameter.
Figure 5.3 In the absence of a nucleation layer droplets aren’t able to wet the rough sapphire substrate and thus no In-Ga droplets are visible.

From the SEM it is evident that the surface is extremely rough unlike in the other cases where the droplets wet the GaN layer and have a smooth interface between the two and the droplets aren’t able to wet the surface, leaving only residue behind.

**InGaN Nanorings**

**Growth Time**

The growth temperature, pressure, ratio of TMGa/TMIn, III/V ratio, and growth time all affected the composition and quality of the resulting nanorings. The rings were grown for 30 sec, 1 min, 1:30 min, 2 min, and 5 minutes, indicating the amount of time ammonia was flowed into the reactor and allowed to react with the In-Ga droplets to form the nanorings.
Figure 5.4 The formation of InGaN nanoparticles after 30 seconds. At this point the particles appear to be completely filled with no holes present.

Figure 5.5 After 1 minute of growth, majority of the nanoparticles have been converted into nanorings.
Figure 5.6 After 1 minute 30 seconds of growth the samples have became hexagonal nanorings with a clearly visible hole in their center.

Figure 5.7 After 2 minutes of growth the nanorings begin to fill up again causing their hole to disappear.
As the amount of time increases where ammonia flows in the reactor, it begins to etch away and react with the In-Ga droplet. A critical point exists where the condition becomes ideal for there to be a hole in the nanostructure. The main reason this occurs is due to the disparity between the surface mobility of In and Ga atoms. As the ammonia flows in and reacts with the In-Ga droplet, to accommodate the extra stress, indium is kicked out and migrates to the edge of the nanostructure, leaving behind a whole. After the critical point, the nitrogen begins to fill into the center once more creating a filled nanoparticle and reducing the number of nanorings present in the sample.

**Temperature**

The second parameter that was changed was the temperature to control the amount of indium incorporated within the nanorings. The temperature of growth was chosen to be 570 C, 670 C, 770 C, and 880 C. As the temperature increased, as expected the amount of indium decreases and therefore a critical amount of indium exists that allows for the formation of nanoring.
Figure 5.8 InGaN nanorings at 670 C

Figure 5.9 InGaN nanorings at 770 C
The more indium that incorporates at lower temperatures, the more deformed the rings appear due to the difficulty of incorporating the larger indium atoms within the nanostructure. Similar to the time of growth, an optimum temperature seems to exist in which the nanorings are more well defined with respect to the size of the holes. Initially at 670 C, there exists 50.4 % indium within the rings, but the rings are less defined due to the instability of the indium atoms. At 770 C as the indium content reduces to 44.67%, the rings become to be more well defined and almost all the droplets are converted to rings. A possible explanation can be that for the size of droplets that are formed, there exists a certain threshold of indium that the ring can thermodynamically stable.
**TMIn/TMGa Ratio**

As the ratio of the TMIn and TMGa was varied, it affected the formation of the nanorings based upon the incorporation of indium. The ratio of TMIn/TMGa was varied as high as 40/1 to as low as 13/1. Initially the droplets were observed with this varying ratio to see how they were affected. With the 40/1 ratio in which the droplets consisted of 40% indium with the total TMGa + TMIn being 205 sccm, the droplets seemed relatively unstable and upon incident excitation from the 20 keV beam of the SEM the droplets seemed to begin migrating, showing the possible initial formations of nanowire growth.

![Image](image_url)

**Figure 5.11 InGa droplets grown using 40/1 TMIn/TMGa ratio**

As the amount of TMGa was increased reducing the TMIn/TMGa ratio to 20/1 but increasing the total amount of TMGa + TMIn to 210 the droplets...
appeared to be more stable and well defined and the amount of indium decreased to about 20%.

Figure 5.12 InGa droplets grown using 20/1 TMIn/TMGa ratio

At the lowest ratio of 13/1 TMIn/TMGa with TMGa increased to 15 sccm and the total amount of TMGa + TMIn being 215 sccm, the amount of indium incorporated within the droplet surprisingly increased to almost 70%, despite the lower TMIn/TMGa ratio. It seems that similar to the temperature case, there exists an ideal ratio between TMIn/TMGa and TMIn + TMGa where the indium incorporation is greatest. But in this case as well, upon incident excitation of 10 kV from the SEM, the droplets begin to transform into nanowires. The reason this may be true is due to the trapping of indium atoms by the increased amount of gallium atoms present thereby increasing the amount of indium atoms that are
incorporated. Secondly, there may be an overpressure present of TMGa and TMIn gases that cause the reduction of indium escaping from the droplets, as they tend to do in other cases.

