Synthesis, Properties and Applications of GaN Nanowires

A dissertation presented

by

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to

The Department of Physics

In partial fulfillment of the requirements

for the Degree of

Doctor of Philosophy

in the field of

Physics

Northeastern University

Boston, Massachusetts

April 24, 2013
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ABSTRACT OF DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the College of Science of
Northeastern University
April 24, 2013
Abstract

This main focus of the work is on controlling the growth morphology in GaN and related nanowires. Two key results are presented: (1) demonstration of GaN nanowire growth in a newly discovered ‘serrated’ morphology and (2) demonstration of Mn-doped, GaMnN nanowires by a new method. In (1) it is shown that simply by controlling the type of catalyst, size of the catalyst and the initial ratio of the precursor materials, GaN nanowire growth in a highly periodic serrated morphology can be obtained. Unlike regular non-serrated wires which grow in the non-polar [10\(\bar{1}0\)] direction, growth of the serrated wires is in the polar [0001] direction. The serrated faces are oriented in the semi-polar directions. Wires with serrated faces in both [10\(\bar{1}1\)] and [11\(\bar{2}2\)] semi-polar directions have been obtained. In (2) it has been shown that by using Au-Mn alloy catalyst method, GaMnN wire growth can be obtained. This is a significant result since this may be the first demonstration wherein Mn doping is achieved by introducing Mn as a catalyst rather than as a source material. The growth direction of these GaMnN wires is in the non-polar direction as in the case of non-serrated wires. Interestingly, unlike the non-serrated GaN wires, in this case the growth direction is [11\(\bar{2}0\)]. A second focus of the work is on the investigation of transport properties of serrated GaN nanowires and comparison with the non-serrated GaN nanowires. For the serrated nanowires our results indicate significant influence of surface effects on the electronic transport resulting in much higher electrical resistivity. A third focus of the work is on the investigation of magnetic properties of the GaMnN nanowires which indicates potential weak ferromagnetic behavior. This is consistent with low hole concentration and low Mn doping concentration (~0.5%) in these nanowires.
Acknowledgement

I would like to express my deepest gratitude to the following people who have helped, supported and inspired me and made important contributions to the work described in this dissertation.

First of all, I would like to thank my advisor Prof. Latika Menon. The luckiest thing for me in my study and research over these years is meeting my advisor. She is a visionary in nanotechnology research and also in life. Her guidance, support and mentoring during the years has really been very important for me. She not only cares deeply about research, but also about individual development. She has very positive attitudes towards work and life and inspires me a lot both in work and spiritually. She has always allowed me to be independent, creative in work and inspires me to see the big picture. She has been a witness to my growth both in research and in life over the years.

I would like to thank Prof. Moneesh Upmanyu for help with the theoretical modeling and analysis of serrated GaN nanowire growth mechanism.

I would like to thank Prof. Swastik Kar for serving on my thesis committee and for supervising my research for two semesters and supporting me extensively. He has always been willing to discuss my work with me whenever I needed it, especially concerning Raman Spectroscopy analysis.

I would like to thank Prof. Donald Heiman for being a part of my thesis committee. I am also grateful for his help in SQUID measurements and analysis of magnetic properties.

I would like to thank Prof. Adrian Feiguin for being on my thesis committee at short notice and also for his valuable feedback during my presentation in Journal Club in Physics Department.
I would like to thank Dr. Eugen Panaitescu, who is always willing to help whenever I have questions concerning research or analysis and I am grateful for his valuable input concerning my presentations.

I would like to thank Dr. Mohamed AbdElmoula, who introduced me to the CVD systems and trained me in the operation of CVD system and provided me help and support whenever I needed it.

I would like to thank Dr. Xiaohong An for her wonderful support and for her help with Raman measurements.

I would like to thank Fangze Liu. He is smart and brilliant at hands-on work and trouble shooting. I am grateful for his help with e-beam lithography training and for his help and guidance in solving research-related problems.

I would like to thank Pegah M. Hosseinpour, my colleague for being a great listener. I am grateful for being able to share my thoughts and feelings with her and for her wonderful support always.

I would like to thank Michelle Jamer for her help with magnetic measurements in SQUID.

I would like to thank Ji Hao who has been a great help with Janis Probe Station for transport measurements.

I would like to thank all staff in Kostas Research Center at Northeastern University, especially Richard Devito, Scott McNamara and David McKee for their help and trainings.

I would like to thank all staff in Physics Department at Northeastern University who give me support and help towards my completion of degree.

I would like to thank Dr. Dezhi Wang, manager of TEM at Boston College for training me on the TEM and help with sample tilting. His suggestions, effort and support have been very important for my work.
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Chapter 1

Introduction

1.1 Motivation

Gallium nitride (GaN) is an important binary direct bandgap III-V semiconductor. With a large direct energy bandgap of 3.4eV, it is a potential candidate for short wavelength emitters (LEDs and diodes lasers), high-power/high-temperature electronic devices and high-speed field effect transistors [1]. GaN has other potential advantages in device applications, such as high thermal conductivity for improved heat dissipation in devices and good thermal stability for high temperature and high power electronics. In the stable state, GaN exhibits a hexagonal wurtzite crystal structure. Because of the non-centrosymmetric structure and significant ionic chemical bonding of the wurtzite structure, they are strongly piezoelectric and exhibit spontaneous polarization [2][3]. Its sensitivity to ionizing radiation is low, making it suitable for solar cell arrays for satellites.

In thin film GaN, many of these advantages have been difficult to realize in device applications mainly due to challenges concerning defect density, strain, threading dislocations and stacking faults [4][5]. In contrast, in nanowire structures which are typically grown by using vapor-liquid-solid (VLS) growth mechanism, the nanowires are single crystal in nature with almost no strain or threading dislocations. Also, in contrast with expensive thin film deposition techniques such as molecular beam epitaxy (MBE) which are used to grow epitaxial GaN, nanowire growth based on VLS growth mechnism is relatively simple and inexpensive. Indeed, as a result of the relative simplicity and ease of synthesis, extensive work is reported in literature on the VLS growth of GaN nanowires [6]-[11]. In spite of many these advantages that nanowires present, GaN nanowire technology has so far not been fully
utilized in advanced nanoscale devices.

