GALLIUM NITRIDE NANOWIRE GROWTH AND CHARACTERIZATION

by

Lorelle M. Mansfield
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

Golden, Colorado

Date 4/8/09

Signed: Lorelle M. Mansfield

Lorelle M. Mansfield

Signed: Timothy R. Ohno

Dr. Timothy R. Ohno
Thesis Advisor

Signed: Kristine A. Bertness

Dr. Kristine A. Bertness
Thesis Advisor

Golden, Colorado

Date 4/8/09

Signed: John J. Moore

Dr. John J. Moore
Professor and Head
Department of Metallurgical, and Materials Engineering
ABSTRACT

GaN nanowires have become scientifically important because they provide an avenue to circumvent the limitations of conventional thin film GaN devices. Nanowires have no crystalline defects and low impurity levels even when grown on lattice-mismatched substrates and with embedded heterostructures. New and better growth and characterization methods for novel nanoscale materials are also necessary for the effective use of these properties in commercial devices. In this work, a chemical beam epitaxy (CBE) system was designed and built for the growth of nitride materials, including GaN nanowires. The effects of various nanowire growth parameters were investigated. In addition, a method to measure the carrier concentration and mobility in GaN nanowires was developed.

A study of growth conditions was performed to optimize nanowire fabrication. The parameters chosen for nanowire runs were based on a three-level Box-Behnken designed experiment. The parameters that varied were substrate temperature, gallium cell temperature, and a combined plasma power and nitrogen flow. GaN nanowires were formed by use of an effusion cell containing gallium and a nitrogen plasma source. Growth rates increased from 0 to 325 nm/h as Ga cell temperature increased. The nanowire morphology was influenced by nitrogen plasma power and flow combination. High power (325 W) and flow (1.7 sccm) caused the nanowires to be more tapered and coalesced than the low power (225 W) and flow
(0.9 sccm) conditions. Substrate temperatures at the low temperature condition (800 °C) produced the best nanowire growth environment.

The carrier concentration and mobility of silicon-doped GaN nanowires was obtained from light and dark resistance data at room temperature. Current-voltage measurements were performed on single-nanowire devices in the dark and under 360 nm illumination. Field-emission scanning electron microscopy was used to measure the device dimensions. The nanowires were modeled with cylindrical geometry, and solutions were computed with a nonlinear fit algorithm. Simulations were also performed to verify the model. The carrier concentration was bounded by $6 \times 10^{17} \text{ cm}^{-3}$ and $1.3 \times 10^{18} \text{ cm}^{-3}$, and the mobility was between $300 \text{ cm}^2/(\text{V} \cdot \text{s})$ and $600 \text{ cm}^2/(\text{V} \cdot \text{s})$. The work described in this dissertation contributes to the understanding of GaN nanowire growth and characterization.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iii
LIST OF FIGURES ................................................................................................................... viii
LIST OF TABLES ................................................................................................................... xi
LIST OF ABBREVIATIONS .................................................................................................. xii
ACKNOWLEDGEMENTS ........................................................................................................ xiv
CHAPTER 1  INTRODUCTION .............................................................................................. 1
  1.1 Motivation .................................................................................................................. 2
  1.2 Research Conducted .............................................................................................. 4
  1.3 Organization of the Chapters ............................................................................... 4
CHAPTER 2 BACKGROUND ..................................................................................................... 7
  2.1 Nitrides .................................................................................................................... 7
    2.1.1 Band Gaps ................................................................................................ 7
    2.1.2 Crystal Structure ....................................................................................... 8
    2.1.3 Dopants ..................................................................................................... 10
  2.2 Nanowires ............................................................................................................... 12
    2.2.1 Growth Substrates ................................................................................... 12
    2.2.2 GaN Nanowire Research ....................................................................... 13
    2.2.3 Nanowire Structures ............................................................................. 14
  2.3 Growth Methods ..................................................................................................... 16
    2.3.1 Metalorganic Chemical Vapor Deposition (MOCVD) .................... 16
### Chapter 2: Nitride Growth

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.2</td>
<td>Molecular Beam Epitaxy (MBE)</td>
<td>18</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Vapor-Liquid-Solid Growth Method (VLS)</td>
<td>19</td>
</tr>
<tr>
<td>2.4</td>
<td>GaN Nanowire Growth at NIST</td>
<td>23</td>
</tr>
</tbody>
</table>

### Chapter 3: Nitride Growth System

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Initial Design and Construction</td>
<td>27</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Ultra-High Vacuum (UHV) Environment</td>
<td>28</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Sample Stage and Temperature Control</td>
<td>31</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Material Sources</td>
<td>34</td>
</tr>
<tr>
<td>3.1.4</td>
<td>RGA and Software Control</td>
<td>36</td>
</tr>
<tr>
<td>3.2</td>
<td>Upgrades to Growth System</td>
<td>39</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Loadlock and Transfer System</td>
<td>41</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Effusion Cells</td>
<td>43</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Manipulator</td>
<td>46</td>
</tr>
<tr>
<td>3.2.4</td>
<td>OM Upgrades</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Conclusions</td>
<td>49</td>
</tr>
</tbody>
</table>

### Chapter 4: Nanowire Growth

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Abstract</td>
<td>51</td>
</tr>
<tr>
<td>4.2</td>
<td>Introduction</td>
<td>52</td>
</tr>
<tr>
<td>4.3</td>
<td>Experiment</td>
<td>54</td>
</tr>
<tr>
<td>4.4</td>
<td>Results</td>
<td>58</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusion</td>
<td>73</td>
</tr>
</tbody>
</table>

### Chapter 5: Nanowire Carrier Concentration

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Abstract</td>
<td>75</td>
</tr>
</tbody>
</table>

vi
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2 Introduction</td>
<td>76</td>
</tr>
<tr>
<td>5.3 Experiment</td>
<td>77</td>
</tr>
<tr>
<td>5.4 Discussion</td>
<td>82</td>
</tr>
<tr>
<td>5.5 Model</td>
<td>87</td>
</tr>
<tr>
<td>5.6 Simulations</td>
<td>98</td>
</tr>
<tr>
<td>5.7 Summary</td>
<td>101</td>
</tr>
</tbody>
</table>

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS ........................................ 103

6.1 Nitride Growth System ......................................................................... 103

6.2 Nanowire Growth .................................................................................. 103

6.2.1 Conclusion....................................................................................... 103

6.2.2 Future Work .................................................................................... 105

6.3 Nanowire Carrier Concentration ........................................................... 107

6.3.1 Conclusions ..................................................................................... 107

6.3.2 Future Work .................................................................................... 108

REFERENCES CITED...................................................................................... 109

APPENDIX A CRACKING PATTERNS.................................................................. 119

APPENDIX B IONIZED DONOR CALCULATIONS.................................................. 121

APPENDIX C NITRIDE GROWTH SYSTEM......................................................... 127

C.1 Conclusion ............................................................................................ 127

C.2 Future Work .......................................................................................... 130
LIST OF FIGURES

Figure 2.1 Band gap energy vs. lattice parameter for the III-nitride semiconductors. 8
Figure 2.2 Wurtzite crystal structure of GaN ................................................................. 9
Figure 2.3 Crystal planes in GaN .................................................................................. 10
Figure 2.4 The focused ion beam (FIB) process for creating an electrical contact. ... 15
Figure 2.5 GaN nanowires grown selectively by MBE .................................................. 15
Figure 2.6 Axial and radial nanowire structures ......................................................... 16
Figure 2.7 Diagram of an MOCVD system ................................................................. 18
Figure 2.8 Diagram of an MBE system ...................................................................... 20
Figure 2.9 Cartoon of the vapor-liquid-solid (VLS) growth method ......................... 21
Figure 2.10 SEM images from reference [35] of GaN grown using nickel catalyst nanoclusters ................................................................. 22
Figure 2.11 Cartoon of GaN nanowire growth shown in cross-section .................... 24
Figure 2.12 Cross-sectional FESEM image of GaN nanowires .................................. 24
Figure 2.13 Cartoon of Ga atom incorporation ............................................................ 26
Figure 3.1 Hand-drawn diagram of the growth chamber ............................................ 29
Figure 3.2 Partial engineering diagram of the growth chamber .................................. 30
Figure 3.3 Chamber and pump connections ............................................................... 32
Figure 3.4 Substrate manipulator .............................................................................. 33
Figure 3.5 Temperature non-uniformity ...................................................................... 35
Figure 3.6 Organometallic (OM) gas lines ................................................................. 37
Figure 3.7 Organometallic source details .................................................................... 38
Figure 3.8 RGA spectra from growth system ......................................................... 40
Figure 3.9 Front panel of the control software for the nitride growth system .... 42
Figure 3.10 Loadlock system .............................................................................. 44
Figure 3.11 Picture of the inside of the loadlock chamber ................................... 45
Figure 3.12 Diagram of an effusion cell ............................................................... 45
Figure 3.13 Magnet rotation drive on manipulator .............................................. 48
Figure 3.14 The completed nitride growth system .............................................. 50
Figure 4.1 Geometric representation of a Box-Behnken design ....................... 54
Figure 4.2 Marginal means plot for growth rate versus substrate temperature, Ga cell bottom temperature, and plasma RF power ........................................ 59
Figure 4.3 Surface plot of growth rate versus substrate temperature and Ga cell bottom temperature at 275 W RF power .............................................. 60
Figure 4.4 The effect of increasing substrate temperature ................................. 61
Figure 4.5 Top-view FESEM images illustrating that an 840 °C substrate temperature is the upper boundary for nanowire growth ..................................... 62
Figure 4.6 The effect of increasing gallium cell temperature ............................... 63
Figure 4.7 FESEM images that compare the morphology of nanowires grown with N2 plasma at different RF powers ................................................. 66
Figure 4.8 Normalized PL intensity vs. photon energy ....................................... 67
Figure 4.9 FESEM images of nanowire density differences based on RF power .... 69
Figure 4.10 Nanowire density graphs ................................................................. 71
Figure 4.11 FESEM images of nanowire runs grown at 800 °C substrate temperature, 950 °C Ga cell temperature, and 225 W RF power .................... 73
Figure 5.1 Top-view FESEM image of a typical four-point device ..................... 79
Figure 5.2 Photocurrent graphs ....................................................................... 83
Figure 5.3 A gate voltage sweep showing hysteresis at constant drain-source bias, $V_{ds}$, of 0.3 V for a nanowire FET. .............................................................. 86

Figure 5.4 Cartoons of nanowire radius and depletion width. ........................................... 88

Figure 5.5 Graphs comparing modeled resistance to actual measured resistance. ..... 93

Figure 5.6 Solution space of carrier concentration vs. mobility. ........................................ 94

Figure 5.7 Measurements of nanowire device resistance between contacts two and three compared to collinear resistance. .......................................................... 96

Figure 5.8 Graph of the solution space for carrier concentration vs. mobility for a simulation with a low starting value of mobility of 270 cm$^2/(V\cdot s)$... 99

Figure 5.9 Graph of the solution space for carrier concentration vs. mobility for a simulation where we overestimated the contact resistivity. .......... 100

Figure 6.1 FESEM image of a nanowire sample which was grown in two steps. .... 106

Figure B.1 Graphical method to determine the Fermi energy level $E_f$ when ionization is not complete. ........................................................................................................ 123

Figure B.2 Mathematica graphs used to find the Fermi energy. ..................................... 125

Figure C.1 Ga flux recorded by change in chamber pressure. ........................................... 129
LIST OF TABLES

Table 4.1 Nanowire growth matrix.......................................................................................56
Table 4.2 Lattice parameters for nanowires and bulk GaN. ...............................................72
Table 5.1 Measurements of two-terminal nanowire devices. .............................................81
Table 5.2 Back-gated FET measurements of two-terminal nanowire devices. ........... 85
Table A.1 Cracking patterns of common vacuum contaminants.......................................119
Table B.1 Values used in ionized donor calculation..........................................................121
LIST OF ABBREVIATIONS

ALD. .......... Atomic layer deposition
AlN........... Aluminum nitride
CAD. .......... Computer-aided design
CBE.......... Chemical beam epitaxy
CL. ......... Cathodoluminescence
Cp2Mg. ....... Bis(cyclopentadienyl)magnesium
DMEAA....... Dimethylethylamine alane
EDX. ......... Energy-dispersive x-ray spectroscopy
FESEM......... Field-emission scanning electron microscope
FET. .......... Field-effect transistor
FIB. .......... Focused ion beam
GaN. .......... Gallium nitride
HCP. .......... Hexagonal close packed
InN. .......... Indium nitride
I-V. .......... Current-voltage
LED. .......... Light-emitting diode
MBE. .......... Molecular beam epitaxy
MESFET. ..... Metal-semiconductor field-effect transistor
MFC. .......... Mass flow controller
MMP. .......... Marginal means plot
MOCVD........ Metalorganic chemical vapor deposition
MOMBE. ...... Metalorganic molecular beam epitaxy
MOVPE......... Metalorganic vapor-phase epitaxy
NIST............ National Institute of Standards and Technology
NSOM............ Near-field scanning optical microscope
OM................ Organometallic
OMCVD......... Organometallic chemical vapor deposition
OMVPE......... Organometallic vapor-phase epitaxy
PAMBE......... Plasma-assisted molecular beam epitaxy
PBN............. Pyrolytic boron nitride
PL................ Photoluminescence
RF................ Radio frequency
RGA. .......... Residual gas analyzer
RHEED......... Reflection high-energy electron diffraction
SEM............. Scanning electron microscope
TEGa............ Triethylgallium
TMA1............ Trimethylaluminum
TMIn. .......... Trimethylindium
UHV............. Ultra-high vacuum
UV.............. Ultraviolet
VLS............. Vapor-liquid-solid
XA............... Free A exciton
XRD............. X-ray diffraction
ACKNOWLEDGEMENTS

I would like to thank my NIST advisor, Dr. Kris Bertness, for being an excellent mentor and supporting me throughout this project. She knew everything that we needed to put the growth system together. Her design and construction savvy made this project possible. I also appreciate her suggestion that I start the resistivity measurement project early on, so that I did not have to wait for nanowires that were grown in the new system.

Thank you to my Colorado School of Mines advisor, Dr. Tim Ohno, for his guidance and input during my graduate school career. Thank you also to the rest of my committee, Dr. Reuben Collins, Dr. Norman Sanford, Dr. Craig Taylor, and Dr. Colin Wolden for your advice along the way, and especially your suggestions during my proposal.

I appreciate the hard work of everyone who helped with this project. Dr. Norman Sanford taught me to use the photoconductivity setup, the x-ray diffraction system, and kept me up to date on his latest discoveries in the lab. Dr. Joy Barker got our group interested in the photoconductivity of GaN nanowires after she returned from her visit to the Julich group (Calarco, et al.) in Germany where she saw some of their early work. Todd Harvey welded the gas lines, helped with the heavy lifting, and kept the lab in working order. Devin Rourke helped put together the OM lines. Matt Brubaker and Ron Propri did the thermal imaging of the substrate manipulator. Dr. Aric Sanders did photoluminescence for the growth paper and provided numerous
helpful suggestions about the carrier concentration paper. Dr. John Schlager was essential to the interpretation of the photoluminescence results. Paul Blanchard, Aric Sanders, Chris Dodson, and Devin Rourke did lots of device fabrication and identified devices that had nanowires present. I also thank Dr. Ben Klein from Georgia Institute of Technology for simulations showing the shape of the electrical potential for hexagonal nanowires. If I have not specifically named your contributions, I apologize, but know that your help was appreciated.

I should also mention my colleagues and friends at CSM. Special thanks to Dr. Joe Beach and Dr. Scott Feldman who I worked with on my first research project. I don’t have time to mention the rest of you, but thank you everyone for your friendship.

Funding sources included the Department of Commerce and the NIST Boulder Laboratory Professional Research Experience Program (PREP) fellowship. The studies conducted by the authors from NIST are supported in part by the DARPA Center on Nanoscale Science and Technology for Integrated Micro/Nano-Electromechanical Transducers (iMINT), funded by DARPA N/MEMS S&T Fundamentals Program (HR0011-06-1-0048).

In the last push to get this document out the door, Dr. Kris Bertness, Dr. Tim Ohno, and Paul Blanchard did some timely proof-reading. Thank you for your input.
CHAPTER 1

INTRODUCTION

Some individuals are always willing to buy the latest technology. Whether it is the newest tiny cell phone or an HD DVD player, there is a person who needs to have it. Behind these consumers are the businesses who supply the flashy new devices. They must constantly create upgrades in speed and functionality in order to stay competitive in the marketplace. These advances depend on new or improved materials that are suitable for high power and high temperature electronics. Health care providers, too, need better tools to diagnose and treat diseases. Miniature biological sensors and lasers could aid in patient care. Handheld water-sterilization devices could provide sanitary drinking water to people in developing nations.

Scientists envision these applications. We see the possibilities for the advancement of basic materials research and updates to characterization tools such as near-field scanning optical microscope (NSOM) tips. Many also believe that the world could be a better place if only more electricity were derived directly from the sun. Efficient blue light-emitting diodes (LEDs) and solid state lighting could also allow energy conservation without compromise. All of the aforementioned technology currently utilizes nitride materials, or may in the future use nitride nanowires in its operation.
1.1 Motivation

The primary reason for gallium nitride nanowire research is to facilitate their use in optoelectronic devices. Bulk and thin films of gallium nitride are already important for applications such as ultraviolet and blue lasers. Cell phone backlighting and Blu-ray DVD players also contain nitride materials. Although these products are already commercially successful, the cost of these devices limits their use in broader applications like solid state lighting and city water system purification. Because of the higher material quality on less expensive substrates, nitride nanowires offer improved performance at lower cost. In some cases, nanotechnology opens up entirely new applications that were not possible before. Some of the most novel and intriguing ideas are in the fields of biological sensing and health care. If nanowire sensors could be used for biopsies or nanowire lasers could be used for tumor removal, patients would recover faster and have a lower risk of infections than they do after surgical procedures today. Because of the high-quality material in nanowires, products could be made more efficient, which is increasingly important as energy prices continue to rise. As the world faces dwindling resources, products incorporating nanoscaled semiconductor devices will use less material than their traditional counterparts. Miniaturization of components can also lead to transportation cost savings. Manufacturers and consumers both benefit when products employ less-expensive and higher-quality materials.

Previously at the National Institute of Standards and Technology (NIST), nanowires were grown in a singular molecular beam epitaxy system (MBE), which presented some problems and limitations. The biggest issue was that the primary $p$-
type dopant for GaN, magnesium, could not be introduced into the multi-user MBE system because it is a contaminant in GaAs. A new growth system was required that would allow p-type doping and additional options such as organometallic sources and catalysts if desired.

For use in high-quality optoelectronic devices, gallium nitride nanowires must be straight, well separated, and contain few defects. Although it results in material that has higher purity and fewer defects, catalyst-free nanowire growth is not as easily controlled as catalytic growth. Nanowire position, diameter, and taper are more difficult to regulate without a catalyst. The nanowire growth is sensitive to substrate temperature, the amounts of gallium and nitrogen in the growth chamber, and the nitrogen plasma conditions. Nanowire morphology is also highly influenced by the type of buffer layer that is deposited on the substrate before nanowire growth. Especially in a new system, nanowire growth must be attempted and optimized.