Figure 5.13 InGa droplets grown using 13/1 TMIn/TMGa ratio with the droplets being much more mobile then the other cases

Nanoring shape increases indium incorporation

Thereafter, the effect of the TMIn/TMGa ratio was observed on the nanorings by varying the ratio from 10, 13.3, 15, 20, 23 and 30 to 1. As the ratio of TMIn/TMGa increased, as expected the amount of indium incorporated increased with the exception of a ratio of 15 where it decreased as compared to 13.3. A plausible explanation for this decrease exists in the shape of the nanostructure that formed. In the case of 13.3, the structures formed nanorings with significant hole in the center. In the
case of 15 however, the nanostructures were particles without a hole in the center. From this it indicates that the nanoring shape assists in better accommodating indium into the structure by allowing the structure to relax as the ring is formed whereas in the non-hole structure there exists more stress that causes indium to have difficulty remaining within the structure. As the ratio was then increased to 20, nanorings formed again with a well defined hole in the center and as expected with this theory the amount of indium significantly increased again to over 20%. Then as the ratio was pushed higher to 23, once more the nanostructures that formed were particles without any hole and again the amount of indium incorporated significantly reduced down to 7%. This observation agrees with the explanation that was given that the nanoring structure allows for higher indium incorporation due to the accommodation of stress by significant material migration with the formation of the hole.

Figure 5.14 InGaN nanorings grown using 10/1 TMIn/TMGa ratio
Figure 5.15 InGaN nanorings grown using 13/1 TMIn/TMGa ratio

Figure 5.16 InGaN nanorings grown using 15/1 TMIn/TMGa ratio
Figure 5.17 InGaN nanorings grown using 20/1 TMIn/TMGa ratio

Figure 5.18 InGaN nanorings grown using 23/1 TMIn/TMGa ratio
Figure 5.19 InGaN nanorings grown using 30/1 TMIn/TMGa ratio

*NH₃ Effect on Growth*

From the SEM images the evolution of the nanorings and the effects of various parameters was discussed. Next the effect of ammonia was observed on the morphology and nature of the nanoring. The amount of ammonia was varied from 500, 1000, 1500, and 2000 sccm. As the amount increased, the quality of the nanoring also seemed to increase as well as the amount of indium incorporated. In the case of 1000 sccm, the amount of indium incorporated was only 5.73 % while for the same conditions at 2000 sccm, that amount dramatically increased to 20.5%. The reason attributed for this increase was the increased pressured exhibited upon the droplets upon growth. Since indium has a tendency to escape from the material, the increased ammonia content forces the indium to stay within and remain part of the final nanostructure.
Furthermore energetically more nitrogen atoms are available to form bonds with indium, reducing its chances of migrating away.

Figure 5.19 InGaN nanorings grown using 500 sccm NH3

Figure 5.20 InGaN nanorings grown using 1000 sccm NH3
Figure 5.21 InGaN nanorings grown using 1500 sccm NH3

Figure 5.22 InGaN nanorings grown using 2000 sccm NH3
Photoluminescence

One of the key characteristics that make InGaN unique as discussed in the introduction is its ability to be tuned to span a major portion of the visible spectrum. Photoluminescence (PL) is one technique that allows for measuring the wavelength that is active for a given material. In this case PL measurements were taken for various compositions of nanoring samples to see which wavelengths were active throughout and approximate the band gap of the material.

In the first PL spectra, there is a very well defined and relatively sharp peak appearing at 500 nm, which corresponds to 2.48 eV, which makes it active in the green region of the color spectrum. This sample was grown under 880 °C with ratio of 20/10 TMGa/TMIn for 1 minute.

As the time of growth was increased to 1 minute 30 seconds, considerable amount of peak broadening occurred at about the same wavelength peak, indicating that significant fluctuation in indium composition in InGaN exists. This may be probable due to the increased time ammonia has to follow into the system, which could give enough time for more indium to escape as the nitrogen atoms are deposited.

The temperature effect on photoluminescence was also observed between samples grown at 670, 770, and 870 °C. As the temperature of growth decreased, there was a redshift towards higher wavelengths.
indicating the increased incorporation of indium. Another observation is the quality of the peak decreases as the temperature increases, also indicating composition fluctuation occurring at higher temperatures, which could be due to phase separation. Therefore it has been demonstrated that the active wavelength of the nanorings can be tuned across at least a part of the visible spectrum from the blue to green region. Growths performed at extremely low temperatures below 500°C resulted in the formation of small nanoparticles but nanorings did not form, possibly due to the absence of enough thermodynamic energy in the system to drive the atoms to migrate from the particles to the surface.