For device applications, it is important to have a better understanding of the growth mechanism. For applications in LEDs and solar cells, controlling the material composition along the radius or along the length of the nanowire can result in p-doped/n-doped junctions perfect for radial or longitudinal p-n junction diodes or solar cells [12]. For applications in solar cells, controlling the morphology to enhance the effective surface area is a desirable feature since this can result in increased light absorption. While the one-dimensional nanowire morphology naturally presents enhanced effective surface area spanning the entire cylindrical surface, this may be further enhanced by modulating the diameter along the length of the wire. Enhancement in solar absorptivity may also be realized by controlling the growth mode so that the wires are perfectly aligned in the vertical direction (with respect to substrate resulting in a photonic band gap structure with increased solar absorption over specific wavelength regimes). By controlling the nanowire parameters namely diameter, spacing, etc., the absorption regime may be tuned to the visible region. Diameter modulation can lead to additional benefits such as reduced reflections from the surface thus also enhancing the absorption [13]. The ability to control alignment of the nanowires, particularly large-scale assembly of nanowires horizontally aligned with the substrate, is highly desirable since such morphology is directly compatible with MEMS processing and device assembly. Controlling the crystal structure to produce GaN in cubic structure may be potentially significant due to superior optical and electrical properties such as higher electrical mobility, absence of spontaneous and piezoelectric polarization due to the cubic symmetry and high optical gain [14]-[16]. Finally, the polarity or growth direction of the nanowires will play a significant role in controlling the electrical properties due to polarization effects. So a detailed understanding as to how the growth conditions translate to good control over the composition and morphology of the nanowires and how in turn this influences optical and electrical
properties is important.

### 1.2 Overview of thesis

The objective of this thesis is to investigate the growth of GaN and related nanowires, their properties and applications out of them. A new “serrated” morphology in GaN nanowires has been discovered in our work from where controlling of growth of GaN and related nanowires has been investigated, such as controlling of growth morphologies, growth direction and enhancing production of nanowires. A new “Au-Mn alloy catalyst” method has also been discovered in our work for Mn doping in GaN where may be the first time demonstrating Mn doping by introducing Mn as a metal catalyst rather than as a reaction source. Their structural, transport, magnetic properties, etc. have also been investigated for potential applications purposes.

Chapter 1 describes the motivations and overview of this thesis.

Chapter 2 describes Chemical Vapor Deposition (CVD) method by which synthesis of GaN and Mn-doped GaN nanowires has been carried out. Detailed descriptions are given in vapor-liquid-solid growth mechanism, introduction of chemical vapor deposition system, procedures in CVD system of synthesis of GaN nanowires and growth conditions in CVD process. Results of “serrated” GaN nanowires (in contrast with regular non-serrated morphology) have also been illustrated, such as measurements of morphological parameters and optimal growth conditions. Comparison of serrated and non-serrated GaN nanowires is carried out as well and a hypothesis of serrated nanowire growth mechanism has also been demonstrated. Finally, the growth conditions have been optimized for increased production of the serrated nanowires and the optimal window of growth conditions has also been determined.

Chapter 3 describes structural characterization and comparison of serrated and
non-serrated GaN nanowires. Results of X-ray diffraction, Raman Spectroscopy, Transmission Electron Microscopy and Electron Backscatter Diffraction on the two types of nanowires have been demonstrated and discussed. It enables a better understanding of crystal structure, growth direction, crystal orientations, etc. of nanowires in different morphologies. This information might shed further light on their properties.

Chapter 4 describes a newly discovered “Au-Mn alloy catalyst” method for synthesis of Mn-doped GaN nanowires. Based on VLS growth mechanism with Au catalyst, it introduces Mn as a metallic catalyst instead of a solid reaction source. This enables a more flexible control of Mn/Au ratio and enhances Mn solubility in Au. Description of growth conditions in CVD process is given and results of Mn concentration has been demonstrated. Structural characterization of Mn-doped GaN nanowires has also been carried out by using Transmission Electron Microscopy and X-ray diffraction.

Chapter 5 describes magnetic property characterization of Mn-doped GaN nanowires using the SQUID magnetometer for applied magnetic fields in the range of xx-xxOe and for temperatures in the range of 4-300K.

Chapter 6 describes investigation of transport properties of GaN nanowires in the two morphologies and Mn-doped GaN nanowires. Fabrication procedures and trouble shooting of single nanowire transport measurement device have been illustrated in detail. Transport measurement results have been demonstrated separately for serrated and non-serrated GaN nanowires and for GaMnN nanowires as well.

Chapter 7 describes a summary of this thesis and outline of future work.

Experiments of device fabrication and X-ray diffraction characterization have mainly been carried out in Kostas Research Center at Northeastern University. Besides these, Raman Spectroscopy has been carried out in Prof. Swastik Kar’s laboratory and Transmission Electron Microscopy has been carried out at Boston College. Electron Backscatter Diffraction
results have been obtained by Albert V Davydov at National Institute of Standards and Technology (NIST). Some transport measurements reported in the thesis have been carried out by Adam Friedman at US Naval Research Laboratory (NRL).
Chapter 2

Synthesis of GaN nanowires by means of Chemical Vapor Deposition

2.1 Introduction

There are several reports in literature that describe the growth of GaN in many different forms, such as thin films, nanowires, etc. For example, molecular beam epitaxy has been routinely used to grow GaN thin films [17]. Methods such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD) have been used to grow single crystal GaN nanowires [18]-[21]. GaN nanowires can have non-polar or polar growth direction which are reported to have a non-polar growth direction [18]-[20] with triangular cross-section; and also reported to have a polar growth direction [19][21] with hexagonal cross-section. It is also reported GaN nanorods with polar growth direction by means of molecular beam epitaxy [22].

Among these methods of nanowire or thin film synthesis, Chemical Vapor Deposition (CVD) is known to be one of the most effective. Chemical Vapor Deposition has been used to deposit a variety of materials in many forms, such as single-crystalline, poly-crystalline, amorphous and epitaxial. In our work both GaN and Mn-doped GaN nanowires were synthesized by means of CVD.

As Ga and N reaction sources for GaN synthesis, there are several options are reported: Ga/Ga$_2$O$_3$ mixtures with ammonia [7]; direct reaction of Ga with ammonia [23]; Trimethylgallium (TMG) and ammonia [31].
In this chapter, we will show the demonstration of a newly discovered “serrated” morphology in GaN nanowires. They co-exist with regular nanowires. In contrast with regular non-serrated GaN nanowires which have been widely reported in literatures, diameter of serrated nanowires is changing with periodical serrations along the length of nanowire. Previously, epitaxially grown versatile GaN nanowire networks which form hexagonal symmetry have been discovered in our laboratory [32] (as shown in Figure 1). The nanowires bend along certain angles forming specific symmetries along the substrate surface. The nanowire networks were prepared with Ni catalyst dots on c-plane sapphire substrates by using chemical vapor deposition method. The diameters of epitaxial nanowires were very small (typically less than 50nm). Photoluminescence results indicated a possible cubic zinc blende crystal structure and transport measurements demonstrated excellent current-carrying capacity.