NIST is interested in nanowire characterization because of its position as a world leader in metrology. With the explosion of new research in nanostructures, NIST needs to develop measurement techniques that operate on nanoscaled materials. Materials characterization of nanowires can be challenging due to their size and geometry. To date, Hall measurements have not been demonstrated. While current-voltage measurements on nanowires are now common, extracting electrical properties such as carrier concentration and mobility is in its infancy. NIST has an opportunity to create measurement standards that help advance the use of nanotechnology in industry.
1.2 Research Conducted

A broad range of work relating to gallium nitride nanowires was conducted during the course of this dissertation project. The first and most time-consuming task was the design and construction of a nitride growth system. Each part of the system required thorough research for commercial availability and optimal vendor selection. Substantial planning and design work was essential to assembling the system within laboratory space constraints. After the nitride growth system was operational, nanowire growth was achieved. A growth study using design-of-experiments principles was conducted to find the optimal parameters for nanowire formation. Growth parameters were systematically varied, and field-emission scanning electron microscopy (FESEM) was used extensively to observe the nanowire morphology. An electrical characterization study of nanowires was also performed. The carrier concentration of gallium nitride nanowires grown in the older molecular beam epitaxy system was calculated from current-voltage measurements taken in the dark and under ultraviolet illumination. All three components of the materials science paradigm, nanowire processing, structure, and properties, were explored in this research project.

1.3 Organization of the Chapters

Five additional chapters follow the introduction in this dissertation. Chapter 2 contains background information on nitride materials, nanowires, and growth methods. Chapter 3 gives a detailed description of the nitride growth system that was designed and constructed during the first part of this project. In Chapter 4, a nanowire growth experiment, that was conducted using the new system, is described. A new
method for calculating the carrier concentration of nanowires is presented in Chapter 5. It is compared to and deemed superior to the often-used, back-gated field-effect transistor method for determining the carrier concentration and mobility of nanowires. Finally, Chapter 6 summarizes the conclusions from this work. Suggestions for future work to extend the current research are also provided.
CHAPTER 2
BACKGROUND

Background information for the materials and the growth methods that were employed are given in the following sections. First, the band gap, crystal structure, and doping of nitride materials are discussed. Second, an introduction to nanowires and multi-layer nanowire structures is given. Third, the most common growth methods for nitride materials and nanowires are presented. Finally, the nanowire growth procedure at NIST is explained.

2.1 Nitrides

The nitrides are a unique subset of the III-V semiconductors. Their band gaps, crystal structure, and dopants are presented below.

2.1.1 Band Gaps

Nitride materials have direct band gaps, and their alloys cover a full range of band gap energies. Aluminum nitride (AlN) has the highest band gap of 6.2 eV, and gallium nitride (GaN) falls in the near ultraviolet at 3.4 eV. InN was once generally reported to have a band gap of 1.9 eV. However, now the common belief is that indium nitride (InN) has an even lower band gap, between 0.7 eV [1] and 1.1eV [2, 3]. This discrepancy is due to the difficulty in growing bulk InN. Its low melting point and high indium vapor pressure lead to dissociation at temperatures as low as 600 °C. Figure 2.1 shows the band gaps and lattice constants for the III-N
semiconductors. GaN or AlGaN would be ideal for ultraviolet lasers, and InGaN, with a band gap around 1.5 eV, could be used in solar cells. Direct band gaps make these materials ideal for optoelectronic devices, while the range of band gaps makes them versatile enough to fit many different applications.

![Band gap energy vs. lattice parameter for the III-nitride semiconductors.](image)

**Figure 2.1** Band gap energy vs. lattice parameter for the III-nitride semiconductors.

### 2.1.2 Crystal Structure

Another characteristic that sets the III-nitrides apart from other III-V semiconductors is their crystal structure. Most III-V compounds have the zincblende structure as their stable form, but III-nitrides are stable in the wurtzite crystal structure. Figure 2.2 shows a ball and stick representation of the wurtzite structure which can be thought of as two interpenetrating hexagonal close packed (HCP) sublattices that are separated by $5/8 \ c$. Since wurtzite is a hexagonal structure, it has
two lattice parameters, \( a \) and \( c \). The in-plane distance from one atom to another of the same element is referred to as \( a \), and \( c \) is the height of the unit cell, or the distance between planes of like atoms. In the bulk, each group III atom is surrounded by four nitrogen atoms. The zincblende structure is also tetrahedrally coordinated. The main difference between the two crystal structures is that the stacking sequence in the \(<0001>\), or \( c \), direction is \( ...ABAB... \) for wurtzite, while zincblende has an \( ...ABCABC... \) stacking sequence.

![Wurtzite crystal structure of GaN](image)

Figure 2.2 Wurtzite crystal structure of GaN. Note that the stacking sequence is ABAB in the \( c \) direction.[4]

Plane indexing for hexagonal crystals is not as straightforward as it is in cubic crystals. The hexagonal system uses four Miller-Bravais indices (\( hkil \)). To find these indices, take the inverse of the plane intersects with the basal plane axes that are 120° apart \( (a_1, a_2, \text{ and } a_3) \), and the inverse of the plane intersect with the \( c \) axis, which is \( l \).
The same plane can also be expressed with three Miller indices, where \( h + k = -i \).

For example, (100) and (1010) are equivalent in the hexagonal system. Figure 2.3 shows the crystal planes that are important in the hexagonal crystal structure. Unlike cubic crystals, the plane and the direction perpendicular to the plane do not necessarily have the same indices. The \( c \)-plane (0001) and the \( c \) direction [0001] are an exception.

![Crystal planes in GaN](image)

Figure 2.3 Crystal planes in GaN. Notice that a plane and the direction perpendicular to it do not necessarily have the same indices. Adapted from reference [5].

### 2.1.3 Dopants

Both \( n \)-type and \( p \)-type doping are necessary in order to make the nitrides viable for use in optoelectronic devices. Gallium nitride (GaN), which is usually slightly \( n \)-type due to nitrogen vacancies or oxygen contamination, has been studied the most. Not surprisingly, intentional \( n \)-type doping is more easily achieved than \( p \)-type doping. Silicon, germanium, and selenium have all been successfully incorporated in GaN films to produce carrier concentrations on the order of \( 10^{19} \text{ cm}^{-3} \). Se acts as a donor by substituting for N atoms in the lattice, while Si and Ge substitute for Ga. Likewise, silicon can also create \( n \)-type conductivity in AlN and
InN. Doping with Si is well studied and controllable, and silicon is therefore the most commonly used n-type dopant for the nitrides.

P-type doping is much more difficult. As with most III-V compound semiconductors, group II elements would be expected to act as acceptors and create p-type material. However, beryllium, mercury, and zinc all create resistive films when added to GaN. Unfortunately, they form rather deep acceptor levels (~370 meV above the valence band for Zn [6]) that do not fully ionize at room temperature. Calcium may form a more shallow acceptor level when introduced by ion implantation of Ca+ [7], but high hole concentrations have not been achieved. Although many were tried, no suitable acceptor was realized for GaN until 1989 when Amano and Akasaki demonstrated that a resistive, magnesium-doped film could be converted to p-type material by irradiating it with a low energy electron beam [8]. Hole concentrations were relatively low (~ 2x10^{16} cm^{-3}), but they were sufficient to create the first GaN p-n junction LED. Magnesium is currently the most successful p-type dopant for GaN. Its acceptor level, which falls around 170 meV above the valence band [6], is also rather deep and therefore has low ionization efficiency. Hydrogen, which is present in many growth systems, will neutralize magnesium acceptors as well. Thus most Mg-doped GaN must be irradiated with an electron beam or thermally annealed to render it p-type [9] by driving off hydrogen. It has also been suggested that the presence of hydrogen is beneficial to p-type doping during growth because it prevents donor defects from forming [10].

Even with the post-growth treatments, difficulties remain in achieving high p-type doping. For one, unintentional (n-type) doping must be extremely low, at or
below $10^{17}$ cm$^{-3}$. Oxygen contamination is the most common source of unintentional $n$-type doping. Silicon diffusion from the growth substrate may also play a role, and silicon is a common contaminant in refined metals such as Ga and Al. These factors have limited free hole concentrations to 1 to $3 \times 10^{18}$ cm$^{-3}$.

2.2 Nanowires

Nanowires, also known as nanocolumns, semiconductor whiskers, and nanorods, have attracted significant interest in the last decade. This is largely due to the possibility of creating electronic devices that are smaller than those currently fabricated by “top-down” methods, which are often limited by the resolution of lithographic techniques. It is generally believed that employing “bottom-up” device construction would also decrease the defects that are associated with “top-down” processes such as chemical etching and ion milling. Nanowires are typically tens to hundreds of nanometers in diameter and micrometers in length, though this varies greatly depending upon materials and growth methods. At these dimensions, it is not expected that quantum confinement will affect nanowire properties.

2.2.1 Growth Substrates

Native substrates are not widely available for nitride materials. A few companies, such as Sumitomo Electric Industries and Hitachi Cable Ltd., do have two-inch GaN substrates available, but they are cost prohibitive for use in most applications. Gallium nitride films are often grown on sapphire or silicon carbide substrates, which are also expensive. When these substrates are used, defects and cracking of films can be a problem, since the lattice mismatch is 16% for sapphire
and 3.5 % for SiC [11]. Nitride nanowires, however, can be grown with very few
defects and low strain on less expensive substrates such as silicon.

2.2.2 GaN Nanowire Research

The number of groups working in the field of nitride nanowires has increased
dramatically in the past few years. The first $p$-type GaN nanowires were reported in
2003 by Zhong et al. in the Lieber group at Harvard [12]. They were able to fabricate
ultraviolet LEDs from a pair of crossed nanowires, one $n$-type and the other $p$-type.
Many researchers use a catalyst and employ the vapor-liquid-solid method of GaN
nanowire growth that will be discussed later in section 2.3.3. A new approach to GaN
nanowire growth by metallorganic chemical vapor deposition (MOCVD) without a
catalyst was developed by Hersee et al. [13]. It involved depositing a thin silicon
nitride film mask on previously grown GaN films. Nanowires grew perpendicular to
the substrate and retained the diameter of the hole in the mask. A few research teams
around the world are fabricating nanowires using catalyst-free molecular beam
epitaxy. In addition to the NIST group, they include groups from Spain [14], Japan
[15, 16], Korea [17], and Germany [18].

NIST researchers have written and co-authored several papers in the field of
GaN nanowires. Many of the articles describe the catalyst-free nanowire growth by
molecular beam epitaxy and provide explanations of the growth mechanisms involved
[19-22]. The most recent work to be submitted for publication was on steady-state
and transient photoconductivity measurements that were used to calculate the carrier
concentration and mobility of the nanowires [23]. Top-gated metal-semiconductor
field-effect transistors (MESFETS) with improved performance compared to other
single nanowire devices have also been fabricated [24]. Polarization-resolved photoluminescence (PL) on single nanowires was consistent with strain-free GaN [25]. Steady-state PL on GaN nanowires with induced strain due to coatings showed the predicted shifts from the unstrained peaks, and time-resolved PL demonstrated low surface recombination velocities of $9 \times 10^3$ cm/s [26] relative to GaAs at $\sim 10^6$ cm/s [27, 28]. Cathodoluminescence (CL) spectroscopy was also used to characterize both as-grown and dispersed nanowires [29, 30]. NIST’s nanowires have even been studied as nanoelectromechanical resonators with high mechanical quality factors [31].

In addition to the published work, NIST has ongoing GaN nanowire research in several areas. Optically pumped laser action, similar to work by J.C. Johnson, et al. [32] has been achieved. One of the main goals of the nanowire project is to create an electrically-pumped GaN nanowire laser. Growing $p$-type GaN nanowires is also a top priority. Progress has been made in contacting $n$-type nanowires with $p$-type GaN shells by using a focused ion beam (FIB) as shown in Figure 2.4. Nanowire light-emitting diodes (LEDs) with wavelengths near 385 nm were created from $n$-type GaN nanowires on $p$-type GaN films. NIST has also had some success with selective growth of nanowires. Figure 2.5 shows nanowires grown in etched pits of a silicon nitride layer on top of a Si(111) wafer.

2.2.3 Nanowire Structures

A variety of devices can be fabricated with novel nanowire growth schemes. “Axial” structures are those where the material composition varies along the length (or growth axis) of the nanowire. Examples of axial structures in the literature are
Figure 2.4 The focused ion beam (FIB) process for creating an electrical contact. The nanowire shown is an $n$-type GaN nanowire as the inner core with a $p$-type GaN outer shell.

Figure 2.5 GaN nanowires grown selectively by MBE. (a) Si(111) wafer coated with AlN and SiNx with multiple patterns etched in the SiNx layer. (b) Field-emission scanning electron microscope (FESEM) image of an array of etched pits on the wafer in (a). (c) FESEM image of a single GaN nanowire growing in an etched pit.

GaN quantum discs in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ nanowires [33] and nanocolumn LEDs with multiple quantum disks made of GaN and InGaN [16]. The term “radial” is given to structures with an inner core nanowire and an outer shell with different properties, which can be created by varying the material or the doping. Figure 2.6 shows a cartoon of each of these structures. GaN nanowires with radial $p$-$n$ junctions have been synthesized and characterized [34]. Nanowire core/shell structures have also been grown with more complicated heterostructures such as $n$-GaN cores with InGaN/$p$-GaN shells [35] and $n$-GaN cores with In$_x$Ga$_{1-x}$N/$p$-AlGaN/$p$-GaN shells [36], which behave as light-emitting diodes (LEDs) when forward-biased. These studies involve initial nanowire growth along the $a$ axis by catalyst-assisted
metallorganic chemical vapor deposition (MOCVD), followed by epitaxial film growth to create the shell layers.

![Axial and radial nanowire structures](image)

**Figure 2.6** Axial and radial nanowire structures. The image on the left shows an axial nanowire structure created by initiating nanowire growth with p-type material and then switching to n-type material half way through the growth process. The image on the right is a radial nanowire structure. It can be created by growing n-type nanowires and then coating them with p-type material.

### 2.3 Growth Methods

Nanowires are synthesized by several methods. They include various solution-based processes, and vapor-based growth such as metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The last two processes are particularly suited to growing GaN nanowires. Following are brief introductions to MOCVD and MBE. Also included is a description of the vapor-liquid-solid growth method.

#### 2.3.1 Metalorganic Chemical Vapor Deposition (MOCVD)

The MOCVD process [37, 38] also goes by other names such as organometallic vapor-phase epitaxy (OMVPE), organometallic chemical vapor deposition (OMCVD), and metalorganic vapor-phase epitaxy (MOVPE). These
techniques are essentially the same when used for semiconductor epitaxial crystal growth. The defining characteristic is the use of organometallic compounds to transport at least one of the elements in the resulting material. MOCVD of III-V compounds is based on the reactions of group III alkyls with group V hydrides. The generic chemical equation for the process is \( R_3M + EH_3 \rightarrow ME + 3RH \). In this formula \( R \) represents a methyl (CH\(_3\)) or ethyl (C\(_2\)H\(_5\)) group, \( M \) is the group III element Al, Ga, or In, and \( E \) is a group V element which could be P, As, Sb or N in the case of nitrides.

MOCVD precursors require special handling. Group III alkyls are extremely reactive with water and air, so growth systems must be leak-tight and kept free of trace amounts of oxygen and water vapor. They are termed pyrophoric because they can spontaneously combust in air. Most organometallics (OMs) are liquid at room temperature, except for bis(cyclopentadienyl)magnesium (C\(_2\)Mg) and trimethylindium (TMIn), which are solid. They are contained in stainless steel cylinders with inlet and outlet ports. The compounds either evaporate or sublimate, and are often moved to the growth zone with a carrier gas. One of the problems that can occur during growth is the reaction of these chemicals in the gas phase during transport to the substrate. Another is carbon incorporation in the resulting film.

Many MOCVD reactors run at near-atmospheric pressure and use a carrier gas like H\(_2\) or N\(_2\) to transport the precursors to the hot zone near the substrate. Flow dynamics are important in these cases. Turbulent flow can adversely affect the material quality and uniformity. One way to reduce turbulence is to operate at lower pressures. This reduces the time available for the gases to interact before reaching the...
deposition zone which minimizes premature reactions. The drawback is higher consumption of organometallics and group V gases. Another approach is to perform MOCVD at high vacuum so that the precursors are in the molecular flow regime. This method is similar to MBE (which will be discussed later) because the gas flow is no longer an issue. The four main components of an MOCVD reactor are (1) gas handling system (sources, valves, plumbing, and mass flow controllers), (2) reactor chamber, (3) heating system, (4) exhaust or low pressure pumping system. A diagram of an MOCVD system can be seen in Figure 2.7.

![Diagram of an MOCVD system](image)

Figure 2.7 Diagram of an MOCVD system.

2.3.2 Molecular Beam Epitaxy (MBE)

In molecular beam epitaxy (MBE) growth, beams of atoms or molecules in the gas phase travel to a hot substrate where they combine. The term molecular beam
epitaxy [39] was first used in 1970. Advances in vacuum technology made it possible to attain ultra-high vacuum pressures of $10^{-10}$ torr (1.3×10$^{-8}$ Pa), allowing material of high purity to be grown. Materials for MBE are evaporated onto the heated substrate from Knudsen effusion cells. The cells consist of a crucible, filaments for heating, a thermocouple, cooling water, and some type of shutter system. The crucible is generally made of pyrolytic boron nitride (PBN) and filled with a source material that is solid at room temperature. As current runs through the filament(s), the material is heated. Shutters can precisely control the release of evaporated molecules or atoms of the material. MBE systems sometimes have gas sources as well. For nitride growth, for example, a nitrogen plasma source and ammonia are often available. Other components of the MBE system include a rotating substrate heater and often a reflection high-energy electron diffraction system (RHEED) for in-situ growth monitoring. Liquid nitrogen cooled cryopanels trap impurities so that they do not incorporate into the growing film. A diagram of an MBE system can be seen in Figure 2.8.

2.3.3 **Vapor-Liquid-Solid Growth Method (VLS)**

The formation of nanowires with a catalyst is attributed to the vapor-liquid-solid (VLS) growth method. VLS was first described in 1964 by Wagner and Ellis [40]. They grew crystalline silicon whiskers atop a Si (111) substrate using a SiCl$_4$ gas precursor and a gold catalyst. An illustration of the mechanism for VLS is shown in Figure 2.9. When heated to growth temperature, the catalyst forms a liquid droplet on the surface of a substrate. This is a preferred site for the vapor precursors to deposit, and together they form a supersaturated liquid alloy. Solid crystalline
material is precipitated from the droplet, which causes the liquid to be pushed upward on top of the growing crystal.