The band gap of the material can be extrapolated from the PL spectra using the relationship:

$$E_{\text{InGaN}}(x) = (1 - x)E_{\text{GaN}} + E_{\text{InN}} - bx(1 - x) \ [\text{Eq 6}]$$

In this case the $b$ is known as the bowing factor that is responsible for taking account the non-linearity that is present with InGaN alloys. As discusses previously, the bowing factor varies throughout literature. In this case the bowing factor was taken to be 3.8 eV, GaN is 3.4 eV and InN 0.7 eV. Using these values, the composition was back calculated to be 16.8% that is very close to the value determined through EDX of 17.1%.
Figure 5.23 InGaN nanoring grown at 880°C for 1 minute.

Figure 5.24 InGaN nanoring grown at 880°C for 1:30 minute.
Figure 5.25 InGaN nanoring grown at 770 C

Figure 5.26 InGaN nanoring grown at 670 C
**XRD Analysis**

XRD analysis was used to determine if phase separation was occurring in the samples and the crystallinity of the nanorings that were grown. In a θ-2θ scan, the 31.4° corresponds to pure InN while 34.5° corresponds to a pure GaN peak, relating to the (0002) reflection. Therefore it was expected that InGaN would fall between the two values depending upon the amount of indium present in the alloy. In each of the samples it was also expected that the GaN peak from the buffer layer would also be present. The shift and variation of the XRD peaks was observed with respect to change in temperature growth, growth time, and III/V ratio. In this case XRD was compared between nanorings grown at 670 C, 770 C, and 870 C. As the temperature decreases, the InGaN peak becomes sharper and the noise significantly decreases, indicating a high crystalline InGaN. The other observation is that at higher temperatures there seems to be additional smaller InGaN peaks, indicating that phase separation is occurring where there are indium-rich and indium-deficient regions present in the nanorings. It appeared however the trend seen in the XRD results was not as expected. The highest 870 C sample had its InGaN peak at 32.88 compared to 32.93 for the 770 C peak and 33.15 for the 670 C peak. If the peaks were solely due to the composition, which have been confirmed via EDX and PL previously as increasing in indium content in lower temperatures, then the 670 C sample should have had the peak closest to
the 31.5 InN peak, but the opposite was the case. One plausible explanation for this shift is that XRD peaks are very sensitive to the strain present in the material. It is evident that as the amount of indium incorporates within the material, due to its larger atom size causes the rings to become more strained as it grows causing the lattice to become contracted and shift towards the InN peak, despite the inability of the material to keep the indium incorporated.

Figure 5.27 InGaN nanoring grown at 670 C, with InGaN peak at 33.15°
Figure 5.28 InGaN nanoring grown at 770 C, with InGaN peak at 32.93°

Figure 5.29 InGaN nanoring grown at 870 C, with InGaN peak at 33.15°

The effect of pressure on indium incorporation on the rings was then subsequently studied. In one sample the pressure of the system during
droplet deposition and growth of the nanoring was kept at 300 mbar and then for another sample it was increased to 600 mbar for both to see the effect. In the first case there was a significant InGaN peak present in the sample along with a higher GaN peak and smaller InN peak, indicating some phase separation occurred. However for the sample grown at 600 mbar the InGaN almost completely disappeared leaving only the major GaN peak. Other papers have mentioned that higher overpressures are needed to increase indium incorporation. But in this case as the pressure is increased for both the droplets and ring, it seemed to increase the indium desorption from the sample. This may be explained by the fact that initially during the droplet formation phase, the high pressures keep indium from full incorporating into the droplet from the beginning. Thus when ammonia is introduced into the system, already there is very little indium present in the droplets causing mainly Ga rich rings to form.

Figure 5.30 InGaN nanoring grown at 300-mbar pressure
To confirm this theory, another sample was grown during which the droplets were grown at the lower 300 mbar and then when ammonia was introduced to form the nanorings, the pressure was raised to 600 mbar to see if the desired increased indium incorporation could be seen using this methodology. From the XRD plot, it is conclusive that this indeed did occur and there was a significantly sharp InGaN peak at about 33°, indicating about 15% indium is present within the rings. Therefore the ideal growth method was determined to be to grow the droplets at lower pressures to allow for high indium content droplets to form and then subsequently increase the pressure upon release of ammonia to prevent indium from escaping the droplets.