In this thesis, we go one step forward and try to understand what happens when the catalyst size is large and whether it is possible to stabilize other forms of GaN with new morphologies and symmetries. Before describing the results, a brief introduction is provided into the chemical vapor deposition system and the nanowire synthesis method.
Figure 1 - (a) Typical SEM image showing epitaxially grown versatile GaN nanowire networks forming hexagonal symmetry. (b) High resolution images showing the hexagonal symmetry and the characteristic “bends” where the wire growth changes direction. Taken from work of Zhen Wu, et al. [32].
2.2 Chemical Vapor Deposition Method

2.2.1 Vapor-Liquid-Solid growth mechanism

CVD nanowire growth is based on vapor-liquid-solid (VLS) growth mechanism. In VLS mechanism [23], the reaction speed is accelerated by introducing a catalytic liquid alloy phase which is much faster than VS growth mechanism [25][26]. The liquid phase acts as a preferential adsorption area for the incoming vapor species, until a supersaturation condition is reached. Then the liquid phase supersaturation drives the condensation of species at the liquid-substrate interface at a rate higher than the growth rate on the free substrate surface [27]. Many metals can be candidates for this type of catalyst for nanowire growth, such as Au, Fe, Ni, Co, In, etc. [21][28][29][30]. The liquid metal catalyst rapidly absorbs the vapor of reaction sources and they form an alloy phase. Thus a crystal (solid) is formed at the liquid-solid interface which continues to grow resulting in the formation of nanowires. Several parameters such as the growth temperature, pressure, ratio of precursor materials, size and type of the catalyst play a significant role in determining the growth morphology, growth direction and alignment of the nanowires.

2.2.2 Chemical Vapor Deposition system

CVD system typically contains a furnace as heating source with temperature controller, horizontal quartz tube inside the furnace as growth chamber where the reaction sources and substrates are placed, several gas cylinders which carry different compressed air as reaction gases and a mechanical pump which maintains low pressure inside the quartz tube. Mass Flow Controllers (MFC) are connected between gas cylinders and horizontal quartz tube and they monitor the gas flow rates in units of standard cubic centimeter per minute (sccm). Mass Flow Controller can be calibrated for different gases. Needle valve is connected between
horizontal quartz tube and mechanical pump, controlling the pressure inside the tube. Figure 2 shows schematic view of Chemical Vapor Deposition in our laboratory [30]. Figure 3 shows schematic view of horizontal quartz tube for synthesis of GaN nanowires.

2.2.3 Procedures in Chemical Vapor Deposition

2.2.3.1 Prepare Chemical Vapor Deposition system

Synthesis of GaN nanowires is processed in a horizontal quartz tube inside CVD furnace.
Before starting preheating and synthesis, the system is sealed by connecting gas cylinders and horizontal quartz tube and connecting quartz tube and mechanical pump. All gases are turned off and the system is pumped down. Ideally, the pressure inside the quartz tube reaches around 50mtorr in about 2 hours. Following this, the pumping is stopped and Ar gas is allowed to flow into quartz tube until pressure inside quartz tube reaches 760torr. Ar flow is turned off and the quartz tube is opened.

2.2.3.2 Deposit metal catalysts on substrates

Prior to CVD synthesis, catalyst metals are deposited on Si/sapphire substrates by using thermal evaporation or E-beam evaporation. We mainly used Au (in some cases Ni) as metal catalysts for GaN nanowire growth. The substrate is typically Si (100) or sapphire (c-plane).

Substrates were sonicated for 10 minutes in acetone for cleaning which was followed by IPA spray for several seconds for cleaning acetone. Then the clean substrates are placed inside thermal evaporator or the e-beam evaporator. Deposition is carried out for about 2 mins until a thin layer of metal has deposited on the substrate. Typically, e-beam evaporation has been found to provide better control over the deposition thickness. In order to maintain uniformity of the samples through different runs, we typically deposited Au/Ni on an entire 3-inch clean Si wafer. After deposition we used dicing saw to dice the 3-inch wafer (with metals on it) into small pieces (typically 1cm by 1cm) for use in different runs.

2.2.3.3 Synthesis in Chemical Vapor Deposition

We chose powder of gallium oxide as reaction source for Ga and gas of ammonia as reaction source of N. The powder of Ga$_2$O$_3$ that we used has purity of 99.999%. Gas of H$_2$ helps decompose Ga$_2$O$_3$. Gas of Ar was used during preheating and cooling processes.
Powder of Ga$_2$O$_3$ (placed in white alumina crucible) and metal-catalyst-patterned Si/sapphire substrate (placed in white alumina crucible) are placed in the center of the horizontal quartz tube, with 2cm separation. Ga$_2$O$_3$ powder is at upstream of gas flow and substrate is at downstream of gas flow.

The CVD system is sealed and pumped for 15 minutes for purging. Then Ar is allowed to flow into the quartz tube. Heating in furnace is turned on when pressure reaches desired value. When temperature inside the furnace reaches desired value, the Ar flow is turned off and H$_2$ and NH$_3$ flow is tuned on through two different tubes converging finally into quartz tube.

When the growth is completed, the furnace heating is turned off, H$_2$ and NH$_3$ flow is turned off and Ar flow is turned on. The system is then allowed to cool for several hours.

During all the processes, the needle valve is adjusted to maintain stable pressure in quartz tube within very small fluctuations.

When the temperature in furnace reaches room temperature and the pressure reaches 760torrs, the needle valve is closed and the substrate is removed.

The chemical reactions during growth of GaN nanowires are as follows [30]:

\[
\text{Ga}_2\text{O}_3 \text{(s)} + 2 \text{H}_2 \text{(g)} \rightarrow \text{Ga}_2\text{O} \text{(g)} + 2 \text{H}_2\text{O} \text{(g)}
\]

\[
\text{Ga}_2\text{O} \text{(g)} + 2\text{NH}_3 \text{(g)} \rightarrow 2\text{GaN} + \text{H}_2\text{O} \text{(g)} + 2\text{H}_2 \text{(g)}
\]

Ga$_2$O$_3$ powder and gas of NH$_3$ were used as reaction sources. Gas of H$_2$ was introduced to help decomposition of reaction sources and increase the reaction speed.

### 2.3 Growth conditions

Mass of Ga$_2$O$_3$ powder was typically in the range of 0.5grams to 1.2grams. Thickness of Au on Si/sapphire substrates was typically in the range of 5nm to 13nm.

During the reaction, growth temperature inside the tube is typically maintained at 960°C [30]. GaN nanowires occur at growth temperature of 800-1000°C [31]. Gas flow rate of H$_2$
and NH$_3$ are at 50sccm and 30sccm separately. During the preheating (before reaction) and cooling (after reaction) processes, gas flow rate of Ar is at 70sccm. Pressure in the horizontal quartz tube is maintained at 100torrs within a small fluctuation all the time. Typical growth time lasts for 1 hour. Sometimes, we increased growth time to 2 hours or even 3 hours to obtain longer GaN nanowires.

All the factors of growth conditions for nanowire synthesis in CVD, namely the mass of Ga$_2$O$_3$ powder, the thickness of metal catalyst, growth temperature, pressure inside quartz tube, flow rates of all gases and growth time, are acceptable within a range. They could all play significant roles in affecting the sample growth.