Figure 2.8 Diagram of an MBE system.
For GaN nanowire growth via the VLS method, several catalysts have been studied, such as Au, Ni, Ag, and Cu. The advantage of using a catalyst is the ability to precisely place nanowires as desired and to have better control over nanowire diameters [41]. Unfortunately, growing crystals in this manner leaves a metal droplet on the extended end of the nanowire as shown in Figure 2.10 [35]. One of the concerns about using the VLS method is that catalyst material will be incorporated in the semiconductor crystal. This would affect the electrical and optical properties, and possibly create difficulties in achieving reproducible doping densities. VLS catalyst growth is often performed in tube furnaces whose environments tend to produce material with high impurity concentrations.
Figure 2.10 SEM images from reference [35] of GaN grown using nickel catalyst nanoclusters. (a) The scale bar is 20 μm. (b) and (c) The arrows point to the nanoclusters. The scale bars are 50 nm. The inset is an energy-dispersive x-ray spectroscopy (EDX) map of nickel (red) and gallium (blue) for the nanowire pictured.
2.4 **GaN Nanowire Growth at NIST**

As shown by several groups worldwide, catalyst-free growth can be achieved with molecular beam epitaxy [19]. Nanowire growth in the MBE system at the National Institute of Standards and Technology (NIST) includes several steps[22] as depicted in Figure 2.11. First, the silicon (111) wafers are prepared by chemical cleaning for two minutes in a 10% hydrofluoric acid (by volume) solution. Next, they are placed in a sample introduction chamber, where they are baked at 750 °C for 15 min. After being transferred into the MBE growth chamber, they are again heated up to 850 °C for 10 minutes. These outgasing steps remove any remaining water or atmospheric contaminants from the wafer. A thin layer of aluminum is then deposited as a barrier between the silicon wafer and the aluminum nitride to prevent the formation of silicon nitrides. Unintentional SiNₓ growth is undesirable because it prevents GaN nucleation. Next, the aluminum nitride buffer layer is deposited at 630 °C using N₂ plasma and aluminum from an effusion cell. This layer is generally 50-80 nm thick. The gallium cell is opened next, and together with the N₂ plasma they form a defect-ridden, GaN matrix layer on the substrate. At some point, crystals of GaN begin to form in the hexagonal pits created by intersecting GaN {1102} planes in the matrix layer [19]. These crystals grow into nanowires. Nanowire growth continues at 820 °C for tens of hours. The growth rate for the nanowires is very slow, generally 100-200 nm/h. Nanowires grown in this way are c axis wires with growth in the <0001> direction. A cross-sectional FESEM image of the nanowires is shown in Figure 2.12.
GaN nanowires

AlN buffer 50-80 nm

Al prelayer 0.5 nm

GaN matrix layer

Si (111) substrate

<0001>

Figure 2.11 Cartoon of GaN nanowire growth shown in cross-section.

Figure 2.12 Cross-sectional FESEM image of GaN nanowires. False color was added for contrast.
Nanowires grown by catalyst-free MBE have a different growth mechanism than those grown with a catalyst. It was suggested that a self-catalytic process involving Ga droplets caused the longitudinal growth [42]. However, no evidence of Ga droplets exists on the tips of the completed nanowires. The nanowires formed via MBE grow perpendicular to the substrate due to differences in the sticking coefficient of the Ga adatoms on the different crystal planes [20]. Figure 2.13a displays the mechanism of Ga atom incorporation. The sticking coefficient for Ga is higher on the c-plane (tip of nanowire) than it is on the m-plane (nanowire sidewall). Ga atoms will incorporate on the tips of the nanowires when they land on the tip, or within a diffusion length of the tip, while atoms that land on the sidewalls often desorb. The re-evaporation of Ga also explains the tendency of MBE-grown nanowires to taper along their length. When a high density of nanowires exists, Ga atoms that desorb from a sidewall of one nanowire may stick to an adjacent nanowire as shown in Figure 2.13b. Ga re-evaporation near the substrate due to high substrate temperatures and shadowing by adjacent nanowires may also keep the base diameters of the nanowires small. Because GaN nanowire growth occurs when the nitrogen to gallium ratio is high, nitrogen transport does not limit nanowire growth.
Figure 2.13 Cartoon of Ga atom incorporation. (a) Ga atoms will incorporate on the tips of the nanowires when they land on the tip or within a diffusion length of the tip. From Bertness et al. [20]. (b) Tapering and coalescence of nanowires may be increased when the nanowires are densely packed. Ga atoms that do not stick to one sidewall may stick to the sidewall of an adjacent nanowire. Ga re-evaporation near the substrate due to high substrate temperatures and shadowing by nearby nanowires may keep the base diameters small.
The first goal of this project was to design, build, and test a new system for the growth of nitride materials and nanowire crystals. The apparatus is a hybrid MOCVD/MBE system, also known as a chemical beam epitaxy (CBE) or metalorganic molecular beam epitaxy (MOMBE) system. It allows maximum flexibility for growing nitride materials at a variety of pressures and substrate temperatures, and also allows precise control over the material layers so that superlattices, quantum wells, and core-shell structures can be created. Parts of the new system included ultra-high vacuum (UHV) deposition chamber and pumps for achieving vacuum conditions (3.1.1), Substrate manipulator (3.1.2), OM gas handling and nitrogen sources (3.1.3), residual gas analyzer (RGA) and control software (3.1.4), loadlock chamber and transfer system (3.2.1), and MBE-type effusion cells (3.2.2). Each of these will be discussed in more detail in the following sections.

3.1 Initial Design and Construction

This section describes the initial stages of the growth system design and construction. During the design process, individual parts were modeled in computer aided design software to ensure that they would fit together. Several items that are not discussed in detail were also completed during the initial system construction. These components included the plumbing for the water lines to cool the pumps and manipulator, the system enclosure, the electronics rack, and the wireway for carrying
the ammonia and nitrogen lines. The control system also required several interlocks for safe shutdown of the system in case of power failure or vacuum failure. After assembly of the major components, the growth system was operational.

3.1.1 Ultra-High Vacuum (UHV) Environment

The deposition chamber and the pumps created the UHV environment. We designed an 18” spherical chamber of stainless steel that was subsequently custom built by a vacuum products company. An early hand-drawn diagram of the growth chamber can be seen in Figure 3.1. The chamber had ports for pressure gauges, an RGA, a manipulator, a load lock, a reflection high-energy electron diffraction (RHEED) system, sources, and windows. All the ports had conflat flanges to be used with copper-gasket seals. Instead of the liquid nitrogen cryopanels that would be found on an MBE system, the chamber had a double-walled design that acted as a water-cooling jacket around the spherical center. The volume between the two walls was filled with water that was circulated by a chiller and was cooled to 25 °C. Figure 3.2 shows a section of the final engineering diagram provided by the company that built the chamber.

A custom tee, placed directly below the chamber, was designed to connect the chamber to the pumps, as shown in Figure 3.3. A 2.75” port on the tee was fitted with a manual angle valve that led to the foreline between the mechanical pump and the turbomolecular (turbo) pump. The mechanical roughing pump was used to evacuate the chamber from atmospheric pressure to pressures below 0.13 Pa (1 × 10⁻³ torr). The mechanical pump was also used to back a turbo pump. The turbo pump was attached to the bottom of the tee with a gate valve, and below that a bellows was
Figure 3.1 Hand-drawn diagram of the growth chamber. It was used during initial consultations with chamber manufacturers.
Figure 3.2 Partial engineering diagram of the growth chamber. The front view of the chamber is on the left and the right side view on the right. Cooling-water ports can be seen near the bottom of the front view diagram.
installed to reduce vibrations. To prevent debris from entering into the turbo pump, the flanges for the chamber connection and the turbo pump connection to the tee were offset, and a screen was placed inside the tee. After thoroughly baking the system, the base pressure was expected to drop to the mid $10^9$ torr ($10^{-7}$ Pa), and it did reach $5 \times 10^9$ torr ($6.7 \times 10^{-7}$ Pa).

3.1.2 Sample Stage and Temperature Control

The sample stage was customized by the supplier for our application. Complicated sample stages like this one are often called substrate manipulators. The “manipulator” part refers to the ability to move the sample stage in various directions. Often substrate manipulators have x, y, and/or z motion in addition to rotation. In our case, the manipulator was designed to simply rotate so that an entire wafer could be coated evenly with material. The substrate manipulator is pictured in Figure 3.4 with some of the components labeled. It was made to hold a three-inch wafer vertically at a position two inches back from the center of the chamber. This position was chosen to allow the best coverage from all of the material sources attached to the chamber.

The substrate manipulator also supported a pyrolytic boron nitride (PBN) encased graphite heating element that could attain temperatures of 1300 °C. The heater was connected to a power supply that was regulated by a temperature controller. In order to protect the walls of the chamber from excess heat, the sample stage included a water-cooling shroud and a heat shield. A thermocouple measured the temperature near the center of the substrate. Finally, since the thermocouple did not touch the substrate and therefore could not measure its true temperature, a sapphire rod ran from the back of the substrate, through the heater and the length of
Figure 3.3 Chamber and pump connections. The components that are mentioned in the text are labeled.
the manipulator to a mini view port where a photodiode detected the radiation from
the substrate. Calibration tests were performed to match the voltage returned from the
detector to the temperature of a silicon wafer measured from the front side with an
optical pyrometer. By fitting the calibration data, constants were obtained that
enabled the computer to convert the input voltage from the photodiode into a
substrate temperature. The backside pyrometer is needed because it continues to read
the true wafer temperature. Frontside pyrometer readings vary from the actual
temperature as material is deposited on the wafer. The temperature uncertainty for the
back pyrometer is ± 6 °C, but it only measures a small spot on the wafer.
The temperature also varied across the diameter of the wafer. Figure 3.5a shows the temperature measurements taken by the frontside pyrometer at various points on a wafer. Thermal imaging was performed on the bare substrate heater (Figure 3.5c) and a Si wafer (Figure 3.5d). The temperature non-uniformity for the bare heater was around 200 °C. It was not as extreme for the Si wafer, where temperature varied by about 50 °C over most of the wafer, and by about 20 °C over the center 2 inches of the wafer. The temperature variation could be seen clearly in some of the as-grown wafers (Figure 3.5b).

3.1.3 Material Sources

Initially, three organometallic sources were available. They included triethylgallium (TEGa) as a gallium source, bis(cyclopentadienyl)magnesium (Cp₂Mg) for p-type doping with magnesium, and dimethylethylamine alane (DMEAA) as an aluminum source. Figure 3.6 shows a picture and diagrams of the OM lines. The sources were contained in stainless steel cylinders (bubblers) that were encircled with copper coils containing temperature-controlled water circulated by a heater/chiller. For added thermal isolation, the bubblers were also enclosed in foam coolers that were filled with water. The bubblers were connected to the chamber with ¼ inch stainless steel lines that were warmed with heater tapes. Bellows-sealed diaphragm valves and mass flow controllers (MFCs) directed the flow of gases in the system. All connections were made with face-sealed fittings and checked for leaks. Unlike most MOCVD systems, the OM vapors were not transported into the chamber with a carrier gas. Instead, OM vapors flowed through the lines due to the difference in pressure between their canisters and the vacuum environment. The vapor pressure
Figure 3.5 Temperature non-uniformity. (a) Temperature measurements taken with a frontside pyrometer at various points on a wafer. (b) Picture of a wafer with nanowires. The rings are evidence of the temperature gradient. (c) Thermal image of the substrate heater without a wafer present. (d) Thermal image of a wafer in front of the substrate heater. Each of these images shows that the temperature is not uniform across the diameter of the wafer.
equations for the OM sources are shown in Figure 3.7a. The temperature of the bath controlled the OM vapor pressures. For example, if the bath temperature was set to 35 °C, the vapor pressure of TEGa would be 11.5 torr, of DMEAA would be 4.7 torr, and of Cp₂Mg would be 0.11 torr. Figure 3.7b shows the vapor pressure curves for the OM sources that were available in the growth system.

The first available nitrogen source was ammonia (NH₃). Nitride materials grown by MOCVD often use ammonia as their nitrogen source. An ammonia purifier was installed in the gas line to remove any trace amounts of water. The ammonia entered the chamber through a gas injector that could be heated. Gas lines for a nitrogen plasma source were also included in the system. The source was added later as a system enhancement.

### 3.1.4 RGA and Software Control

The residual gas analyzer (RGA) served many purposes in the nitride growth system. Initially, it aided in leak checking throughout system construction. During bake-out, the RGA enabled us to see what impurities were being removed from the system. Figure 3.8a shows an RGA scan when the chamber was not fully baked and had a pressure of 7 × 10⁻⁹ torr. Figure 3.8b shows another RGA scan when the chamber was fully baked and had a chamber pressure of 2.5 × 10⁻¹⁰ torr. Note that this was taken with the sources warm and after some of the system improvements that will be discussed in the next section. Also, the calibration of the RGA may be off, because the partial pressures registered are higher than the chamber pressure. Peaks from ammonia, water, and ethane that are visible in Figure 3.8a are almost completely gone in Figure 3.8b. A table of the cracking patterns of common vacuum system
Figure 3.6 Organometallic (OM) gas lines. (a) Picture of partially-constructed OM lines in the system. (b) Diagram of the set of 4 OM lines. (c) Diagram showing one OM line with the valves, mass flow controller (MFC), and bubbler locations labeled.
Figure 3.7 Organometallic source details. (a) Properties of OMs and (b) vapor pressure curves. Data is from reference [43].
contaminants can be found in Appendix A. The peak at 19 is large and often attributed to fluorine, but Cole et al. claim that it is due to the hydronium ion (H$_3$O$^+$) [44]. Regardless of the source, the mass 19 peak was always present in the RGA scans for this system. Finally, the RGA was used to determine the concentration of source elements that were admitted into the chamber for growth runs.

Software was developed in LabVIEW to allow computer control of various system components and processes. The main user interface is shown in Figure 3.9. It is a system overview program that constantly monitors the pressures and checks for problems. It allows MFCs to be controlled by the operator. The valves and shutters were pneumatically actuated with solenoids that were wired to National Instruments Field Point modules and controlled through the computer interface. Programs were also created for performing routine tasks like venting and evacuating the growth chamber. The programs guide the user through the steps so that errors are less likely to occur.

3.2 Upgrades to Growth System

Several system upgrades were necessary in order to allow nanowire growth. A loadlock kept the growth chamber cleaner. Effusion cells for solid sources were added and the nitrogen plasma source was installed. After the following system enhancements, a base growth chamber pressure of $2.3 \times 10^{-10}$ torr ($5.3 \times 10^{-8}$ Pa) was achieved when the sources were all warm.
Figure 3.8 RGA spectra from growth system. (a) The chamber pressure was $7 \times 10^{-9}$ torr. Small amounts of water, ammonia, and ethane are contaminating the chamber. (b) The chamber pressure was $2.5 \times 10^{-10}$ torr. Some hydrogen and carbon monoxide remain in the chamber. Note that the RGA calibration may be off in these scans.
3.2.1 Loadlock and Transfer System

A loadlock chamber and transfer arm were added to the growth system to improve the base pressure of the growth chamber and shorten the time between growth runs. In the early uses of the growth system, substrates were manually placed on the substrate manipulator. This required that the chamber be vented to atmosphere after every growth run. Constant venting made low base pressures impossible to achieve. Because contamination of the sources was likely, it also prevented the use of MBE effusion cells. A loadlock chamber and wafer transfer system alleviated these issues. Figure 3.10a shows a picture and Figure 3.10b shows an engineering drawing of the loadlock chamber. One of the features of the loadlock chamber was a heated stage so that wafers could be outgassed before moving them into the higher-vacuum environment of the growth chamber. The loadlock chamber also had a parking stage so that one wafer could be outgassed while a run was taking place in the growth chamber. Both stages had rotation feedthroughs in order to move a wafer from the stage to the sample transfer cup on the transfer arm and back again. Figure 3.11 is a close up view of the sample stages. A manual gate valve was placed between the loadlock chamber and the growth chamber so that the transfer arm could pass between chambers. The transfer arm had linear motion and rotating the magnet drive moved the transfer cup laterally (at 90° to the linear motion) to engage with the manipulator and stages. Lining up the transfer arm was tricky because the sample transfer cup had to fit into three separate positions on a horizontal axis. After the first attempt at installing the loadlock and transfer arm, the sample transfer cup would not engage with the manipulator sample stage. Tightening the transfer arm gaskets more
Figure 3.9 Front panel of the control software for the nitride growth system. The circles with lighted centers represent open valves.
on one side than the other was required to fix the alignment. A small pumping station was purchased for evacuating the loadlock chamber. It consisted of a small mechanical pump and a mini turbo pump that could pull the pressure down below $1 \times 10^{-5}$ torr ($1.33 \times 10^{-3}$ Pa) in about 10 minutes. The loadlock could be vented and evacuated in a fraction of the time necessary to vent and evacuate the entire growth chamber.

3.2.2 Effusion Cells

Effusion cells were added to allow MBE type growth. Three of the cells were purchased new for the nitride growth system and one was borrowed from another system. Figure 3.12 shows a diagram of an effusion cell. Specifications for the purchased cells included integral pneumatic shutters, water cooling, and bakeable cables. All the crucibles were installed and heated to remove adsorbed gases before the source materials were added.

The gallium cell was the first to be installed. Because liquid Ga tends to creep toward lower temperature regions in the cell, it requires a cell with two thermocouples and two heating elements. Thus it also requires two power supplies and two temperature controllers. The top heating element is kept at a higher temperature than the bottom heating element to prevent the Ga from spilling out of the crucible. Since Ga freezes at just above room temperature (~30 °C), once the cell is loaded and the Ga ingots are melted, the Ga must be kept warm to prevent freezing and subsequent cracking of the crucible. Although it has a low melting point, Ga has a very high boiling point of around 2200 °C at one atmosphere. Under vacuum
Figure 3.10 Loadlock system. (a) Picture of the loadlock chamber. The transfer arm extends approximately 1 meter to the left of the picture. The growth chamber is to the right of the gate valve. (b) CAD object of the loadlock chamber supplied by Transfer Engineering.
Figure 3.11 Picture of the inside of the loadlock chamber. The parking stage, heating stage, transfer arm, and sample transfer cup are visible.

Figure 3.12 Diagram of an effusion cell. Water cooling and an integrated shutter were two requirements for the effusion cells in the nitride growth system.

conditions in the growth chamber, the Ga cell must be heated to over 850 °C to obtain significant Ga flux.

Magnesium, the primary p-type dopant for GaN, has the lowest boiling temperature of all of the elements that were added to the nitride growth system. Temperatures during growth were between 350 °C and 400 °C. Mg is solid at room temperature, and it is reactive with air. Pure Mg is packaged in vacuum sealed
ampoules to prevent oxidation. The time between opening the ampoule and placing the sample into the vacuum chamber must be kept to a minimum. The Mg cell was mounted horizontally in the chamber, so it required a perforated crucible cover to prevent the ingot from rolling out of the crucible. The Mg cell had standard single-filament heating and therefore one thermocouple, one power supply, and one temperature controller were required for its operation.

A silicon cell was added for n-type doping of GaN. Si can be sintered into its crucible with the opening facing upward, and then moved into another orientation and it will not fall or drip out. The melting point of Si is 1414 °C. Other members of our research group sintered the Si into the crucible with a temperature of 1500 °C and installed the silicon cell in a horizontal port on the chamber. The Si cell was borrowed from another system and it does not have integrated water cooling. A fan was directed on the Si cell tube to help reduce the local heating. Normal operating temperatures for the single-filament Si cell are between 1175 °C and 1225 °C.