**Figure 5.31 InGaN nanoring grown at 600-mbar pressure**
Figure 5.32 InGaN droplets grown at 300 mbar and nanorings at 600 mbar

**Growth Time**

The next analysis was done to observe the effect of the droplet growth time on the overall quality of the InGaN ring. Therefore the droplet time was increased to 1 minute and compared to the original 30 seconds as in the sample data previously presented.
Figure 5.33 InGaN droplet time increased to 1 minute

The XRD revealed that significant phase separation began to occur as the droplet time was increased, indicated by the multiple smaller InGaN peaks that emerged between 32.5° and 34°, ranging from 25% to 5% indium in InGaN. Therefore the droplet growth time should be kept as low as possible but at the same time enough to achieve desired amount of indium incorporation without causing phase separation to occur.
Figure 5.34 InGaN nanoring grown for 45 seconds

Figure 5.35 InGaN nanorings grown for 1 minute
Figure 5.36 InGaN nanorings grown for 1 minute 30 seconds

Figure 5.37 InGaN nanoring grown for 2 minutes
Figure 5.38 InGaN nanoring grown for 5 minutes

The growth time of the rings was varied between 45 seconds to 5 minutes to see where the ideal time of growth lay that would allow for the best InGaN nanorings with little phase separation and high indium incorporation. The samples grown at 45 seconds and 1 minute have small InGaN peaks, but the GaN peak greatly overwhelms it indicating that the InGaN rings are very sparse as compared to GaN. But when the growth time was increased to 1 minute 30 seconds, the ratio of InGaN peak to GaN was greatly reduced showing that the rings are overwhelmingly InGaN with high indium content (~20%), showing that this growth time is much better than the lower growth times. But if the growth time is increased further to 2 minutes, then the nanorings begin to lose their crystallinity and multiple InGaN peaks emerge showing significant phase...
separation is occurring. This may be due to the fact the additional time allows for indium atoms to be kicked out as the additional nitrogen atoms enter. As the time is increased to 5 minutes, the atoms have time to achieve their thermodynamically ideal state in which GaN once more overwhelms and the ratio of GaN to InGaN peaks is 10 times as compared to the original 4x. Therefore from this study we conclude that the ideal growth time for InGaN nanorings with high indium content and low phase separation occurs at around 1 minute 30 seconds.

**Conclusion**

From this study we developed a systematic method to grow and synthesize InGaN nanorings along with the ability to control the amount of indium content present in the rings. The study also further enhanced our understanding of the effects of various external factors such as growth pressure, temperature, TMGa/TMIn ratio, III/V ratio on indium incorporation within InGaN in general and nanorings in particular. The nanorings grown through this study were shown to be optically active in the green and blue regions with high intensity, allowing for their potential applications for optoelectronic devices. Droplet epitaxy allowed for the control of the nanoring size and has shown to be a good method to achieve fast growth of nanostructures while maintaining relatively good control over the ultimate size and shape of the nanostructures. As nanorings have only been shown thus far in few material systems, with
this being the first research into InGaN nanorings, there exists great potential for further research into the unique properties of nanorings as compared with other nanostructures. It can be envisioned for them to be used as a platform for other nanostructures such as nanowires to be grown from the center hole and create very good electrical contact with the underlying substrate. Further research should be conducted to gain a better understanding of InGaN nanorings and investigate potential applications.
REFERENCES


APPENDIX A
SAMPLE INGAN NANORING RECIPE USED IN AIXTRON REACTOR
ReactorStat = Power ReactorPress ReactorTemp;

layer {

  # Set-up the system:
  0:00:10 N2.line close, H2.line open, N2.run close, H2.run open,
           RunHydride.H2 open, LinerPurge.H2 open, Rotation.H2 close, Cooling on,
           MainPump on, Heattape on;
  0:03:00 Heather on, VentVac open, Control on, IGS on, ReactorPress to 100;
  0:03:00 RunHydride to 2500, PushHydride to 500, VentHydride to 500,
           RunMO to  1500, PushMO to 500, VentMO to 500, RunDopant to 500,
           PushDopant to 500, VentDopant to 500, LinerPurge.source to 1000,
           LinerPurge to 1000, Rotation to 400,
           TMGa_1.source to 10, TMGa_1.push to 50,
           TMAI_1.source to 10, TMAI_1.push to 50,
           TMIn_1.source to 10, TMIn_1.push to 50,
           Cp2Mg_1.source to 10, Cp2Mg_1.dilute to 50, Cp2Mg_1.inject to 10,
           TBAs_1.source to 10, TBAs_1.push to 50,
           NH3_1.source to 400, NH3_1.push to 100,
           HCl_1.source to 10, HCl_1.push to 50,
           SiH4_1.source to 10, SiH4_1.dilute to 50, SiH4_1.inject to 10;
  0:03:00 "prepare reactor pressure", ReactorPress to 300;