NH$_3$ Mass Flow Controller was used for monitoring NH$_3$ flow rate. However, Ar Mass Flow Controller was used for monitoring both Ar and H$_2$ (they were not flowing at the same time). Display value of gas flow rate on Ar Mass Flow Controller is calibrated for Ar. Therefore, conversion is needed for actual H$_2$ flow rate based on displaying value of flow rate. K factor (relative to N$_2$) is 1.4573 for Argon gas and is 1.0106 for H$_2$ gas (given in mass flow controller manual). The displaying value of H$_2$ flow rate (using Ar mass flow controller) was set to 70sccm. Thus, actual flow rate of H$_2$ is 50sccm:

\[
\text{Actual flow rate of } H_2 = \text{Displaying flow rate} \times \frac{1.0106}{1.4573} = 49 \text{sccm} \sim 50 \text{sccm}
\]

### 2.4 Two different morphologies in GaN nanowires

In literature, growth of regular GaN nanowires/nanorods (with either non-polar or polar growth direction) has been reported [18][19][20][22]. Regular nanowire refers to wires in which the surface along the length of nanowire is smooth. To distinguish it from serrated GaN nanowires (see Chapter 2.4.2) which has been newly discovered by our laboratory, we refer to the regular wires as non-serrated GaN.
2.4.1 Non-serrated (regular) GaN nanowires

Figure 4 is a typical Scanning Electron Microscopy (SEM) view of non-serrated GaN nanowires grown using Ni catalyst on c-plane sapphire substrate. Figure 5 shows non-serrated GaN nanowires with Au catalyst grown on Si (100) substrate. The wires are vertically aligned. The diameter of each non-serrated nanowire is determined by the Au/Ni catalyst size during the growth. Generally, thinner non-serrated nanowires grow faster and longer. In some cases, the metal catalyst is not visible at the end of the nanowire which could be due to metal catalyst consumption during the growth process. Figure 6 shows one case of a single non-serrated GaN nanowire with “needle” shape at the end.

Figure 4 - Non-serrated GaN nanowires with Ni catalyst grown on c-plane sapphire substrate
Figure 5 - Non-serrated GaN nanowires with Au catalyst grown on Si (100) substrate

Figure 6 - A single non-serrated GaN nanowire with “needle” shape at the end

Side view of vertically grown GaN nanowires (Figure 7) shows the sample has a thickness of 6microns.
For a better observation of morphology of individual nanowires, we released nanowires on grids or clean substrates. For this, the original GaN sample with Si substrate was placed in solution of IPA followed by 5 seconds sonication. The nanowires were easily detached from Si substrate into IPA solution. We dropped one droplet of IPA solution (with GaN nanowires in it) onto clean substrates or grids and let it dry; repeated the step until several droplets were applied so the density of nanowires on substrates or grids was high enough for location of sufficient nanowires under the SEM. Sonication time should not be too long since the nanowires will be broken into very short pieces in this case. Typical sonication time is in the range of 5-10 seconds.

Figure 8 and Figure 9 are typical SEM images showing general views of single non-serrated GaN nanowires (released onto grids) with Au catalyst at the end.
For investigation of detailed morphology of nanowires, Figure 10 is SEM image of a single non-serrated GaN nanowire with triangular cross-section. Figure 11 is SEM image of two single non-serrated GaN nanowires with faceted Au catalyst and with triangular
cross-section. The shape of cross-section is related to growth direction of wurtzite GaN nanowires which will be illustrated in details in Chapter 3.4.

Figure 10 - View of a single non-serrated GaN nanowire with triangular cross-section

Figure 11 - Non-serrated GaN nanowires with faceted Au catalyst showing triangular cross-section

This is similar to what is reported by Tevye Kuykendall et al. [31] as shown in Figure 12. Large-scale GaN nanowires were grown on Ni-coated c-plane sapphire substrates where
Trimethylgallium (TMG) and ammonia source materials were used as Ga and N precursors. Electron diffraction pattern was taken along the [001] zone axis. GaN nanowire had wurtzite structure and a triangular cross-section.

Figure 12 – FESEM and TEM images of GaN nanowires grown on a nickel-coated c-plane sapphire substrate, taken from work of Tevye Kuykendall et al. [31].
2.4.2 Serrated GaN nanowires

In our laboratory, we have discovered “serrated” GaN nanowires in large quantities which have very different morphology from regular non-serrated GaN nanowires. In current work, they have been demonstrated only with Au catalyst and only on Si (100) substrates.

Figure 13 shows SEM image of a large quantity (about 15%) of serrated GaN nanowires which coexist with non-serrated GaN nanowires. These serrated nanowires have regular periodical serrations along the length of nanowire with hexagonal cross-section. The density of serrated nanowires (in Figure 13) within focusing range is about 0.4/μm². Serrated nanowires were scattered all over the sample uniformly.

Figure 13 - A large quantity (~15%) of serrated GaN nanowires which coexist with non-serrated GaN nanowires

Figure 14 is an SEM image of a single serrated GaN nanowire (diameter is about 130nm) with faceted Au catalyst at the end. Figure 15 shows hexagonal cross-section of serrated nanowire.
Figure 14 - A single serrated GaN nanowire with faceted Au catalyst at the end

Figure 15 - A single serrated GaN nanowire showing hexagonal cross-section

In an attempt to understand the growth mechanism, we carried out an investigation into the growth as a function of time of deposition. First, we investigate the characteristics of the
catalyst. Au deposited on substrates (used as catalysts during CVD process) formed Au dots when deposition is less. Figure 16 illustrates this case showing Au dots with diameters mainly less than 30nm (preparing by using thermal evaporator). As deposition thickness of Au thin film becomes larger they start to form structures of islands. Figure 17 shows an SEM image of Au thin film of island structures by using thermal evaporator. Deposition time for this sample was 90 seconds (thickness is not known). Since the thickness of Au deposition is difficult to control or calibrate in the thermal evaporator, E-beam evaporation method was used for a second set of samples. Figure 18 shows an SEM image of 7nm thick Au film of island structures by using e-beam evaporation. Au thin film formed dots as catalysts during annealing where nanowires can be synthesized out of it.

Figure 16 - Small Au dots (with diameters mainly less than 30nm) by thermal evaporation
Figure 17 - Au film deposition by thermal evaporation forming islands

Figure 18 - 7nm thick Au film by e-beam evaporation forming islands

Figure 19 shows SEM image of deposition Au under annealing in Argon flow of 70sccm for 10 minutes at 960°C in CVD. This control experiment was carried out to obtain a better
understanding of what happens to the Au under actual experimental conditions. After cooling, it may be noted that the Au forms beautifully faceted catalysts (as shown in Figure 19 and Figure 20). The two samples were under different deposition conditions of Au thin film. The thickness of Au in Figure 19 (with catalyst diameters of 100-600nm) was much higher than that in Figure 20 (with catalyst diameters less than 180nm).

![Figure 19 – Faceted Au catalysts after 10 minutes annealing in Ar flow in CVD, with diameters of 100-600nm.](image1)

![Figure 20 - Faceted Au catalysts after 10 minutes annealing in Ar flow in CVD with diameters less than 180nm.](image2)
In the next set of experiments we were interested in understanding early stage growth in GaN. So we carried out the CVD growth of GaN for very short intervals of time. Figure 21 shows an SEM image of the very early stage of GaN synthesized from Au catalysts based on VLS mechanism. The Au dots became faceted after cooling (this may not be the case in the liquid state at the high temperature). Figure 22 is an SEM image showing the early stage of GaN nanowire synthesis: the Au catalyst can be seen to have moved along the substrate surface catching up Au particles along the way and also forming GaN nanowires along the surface; therefore Au appears to getting accumulated and becoming larger in size. For large catalysts, the net contact forces will become large enough to allow for vertical growth.