The other effusion cell attached to the nitride growth system was intended for aluminum. However, germanium was added instead for use in another experiment. Al requires an effusion cell with a “cool lip” design because it tends to creep to areas of the crucible that have a hotter temperature. Eventually Al will be added so that MBE-type AlN buffer layers can be grown in the nitride system.

3.2.3 Manipulator

The manipulator rotation did not perform as well as expected, so two updates were required. After the loadlock was installed and the system was fully baked, the manipulator rotation became jerky, eventually throwing a wafer off into the growth
chamber. After removing the manipulator, we found that the all-metal, molybdenum-disulfide-coated bearings worked better in the air than under vacuum. When the bearings failed again after replacing them, we decided to try ceramic-metal hybrid bearings that had metal tracks and ceramic beads. These bearings worked much better than the all-metal variety. Replacing most of the bearings in the manipulator required removing the sample holder, the heater, and unhooking part of the water cooling system. At least one set of bearings still needs to be changed, but that will require an even more extensive disassembly of the manipulator.

The other rotation problem stemmed from the use of a polymer belt for turning the magnet. Figure 3.13a shows the original configuration. The belt was prone to slipping when it met with a small amount of resistance while turning the magnet. The belts also stretched out and needed to be replaced often. If a tighter belt was used, dropping a wafer became much more likely because there was backlash since the belt would stretch but not slip. We finally decided to have the belt replaced by a chain that moved on gears. The chain turned on the gears without slipping and without backlash. It also kept the rotation relatively steady even when it encountered resistance to turning. The chain and gear drive is shown in Figure 3.13b.

3.2.4 **OM Upgrades**

Trimethylaluminum (TMAI) was added to the fourth line on the system because growing the aluminum nitride buffer layers with dimethylethylamine alane (DMEAA) was very slow. For example, at a bath temperature of 20 °C, a 40 nm film could be grown from TMAI in 20 minutes, while it took 2 hours to grow the same film thickness with DMEAA. The difference in growth rate was partly due to the
Figure 3.13 Magnet rotation drive on manipulator. (a) Shows the original belt drive for the magnet. (b) Shows the chain and gear drive for the magnet.

difference in vapor pressure between the two compounds. It was also difficult to control the amount of DMEAA that was injected into the chamber. The zero point on the DMEAA mass flow controller kept drifting to higher numbers. Part of the problem may have been DMEAA’s low dissociation temperature of 127 °C [45]. The sensor in a MFC generally heats a gas to 80 °C higher than the ambient. Also, the gas lines and MFC were heated above room temperature to prevent condensation in the lines. Therefore, the temperature in the sensor was likely to be at or near the dissociation temperature of DMEAA, which could have caused aluminum to deposit inside the sensor, resulting in the drifting zero point.

Mass flow controllers were replaced by leak valves. In addition to the drifting zero points, the MFCs were being used at a fraction of their full range where they produce less reliable flow rates. The maximum flow allowed through the MFCs was 5 sccm and the highest setting used was 5.5 %, so only 0.275 sccm was being sent into the growth chamber. The leak valves provided finer tuning of the input gas. Eventually, the organometallic injector was temporarily removed from the system to
make room for the Si effusion cell. The system reached the lowest base pressure after
the OMs ceased to be used in the chamber.

3.3 Conclusions

Building an entirely new system was a significant undertaking. It was
satisfying, however, when things fit together well. The CAD software helped to
visualize the design before construction and ensure that enough space was available
for the various components. Figure 3.14 shows a picture of the completed system. It
successfully grew nanowires within a few runs of the installation of the necessary
sources, and has achieved its primary goal of doping nanowires \( p \)-type with Mg.
Discussion of the primary growth study is given in Chapters 4. Additional
conclusions can be found in Appendix C.
Figure 3.14 The completed nitride growth system. Enclosure windows were removed to allow a better view of the chamber.
Chapter 4 is a paper entitled “Designed Experiment to Examine the Growth Conditions for GaN Nanowire Formation on Si(111) Substrates.” It will be submitted for publication. I wrote the paper, and the coauthors include Kris A. Bertness, Aric W. Sanders, Norman A. Sanford, and John B. Schlager. The entire paper is included here, with modifications to indicate work that was performed by the coauthors. This article is a contribution of an agency of the U. S. government and not subject to copyright.

4.1 Abstract

We performed a systematic study of growth conditions to optimize nanowire fabrication in a chemical beam epitaxy (CBE) growth system. The parameters for each of 15 nanowire runs were based on a three-factor, three-level Box-Behnken designed experiment. The three factors that varied were substrate temperature, gallium effusion cell temperature, and a combined plasma RF power and nitrogen flow. Photoluminescence and x-ray diffraction were performed to assess the crystalline quality of the nanowires. Nanowire morphology was dependent on the nitrogen plasma conditions. High power (325 W) and flow (1.7 sccm) resulted in nanowires that had smaller bases and were more tapered than the low power (225 W) and flow (0.9 sccm) conditions. Substrate temperatures at the low level (800 °C) and
Ga cell temperatures at the high level (950 °C) produced the best nanowire growth environment.

4.2 Introduction

GaN nanowires are being investigated as an alternative to thin films in high-power and high-frequency electronics. Device applications under study range from biosensors to UV laser diodes [46]. Controlled growth of GaN nanowires is important for these emerging technologies. The vapor-liquid-solid (VLS) mechanism is a common method of nanowire growth that allows the placement of nanowires through the use of catalyst droplets. Typically, this method is used in metalorganic chemical vapor deposition (MOCVD) systems [47]. However, VLS growth introduces the possibility of contamination by the metal used as the catalyst. Growing GaN nanowires with catalyst-free molecular beam epitaxy (MBE) [19, 22] has the advantage of removing the possibility of contamination by the catalyst. However, growing by MBE makes controlling the spacing and the diameters of the nanowires more challenging. Even if the growth procedure is well controlled in one system, moving the process to an entirely new growth system is not straightforward.

The purpose of this experiment was to find the best conditions for nanowire growth with several goals in mind. Ideal nanowires should be well-spaced and normal to the substrate so that individual wires are easy to coat with additional material layers and remove from the substrate. The nanowires should have little or no taper along the axial length, since it is easiest to measure their electrical properties when they have a constant diameter. The crystalline quality of the nanowires is also important for devices, so we wanted the nanowires to be as close to strain-free as
possible. Lattice constants calculated from x-ray diffraction peaks were compared to the lattice constants of strain-free GaN. Photoluminescence (PL) peak energies were also compared to the value for strain-free GaN at room temperature. The nanowires should have the highest growth rate possible while preserving the above properties.

In this experiment, growth parameters were varied according to a three-factor, three-level Box-Behnken designed experiment. Optimization of processes such as the nanowire growth is often accomplished in industrial settings through the use of designed experiments [48]. When there are several variables (factors) that influence the outcomes of the process, it is time consuming and expensive to test every variable independently. A statistically designed experiment can dramatically cut the number of trials needed to glean the desired information because several factors are varied at once. The levels (settings for the variables) for each trial are set ahead of time based on proven design techniques. Figure 4.1 shows a geometric representation of a Box-Behnken design for three factors and three levels. The design consists of 13 different runs, plus two additional runs at the middle levels for all factors. Setting up the runs ahead of time ensures that the researcher cannot bias the results by believing that one factor is the most important and ignoring interactions between factors. After the trials are completed, measurements that are also defined ahead of time are made to determine the response or outcome. The response values can be input to a design of experiments software package, such as DOE KISS by SigmaZone, which will statistically analyze the results.
Figure 4.1 Geometric representation of a Box-Behnken design. The design has three factors (variables) with three levels (settings) each. Each factor is represented by an axis, and the levels vary along the axis from low to high. The numbered circles represent the runs. Thirteen distinct runs are performed, plus two additional runs at the mid level for all factors. The diagram was adapted from reference [48].

4.3 Experiment

GaN nanowires were grown in a chemical beam epitaxy system on Si(111) substrates. Wafers were cleaned for two minutes in a 10% by volume HF:H₂O solution, rinsed in deionized water, and blown dry. The substrates were then outgassed in a loadlock chamber for one hour, reaching an average thermocouple temperature of 336 °C. After being transferred to the growth chamber, substrates were heated at ~900 °C for 15 minutes of additional outgassing. The substrate temperature was reduced to 500 °C, and a layer of aluminum was deposited with trimethyl aluminum (TMAI). The TMAI flow rate was controlled with a water bath temperature of 20 °C and a leak valve. Aluminum nitride was then grown with TMAI and ammonia (NH₃) for 20 minutes, resulting in an average film thickness of 35 nm. The substrate was heated up to the nanowire growth temperature and allowed to stabilize.
GaN nanowires were grown for 24 hours with a radio-frequency (RF) nitrogen plasma source and elemental gallium evaporated from a Knudsen effusion cell. Pressures in the chamber during growth were $6.9 \times 10^{-3} \text{ Pa} \pm 1.6 \times 10^{-3} \text{ Pa}$ ($5 \times 10^{-5} \text{ Torr} \pm 1.2 \times 10^{-5} \text{ Torr}$). Samples were cooled in the presence of nitrogen until they reached 200 °C.

Parameters for the growth runs were based on a three-factor, three-level Box-Behnken[49] designed experiment. The three factors that varied were substrate temperature during GaN nanowire growth, gallium effusion cell temperature, and an RF plasma power-N$_2$ flow rate combination. The substrate temperature had levels of 800 °C, 820 °C, and 840 °C, which was measured from the backside of the substrate wafer. Backside emission was collected through a sapphire light pipe and measured with a silicon detector that was previously calibrated to a front-side optical pyrometer. The gallium was evaporated from a dual filament effusion cell. The top of the cell was kept 75 °C hotter than the bottom, which was set at 850 °C, 900 °C, or 950 °C. Plasma power and flow rate combinations were 225 W with 0.9 sccm, 275 W with 1.2 sccm, and 325 W with 1.6 sccm. The combination of low RF power and high N$_2$ flow did not produce a stable plasma, therefore N$_2$ flow was varied with RF power. The list of all growth runs appears in Table 4.1. In addition to the 15 growth runs dictated by the Box-Behnken design, two more were grown at 800 °C substrate temperature, 950 °C Ga cell temperature, and 225 W RF power with 0.9 sccm of N$_2$. One of these started with an aluminum nitride buffer layer grown by molecular beam epitaxy in a separate growth system, while the other had the same TMA1 and NH$_3$ aluminum nitride as the previous 15.
Table 4.1 Nanowire Growth Matrix

<table>
<thead>
<tr>
<th>Row #</th>
<th>Run</th>
<th>Substrate Temp (°C)</th>
<th>Ga Cell Bottom (°C)</th>
<th>RF Power (W)</th>
<th>N₂ Flow Rate (sccm)</th>
<th>Growth Rate (nm/h)</th>
<th>Density (#/μm²)</th>
<th>PL Energy Shift (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N063</td>
<td>800</td>
<td>850</td>
<td>275</td>
<td>1.2</td>
<td>46 ± 30</td>
<td>46 ± 7</td>
<td>-48.7</td>
</tr>
<tr>
<td>2</td>
<td>N062</td>
<td>800</td>
<td>950</td>
<td>275</td>
<td>1.2</td>
<td>325 ± 22</td>
<td>6 ± 4</td>
<td>-48.7</td>
</tr>
<tr>
<td>3</td>
<td>N072</td>
<td>840</td>
<td>850</td>
<td>275</td>
<td>1.2</td>
<td>0 ± 0</td>
<td>0 ± 1</td>
<td>-48.7</td>
</tr>
<tr>
<td>4</td>
<td>N085</td>
<td>840</td>
<td>950</td>
<td>275</td>
<td>1.2</td>
<td>54 ± 18</td>
<td>15 ± 4</td>
<td>10.7</td>
</tr>
<tr>
<td>5</td>
<td>N059</td>
<td>800</td>
<td>900</td>
<td>225</td>
<td>0.9</td>
<td>138 ± 14</td>
<td>26 ± 3</td>
<td>-8.4</td>
</tr>
<tr>
<td>6</td>
<td>N087</td>
<td>800</td>
<td>900</td>
<td>325</td>
<td>1.6</td>
<td>183 ± 25</td>
<td>12 ± 6</td>
<td>-30.4</td>
</tr>
<tr>
<td>7</td>
<td>N060</td>
<td>840</td>
<td>900</td>
<td>225</td>
<td>0.9</td>
<td>0 ± 0</td>
<td>0 ± 1</td>
<td>-48.7</td>
</tr>
<tr>
<td>8</td>
<td>N091</td>
<td>840</td>
<td>900</td>
<td>325</td>
<td>1.6</td>
<td>0 ± 0</td>
<td>0 ± 1</td>
<td>-48.7</td>
</tr>
<tr>
<td>9</td>
<td>N065</td>
<td>820</td>
<td>850</td>
<td>225</td>
<td>0.9</td>
<td>1 ± 1</td>
<td>0 ± 1</td>
<td>-48.7</td>
</tr>
<tr>
<td>10</td>
<td>N092</td>
<td>820</td>
<td>850</td>
<td>325</td>
<td>1.6</td>
<td>10 ± 10</td>
<td>3 ± 2</td>
<td>-48.7</td>
</tr>
<tr>
<td>11</td>
<td>N044</td>
<td>820</td>
<td>950</td>
<td>225</td>
<td>0.9</td>
<td>267 ± 34</td>
<td>15 ± 4</td>
<td>-48.7</td>
</tr>
<tr>
<td>12</td>
<td>N046</td>
<td>820</td>
<td>950</td>
<td>325</td>
<td>1.7</td>
<td>317 ± 42</td>
<td>5 ± 2</td>
<td>-45.3</td>
</tr>
<tr>
<td>13</td>
<td>N061</td>
<td>820</td>
<td>900</td>
<td>275</td>
<td>1.2</td>
<td>36 ± 10</td>
<td>41 ± 5</td>
<td>5.9</td>
</tr>
<tr>
<td>14</td>
<td>N086</td>
<td>820</td>
<td>900</td>
<td>275</td>
<td>1.2</td>
<td>21 ± 15</td>
<td>11 ± 3</td>
<td>-8.6</td>
</tr>
<tr>
<td>15</td>
<td>N093</td>
<td>820</td>
<td>900</td>
<td>275</td>
<td>1.2</td>
<td>29 ± 29</td>
<td>44 ± 6</td>
<td>-4.6</td>
</tr>
<tr>
<td>E1</td>
<td>N081</td>
<td>800</td>
<td>950</td>
<td>225</td>
<td>0.9</td>
<td>129 ± 21</td>
<td>2 ± 1</td>
<td>-40.1</td>
</tr>
<tr>
<td>E2</td>
<td>N082</td>
<td>800</td>
<td>950</td>
<td>225</td>
<td>0.9</td>
<td>238 ± 3</td>
<td>17 ± 4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 4.1 Nanowire growth matrix. Row # is the row number given according to the Box-Behnken experimental design. The last two growth runs (E1, E2) were additional sets of conditions that represent the best growth parameters, but were not included in the original design. Growth runs were performed randomly with respect to the Row #. The chronological order is sequential with the last three digits in the Run column. Photoluminescence (PL) energy shift is given in meV away from 3.41 eV, the peak energy for unstrained GaN at room temperature given by reference [50]. * Grown on MBE AlN.
The nanowires were first characterized by field-emission scanning electron microscopy (FESEM). FESEM was performed on the as-grown material in both cross-section and top views. Images were taken at working distances around 6 mm with a secondary electron detector, except for the highest resolution images, which employed a through-lens detector. The electron beam accelerating voltage was set low (5 keV) to ensure that the samples would not be damaged. Growth rate was calculated by dividing the nanowire length that was measured from the cross-sectional FESEM images by the growth time. Image analysis was attempted on top-view FESEM images in order to obtain nanowire density numbers. This proved to be difficult, because in many cases the nanowires started growing narrowly at the base and then tapered outward and coalesced at the tips. Instead of using the numbers acquired with the image analysis tool, we counted the individual nanowires in FESEM images that were magnified 25×10^3 times. When a coalesced group of nanowires was encountered, the number of nanowires in that group was estimated and added to the count.

X-ray diffraction (XRD) on as-grown nanowire assemblies was carried out in a triple-axis diffractometer with a Cu Kα x-ray source. 2θ-ω (2 theta-omega) scans were performed to obtain the peaks at three symmetric (002, 004, 006) and three asymmetric (104, 105, 205) diffraction conditions. The c lattice parameter was calculated from the peak position in a symmetric scan. The a lattice parameter was then calculated with the average c lattice parameter and the peak position in an asymmetric scan. Uncertainties are one standard deviation of the mean for the three calculated values for each lattice parameter.
The photoluminescence spectra of these nanowires was taken on as-grown material at room temperature by exciting the wires above the bandgap at 3.8 eV (325 nm) with a HeCd laser (5 mW maximum power). The laser beam was focused with a reflective objective to a spot roughly 2-5 μm in diameter. Light emitted from the sample was then collected through the same objective and filtered from the excitation beam by a dichroic mirror. The collected light was then detected using a spectrometer. Aric W. Sanders described the apparatus to me, and performed the PL. Kris A. Bertness and John B. Schlager helped to interpret the PL results.

4.4 Results

The most important factors determining the growth rate of the nanowires were the substrate temperature and the Ga bottom cell temperature. Some growth runs had virtually no nanowire growth, while others had wires up to 7.8 μm long. In addition to conventional data plotting, the results from the nanowire characterization were analyzed with standard design of experiments software that is often used in industry. A marginal means plot, also known as an effects plot, is constructed by plotting the average response at each setting (level). A section of the graph is devoted to each factor, and the steepness of the slope indicates the importance of the factor. The marginal means plot (MMP) in Figure 4.2 shows a negatively sloping line in the Substrate Temp column, which indicates that a lower substrate temperature increased the nanowire growth rate. The line in the Ga Cell Bottom Temp column has positive slope, so a higher Ga cell temperature increased the nanowire growth rate. The Plasma RF Power column in the MMP does not have a definite slope. Therefore, the growth rate is not strongly dependent on RF power. Higher RF power and N₂ flow
rate did slightly increase the growth rate, but this is most likely a function of flow rate rather than plasma power. The results from the MMP are validated by the surface plots. Figure 4.3 displays a surface plot showing the growth rate as a function of substrate temperature and Ga cell temperature for an RF power of 275 W. The growth rate is clearly the highest, between 300 nm/h and 350 nm/h, for low substrate temperature and high Ga cell temperature. The surface plots at 225 W and 325 W RF power are not shown here, but they have a similar shape.

Figure 4.2 Marginal means plot for growth rate versus substrate temperature, Ga cell bottom temperature, and plasma RF power. The negative slope of the line in the Substrate Temp column indicates that the growth rate decreases with increasing substrate temperature. The positive slope in the Ga Cell Bottom Temp column indicates that the growth rate increases with increasing Ga cell temperature. A definite slope is not observed in the Plasma RF Power column. Therefore, no strong correlation exists between the RF power and the growth rate.
Figure 4.3 Surface plot of growth rate versus substrate temperature and Ga cell bottom temperature at 275 W RF power. The surface plot confirms that lower substrate temperature and higher Ga cell temperature increase the nanowire growth rate.