  #**Start H2 Desorption**#
  0:15:00 ReactorTemp to 1100, "ramp temperature";
  0:02:00 ReactorTemp to 1190, "ramp temperature";
  0:10:00 ReactorTemp = 1190, "H2 desorption";
  #**End H2 Desorption**#

  #**Start Nitridation**#
  #2 L NH3 & 15 mL TMGa @ 560 C in 300 mbar H2
  0:00:01 NH3_1.line open, TMGa_1.line open;
  0:05:00 ReactorTemp to 570, "ramp temperature";
  0:00:01 ReactorTemp = 560;
0:03:00  

NH3_1.run open, NH3_1.source to 2000, NH3_1.push to 500, "open NH3",

RunHydride to 250, PushHydride to 250, VentHydride to 1000;
0:01:00  "stabilize NH3";

#####################**End Nitridation**#
###**Start Growth Nucleation Layer**###
0:01:00  begin stat ReactorStat, TMGa_1.run open, "grow nucleation layer";

0:00:01  end stat ReactorStat, TMGa_1.run close, TMGa_1.line close, NH3_1.run close;
###**End Growth Nucleation Layer**###

###**Start Annealing**###
#3 L NH3 @ 1170 C in 300mbar H2
0:15:00  ReactorTemp to 1130, "ramping anneal",

    TMGa_1.source to 45, TMGa_1.push to 205,

    RunMO to 2000, RunDopant to 1000;
###**End Annealing**###

###**Start Growth InGaN Nanorings**###
#TMGa & 200 mL, TMIn @ 880 C in 300 mbar N2
0:05:00  ReactorTemp to 890, "lower temperature",

    TMGa_1.source to 30, TMGa_1.push to 220,
    LinerPurge.source to 800, LinerPurge to 800;
0:00:01  ReactorTemp = 880,

    N2.line open, H2.line close, N2.run open, H2.run close, # switch from H2 to N2  RunHydride.H2 close, LinerPurge.H2 close, Rotation.H2 close;
0:00:01  TMGa_1.line open;
0:00:30  TMGa_1.source to 10, TMGa_1.push to 240, TMIn_1.source to 200, TMIn_1.push to 50, "prerun sources";
0:00:30  TMIn_1.line open, "stabilization";
0:00:30  begin stat ReactorStat, TMGa_1.run open, TMIn_1.run open, "grow InGa droplets";
0:00:01   end stat ReactorStat, TMIn_1.run close, TMIn_1.line close, TMGa_1.run close, TMGa_1.line close;

0:01:30   NH3_1.run open, "Grow InGaN Rings";
0:00:01   NH3_1.run close;

#***End Growth InGaN Nanorings***#

#***Start Cool in NH3***#
# 3 L NH3 in 300 mbar H2

0:10:00   ReactorTemp to 450, "ramp down temperature",
           TMGa_1.source to 10, TMGa_1.push to 50,
           TMIn_1.source to 10, TMIn_1.push to 50;
0:00:01   ReactorTemp = 0, Heater off;
0:05:00   NH3_1.source to 2000, "decrease NH3",
         RunMO to 1500, RunDopant to 500;
         "cool down to 250",
         until ReactorTemp << 250;

#***End Cool in NH3***#

#***End Cool in N2***#

0:03:00   NH3_1.line close, NH3_1.source to 400, NH3_1.push to 100,
           "close NH3", RunHydride to 2500, PushHydride to 500, VentHydride to 500;
#***End Cool in N2***#

#***Start Cycle Purge***#

0:03:00   ReactorPress to 80;
0:05:00   ReactorPress to 1000;
"go to idle conditions",

NH3_1.source to 100,

RunHydride to 200, PushHydride to 200, VentHydride to 200,

RunMO to 100, PushMO to 100, VentMO to 100,

RunDopant to 100, PushDopant to 100, VentDopant to 100,

LinerPurge.source to 100, LinerPurge to 100,

Rotation to 100;

"cool down to 65",

until ReactorTemp <<65;

0:00:01 Cooling off, Control off, VentVac close, IGS off, Heattape off;

} #end