Figure 21 – The very early stage of GaN synthesis from Au catalysts based on VLS growth mechanism
For better observation of morphology of serrated GaN nanowires, we released the nanowires onto Si substrate with a layer of Au on top. Figure 23 is a Back-scattered Electron (BSE) image of a single serrated GaN nanowire. The Au catalyst surface is faceted with a small amount of GaN on it. The diameter of Au catalyst is about 230nm. Back-scattered Electron image can distinguish different elements by contrast. So Au catalyst is brighter and GaN is darker. Figure 24 is a zoom-out view of a single serrated nanowire. It has a length of about 5-6μm with more than 30 serrations. Figure 25 shows a serrated nanowire with disturbance in growth. In the middle it does not form perfect serrations and tries to grow in a semi-polar direction rather than the normal growth direction. The disturbance occurs for several serrations and then the nanowire switches back to normal growth. Local growth variations could result in this phenomenon.
Figure 23 - Back-scattered Electron (BSE) image of a single serrated GaN nanowire with faceted Au catalyst

Figure 24 - A single serrated nanowire in zoom-out view
In an extreme case, one serrated nanowire has an outer diameter of 1.2 µm (in Figure 26) which is extremely large. It turns out to become “micronwire”. It has a length of 12 µm.
By demonstration of serrated GaN nanowires, we have realized one of the approaches of controlling diameter, spacing, side face angle and morphology of semiconductor nanowires. Semiconductor nanowires have many advantages compared with bulk materials. And the ability to control structure, size and morphology etc. of nanowires enables reaching their full potentials in advanced applications.

Similar in-situ modulation of the diameter, length, and composition of individual segments within (In,Ga)N nanowires has been realized in Sung Keun Lim et al.’s work [33] (shown in top Figure 27) by tuning the seed particle supersaturation and size via the supply of III and V sources during the growth. They have also demonstrated the synthesis of axial InN/InGaN nanowire heterojunctions in the nonpolar m-direction (bottom in Figure 27). What is important to note is that the serrated wires reported in this thesis is distinct from the report by Lim et al. In our work only the initial growth parameters, namely the type of catalyst (namely Au), size of the catalyst and the ratio of Ga:N needs to be controlled. No further control over the growth conditions is required during the growth process. Also, the periodicity that is observed in our wires is more perfect in comparison with the work of Lim et al. As shown in the Figure 27, their wires appear to wavy and less regular in comparison to our work.
Figure 27 – Modulation in situ the diameter, length, and composition of individual segments within (In,Ga)N nanowires; synthesis of axial InN/InGaN nanowire heterojunctions in non-polar m-direction. Taken from work of Sung Keun Lim et al. [33]

2.5 Measurement of parameters of serrated GaN nanowires

To investigate the morphology and parameters of serrated GaN nanowires, we first define some terms such as outer diameter of the serrated, inner diameter of the serration, period of the serration, Au diameter and angle of $2\alpha$ made by two side facets of one serration (illustrated in Figure 28).
Measurements on many individual serrated nanowires were carried out to investigate morphology (please see Table 1).

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<td>170</td>
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<td>0.965909</td>
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</table>

**Table 1 - Measurements of parameters of individual serrated GaN nanowires**

Based on these measurements, we have found that:

1. For different nanowires, the outer diameter ranges from 100nm to 400nm with an average of about 200nm. (For comparison, the diameter of non-serrated GaN nanowires is mainly from 50nm to 100nm.) Histogram of outer diameter of many serrated nanowires is shown (please see Figure 29).
For each individual nanowire, the outer diameter of the serrations is almost the same as the Au catalyst diameter. The measured ratio of Au diameter to outer diameter is from 0.83 to 1.06 with the average of 0.98 and standard deviation of 0.06 (please see the histogram of ratio of Au diameter to outer diameter in Figure 30).

Figure 29 - Histogram of outer diameter of many serrated nanowires

Figure 30 - Histogram of ratio of Au diameter to outer diameter of many serrated nanowires
3. The ratio of outer diameter to inner diameter for different serrated nanowires varies from 1.44 to 1.98 with an average of 1.58 and standard deviation of 0.13 (please see the histogram of ratio of outer diameter to inner diameter in Figure 31). Therefore, this ratio varies in a small range indicating that serrations of nanowires have a stable and constant structure with certain ratios of outer diameter/inner diameter/spacing.

![Histogram of outer diameter to inner diameter of many serrated nanowires](image)

**Figure 31 - Histogram of outer diameter to inner diameter of many serrated nanowires**

4. For more accurate measurements of angle of serrations $2\alpha$, nanowires were released on Au layer on Si substrates. A thin layer of Au is to help to reduce charging problem when observing under SEM. Angle of $2\alpha$ has been measured at different serrations on same wire and also at five individual wires (please see Table 2). Based on these measurements, the average angle $2\alpha$ ranges from 117.1° to 122.5° with an average of 119.9° and standard deviation of 2.57°. The angle is about 120° which indicates the angle between crystal orientation of side facets of serration and the growth direction is about 60°. We can
determine the crystal orientation of side facets based on this angle and growth direction (detailed discussion is in Chapter 3.4).

<table>
<thead>
<tr>
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<th>Average of angle $2\alpha$ (°)</th>
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<tbody>
<tr>
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<tr>
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<td>122.2</td>
</tr>
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<td>122.5</td>
</tr>
<tr>
<td>5th nanowire</td>
<td>117.1</td>
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</table>

Table 2 – Measurements of average value of $2\alpha$ for five individual serrated nanowires

2.6 Optimal growth conditions for serrated and non-serrated GaN nanowires

By controlling the growth conditions, optimal growth conditions has been determined for serrated and non-serrated GaN nanowires. For these studies one variable at a time was varied to obtain a clear understanding of the dependence.

2.6.1 Serrated nanowires

We have demonstrated two critical growth factors for synthesis of large quantity of serrated GaN nanowires: large Au diameter and large Ga/N ratio.

1. Large Au diameter

If we compare the samples of purely non-serrated nanowires and large quantity of serrated nanowires (coexisting with non-serrated nanowires), the average outer diameter
of serrated nanowires is obviously larger than average diameter of non-serrated nanowires. In Figure 32, a) is sample of purely non-serrated nanowires and b) is partially serrated nanowires. From scale bars, diameter of non-serrated sample is about 100nm or less while outer diameter of serrated nanowires is above 200nm. Since value of outer diameter (or diameter) is determined by Au catalyst diameter, larger average Au diameter is critical for synthesis of large quantity of serrated GaN nanowires. Average Au diameter of one sample can be controlled by thickness of Au catalyst deposition during e-beam evaporation or thermal evaporation. For our samples of large quantity serrated nanowires 7-11nm thickness of Au during e-beam evaporation was carried out. Samples of 11nm thick Au catalyst could have about 15% to 20% serrated nanowires.