Cross-sectional FESEM images visually illustrate what is displayed in the surface plot, that lower substrate temperature and higher Ga cell temperature accelerate the nanowire growth rate. The two FESEM images in Figure 4.4 are of growth runs that had the RF power set at 275 W and the Ga cell temperature set at 950 °C. They were both grown for 24 hours, so the only difference in these two samples was the substrate temperature, which was 800 °C for the left image and 840 °C for the right image. The average length of the nanowires in the left image is 7.8 µm, and the average length of the nanowires in the right image is 1.3 µm. The large difference in nanowire lengths due to substrate temperature indicates that the
desorption rate for Ga atoms is higher at higher temperatures. This has been reported for GaN grown on GaN(0001) surfaces. Guha et al. found that the residence time of Ga adatoms on the substrate decreases with increasing temperature, thus reducing the time available for binding with nitrogen on the surface of the substrate and becoming incorporated into GaN [51]. Other early papers also discuss the re-evaporation of Ga grown on Si(111) substrates [14, 52].

The upper limit of substrate temperatures for successful nanowire growth was around 840 °C. The inhibited growth at higher substrate temperatures is illustrated in Figure 4.5. Figure 4.5a and Figure 4.5c were both grown with a Ga cell temperature of 900 °C and an RF power of 325 W. The sample with a substrate temperature of 800 °C, shown in Figure 4.5a, has many nanowires. The sample with a substrate temperature of 840 °C, shown in Figure 4.5c, had very few nanowires are present. The circle in Figure 4.5c encloses spots that might be nanowires. Similarly, Figure
4.5b and Figure 4.5d were both grown with a Ga cell temperature of 950 °C and an RF power of 275 W. A substrate temperature of 840 °C is the upper boundary of substrate temperatures that are suitable for nanowire growth.

Figure 4.5 Top-view FESEM images illustrating that an 840 °C substrate temperature is the upper boundary for nanowire growth. (a) and (c) were grown with a Ga cell temperature of 900 °C and an RF power of 325 W. (a) Many nanowires are visible at a substrate temperature of 800 °C. (c) Very few nanowires grew at a substrate temperature of 840 °C. The circle indicates spots that might be nanowires. (b) and (d) were grown with a Ga cell temperature of 950 °C and an RF power of 275 W.

The impact of the Ga cell temperature on growth rate is evident in the series of images in Figure 4.6. All of the samples were grown with a substrate temperature of 800 °C. The RF power was 325 W for the nanowires in the bottom left image and...
275 W for the other two images. Ga cell temperature increases from the top left to the right starting with 850 °C in the top left image, 900 °C in the bottom left image, and 950 °C in the right image. Approximate nanowire lengths are 1.1 µm in the top left image, 4.4 µm in the bottom left image, and 7.8 µm in the right image. The Ga cell temperature has a dramatic effect on the nanowire length because as the cell temperature increases, the Ga flux from the effusion cell increases. Since nanowires generally grow when the nitrogen to gallium ratio is high [15, 19, 21, 53], low Ga flux creates a situation where the nanowire growth is Ga limited. Therefore, additional Ga at the substrate increases the growth rate.

Figure 4.6 The effect of increasing gallium cell temperature. Cross-sectional field-emission scanning electron microscope (FESEM) images of as-grown nanowires. The growth rate increases as the gallium cell temperature increases. The substrate temperature was 800 °C for all of these growth runs.
We expect the Ga flux to increase approximately exponentially with Ga cell temperature, because the vapor pressure has an exponential dependence on the temp of the liquid Ga. Thus, we used a growth rate equation to determine the temperature required for Ga to go into the vapor phase under the conditions in the growth chamber.

\[
GR \propto Ae^{T_{Ga} / T_0}
\]  

(4.1)

In Equation 4.1, \(GR\) is the growth rate, \(A\) is a prefactor that depends on cell geometry, \(T_{Ga}\) is the gallium cell temperature in K, and \(T_0\) is the activation temperature in K. Equation 4.1 can be expressed as

\[
\frac{\Delta \ln GR}{\Delta T_{Ga}} \propto \frac{1}{T_0}
\]

(4.2)

by using the ratio of two growth rates and some mathematical manipulation. \(T_0\) was found by plotting the natural log of the growth rate vs. the gallium cell temperature and inverting the slope of a line fit to the data points. For this set of data, the activation temperature was 43 K ± 13 K, or \(4 \times 10^{-3}\) eV ± 1 \(\times 10^{-3}\) eV. It falls within the uncertainty of a \(T_0\) value, which was determined from reflection high-energy electron diffraction (RHEED) data of GaAs growth, for another Ga evaporator cell. The activation temperature can also be estimated with data taken directly from a vapor pressure curve for Ga. For an effusion cell with an ideal orifice, where the orifice length is less than the orifice diameter, the vapor pressure is proportional to the effusion rate, which is proportional to the condensation rate at the substrate, and thus the growth rate. Therefore we can substitute \(\Delta \ln P_v\) for \(\Delta \ln GR\) in Equation 4.2, where \(P_v\) is the vapor pressure.
According to reference [54], the vapor pressure of Ga is approximately \(2 \times 10^{-4}\) torr at 1123 K (850 °C), and \(2 \times 10^{-3}\) torr at 1223 K (950 °C). Using these values in Equation 4.3, we get an activation temperature of 43 K.

Nanowire morphology was highly influenced by the RF power. The morphology was difficult to quantify, however, so the conclusions are based on the appearance of the nanowires in the FESEM images. Figure 4.7 has two examples of the difference in the base widths of the nanowires that was due to the RF power used for the N\(_2\) plasma. Figures 4.6a and 4.6c show nanowires that were grown at a substrate temperature of 820 °C with a Ga cell temperature of 950 °C. The run in Figure 4.7a had an RF power of 225 W and the run in Figure 4.7c had an RF power of 325 W. The insets zoom in on the nanowire bases. The nanowires on the left appear straighter and less tapered than the nanowires on the right. Images in Figures 4.6b and 4.6d provide a similar example for runs grown at a substrate temperature of 800 °C and Ga cell temperature of 900 °C. The lower RF power corresponds to nanowires with less tapered morphology.

Growing nanowires with different RF powers had an effect on the photoluminescence (PL) spectra as shown in Figure 4.8. Both sets of nanowires had a growth temperature of 820 °C and a Ga cell temperature of 950 °C. The PL spectrum of the nanowires grown with the lowest RF power is shown by the solid trace. The free A exciton (X\(_\text{A}\)) PL peak is close to the unstrained value of 3.41 eV [50] at room temperature. The PL spectrum of the sample grown with high RF power, shown by the dotted trace, has a broader peak at a lower energy. Similar PL shifts are observed
Figure 4.7 FESEM images that compare the morphology of nanowires grown with N\textsubscript{2} plasma at different RF powers. The samples shown in (a) and (c) were both grown with a substrate temperature of 820 °C and a Ga cell temperature of 950 °C. The RF power in (a) was 225 W and the RF power in (c) was 325 W. The samples shown in (b) and (d) were both grown with a substrate temperature of 800 °C and a Ga temperature of 900 °C. The RF power in (b) was 225 W and the RF power in (d) was 325 W. The insets show higher magnification images of the nanowire bases. Nanowires grown with an RF power of 225 W are straighter and less tapered than those grown with an RF power of 325 W.
Figure 4.8 Normalized PL intensity vs. photon energy. The solid trace is data from row #11, a run that was grown at 820 °C, 950 °C Ga cell temperature, and 225 W RF power. The dotted trace is data from row #12, which was grown with the same substrate temperature and Ga cell temperature, but it had 325 W RF power. The dashed line at 3.41 eV marks the peak location of the free A exciton for unstrained GaN at room temperature. See the text for possible explanations for the shift in the PL peak.
for the other sets of nanowires that had RF power as the only difference in growth conditions. The shift to lower energy, or red shift of approximately 0.04 eV in Figure 4.8, was most likely caused by the nanowires acting as waveguides for the emitted light. Light in the nanowires can become trapped by total internal reflection, causing those wavelengths that correspond to waveguide modes of the nanowire to be transmitted more effectively. The modal structure is superimposed on the broad emission peak of GaN in the PL spectrum. The superimposed peak can shift the GaN PL peak, or appear as a double peak in the spectrum. The PL peak shift could also be due to increased tensile stress in the nanowires. If this is the case, the peak broadening could be caused by variations in the strain between individual nanowires in the collection of nanowires that was sampled. Another possible explanation for the shift in the PL peak is that defects occur at coalescence points in the nanowires, and they emit at a different wavelength than defect-free GaN.

The PL peak shifts were correlated with the level of RF power used during the nanowire growth. As RF power increased, the average diameter of the nanowire clusters increased, which shifted the modal emission pattern of the PL. Figure 4.9 shows three examples of growth runs that had the same growth temperature and Ga cell temperature, but had different RF powers for the nitrogen plasma. The density of nanowires in Figure 4.9d, grown with an RF power of 325 W, is lower than the density of nanowires in Figure 4.9a, which were grown with an RF power of 225 W. A decrease in nanowire density was one of the goals of this experiment. However, instead of a decrease in nucleation density, the density decrease comes from an increase in nanowire coalescence. It is not as visible from the top-view images as it
Figure 4.9 FESEM images of nanowire density differences based on RF power. The images on the left were runs grown with RF powers of 225 W. They have a higher density of nanowires than the images on the right. (d) and (e) had RF powers of 325 W and (f) had an RF power of 275 W. (a) and (d) were both grown at substrate temperatures ($T_{sub}$) of 820 °C and Ga cell temperatures ($T_{Ga}$) of 950 °C. (b) and (e) had $T_{sub} = 800$ °C and $T_{Ga} = 900$ °C. (c) and (f) had $T_{sub} = 800$ °C and $T_{Ga} = 950$ °C.
was in Figure 4.7, but the nanowire tips shown in the right-hand images are made up of several nanowires grown together. Figure 4.10a shows a graphical view of decreasing nanowire density with increasing RF power. In Figure 4.10b, the PL peak shift in meV is plotted against the nanowire density. The samples with lower densities of nanowires, those grown with high RF power, had larger shifts away from the unstrained PL peak.

The differences in lattice parameters calculated from x-ray diffraction and the lattice parameters for unstrained GaN were statistically analyzed. The marginal means plots for both the \(a\) lattice parameter and the \(c\) lattice parameter indicated that nanowires grown with a lower RF power were closer to the unstrained values. However, most of the lattice parameter measurements had wide error bars that were not displayed on the MMP. The contour plots produced by the software also showed contradictory results. Therefore, we cannot say with certainty that the lattice parameters are correlated to the RF power.

The best level for each of the three factors was selected for two additional growth runs. As shown in rows E1 and E2 of Table 4.1, the substrate temperature was set to 800 °C, the Ga cell temperature was set to 950 °C, and the RF power was set to 225 W. One run, row E1, was grown on a very smooth AlN buffer layer produced by MBE with solid source Al from an effusion cell and \(N_2\) from a plasma source. The other, row E2, was grown on the same AlN buffer layer as the other 15 runs. Table 4.2 lists the lattice parameters for rows E1, E2, and unstrained bulk GaN. The \(c\) lattice parameter calculated for run E1 was closer to the \(c\) lattice parameter for unstrained GaN than the \(c\) lattice parameter for run E2. The \(c\) lattice parameter did not fall within
Figure 4.10 Nanowire density graphs. (a) Nanowire density vs. RF power. Density decreases with increasing RF power. (b) PL peak shift vs. nanowire density. The strain-induced red-shift is greater for nanowires with lower densities because the nanowires are more coalesced.
the uncertainty limits for row E2, even though row E2 had wider a wider uncertainty range. The $a$ lattice parameter for both runs was within the uncertainty bars for unstrained GaN. However, run E1 had a smaller uncertainty range, which may point to more consistency from nanowire to nanowire on the substrate. The lattice constants of the nanowires were closer to those of strain-free GaN for the nanowires grown on a high-quality AlN buffer layer.

<table>
<thead>
<tr>
<th>Row #</th>
<th>Run</th>
<th>NW Length (μm)</th>
<th>Lattice Parameter $c$ (nm)</th>
<th>Lattice Parameter $a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>N081</td>
<td>4.6</td>
<td>0.518 50 ± 0.000 01</td>
<td>0.318 90 ± 0.000 01</td>
</tr>
<tr>
<td>E2</td>
<td>N082</td>
<td>5.7</td>
<td>0.518 60 ± 0.000 06</td>
<td>0.318 90 ± 0.000 08</td>
</tr>
<tr>
<td>GaN</td>
<td>Bulk</td>
<td></td>
<td>0.518 53</td>
<td>0.318 91</td>
</tr>
</tbody>
</table>

Table 4.2 Lattice parameters for nanowires and bulk GaN. Lattice parameters calculated from x-ray diffraction for nanowire runs grown on two different AlN buffer layers are listed. Row E1 was grown on high-quality AlN, while row E2 was grown on rougher AlN. The $c$ lattice parameter in row E1 is closer to the value for unstrained GaN than in row E2. Row E2 also has a wider error range for the $a$ lattice parameter, suggesting more variability from nanowire to nanowire. The bulk GaN lattice parameter values are from reference [55].

The choice of AlN buffer layer also had a distinct impact on the nanowire morphology. The FESEM images in Figure 4.11 show that the two runs have different morphologies. In the cross-sectional image of E1 (Figure 4.11a), the nanowires grow through a defect-ridden layer of GaN commonly known as the matrix layer. They are also well separated in the top-view image (Figure 4.11b), and many have hexagonal cross-sections. The nanowires in E1 have little taper compared to the cross-sectional image of E2 in Figure 4.11c. The top-view image of E2 (Figure 4.11d) shows that many of the nanowires are coalesced and do not have hexagonal cross-sections. The GaN matrix layer in growth run E1 can explain the large PL shift that
was observed. Run E1 was grown with an RF power of 225 W, so it looks like a contradiction to the earlier claims. However, since the nanowires are so well separated, much of the PL signal is due to the matrix layer which is known to contain many defects.

\[ T_{\text{sub}} = 800 \, ^\circ C, \quad T_{\text{Ga}} = 950 \, ^\circ C, \quad \text{RF Power} = 225 \, \text{W} \]

Figure 4.11 FESEM images of nanowire runs grown at 800 °C substrate temperature, 950 °C Ga cell temperature, and 225 W RF power. Row E1 shown in images (a) and (b) was grown on a smooth MBE buffer layer. (a) is the cross-sectional image and (b) is the top-view image. Row E2 was grown on a rougher buffer layer produced by TMA1 and ammonia. Image (c) shows the cross-section and image (d) is the top-view. Row E1 has the better nanowire morphology.

4.5 Conclusion

Using a designed experiment, we investigated the nanowire growth parameters of substrate temperature, Ga cell temperature, and RF power. For each of
these factors, three levels were explored so that a wide range of growth conditions could be covered in the fewest number of growth runs. A statistical analysis software package was employed to identify the influence that each parameter had on quantifiable values such as growth rate, PL peak position, and lattice parameters measured with x-ray diffraction. The best conditions for nanowire growth in this experiment were substrate temperature equal to 800 °C, Ga cell temperature equal to 950 °C, and RF power equal to 225 W. The high temperature level of 840 °C was the upper boundary of substrate temperature at which nanowires grew. Growth rate increased with increasing Ga cell temperature, indicating that the growth was Ga limited. The RF power used for the nitrogen plasma increased nanowire coalescence, which sometimes altered the modal structure in the PL emission. We also found that smooth, high-quality aluminum nitride buffer layers were a significant factor in achieving well-separated nanowires. Additional work is necessary to further optimize the nanowire spacing on AlN grown by molecular beam epitaxy.
Chapter 5 is a paper entitled “GaN Nanowire Carrier Concentration Calculated from Light and Dark Resistance Measurements.” It was published in Journal of Electronic Materials, volume 38, issue 4, page 495 [56]. I wrote this paper, and coauthors include Kris A. Bertness, Paul T. Blanchard, Todd E. Harvey, Aric W. Sanders, and Norman A. Sanford. The entire paper is included here, with modifications to indicate work that was performed by the coauthors. This article is a contribution of an agency of the U. S. government and not subject to copyright. Please see Appendix B for the calculation of ionization energy for donors and the percentage of ionized donors in GaN at room temperature.

5.1 Abstract

We obtained the carrier concentration and mobility of silicon-doped gallium nitride nanowires at room temperature with light and dark resistance data. Current-voltage measurements were performed on single-nanowire devices in the dark and under 360 nm illumination. Field-emission scanning electron microscopy was used to measure the device dimensions. The nanowires were modeled with cylindrical geometry, and solutions were computed with a nonlinear fit algorithm. Simulations were also performed to verify the model. The carrier concentration was bounded by $6 \times 10^{17} \text{ cm}^{-3}$ and $1.3 \times 10^{18} \text{ cm}^{-3}$, and the mobility was between $300 \text{ cm}^2/(\text{V} \cdot \text{s})$ and $600 \text{ cm}^2/(\text{V} \cdot \text{s})$. 
5.2 Introduction

GaN nanowires are being investigated for a variety of applications [57] from biosensors to field-effect transistors (FETs) [58, 59] to UV laser diodes [46]. They could also be an alternative to thin films in high-power and high-frequency electronics. Our nanowires, grown by plasma-assisted molecular beam epitaxy (PAMBE), are well suited to these devices because they have high crystalline quality [25, 29, 30]. While researchers are well on the way to refining the growth and processing steps required for these devices, measurement of the material properties of nanowires has not been perfected.

It is important that additional methods for nanowire characterization be developed. Simple resistance and depletion region models are difficult to apply to c-axis GaN nanowires because of their small size and hexagonal cross-sections. Traditional thin-film techniques such as Hall measurements may not be possible on the nearly one-dimensional geometry of nanowires. Carrier concentration and mobility calculations are also complicated, because the two parameters are interrelated. Capacitance-voltage measurements have recently been performed on arrays of nanowires [60] and FET measurements are widely used to extract nanowire properties [57, 58, 61-68]. However, the accuracy of the nanowire FET model is still in question [68, 69], and errors of factors of ten or more are possible. Therefore, additional measurement techniques are necessary for comparison to and verification of the currently used methods.

We have determined the carrier concentration and mobility for a group of GaN nanowires from a single growth run using resistance measurements with and
without UV illumination. Resistance measurements were performed on four-terminal and two-terminal devices with ohmic contacts. We used a nonlinear fit of the dark and UV resistance data to extract the carrier concentration and mobility, and included corrections for the transfer length and depletion width of the nanowires. The model was verified with several simulations, and results were compared to field effect transistor measurements. This method provides values of carrier concentration and boundaries on nanowire mobility. It applies to nanowire batches for which there is a reasonable expectation of material uniformity in electrical properties.