![Figure 32 - Comparison of nanowire diameters of purely non-serrated sample and serrated sample](image)

2. Large Ga/N ratio

For convenience, we set the flow rate of NH₃ at constant 30sccm. By varying mass of Ga₂O₃ powder placed in horizontal quartz tube, the partial pressure of Ga during reaction is also varied. Under conditions of same Au deposition thickness (11nm) and same flow
rate of NH₃, different mass of Ga₂O₃ powder (0.61g, 0.75g, 1.02g and 1.91g) were applied to investigate the change of morphology of GaN samples (please see Figure 33).

Generally, there are mostly non-serrated nanowires in samples when mass of gallium oxide is smaller than 0.5g (even if average Au diameter is large). As the mass of gallium oxide increases (0.5g<m<0.7g, moderately small), there is a transition from non-serrated nanowires to serrated nanowires (Figure 33 a), the percentage of serrated nanowires is relatively low). When the mass of gallium oxide is excess (0.7g<m<1.5g, large) there will be a large quantity of serrated nanowires (Figure 33 b) and c), percentage of serrated nanowires is up to 20%). Within this range (0.7g<m<1.5g), percentage of serrated nanowires increases as mass of gallium oxide increases. However, when too much gallium oxide (>1.5g) is used there is almost no nanowires (Figure 33 d)). The reason is that Ga/N ratio is too large in this case which excesses the limitation for synthesis of GaN (1:1) nanowires therefore GaN nanowire growth cannot be maintained.
In conclusion, for synthesis of large quantity of serrated GaN nanowires, two critical growth conditions must be satisfied at the same time: large average Au catalyst diameter (namely, large Au deposition thickness) and large Ga/N ratio (namely, excess amount of gallium oxide when ammonia flow rate is a constant).

2.6.2 Non-serrated nanowires

Generally, small Au catalyst diameter (50-100nm) results in purely non-serrated nanowires no matter how much gallium oxide is used. Or small Ga/N ratio (mass of gallium oxide smaller than 0.5g at 30sccm flow rate of ammonia) also results in purely non-serrated
nanowires even if average Au catalyst diameter is large.

2.6.3 Nanowires with Ni Catalyst

We also carried out CVD growth using Ni catalyst. The purpose was to synthesize Mn-doped GaN nanowires by using MnO₂ and Ga₂O₃. Some nanowires were grown as shown in Figure 34. However, in our case Mn doping was not confirmed by EDS although by using Ni catalyst (in contrast with [30]). Multi-factors can influence the growth and doping of nanowires therefore this is not uncommon. Namely, we obtained GaN nanowires with Ni catalyst. Growth conditions were large Ga/N ratio and large Ni catalysts. In contrast with regular, beautiful serrations of GaN wires with Au catalysts, GaN wires with Ni catalyst did not form regular serrations (although the surface of nanowires along the length was not smooth). This clearly implies that the type of catalyst is definitely important for the stabilization of the serrated morphology.

Figure 34 – GaN nanowires using Ni catalysts
2.7 Hypothesis of growth mechanism of serrated GaN nanowires

To explain how serrations of GaN nanowires are formed, the first point to note is that the type of catalyst is critical for their formation. As mentioned above, with similar experiments using large Ni catalysts, serrated nanowires do not form. This is an important observation indicating that the serrated morphology may be related to the solubility of Ga and N in Au. We note that while Ga is soluble in both Au and Ni, N has poor solubility in Au and good solubility in Ni. This is consistent with the fact that we are also using a large amount of gallium oxide in the reaction source. Hence a large amount of Ga is absorbed by the Au. However, due to the slower process of N absorption, the rate of growth of the wires will be slow. This is indeed consistent with our observation that the serrated wires are much shorter in length compared to the regular wires for the same time of deposition. Roughly, one can estimate that the rate of Ga absorption is proportional to the entire surface area of the Au catalyst (> $2\pi r^2$) and the rate of N absorption is proportional to the interface area, approximately equal to the circumference area at the interface ($\sim 2\pi r\delta r$). Thus because the rate of Ga absorption is so high the nanowire is forced to continue to grow albeit at a very slow rate which depends on how fast the N atoms can be absorbed in the Au.

The following hypothesis is made for the process of forming serrations and is illustrated in Figure 35. When the contact angle between Au liquid droplet and interface is an acute angle (Figure 35 left) it forces the nanowire to grow inward so diameter of the interface between liquid Au and solid GaN decreases. At some point the contact angle becomes an obtuse angle after it reaches right angle of 90°. Then it forces the nanowire to grow outward and the diameter of interface between liquid Au and solid GaN increases. This process is repeated during the growth thus forming serrations along the way.

In this hypothesis, large Au catalyst is critical because obtuse contact angle can only occur when the Au catalyst is large enough.
In conclusion, we have demonstrated serrated morphology in GaN nanowire in contrast with regular non-serrated nanowires. The key requirements are type of catalyst (for example Au can produce serrated morphology under specific conditions), size of the catalyst (large Au catalyst is needed) and the ratio of Ga/N must be large. Only under these conditions can we realize diameter-modulation of nanowires along the length with stable periodical serrations. The percentage of serrated nanowires is also easy to control. The higher surface-to-volume-ratio of serrated nanowires (compared with that of non-serrated nanowires) makes it a good candidate for potential applications in sensors. Diameter control along the nanowire length could be used to enhance device performance, such as improving light trapping by minimizing reflection and maximizing absorption [34] and enhancing thermoelectric conversion by increasing phonon scattering in structures with multiple diameter modulations [35].
These results pave the way for transferring similar approaches of controlling of nanowire diameter, spacing, and morphology to other semiconductor materials. Therefore, more advanced potential applications of semiconductor nanowires can be achieved. In the next step, further analysis on the crystal structure, orientation of the wire and the orientation of the serrations is needed in order to obtain a better understanding of how the growth conditions may be controlled to obtain desired morphologies in general for other semiconductor systems.
Chapter 3

Structural Characterization of GaN nanowires

3.1 Introduction

From the discussion in the previous chapter, it is clear that we have been able to successfully demonstrate growth of GaN nanowires in a new ‘serrated’ morphology. However, since the serrated and regular nanowires grow intermixed with each other, it is challenging to obtain independent structural characterization. We have attempted a few different techniques wherein the individual nanowires have been isolated and characterized, such as Transmission Electron Microscopy, Selected-area Electron Diffraction and Electron Backscatter Diffraction. Also in other techniques, such as X-ray diffraction and Raman Spectroscopy we have studied the mixed nanowires to obtain qualitative information.

For GaN material, both results of thin film and nanowires have been widely reported. GaN has two possible crystal structures, wurtzite (hexagonal) and zinc-blende (cubic). Hexagonal GaN thin films are reported to grow on (001) GaAs substrates by means of molecular beam epitaxy (MBE) [36]; and cubic GaN thin films are reported to grow on (001) or (100) GaAs substrate by MBE [36][37]. Concerning growth orientations, GaN thin films can be grown with either polar (c-plane) or non-polar (m-plane) surfaces on Si substrates by controlling deposition conditions [38]; while semi-polar GaN thin film can be grown on intentionally miscut m-plane sapphire substrates using metal organic chemical vapor deposition [39], or grown on r-plane sapphire substrates by metalorganic vapor-phase epitaxy [40]. Controlling the polarity difference of GaN film with different crystal orientations is very
appealing because the internal polarization field along the film growth direction affects the performance of GaN based devices [41][42].

For GaN nanowires, they are mainly reported to have wurtzite crystal structure [19][21]. In work of Baodan Liu, et al. [21], GaN nanowire arrays are reported to have wurtzite structure with hexagonal cross-sections (as shown in Figure 36). Figure 37 shows low magnification TEM images and high magnification TEM where indicating crystal planes in (10\Bar{1}0) and (0001) with interplanar distances of 0.28nm and 0.52nm respectively.

Figure 36 – GaN nanowire arrays with hexagonal cross-section, XRD spectrum of GaN nanowires. Taken from work of Baodan Liu, et al. [21].
Figure 37 – TEM images of individual GaN nanowire, taken from work of Baodan Liu, et al. [21].
In work of T. Kuykendall, et al. [19], results of GaN nanowires have been shown in Figure 38, with non-polar growth direction in [1\(\overline{1}\)00] (triangular cross-section) and polar growth direction in [0001] (hexagonal cross-section) respectively. Epitaxial growth of wurtzite gallium nitride was carried out by metal–organic chemical vapour deposition (MOCVD). The selection of single-crystal substrates is critical for achieving deterministic control of growth direction. Single crystal substrates of (100) \(\gamma\)-LiAlO\(_2\) and (111) MgO resulted in the growth directions of nanowires in the orthogonal [1\(\overline{1}\)00] and [0001] directions. From photoluminescence results, GaN nanowires with orthogonal growth directions have drastically different optical emission. In general, the emission for the [1\(\overline{1}\)00] nanowires is blue-shifted by \(~100\) meV from that of [0001] nanowires.

Figure 38 - GaN nanowires with growth directions in [1\(\overline{1}\)00] (a-c) and in [0001] (d-f) respectively, taken from work of T. Kuykendall, et al. [19]
GaN nanowires generally grow in polar or non-polar directions. Work of David Tsivion et al. [43] has demonstrated modulations of even more complicated growth orientations. VLS growth of aligned, millimeter-long, horizontal GaN nanowires with controlled crystallographic orientations on different planes of sapphire has been carried out (as shown in Figure 39 and Figure 40). Despite their interaction with the surface, these horizontally grown nanowires display few structural defects, exhibiting optical and electronic properties comparable to those of vertically grown nanowires.

These reports clearly indicate the importance of achieving control in nanowire synthesis. Often, one requires wires with uniform diameter, specific growth orientation and also maybe good alignment with respect to each other. Our work contributes to the overall knowledge in this area by demonstrating the importance of the type of catalyst, catalyst dimensions and other CVD parameters.
Figure 39 - Guided VLS growth of horizontal nanowires: Concept and realization. (A) Schematic view of guided VLS growth (right) versus conventional VLS growth (left). (B) Three postulated modes of guided VLS growth (schematic cross-sectional views): (a) epitaxial growth along specific lattice directions, (b) graphoepitaxial growth along L-shaped nanosteps of an annealed miscut substrate, and (c) graphoepitaxial growth along V-shaped nanogrooves of an annealed unstable low-index substrate. (C) Experimental realization of (B) for GaN nanowires on different planes of sapphire (cross-sectional TEM images): (a) C (0001), (b) annealed miscut C (0001) by 2° toward [-1100], and (c) annealed M (10-10). (D) Ultralong (>1mm), unidirectional GaN nanowires grown on R (1-102) sapphire. (E) Perfectly aligned GaN nanowires grown on annealed M-plane sapphire. Detail: magnification of the dense nanowires (highlighted in yellow) along the sapphire nanofacets. (Note that nanowires in SEM images may appear broadened as a result of static charging.) (F) Atomic force microscope (AFM) image of unidirectional GaN nanowires grown on nonannealed M-plane sapphire. Taken from work of David Tsivion et al. [43]
Figure 40 - Different morphologies of guided GaN nanowires (cross-sectional TEM images, white-line squares indicating the zoom areas to the right): (A) Perfectly matched epitaxial nanowires, exemplified by a GaN nanowire on R-plane sapphire. The nanowire and substrate fringes display a perfect 3:2 ratio with no misfit dislocations (sample slightly tilted to highlight vertical fringes). (B) Mismatched epitaxial nanowires, exemplified by a GaN nanowire on M-plane sapphire. The 16% lattice mismatch is released by the formation of misfit dislocations (indicated by white arrows) consistent with the 6:7 ratio between the nanowire and substrate lattice parameters in this orientation. (C) Graphoepitaxial nanowires along L-shaped nanosteps, exemplified by a GaN nanowire on annealed C-plane sapphire miscut 2° toward [1-100]. (D) Graphoepitaxial nanowires along V-shaped nanogrooves, exemplified by a GaN nanowire on annealed M-plane sapphire. The atomic models on the right are consistent with fringes and TEM simulations. Taken from work of David Tsivion et al. [43]
3.2 **X-ray Diffraction analysis of non-serrated and serrated GaN nanowires**

For comparison, we carried out X-ray Diffraction (XRD) for two samples: one with purely non-serrated GaN nanowires (Figure 41) and the second with about 20% serrated GaN nanowires (Figure 42, coexisting with non-serrated nanowires). XRD is a common and effective method of determining crystal structures of materials.

![X-ray Diffraction Pattern](image)

*Figure 41 - X-ray diffraction pattern of purely non-serrated GaN nanowires with reported peak positions of bulk wurtzite GaN and Au*
Figure 42 - X-ray diffraction pattern of about 20% serrated GaN nanowires (coexisting with non-serrated nanowires) with reported peak positions of bulk wurtzite GaN and Au

Bulk hexagonal wurtzite GaN XRD peak positions $\theta$ and interplanar distance $d$ are reported in Powder Diffraction File # 65-3410 (please see) where miller index is $(h k l)$ with $i=-(h+k)$. Reported lattice parameters for wurtzite GaN is $a=3.19\text{Å}$ and $c=5.19\text{Å}$.

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Table 3 - XRD data reported in Powder Diffraction File # 65-3410 for Bulk hexagonal wurtzite GaN
Diffraction peaks in both XRD patterns of GaN samples have been indexed to hexagonal wurtzite GaN and cubic Au (catalyst of nanowires). Therefore, both non-serrated and serrated GaN nanowires are pure, single-phase hexagonal wurtzite GaN based on XRD analysis.