5.3 Experiment

Gallium nitride nanowires were grown by plasma-assisted molecular beam epitaxy on silicon (111) substrates. Our nanowires grow perpendicular to the substrate in the c-axis direction and have hexagonal cross-sections. Nanowires were grown for this experiment by Kris Bertness and Todd Harvey. Details of the growth procedure can be found elsewhere [19, 21, 22]. For this experiment, silicon was introduced during the GaN growth process. Silicon is a known n-type dopant in GaN, and the resulting nanowires were doped and conductive as confirmed by current-voltage measurements. At 1 V bias, devices made from undoped nanowires have currents in the low $10^{-9}$ A, compared to currents in the $10^{-5}$ A or even higher for Si doped nanowires at the same bias. The nanowires were typically ~15 μm long and had average diameters between 200 nm and 300 nm. Some nanowires were found with diameters outside of the average range and were specifically chosen for this experiment.
Paul Blanchard and Aric Sanders fabricated four-point devices from single GaN nanowires. Pieces of the as-grown material were placed in isopropanol and ultrasonically agitated to remove the nanowires from the growth substrate. The resulting nanowire suspension was dispersed via pipette onto a Si wafer with a 100 nm SiO$_2$ wet oxide grown at 1000 °C. After the solvent evaporated, the nanowires were left behind with enough surface adhesion to remain in place during photolithographic patterning. The exposed sections of the nanowires were cleaned with a reactive ion etch (30 W, 20 Pa, 20 s, O$_2$ at 75 sccm) to remove organic contaminants. Metal pads were fabricated with 20 nm of Ti and 200 nm of Al deposited by electron-beam evaporation followed by an acetone liftoff. The samples were annealed at 500 °C for 60 s in 5 % H$_2$/95 % Ar ambient to form ohmic contacts. This recipe was previously shown to make ohmic contacts to $n$-type GaN films [70].

Device dimensions were obtained with field-emission scanning electron microscopy (FESEM). The FESEM image in Figure 5.1 shows a typical four-point device. We measured nanowire diameter on both sides of each contact. Nanowire length between contacts and contact lengths were also recorded.

Current-voltage (I-V) measurements were taken for each working device. Two-point resistance values were calculated from the I-V curves by taking the inverse slope of a line fit through zero. The I-V curves were linear, with all of the devices used here showing ohmic contact behavior. Control measurements were also performed to ensure that contacts without a spanning nanowire were electrically isolated. In addition to every two-terminal combination, four-point collinear I-V measurements were obtained. The collinear resistance, $R_{\text{collinear}}$, was measured by
Figure 5.1 Top-view FESEM image of a typical four-point device. C1, C2, C3, and C4 are the Ti/Al contact leads. Four-point collinear resistance was measured by driving current through the outer two leads, C1 and C4, and measuring the voltage between the inner two leads, C2 and C3. Two-terminal measurements were made by applying voltage and measuring current on adjacent contacts.

driving current through the outer two leads and measuring the voltage between the inner two leads. This strategy for isolating the contact resistance was insufficient, however, because of the unusual geometry of the nanowires, and will be discussed in detail below.

In addition to the four-terminal measurements, we took two-terminal I-V measurements in the dark and under ultraviolet (UV) illumination on the same devices. For this portion of the experiment, we chose two-terminal combinations that spanned a variety of nanowire radii. Measurements were taken at room temperature, and maximum bias voltages were 3 mV to 7 mV. The UV measurements were performed under steady-state illumination at 360 nm wavelength supplied by a 75 W Xe arc lamp with a monochromator. UV light was focused on the sample with fused-
silica optics. The resulting beam had an approximate intensity of 3.6 mW/cm² and a
spot size of approximately 1 mm diameter, which is approximately 100 times greater
than the nanowire length. This experimental setup was built and maintained by
Norman Sanford. Dark I-V measurements were taken inside a closed black box. Since
they display persistent photoconductivity, nanowire samples were placed in the dark
for at least 15 hours before dark I-V scans were performed. During the time between
two hours in the dark and 15 hours in the dark, the current in average-sized nanowires
fell 3 % to 4 %, but the current in small diameter nanowires fell as much as 20 %.
Device resistances in the dark and under illumination were calculated from the
inverse slope of a line fit through zero on the I-V curves. Resistance values were
repeatable, with measurements of the same device made on different days varying by
less than 0.6 %. Table 5.1 lists the resistance values along with the dimensions of the
two-terminal nanowire devices.

Photocurrent measurements were taken at various UV intensities using the
apparatus described above. The power intensity of the lamp dropped from
3.6 mW/cm² to approximately 2.7 mW/cm² between the I-V measurements taken at
100 % illumination and the photocurrent measurements. Fused-silica neutral-density
filters were placed between two of the lenses before the light was focused on the
sample. Combinations of filters were used to attenuate the intensity, spanning almost
five orders of magnitude. At each UV intensity, the devices were set at a constant bias
voltage and a current reading was taken every second for at least one-half hour.
Figure 5.2a shows two typical photocurrent scans. The first jump in current occurs
when the light is allowed onto the sample. Variation in current that occurs after
Table 5.1 Measurements of Two-terminal Nanowire Devices

<table>
<thead>
<tr>
<th>Device</th>
<th>$R_{\text{dark}}$ (Ω)</th>
<th>$R_{\text{uv}}$ (Ω)</th>
<th>$r_m$ (nm)</th>
<th>$L_{\text{nw}}$ (nm)</th>
<th>$L_{c1}$ (nm)</th>
<th>$L_{c2}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>954900</td>
<td>132200</td>
<td>48</td>
<td>1950</td>
<td>245</td>
<td>1820</td>
</tr>
<tr>
<td>2</td>
<td>17090</td>
<td>10800</td>
<td>122</td>
<td>1260</td>
<td>1940</td>
<td>1900</td>
</tr>
<tr>
<td>3</td>
<td>29440</td>
<td>17680</td>
<td>122</td>
<td>1905</td>
<td>1495</td>
<td>1585</td>
</tr>
<tr>
<td>4</td>
<td>17320</td>
<td>11640</td>
<td>138</td>
<td>1655</td>
<td>1710</td>
<td>1760</td>
</tr>
<tr>
<td>5</td>
<td>22810</td>
<td>14910</td>
<td>152</td>
<td>3585</td>
<td>2385</td>
<td>2385</td>
</tr>
<tr>
<td>6</td>
<td>15500</td>
<td>9458</td>
<td>156</td>
<td>1555</td>
<td>1625</td>
<td>1620</td>
</tr>
<tr>
<td>7</td>
<td>12590</td>
<td>8948</td>
<td>158</td>
<td>2100</td>
<td>2175</td>
<td>2110</td>
</tr>
<tr>
<td>8</td>
<td>14730</td>
<td>9405</td>
<td>160</td>
<td>2045</td>
<td>1545</td>
<td>1520</td>
</tr>
<tr>
<td>9</td>
<td>9274</td>
<td>6615</td>
<td>168</td>
<td>1620</td>
<td>1610</td>
<td>1600</td>
</tr>
<tr>
<td>10</td>
<td>10060</td>
<td>6809</td>
<td>178</td>
<td>1595</td>
<td>1620</td>
<td>1620</td>
</tr>
<tr>
<td>11</td>
<td>5371</td>
<td>3967</td>
<td>274</td>
<td>1700</td>
<td>1675</td>
<td>1685</td>
</tr>
<tr>
<td>12</td>
<td>3696</td>
<td>3045</td>
<td>328</td>
<td>2025</td>
<td>2290</td>
<td>2285</td>
</tr>
</tbody>
</table>

Table 5.1 Measurements of two-terminal nanowire devices. Devices are sorted by radius from smallest to largest. $R_{\text{dark}}$ is the nanowire resistance obtained from the I-V curve taken in the dark, $R_{\text{uv}}$ is the nanowire resistance under UV illumination, $r_m$ is the average measured radius of the nanowire rounded to the nearest even number, $L_{\text{nw}}$ is the length of the nanowire between the contacts, $L_{c1}$ is the length of nanowire covered by contact 1, and $L_{c2}$ is the length of the nanowire covered by contact 2. Length measurements were rounded to the nearest 5 nm, to reflect the precision with which they could be measured.

300 seconds is due to fluctuations in the Xe lamp intensity. Photocurrent data presented in Figure 5.2b is the average photocurrent taken from 500 seconds to the end of the scan. Notice that the photocurrent begins to level off at 50 % of the UV power intensity, showing that the surface band bending in the nanowire is nearing 0 V. It should be noted that photocurrent in the nanowires occurs due to the ionization of donor atoms.

On several of the devices, back-gated FET measurements were performed under local atmospheric pressure (Boulder, CO, USA) in air. Gate voltage was applied through the conductive silicon substrate with silver paint as a back contact.

The Ti/Al metal pads fabricated earlier were used as source and drain contacts. The devices displayed channel current modulation as the gate bias was varied from -35 V to...
to 35 V, while the drain-source voltage was held constant at values from 0.1 V to 1 V. Consecutive forward and backward sweeps of gate voltage revealed noticeable hysteresis in all of the devices tested.

5.4 Discussion

Carrier concentration and mobility for nanowires are sometimes obtained from nanowire FET measurements, but the standard equations often use assumptions that do not fit most nanowire devices and thus introduce large systematic errors. Typically the gate-nanowire capacitance is calculated with

\[
C = \frac{2\pi L_{nw} \varepsilon_o \varepsilon_{ox}}{\ln(2t_{ox}/r_m)}
\]  

(5.1)

where \(L_{nw}\) is the length of the nanowire, \(\varepsilon_o = 8.854 \times 10^{14} \text{ F/cm}\), \(\varepsilon_{ox}\) is the dielectric constant of the oxide, \(t_{ox}\) is the oxide thickness, and \(r_m\) is the nanowire radius. This method assumes that the nanowire is encased in oxide, so Wunnicke[68] suggests changing the oxide dielectric constant, \(\varepsilon_{ox}\), from 3.9 for silicon dioxide, to an effective dielectric constant of 2.2. The dielectric constant change immediately cuts the capacitance almost in half. In equation 5.1, the oxide thickness is assumed to be much greater than the nanowire radius, which was not true in our case. Removing this assumption takes the capacitance calculation back to

\[
C = \frac{2\pi L_{nw} \varepsilon_o \varepsilon_{ox}}{\cosh^{-1}((r_m + t_{ox})/r_m)}
\]  

(5.2)

and can easily result in more than five-fold reductions in capacitance for devices with and can easily result in more than five-fold reductions in capacitance for devices with nanowires of large radius and thin oxide layers, in other words, as \(r_m\) approaches

82
Figure 5.2 Photocurrent graphs. (a) Two typical photocurrent vs. time scans taken at a drain-source voltage of 7 mV. The grey scan is at 79% UV power intensity and the black scan is at 3.2% UV power intensity. The first jump in current occurs when the light is allowed onto the sample. Variation in current that occurs after 300 seconds is due to fluctuations in the Xe lamp intensity. (b) Photocurrent vs. UV power intensity. The photocurrent data presented is the average photocurrent, in scans similar to Figure 5.2a, taken from 500 seconds to the end of the scan. The inset shows the same data with the UV power intensity on a linear scale. Notice that the photocurrent begins to level off at 50% of the UV power intensity, showing that the surface band bending in the nanowire is nearing 0 V. Two terminal I-V measurements taken under illumination were all performed with 100% of the UV power intensity.
The capacitance error propagates causing an artificially high carrier concentration, \( N_d = \frac{V_{th} C}{q \pi (r_m)^2 L_{nw}} \), and an artificially low mobility, \( \mu = \frac{g_m L_{nw}^2}{V_{ds} C} \), where \( V_{th} \) is the threshold voltage, \( g_m \) is the maximum transconductance, and \( V_{ds} \) is the drain-source voltage.

Using the standard FET analysis, the average mobility of our nanowires was \( 32 \text{ cm}^2/(\text{V} \cdot \text{s}) \) and the average carrier concentration was \( 1.7 \times 10^{18} \text{ cm}^{-3} \). After applying corrections for the effective dielectric constant and the thickness of the oxide compared to the nanowire radius, the average mobility increased five times to \( 160 \text{ cm}^2/(\text{V} \cdot \text{s}) \) and the average carrier concentration fell to \( 4.7 \times 10^{17} \text{ cm}^{-3} \). FET measurements, for tested devices that showed channel pinchoff and with Equation 5.2 for capacitance, are detailed in Table 5.2. Although wire-to-wire differences in carrier concentration and mobility of almost an order of magnitude were observed, the variation was not a function of nanowire diameter. For nanowires from the same growth run, the range of carrier concentrations obtained from FET measurements was \( 1.5 \times 10^{17} \text{ cm}^{-3} \) to \( 1.3 \times 10^{18} \text{ cm}^{-3} \), which was larger than the carrier concentration range obtained from the model described below.

In addition, the FET measurements were not reproducible. Hysteresis and drift were displayed by the FET devices. In a gate voltage sweep at constant drain-source bias, \( V_{ds} \), the current at a given gate voltage varied depending on the direction of the sweep. Figure 5.3 shows a gate voltage sweep at a \( V_{ds} \) of 0.3 V with an average gate voltage offset of 6.6 V. The forward scan ran first, followed immediately by the backward scan. As shown in the figure, two different threshold voltages could be
Table 5.2 Back-gated FET Measurements of Two-terminal Nanowire Devices

<table>
<thead>
<tr>
<th>Device</th>
<th>( r_m ) (nm)</th>
<th>( C ) (fF)</th>
<th>( V_{th} ) (V)</th>
<th>( g_m ) (nS)</th>
<th>( N_d ) (cm(^{-3}))</th>
<th>( \mu ) (cm(^2)/(V·s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
<td>0.13</td>
<td>-22</td>
<td>76</td>
<td>1.3 \times 10^{18}</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>122</td>
<td>0.13</td>
<td>-30</td>
<td>770</td>
<td>4.1 \times 10^{17}</td>
<td>170</td>
</tr>
<tr>
<td>3</td>
<td>122</td>
<td>0.19</td>
<td>-14</td>
<td>700</td>
<td>1.9 \times 10^{17}</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>152</td>
<td>0.40</td>
<td>-29</td>
<td>150</td>
<td>2.8 \times 10^{17}</td>
<td>65</td>
</tr>
<tr>
<td>8</td>
<td>160</td>
<td>0.24</td>
<td>-16</td>
<td>820</td>
<td>1.5 \times 10^{17}</td>
<td>270</td>
</tr>
</tbody>
</table>

Table 5.2 Back-gated FET measurements of two-terminal nanowire devices. Device numbers match those in Table 5.1. \( r_m \) is the measured radius, \( C \) is the capacitance calculated with Equation 5.2, \( V_{th} \) is the gate threshold voltage found by extrapolating the linear region around the point at \( g_m \) in the \( I_d \) vs. \( V_{gs} \) graph to \( I_d = 0 \), \( g_m \) is the maximum transconductance \( (\partial I_d / \partial V_{gs}) \), \( N_d \) is the carrier concentration, and \( \mu \) is the mobility. The range of carrier concentration calculated with our model was from 6 \times 10^{17} cm\(^{-3}\) to 1.3 \times 10^{18} cm\(^{-3}\) and the mobility was between 300 cm\(^2\)/(V·s) and 600 cm\(^2\)/(V·s).

calculated from the two curves, which would result in different values for carrier concentration and mobility. Consecutive measurements on the same device but with a slower scan speed also gave different results. By simply changing the gate voltage scan speed for one example device, the mobility value increased over 30 % from 187 cm\(^2\)/(V·s) with a continuous scan to 248 cm\(^2\)/(V·s) with a scan speed of 0.5 s per point. Some of the inconsistency might be caused by charge trapping due to condensation, since the measurements were made in air rather than in vacuum, but some surface charge trapping would also occur in vacuum. Similar hysteresis has been observed in other GaN FET experiments[58, 61, 66], and they propose that it is due to charge trapping in the gate oxide. Regardless of the mechanism, accumulated charge shifts the effective threshold voltage which results in inconsistent values for carrier concentration and mobility.
Figure 5.3 A gate voltage sweep showing hysteresis at constant drain-source bias, $V_{\text{ds}}$, of 0.3 V for a nanowire FET. The current, $I_d$, at a given gate voltage, $V_{\text{gs}}$, varied depending on the direction of the sweep. Two different threshold voltages could be calculated from the two curves, which would result in different values for carrier concentration and mobility. The maximum gate voltage shift is 9.5 V and the average gate voltage shift is 6.6 V.

We suspect that there are other fundamental problems with the FET measurements. One concern is that the capacitance was originally derived from a model using an infinitely long metal wire\cite{71} which does not allow for depletion effects in the semiconductor nanowire. Trapped charges at the nanowire-oxide interface and contact resistance are also not considered in the model. A full analysis of errors and their causes is beyond the scope of this paper. The inconsistencies in the FET model prompted us to develop a new model based on simple resistance measurements taken in the dark and under illumination.
5.5 Model

In order to fit a carrier concentration and mobility to the resistance data, we made several assumptions. As with any model, the degree to which the model fits the data is a test of the assumptions of the model. First, we assumed that nanowires from the same growth run had the same carrier concentration and mobility, and that carrier concentration and mobility are materials properties that do not change with exposure to illumination. When electron-hole pairs are created during illumination, the hole density remains orders of magnitude lower than the electron density because many are swept toward the nanowire surface and trapped by the negative surface charges. Therefore, the resistance and the corresponding mobility are affected only by the electrons. Mobility and carrier concentration may vary slightly from wire to wire, but fitting with a single value should yield the average of these values for the group of nanowires. As mentioned earlier, the random variation in resistance measurements was 1%. Next, contact resistivity was given a value of $1 \times 10^{-5} \ \Omega \cdot \text{cm}^2$, since this value is commonly reported for nanowire devices [72, 73]. FESEM measurements were repeatable within $\pm 10 \ \text{nm}$, therefore we assumed a variation of $\pm 10 \ \text{nm}$ in length and $\pm 5 \ \text{nm}$ in radius. We accounted for the uncertainty in nanowire measurements by repeating the fit using the low values for length and radius, and again using the high values for length and radius. Each nanowire radius was one-half of the average diameter measured at the contacted ends. Radius values were modified to approximate the nanowire cross-section as a circle inscribed within a hexagon whose point-to-point diameter was measured as shown in Figure 5.4a. This cylindrical geometry was used for the calculations.
Depletion width was also considered in our model. Since there is negative surface charge on the nanowires, a portion of the semiconductor will be depleted of charges, and current will not flow through the entire nanowire, as shown in Figure 5.4b. The cross-sectional area, $A_{xs}$, in the nanowire resistance calculation,

$$R_{nw} = \frac{\rho_s L_{nw}}{A_{xs}},$$  

needs to be modified to account for this depletion width. Equation 5.3 then becomes

$$R_{nw} = \frac{\rho_s L_{nw}}{\pi (r_m - d)^2}.$$
where $\rho_s$ is the semiconductor (nanowire) resistivity, $L_{nw}$ is the nanowire length, and $r_m$ is the nanowire radius. We calculated the depletion width, $d$, using an equation for the surface band bending, $\Phi$, that was derived by use of cylindrical symmetry and Gauss's law [74].

\[
\Phi = \frac{q N_d}{2 \varepsilon} \left[ \frac{r_m^2 - (r_m - d)^2}{2} - (r_m - d)^2 \ln \left( \frac{r_m}{r_m - d} \right) \right].
\] (5.5)

In Equation 5.5, $q = 1.602 \times 10^{-19}$ coulomb, $N_d$ is the carrier concentration, and $\varepsilon = \varepsilon_o \varepsilon_r$, where $\varepsilon_o = 8.854 \times 10^{-14}$ F/cm and $\varepsilon_r = 8.9$ [75]. Typical depletion widths in the dark were around 25 nm for these Si-doped nanowires. Illuminating the nanowires with ultraviolet light above the band gap decreases the depletion width. Photo-generated carriers partially neutralize the surface states, reducing the surface band bending and opening the conducting channel in the nanowire. The illuminated resistance values were around 70% of the original measurement for average-sized nanowires. For the smallest diameter nanowire, however, the illuminated resistance value was only 14% of the dark resistance measurement.

Fitting the data to obtain carrier concentration and mobility values was complicated because the two parameters are related by $\rho_s = \frac{1}{\mu q N_d}$, where $\mu$ is the mobility. Rather than solving a simple linear system of $n$ equations and $n$ unknowns, getting solutions for these two coupled values required a nonlinear fit to the data. We made some initial guesses for $N_d$ and $\mu$ that were used as starting values in the fitting routine, and fixed the value of the surface band bending within each fit. Then the device resistance, $R_{device}$, was calculated based on those starting values:

89
Nano wire resistance was modeled using Equation 5.4 along with Equation 5.5 to account for the depletion width. Contact resistance was calculated using the transfer length correction explained later in Equation 5.7.

A Levenberg-Marquardt[76] nonlinear least-squares fitting routine was used to solve simultaneously for the carrier concentration and mobility that provided the best fit to the entire data set, including both dark and illuminated resistances. Inputs to this routine were initial guesses for the fitting parameters $N_d$ and $\mu$, constants for both surface band bending values, and the nanowire dimensions. Software written in Igor computed the device resistances as described above and summarized in Equation 5.6. Prior to analyzing the data with Igor, I had been working with the data in an Excel file. My NIST advisor, Dr. Kris Bertness, wrote the original Igor functions to perform the fit, and I added to and modified the functions. Each modeled resistance was compared to the actual measured resistance via the chi-squared parameter,

$$\sum_{i=1}^{n} \left( \frac{y - y_i}{\sigma_i} \right)^2$$

where $y$ was the modeled device resistance, $y_i$ was the measured device resistance, and $\sigma_i$ was the standard deviation of the measured resistance. The algorithm then chose new values of $N_d$ and $\mu$, and the process repeated. Iterations continued until chi-squared was minimized. The resulting $N_d$ and $\mu$, along with their uncertainties, were solutions to the experimental data.

We ran the routine several times, varying surface band bending in the dark from 0.3 to 0.7 V and surface band bending under illumination from 0 to 0.05 V. The actual surface band bending for our GaN nanowires is unknown. For nanowire
devices measured in the dark, we chose values within the literature range of 0.1 V to 1.1 V [77-79]. Surface band bending for illuminated nanowires was much lower.

Equation 5.5 supplies a good depletion region model for the surface band bending in the dark. However, it does not hold for small values of surface band bending. The intention was to reduce the surface band bending to 0 V, so that the conducting channel would be the entire nanowire and the upper limit of the radius would be the inscribed radius. Since this could not be confirmed, a range of low values was used even though the depletion model was not perfect. Figure 5.2b does show, however, that the nanowires are tending toward the flat band condition under UV illumination. The inset clearly shows that the current vs. UV intensity begins to level off at around 50 % power intensity. Also note that average-sized nanowires still have a depletion width of around 3.6 nm when the surface band bending is 0.01 V and the carrier concentration is $7.8 \times 10^{17}$ cm$^{-3}$. Additional studies are underway to obtain experimental values for surface band bending, and they will be reported at a later time.

The model provides a good fit to the data. The points in Figure 5.5a show the measured resistance, $R_{\text{meas}}$, minus the modeled contact resistance, $R_{\text{contact}}$, vs. length/radius$^2$ on a log-linear scale. The lines are the model values calculated with surface band bending in the dark at 0.5 V and surface band bending under illumination at 0.01 V. Based on a carrier concentration of $7.8 \times 10^{17}$ cm$^{-3}$ and a mobility of 470 cm$^2$/(V·s), all modeled resistance values were within 25 % of the measured resistance values. Figure 5.5b shows the fractional difference for each point, $(R_{\text{meas}} - R_{\text{fit}})/R_{\text{meas}}$, where $R_{\text{fit}}$ is the modeled resistance. It proves that the
change in resistance between nanowires kept in the dark and nanowires that are illuminated with UV can be explained by the difference in the size of the conducting channel. Using the above parameters, the diameter of the conducting channel in the dark is 78% to 85% of the conducting channel under UV illumination for average-sized nanowires. Whether the current is confined to an inner core of the nanowire or is spread throughout most of the nanowire diameter, the values of carrier concentration and mobility do not change dramatically. Figure 5.5b confirms that our model fits the resistance data and therefore our earlier assumptions were reasonable.

The results of the many fit iterations were constructed into a solution-space graph shown in Figure 5.6. The shapes of the solution spaces are more complicated than what is shown in the figure, but the rectangles provide a good visual representation of the extent of each solution space. The area inside each rectangle represents solutions for the carrier concentration and mobility of the group of nanowires at a given surface band bending in the dark. Included in the solution space are multiple fit results obtained by changing the nanowire dimensions based on the measurement uncertainty, and by varying the surface band bending under illumination from 0 to 0.05 V.

The procedure described does not converge on a single unique solution for carrier concentration and mobility, because of the nonlinear interrelatedness of the two parameters. The fitting algorithm returns an uncertainty associated with each parameter, and the magnitude of this uncertainty increases with the uncertainty in the nanowire resistance and dimension measurements. One such point with uncertainty bars is illustrated within the Φ= 0.4 rectangle in Figure 5.6. Between 97% and 98%
Figure 5.5 Graphs comparing modeled resistance to actual measured resistance. (a) The measured resistance, $R_{\text{meas}}$, minus the modeled contact resistance, $R_{\text{contact}}$, vs. length/radius$^2$ on a log-linear scale. The lines are the model values calculated with surface band bending in the dark at 0.5 V, surface band bending under illumination at 0.01 V, a carrier concentration of $7.8 \times 10^{17}$ cm$^{-3}$, and a mobility of 470 cm$^2$/V·s. (b) The fractional difference for each point, $(R_{\text{meas}} - R_{\text{fit}})/R_{\text{meas}}$, where $R_{\text{fit}}$ is the modeled resistance. Modeled resistance values were within 25% of the measured resistance values.
Figure 5.6 Solution space of carrier concentration vs. mobility. The area inside each rectangle represents solutions for the carrier concentration and mobility of the group of nanowires for a given surface band bending in the dark. Included in the space are the uncertainty in measured nanowire dimensions and variation in surface band bending under illumination from 0 to 0.05 V. The point with error bars is an example fit solution for surface band bending in the dark of 0.4 V and surface band bending under illumination of 0.01 V. Each rectangle contains six points similar to the one shown, and each point is a solution for a given value of surface band bending under illumination. Note that the solution-space shape is not actually a perfect rectangle.

of each uncertainty bar is due to uncertainty in the nanowire dimensions. Another way to interpret these uncertainty limits is to say that they represent the range of combinations of carrier concentration and mobility that would fit the data equally well when the fit is constrained to particular surface band bending value. Even with several data points covering a range of nanowire radii, we find that the range of equally probable carrier concentration and mobility values is on the order of 30% of the average value for these parameters. Our experience also shows that it is easy to find false minima when using a grid search approach rather than the nonlinear curve-
fitting algorithm. The full range of equally probable values is only seen when searching in steps on the order of the third significant digit in each parameter.

For this nanowire growth run, the fitting procedure indicated that the carrier concentration was between $6 \times 10^{17}$ cm$^{-3}$ and $1.3 \times 10^{18}$ cm$^{-3}$, and the mobility was between $300$ cm$^2$/V·s and $600$ cm$^2$/V·s. The mobility range was higher than the $150$ cm$^2$/V·s to $250$ cm$^2$/V·s that Fu et al. and others reported for similarly doped, bulk GaN [80, 81]. GaN films often have dislocation densities of $8 \times 10^9$ cm$^{-2}$ [81]. TEM examination of individual nanowires shows that our MBE grown nanowires are free of dislocations [22]. Our mobility is higher than most reported nanowire mobilities [47, 67, 82], but it is similar to the $300$ cm$^2$/V·s at $2 \times 10^{18}$ cm$^{-3}$ reported for GaN nanowire FETs by Huang et al. [57], whose nanowires are also single crystalline and grow in the [100] direction [83]. The elevated mobility range is probably due to the defect-free nature of our material.

One source of systematic uncertainty in our model is imprecise knowledge of the contact resistance. Generally the contact resistance, $R_{contact}$, can be determined by subtracting the collinear resistance, $R_{collinear}$, from the two-point resistance between the inner two leads, $R_{23}$, $R_{contact} = R_{23} - R_{collinear}$. Then the contact resistivity can be calculated using the device geometry, $R_{contact} = \rho_c / (2 \pi r_m L_c)$, where $\rho_c$ is the contact resistivity, $r_m$ is the nanowire radius, and $L_c$ is the contact length. The graph in Figure 5.7 shows that the collinear resistance measurement was nearly identical to the two-point resistance between the inner two leads. In this case the common procedure gave an exceptionally small contact resistivity on the order of $10^{-7}$ Ω·cm$^2$. Although Yan et al. [70] have produced contacts to GaN film with contact resistivity as low as
10^{-7} \, \Omega \cdot \text{cm}^2$, most reported contact resistivities for GaN films are in the high $10^{-6} \, \Omega \cdot \text{cm}^2$ or low $10^{-5} \, \Omega \cdot \text{cm}^2$ range [84-86]. Nanowire contact resistivities have been reported around $1 \times 10^{-5} \, \Omega \cdot \text{cm}^2$ [72, 73].

This discrepancy was resolved by applying a transfer length correction in our model. The transfer length accounts for the distributed current flow near the contact edges. It is discussed in the paper by Mohney, et al. [87] and defined as

$$L_T = \frac{r_m \rho_c}{2 F \rho_s},$$

where $r_m$ is the nanowire radius, $\rho_c$ is the contact resistivity, and $\rho_s$ is the semiconductor resistivity. $F$ is the fraction of nanowire circumference covered by the contact metal, which we estimated from SEM pictures as 2/3. The transfer length
for a nanowire device with average radius of 125 nm is around 300 nm, which is smaller than our photolithographically defined leads, which are typically 1500 nm wide. Contact resistance in the model was calculated with the transfer length correction,

\[
R_{\text{contact}} = \frac{\rho}{2\pi r_m L_T} \left( L_c \tanh \frac{L_c}{L_T} \right),
\]

where \( L_c \) is the contact length. When we used a contact resistivity of \( 1 \times 10^{-5} \, \Omega \cdot \text{cm}^2 \), the resistance of a typical contact was 2200 Ω.

Another consequence of the short transfer length is that the center metal pads were shunting the nanowire current. We tested this effect by comparing the two-terminal resistance between contacts 1 and 4, \( R_{14} \), and the sum of the two-terminal resistances of the individual wire sections between the pads. Residual resistance is defined as

\[
R_{\text{res}} = R_{14} - (R_{12} + R_{23} + R_{34}) - 2R_L
\]

The thin Ti/Al leads to the nanowire have lead resistances, \( R_L \), on the order of half the difference between \( R_{23} \) and \( R_{\text{collinear}} \). After removing the lead resistance, the residual resistance, \( R_{\text{res}} \), was around 1% of the \( R_{14} \) resistance. If current was flowing through the nanowire under the metal pads, it is expected that the residual resistance would be substantially higher due to the additional resistance from the lengths of the nanowire underneath the contacts. If the current flows into the center metal pads even when current is supplied through the outer pads, however, the contact resistance of the center pads makes the same contribution to \( R_{14} \) as it does to \( R_{12}, R_{23} \) and \( R_{34} \), producing the observed result. The only other possible explanation is that the contact resistance was exactly equal to the

97
resistance of the wire segment underneath it for all nanowires and contacts, which is highly unlikely.

5.6 Simulations

In addition to the data fit described above, we also did several simulations to study how different parameters affected the solution space. Nanowire dimensions were chosen to simulate length, radius, and contact length measurements, and values for carrier concentration, mobility, contact resistivity, surface band bending in the dark, and surface band bending under illumination were set. The resistance of the simulated nanowire devices was calculated with those parameters. Gaussian noise based on a standard deviation of 0.6% of the resistance was added to the resistance numbers to simulate the measurement uncertainty. Finally, we solved for carrier concentration and mobility using the same procedure as was used for the actual data.

By varying one parameter at a time, we were able to isolate its influence on the solution space. In Simulation 1, illustrated in Figure 5.8, we calculated the resistances that would have resulted from nanowires with the same dimensions as those in our actual data set, but with a lower mobility of 270 cm$^2/(V\cdot s)$. The other simulation parameters were a carrier concentration of $5.5 \times 10^{17}$ cm$^{-3}$, contact resistivity of $1.0 \times 10^{-5}$ Ω·cm$^2$, surface band bending in the dark of 0.5 V, and surface band bending under illumination of 0.01 V. Comparing Figure 5.8 with Figure 5.6 shows that the fitting procedure accurately tracks the change in mobility. The "x" on the graph marks the starting values that we used and therefore represents the "actual" solution to the simulated data. In Simulation 2, we intentionally overestimated the contact resistivity when we tried to fit the simulated data. Simulated resistance values
were constructed by use of $1.0 \times 10^{-6} \ \Omega \cdot \text{cm}^2$ while the contact resistivity in the fitting routine was set to $3.0 \times 10^{-6} \ \Omega \cdot \text{cm}^2$. The higher, incorrect, contact resistivity used in the fit procedure shifted the solution-space graph toward artificially higher mobility values (Figure 5.9.) Thus, one possible explanation for the higher mobility values we extract from our data is that we have overestimated the contact resistivity by a factor of 100 or more. Finally, we note that in Simulation 2, nanowire dimensions were simulated that included even more variation in radii than found in our nanowire data set. Because of the nonlinear relationship between carrier concentration and mobility, this greater variability in nanowire radii still led to a large solution space rather than single values for these properties.

![Simulation 1](image)

Figure 5.8 Graph of the solution space for carrier concentration vs. mobility for a simulation with a low starting value of mobility of $270 \ \text{cm}^2/(\text{V} \cdot \text{s})$. The starting values are marked with an x.
Figure 5.9 Graph of the solution space for carrier concentration vs. mobility for a simulation where we overestimated the contact resistivity. The simulation values were obtained with $p_c = 1.0 \times 10^{-6}$, but the contact resistivity was assumed to be $3.0 \times 10^{-6}$ for the fit. The starting values are marked with an x.

Many other insights into the validity of the model were gained through additional simulations. The solution-space graph for the actual data could be reproduced by use of the actual device dimensions and starting values of mobility equal to 470 $\text{cm}^2/(\text{V} \cdot \text{s})$ and a carrier concentration of $7.8 \times 10^{17}$ cm$^{-3}$. Contact resistivity and surface band bending were the same as in the first simulation. We also tried separating effects of nanowire measurement errors. As expected, the size of the solution space rectangle was due mostly to the uncertainty in the nanowire radius rather than to the uncertainty in the nanowire length. Adding more noise to the simulated resistance values did shift and slightly enlarge the solution space, but the actual solution was still included. Changing the surface band bending in the dark had a higher relative effect on the mobility than on the carrier concentration. Mobility
solutions shifted to lower values as surface band bending in the dark increased. On the other hand, the solutions shifted to higher values of mobility as assumed surface band bending under illumination increased. Surface band bending in the dark had a much greater affect on the solution space than surface band bending under illumination. Incremental changes to surface band bending under illumination of 0.01 V led to solutions that overlapped the error bars of the previous solution until the surface band bending under illumination reached approximately 42 % of the value for surface band bending in the dark. The starting guesses for mobility and carrier concentration had little effect on the solution space.

5.7 Summary

We have calculated a carrier concentration between $6 \times 10^{17}$ cm$^{-3}$ and $1.3 \times 10^{18}$ cm$^{-3}$ and a mobility between $300$ cm$^2/(V\cdot s)$ and $600$ cm$^2/(V\cdot s)$ for Si-doped GaN nanowires, based on dark and light resistance measurements. The I-V measurements indicated that we created ohmic contacts to the nanowires, and resistance values were repeatable. A nonlinear fit of the light and dark resistances was used to solve for carrier concentration and mobility. We verified the validity of the calculation method with numerous simulations, and discussed problems in the back-gated FET measurements. Future experiments that will benefit this process are measurements of the surface band bending under light and dark conditions, such as scanning Kelvin probe microscopy, and higher-resolution measurements of nanowire radius. Independent methods for extracting the carrier concentration and mobility of nanowires are also needed to confirm the calculations.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

From system design and construction to nanowire growth and finally nanowire characterization, a wide range of study relating to GaN nanowires was explored in this dissertation. Conclusions and recommendations for further work are summarized in this chapter.

6.1 Nitride Growth System

Designing and building a growth system was a great learning experience that took extensive time and effort. The time commitment for this undertaking made less time available for more scientific pursuits. Currently, the nitride growth system is functioning well. We have met goals such as growing nanowires and doping nanowires p-type with Mg. A detailed description of the conclusions and future upgrades to the system is included in Appendix C.

6.2 Nanowire Growth

The nanowire growth study was performed to find the best conditions for nanowire formation in the new system. With the MBE process as a guide, nanowires were successfully grown on AlN buffer layers.

6.2.1 Conclusion

Gallium nitride nanowire growth was investigated with a three-factor, three-level, designed experiment. The variables (factors) chosen were substrate
temperature, Ga cell temperature, and the RF power used to generate the nitrogen plasma. The nanowires were grown on AlN covered Si(111) substrates for 24 h. Nanowires had the highest growth rates when the substrate temperature was 800 °C and the Ga cell temperature was 950 °C. FESEM was used to observe the amount of taper in the nanowire morphology. Straighter and less tapered nanowires were formed when the RF power was at the low setting of 225 W. As the RF power increased, so did the nanowire taper and coalescence. The high RF power increased the high-energy nitrogen in the system and may have caused charging of the nanowires which resulted in nanowires being attracted to one another and coalescing. Ga atoms desorbing near the substrate due to elevated temperatures may diffuse toward the nanowire tips where they become reincorporated on the sidewalls of the forming nanowires. PL peaks farthest from the unstrained value were also correlated to high nanowire coalescence, and hence high RF power. XRD was used to calculate the lattice parameters of the nanowires. Although the uncertainties were often comparable to the variations, the lattice parameters closest to strain-free GaN were found in nanowires that were grown on a smooth, high-quality aluminum nitride buffer layer.

The strength of the designed experiment was the ability to cover a wide range of growth conditions in the smallest number of growth runs. The weakness in this case was that not all of the runs had nanowire growth. The lack of nanowires made correlations between XRD, PL, and growth parameters impossible. The experiment would have been more useful if a few runs had been completed first to narrow down the ranges of substrate temperature and Ga cell temperature that would produce
nanowire growth. Then there would be XRD and PL data for each run and a lower chance of omitted data skewing the results in the statistical analysis program. Additional measureable quantities relating to the nanowires would have also been helpful. The other key to a designed experiment is doing multiple replicates. In this case, however, we did only one growth run for each row on the growth matrix because of time and cost constraints. Multiple replicates would have ensured that our findings were repeatable.

6.2.2 **Future Work**

The results from the designed experiment gave a good starting point for additional optimization of the nanowire growth in the new system. The first recommendation for future studies is to always use high-quality AlN buffer layers. The buffers can be grown in the old MBE, or using solid source Al in the nitride growth system when it becomes available. Since the nanowires grew best at the lowest substrate temperature of 800 °C, some nanowire runs should be attempted at lower temperatures such as 760 °C and 780 °C. It will be beneficial to know the temperature range required for nanowire formation. The substrate temperature should also be monitored for changes if any new source materials are used in the system.

Additional techniques for nanowire growth could be explored. Two-step growth of nanowires should be thoroughly investigated. We have recently found some success with better separated nanowires by starting with a lower temperature GaN layer and then increasing the temperature for nanowire formation. Figure 6.1 shows an example of two-step growth. Attempts at selective growth using silicon nitride masks might be more successful now that a better range of growth parameters...
has been identified. Catalyst growth of nanowires could also be performed. It would be interesting to compare the properties of catalyst-grown and catalyst-free nanowires to see what effect the catalyst has on growth direction, PL, and lattice parameters.

Figure 6.1 FESEM image of a nanowire sample which was grown in two steps. The nucleation layer was grown at a substrate temperature of 750 °C, a gallium cell temperature of 950 °C, and an RF power of 200 W. The nanowire growth layer had a substrate temperature of 800 °C, a gallium cell temperature of 940 °C, and an RF power of 200 W.

The settings for the nitrogen plasma source could be fully investigated. At the time of the growth experiment, the plasma source was in its closest possible position to the substrate. Since that time it has been moved further away from the substrate twice. Now it is at a position one inch further from the substrate than at the time of the experiment in Chapter 4. We are assuming that the optimal setting for RF power should be the same at this position as it was during the growth experiment, but that might not be true. The plasma source aperture plate could be exchanged for one with a single hole. After reading about some tests of different plasma sources, however,
the multi-holed aperture plate is probably the best choice because it should produce
the fewest number of nitrogen ions \[88\]. Finally, an optical spectrometer is now
installed on the system to record the characteristics of the plasma. The recorded
plasma spectra might give useful information about how the intensities of atomic and
molecular nitrogen species affect nanowire growth.

Growth of nanowire-based structures is ongoing and more is planned for the
future. Nanowire \(p-n\) junctions are being studied for their use in nanowire LEDs and
lasers. Recently, NIST has been growing nanowires with axial \(p-n\) junctions. The
collaboration with NIST Gaithersburg on radial \(p-n\) junctions will continue and radial
\(p-n\) junctions will also be grown at NIST Boulder. Although we have not yet
fabricated nanowire solar cells, we have laid the groundwork for future work.

6.3 Nanowire Carrier Concentration

Measuring the electronic properties of semiconducting nanowires is a
challenging task. However, we are making significant progress in nanowire
metrology. Conclusions from the nanowire carrier concentration study are
summarized in the next section. Recommendations for future work are in the final
section of this dissertation.

6.3.1 Conclusions

We developed a method for calculating the carrier concentration and mobility
of Si-doped GaN nanowires based on dark and light resistance measurements. The \(I-V\)
measurements indicated that the contacts to the nanowires were ohmic. The
resistance values were repeatable, unlike the back-gated FET measurements that are
often used for carrier concentration and mobility calculations. Solutions for carrier concentration and mobility were calculated via a nonlinear fit of the light and dark resistance data, along with the nanowire dimensions. Numerous simulations were performed to confirm that the model was valid. The calculated carrier concentration was between $6 \times 10^{17}$ cm$^{-3}$ and $1.3 \times 10^{18}$ cm$^{-3}$ and the mobility was between 300 cm$^2$/V·s and 600 cm$^2$/V·s. Our method provided a way to extract these properties from simple devices with only a moderate time investment.

6.3.2 Future Work

Many opportunities exist to further the nanowire carrier concentration experiments. One of the most obvious is to perform the same experiment on nanowire batches that have a different expected carrier concentration than the ones studied here. It would be beneficial to confirm that the process is valid for very low and very high carrier concentrations. Initial tests with a UV laser light source have indicated that the nanowires are at flat-band conditions under UV illumination, but more experiments should be completed. The I-V measurements should also be performed under vacuum conditions, or on surface-passivated nanowires, to minimize the effects of surface states. Actual measurements of the surface band-bending under light and dark conditions are needed. One such method, comparing photoconductive decay times at varying temperatures, is currently under study. Scanning Kelvin probe microscopy is another possible option. Higher-resolution measurements of nanowire radius would also reduce the margin of uncertainty in the calculations. Experiments to confirm the calculations by independent methods for extracting the carrier concentration and mobility of the nanowires are underway.
REFERENCES CITED


75. Schubert, E.F. Physical data for GaN. Available from:
http://www.rpi.edu/~schubert/.


## APPENDIX A

CRACKING PATTERNS

<table>
<thead>
<tr>
<th>Component</th>
<th>Base Peak</th>
<th>Minor Peak 1</th>
<th>% of Base</th>
<th>Minor Peak 2</th>
<th>% of Base</th>
<th>Minor Peak 3</th>
<th>% of Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>28</td>
<td>32</td>
<td>27</td>
<td>14</td>
<td>6</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td>Ammonia</td>
<td>17</td>
<td>16</td>
<td>80</td>
<td>15</td>
<td>8</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>Carbon</td>
<td>44</td>
<td>16</td>
<td>9</td>
<td>28</td>
<td>8</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>Dioxide</td>
<td>28</td>
<td>12</td>
<td>5</td>
<td>16</td>
<td>2</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>28</td>
<td>12</td>
<td>5</td>
<td>16</td>
<td>2</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Ethane</td>
<td>28</td>
<td>27</td>
<td>33</td>
<td>30</td>
<td>26</td>
<td>26</td>
<td>23</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>16</td>
<td>15</td>
<td>85</td>
<td>14</td>
<td>16</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28</td>
<td>14</td>
<td>5</td>
<td>29</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>32</td>
<td>16</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>18</td>
<td>17</td>
<td>21</td>
<td>16</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A.1 Cracking patterns of common vacuum contaminants. From VG Instruments Cracking Pattern Calculator.
### Table B.1 Values Used in Ionized Donor Calculation

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity effective mass of an electron in GaN</td>
<td>( m^* )</td>
<td>0.2( m_o )</td>
</tr>
<tr>
<td>Rest mass of an electron</td>
<td>( m_o )</td>
<td>9.11 \times 10^{-31} \text{ kg}</td>
</tr>
<tr>
<td>Electronic charge</td>
<td>( e )</td>
<td>1.6 \times 10^{-19} \text{ C}</td>
</tr>
<tr>
<td>Energy state</td>
<td>( n )</td>
<td>1 (lowest)</td>
</tr>
<tr>
<td>Planck’s constant/2( \pi )</td>
<td>( \hbar )</td>
<td>1.054 \times 10^{-34} \text{ J} \cdot \text{s}</td>
</tr>
<tr>
<td>( \pi )</td>
<td>( \pi )</td>
<td>3.14159</td>
</tr>
<tr>
<td>Relative permittivity of GaN</td>
<td>( \varepsilon_r )</td>
<td>8.9</td>
</tr>
<tr>
<td>Permittivity of free space</td>
<td>( \varepsilon_0 )</td>
<td>8.85 \times 10^{-12} \text{ F/m}</td>
</tr>
<tr>
<td>Conversion factor – J to eV</td>
<td>1 eV</td>
<td>1.6 \times 10^{-19} \text{ J}</td>
</tr>
<tr>
<td>Density of electrons in the donor level</td>
<td>( n_d )</td>
<td>\text{ cm}^{-3}</td>
</tr>
<tr>
<td>Thermal-equilibrium concentration of electrons</td>
<td>( n_o )</td>
<td>\text{ cm}^{-3}</td>
</tr>
<tr>
<td>Effective density of states in the conduction band</td>
<td>( N_c )</td>
<td>4.3 \times 10^{14} (T)^{3/2} \text{ cm}^{-3}</td>
</tr>
<tr>
<td>Density of donor impurity atoms (chosen)</td>
<td>( N_d )</td>
<td>\text{ cm}^{-3}</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>( k )</td>
<td>8.62 \times 10^{-5} \text{ eV/K}</td>
</tr>
<tr>
<td>Energy at the conduction band edge</td>
<td>( E_c )</td>
<td>3.4 \text{ eV}</td>
</tr>
<tr>
<td>Energy of the donor level</td>
<td>( E_d )</td>
<td>eV</td>
</tr>
<tr>
<td>Ionization energy</td>
<td>( E_i )</td>
<td>( E_c - E_d ) \text{ eV}</td>
</tr>
</tbody>
</table>

*From reference [75].

The following steps describe the process for calculating the percentage of donors that remains neutral at room temperature.

First, calculate the general ionization energy of donors in GaN.

\[
E_i = \frac{-m^* e^4}{2(\hbar n)^2 (4\pi \varepsilon \varepsilon_0)^2} \quad (B.1)
\]
\[
E_i = -0.0343 \text{ eV}
\]

Then, determine the fraction of total electrons still in donor states at \( T = 300 \text{ K} \).

\[
\frac{n_d}{N_d} = \frac{1}{1 + \frac{1}{2} \exp \left[ \frac{(E_d - E_f)}{kT} \right]}
\]

Equation B.1 and Equation B.2 are from reference [90]. In order to calculate the fraction of neutral donors from Equation B.2, the Fermi energy is needed. Assuming the free hole and acceptor concentrations are much less than the donor atom concentration, then \( N_d^+ = n_c \) due to charge neutrality. The Fermi energy can be found by graphing the density of free electrons in the conduction band,\( n_c = N_c e^{\left(\frac{E_c - E_f}{kT}\right)} \), and the number density of ionized donors, \( N_d^+ = \frac{N_d}{1 + 2 e^{\left(\frac{E_d - E_f}{kT}\right)}} \), together on one graph. The point where the two lines cross is the Fermi energy. An example graph from reference [91] for Si is shown in Figure B.1.

For GaN with \( N_d = 5 \times 10^{16} \), the Fermi energy was found to be \(-3.29825 \text{ eV} \) from the graph in Figure B.2a. Putting this value back into Equation B.2, the fraction of neutral donors at room temperature is

\[
\frac{n_d}{N_d} = \frac{1}{1 + \frac{1}{2} \exp \left[ \frac{(3.3657 - 3.29825)}{0.02586} \right] = 0.128
\]

Thirteen percent of donor electrons are still in donor states at \( T = 300 \text{ K} \). To show the
Figure B.1 Graphical method to determine the Fermi energy level $E_f$ when ionization is not complete. From reference [91].
effect of the donor density, compare this to the case when $N_d = 6 \times 10^{17}$. Putting the Fermi energy, $\sim 3.348$ eV, back into Equation B.2, the fraction of donors that remains neutral is

$$\frac{n_d}{N_d} = \frac{1}{1 + \frac{1}{2} \exp \left[ \frac{(3.3657 - 3.348)}{0.02586} \right]} = 0.502$$

Fifty percent of donor electrons are still in donor states at $T = 300$ K. A value of 0.0308 eV for the Si donor ionization energy in GaN, as calculated by Wang et al. [92], was also substituted for $E_i$ in the calculations to get 0.479, or 48 % of donor electrons still in the donor states when $N_d = 6 \times 10^{17}$. The Fermi energy for this calculation is shown in Figure B.2b.
Figure B.2 Mathematica graphs used to find the Fermi energy. (a) \( N_d = 5 \times 10^{16} \) and (b) \( N_d = 6 \times 10^{17} \). The insets zoom in on the Fermi energy.
APPENDIX C
NITRIDE GROWTH SYSTEM

This section is intended to be helpful to current and future users of the nitride growth system. It contains a detailed description of our findings during growth system construction, and suggestions for future system upgrades. Most of these changes improve upon compromises made during system construction to reduce cost and reach nanowire growth as soon as possible.

C.1 Conclusion

The computer-aided design (CAD) software was essential to the success of the growth system design and construction. Fitting the system within limited laboratory space would have been close to impossible without it. The system enclosure was packed to the point where only 90° power plugs would fit into the outlets on one of the sides. The internet availability of CAD files for common parts was also extremely helpful, especially for designing the OM lines.

Organometallics and ammonia tend to stay in the chamber longer than the elemental sources and nitrogen gas. A practice adopted while using the organometallic sources was to outgas the manipulator, the gas injector, and the OM injector at 600 °C after each growth run. Outgassing helped to remove some of the compounds remaining in the chamber, causing the chamber pressure to drop to lower base pressures. Another discovery was that leak valves should be used instead of mass flow controllers, in order to keep the chamber pressure below $4 \times 10^{-4}$ torr.
during the material deposition. Mass flow controllers did not produce sufficiently low flow settings, and their zero points tended to drift. They were also ineffective for OMs that had low dissociation temperatures like DMEAA.

While the RGA worked well for leak checking, the design was not perfect for detecting all of the source elements in the chamber. It had a collar with 4 holes for vapor to enter. The holes were well placed for the sources in the chamber that were mounted horizontally, but not for those mounted in other orientations. Mg, for example, was detectable in the RGA spectrum. The Mg cell was 45° left of the substrate normal. In spherical polar coordinates, the Mg cell was located at \( \varphi = 90° \) and \( \theta = -45° \), where the center of the chamber is the origin, \( \varphi = 0° \) points up, and \( \theta = 0° \) points to the front of the chamber. The lower sources, Ga for example, were located at \( \varphi = 135° \) and \( \theta = \pm 45° \), which means they were 45° below and to the left of the substrate normal. Ga was not collected by the RGA when the RGA was at the center of the chamber, nor when the RGA was lowered below the center of the chamber. Because of this, accurate flux measurements were not possible for Ga. Instead of using the RGA to measure Ga flux, the change in chamber pressure indicated by the ion gauge was recorded. Figure C.1 shows the Ga flux at various temperatures over a series of 7 runs. The chamber pressure was recorded at times 1 minute after the Ga shutter was opened (Figure C.1a), and at 3 minutes after the Ga cell was opened (Figure C.1b).

A substrate manipulator with x, y, and z positioning would have made the transfer system less complex. The initial problems that we had with perfectly lining up the loadlock system would have been avoided. A moveable manipulator would
Figure C.1 Ga flux recorded by change in chamber pressure. Run identifiers are on the x-axis. (a) The chamber pressure was recorded 1 minute after the Ga shutter was opened. (b) The chamber pressure was recorded 3 minutes after the Ga shutter was opened.
have eliminated the need for lateral movement of the sample transfer cup. One
strange aspect of the design of the transfer system was that the transfer cup and lateral
movement section of the transfer arm could not be installed when the loadlock
chamber was attached to the main growth chamber. The transfer between the parking
and heating stages inside the loadlock had to be tested before the chamber was
installed. Screws that attach these pieces are not easily accessible from the loadlock
door. The transfer works fine at the present time as long as the tabs on the wafer
holding rings are kept clean. If material deposits on the tabs, they can be filed with a
clean jewelers file and then cleaned to remove small particles. Adjusting the transfer
arm may be necessary in the future.

We found that buying parts in the United States was cost effective even when
the items were slightly more expensive to purchase initially. One of the effusion cells
came from France, and it was slightly damaged in transit. Fortunately we could repair
it easily. The shipping cost was excessive, however, when we ordered a replacement
thermocouple. When we started having the bearing problems with the manipulator,
the company suggested that we return it to them - in Finland - for repairs. The down-
time and shipping cost led us to perform the repairs ourselves. Even small items such
as the bearings were expensive to ship.

C.2 Future Work

The following is a list of possible system enhancements.

1. Replace the germanium crucible with a new aluminum crucible. Having
   aluminum as an available source would allow the AlN buffers to be grown in
   the system right before the GaN nanowire growth. There would be no need to
break vacuum and risk contaminating the sample. Growing AlN in the new system will of course require some experimenting to find the optimal parameters for a smooth thin film.

2. Purchase dedicated cell for silicon. As mentioned in Chapter 3, the silicon cell was borrowed from another system. It does not have water cooling or an integrated shutter. In fact, no shutter has been used with the Si cell since its installation. The Si cell needs a shutter to prevent Si from coating the chamber during outgassing. It is necessary for having better control over nanowire structures such as axial p-n junctions or superlattices. The Si cell also needs water cooling so that we can be sure the local heating is kept to a minimum.

3. Establish cleaning procedures for wafer-holding rings. Todd Harvey did attempt to clean the rings, but GaN is resistant to etching. The rings may be the source of carbon that shows up in SiC bumps on the surface of Si wafers that are outgassed in the chamber. This issue was noticed because atomic force microscope (AFM) images of Ge deposited on Si(100) wafers showed bumpy films. RGA scans taken on 12/8/2008 revealed that the presence of hydrogen and carbon monoxide in the system was much greater when a wafer was outgassed than when the manipulator was heated without a wafer present. The rings could be absorbing carbon dioxide and hydrocarbons from the atmosphere, or they may become contaminated during handling.

4. Replace the remaining bearings that originally came with the manipulator. The rotation of the manipulator is currently functional, but it is noisy, indicating that the bearings are not functioning optimally.
5. Develop software to edit and read recipes. This will be needed if more complicated structures, such as superlattices, will be grown in the system. Recipe building software was started in Igor and is almost complete.

6. Purchase heating blankets for baking out the chamber. Wrapping the chamber with blankets would be much faster than the foil and heater tapes that are currently used.

7. Change the RGA collar. It could be removed or replaced with something that has larger holes so that the flux of all of the sources could be measured.

8. Install a reflection high-energy electron diffraction system (RHEED)

9. Replace the current chamber with a bell jar to increase the elemental sources that are available. The current chamber design only allows room for four different elemental sources. Five sources will fit if the gas injector for ammonia is also removed and one of the sources (Si for example) is mounted upside down. Space will eventually be needed to install an indium cell. The new chamber should have ports for the sources that are oriented closer to perpendicular to the substrate than the ports on the current chamber, which are at a 45° angle to the substrate. These ports have 4.5 inch flanges, but they should also have the wide tubing to accommodate dual-dopant effusion cells. A new chamber would also free up the current chamber for the use of organometallics again. The current chamber could possibly be used for atomic layer deposition (ALD) as well. Another option would be to add a cryopump or get another pump with increased throughput to remove organometallics from the chamber more effectively. If the two-chamber option is used, a way
to transfer a wafer between the chambers without breaking vacuum would also be a valuable enhancement. ALD or OM grown films could be layered on top of materials grown in the MBE type chamber without exposing them to the damaging effects of air and condensation.