The calculated lattice parameters from XRD peak positions are $a=3.186\text{Å}$ and $c=5.180\text{Å}$ for non-serrated GaN sample; and $a=3.187\text{Å}$ and $c=5.182\text{Å}$ for 20% serrated GaN sample. They both agree well with those reported in PDF# 65-3410. The percentage differences are both within 0.1%.

### 3.3 Raman Spectroscopy analysis of non-serrated and serrated GaN nanowires

Raman Spectroscopy is one of the effective methods for probing the phononic and electronic excitations in semiconductor nanostructures [44][45]. To compare structural properties of non-serrated and serrated GaN nanowires, Raman Spectrums of four different samples were carried out. The excitation wavelength used in Raman Spectroscopy was 488nm and grating was 1800 lines/mm. Sample1 is purely non-serrated GaN nanowires. Percentage of serrated nanowires increased from Sample2 to Sample4. Raman peak positions observed in bulk and nanowire GaN at 300K and corresponding symmetry assignments are reported in literature [46]. Our Raman Spectrums for four samples are shown in Figure 43. The spectrums presented are baseline-subtracted results. The values of peak positions were obtained by multiple or single Lorentz peak fitting in Origin software (please see Table 4).
Figure 43 - Raman Spectrums of four samples. Sample1 is purely non-serrated GaN nanowires, percentage of serrated nanowires increases from Sample2 to Sample4. The excitation wavelength is 488nm and grating is 1800 lines/mm.

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<th>E₁(TO)</th>
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<th>A₁(LO)</th>
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</table>

Table 4 – Raman peaks fitting for four GaN samples and peak positions in reference
In all the four samples, peak of 568 cm\(^{-1}\) is consistent with reported value which indicates wurtzite GaN. Therefore, both non-serrated and serrated GaN are wurtzite GaN based on Raman Spectrum analysis.

The peak positions of Si (from substrate) and 568 cm\(^{-1}\) within four samples are very consistent with reported values (520 cm\(^{-1}\) is reported for Si). However, the two smaller peaks 531 cm\(^{-1}\) and 556 cm\(^{-1}\) between them are not very consistent with reported values (the shift from reference is up to 8 cm\(^{-1}\)). The possible reasons are as follows:

1. There is no standard for baseline subtraction. Generally, the baseline (background) is increasing as x coordinate increases. Different methods of baseline subtraction could result in different peak positions when peak fitting is carried out.
2. The intensities of two peaks 531 cm\(^{-1}\) and 556 cm\(^{-1}\) are obviously lower than those of 568 cm\(^{-1}\) peak and Si peak. Therefore, they are more easily affected by noise when peak fitting is carried out.
3. Si peak (which is from substrates and cannot be eliminated in our measurements) is at 520 cm\(^{-1}\) and very close to those two peaks. Strong Si signals may easily affect peak positions fitting of the two peaks.

3.4 **Transmission Electron Microscopy analysis of non-serrated and serrated GaN nanowires**

Transmission Electron Microscopy (TEM) images can provide the information of phase composition, lattice planes and interplanar distances. Selected-area electron diffraction (SAED) can be used to identify crystal structures and examine crystal defects. Both results for non-serrated and serrated GaN nanowires have been obtained. Double tilt sample holder
in TEM needs to be used for tilting sample to align the direction perpendicular to horizontal plane of the grid to one of the possible zone axis.

Figure 44 is a high resolution TEM image of an individual non-serrated GaN nanowire. Average interplanar distances in three crystal orientations have been measured directly from TEM image which are 2.88Å, 2.90Å and 2.78Å. Hexagonal symmetry pattern of SAED indicates zone axis in [0001] and interplanar distance of 2.88Å in growth direction indicates growth direction of nanowire is in $\overline{1}0\overline{1}0$ which is non-polar growth. Orientations of [0001] and $[10\overline{1}0]$ are perpendicular to each other.

Figure 45 is Fast Fourier Transform of TEM image Figure 44 by using ImageJ software. It also has hexagonal symmetry which looks similar to SAED pattern. Interplanar distances in three directions can also be measured directly from FFT which are 2.92Å, 2.88Å and 2.94Å. These values are consistent with those measured directly from TEM images. Figure 46 is zoomed-out view of nanowire in Figure 44. The scale bar is 50nm. The diameter of this nanowire is not uniform which is about 50-70nm.
Figure 44 – High resolution TEM image of non-serrated GaN nanowire with average interplanar distances in three orientations

Figure 45 - FFT of TEM image of non-serrated GaN nanowire
TEM image of Figure 46 shows an individual serrated GaN nanowire with faceted Au catalyst at the end. The outer diameter of nanowire is about 320nm; diameter of Au catalyst is about 310nm; inner diameter of nanowire is about 215nm; period of serration is about 225nm.

TEM images have been obtained showing serrated nanowires and crystal planes in different orientations (Figure 48). a) is an individual serrated nanowire showing 6-7 periodical serrations with outer diameter of about 210nm. Inset is selected-area electron diffraction pattern with rectangular symmetry where zone axis is [110]. Zone axis is confirmed by the measured value of 27.7° for the angle between the diagonal and the long side of rectangular pattern. (Crystal studio software can simulate the SAED pattern in given zone axis of materials [30].) b) and d) shows “crest” of serrations and c) shows “crevasse” of serrations. The crystal planes are consistent throughout the wire although the facet of
serration shifts by a certain angle at both crest and crevasse of serrations (Figure 48 c) and d)). Therefore, it is single crystalline throughout the entire nanowire.

Figure 48 b) shows crystal planes in growth direction of the nanowire. Average interplanar distance is measured as 2.72Å which reveals growth direction in [0001], polar growth. c) and d) both show crystal planes aligned with one of the side facets of serrations. Average interplanar distances are measured as 2.60Å and 1.40Å which reveal orientations in \( [10\overline{1}1] \) (reported as 2.434Å) and \( [11\overline{2}2] \) (reported as 1.356Å) respectively. Measured interplanar distances are all slightly larger than those reported in PDF# 65-3410 for bulk wurtzite GaN.

Figure 47 – TEM image of a serrated GaN nanowire with faceted Au catalyst. The outer diameter of the nanowire is about 320nm.
Figure 48 – TEM images of serrated GaN nanowires. A zoomed-out view of serrated nanowire with outer diameter of about 210nm in a). Inset shows selected-area electron diffraction pattern with rectangular symmetry where zone axis is [110]. b) shows crystal planes in growth direction. c) and d) show crystal planes aligned with one of the side facets of serrations which indicates two possibilities of crystal orientations based on different interplanar distances.

As mentioned in Chapter 2.5, the measured average value of angle $2\alpha$ is about $120^\circ$ therefore the angle made by growth direction and crystal orientation of side facet of serration is about $60^\circ$. Both orientations $[10\bar{1}1]$ and $[11\bar{2}2]$ are semi-polar directions. The angle
between semi-polar [11\overline{2}2] and c-axis [0001] is reported as 58.4° [47]. The angle between semi-polar [10\overline{1}1] and c-axis [0001] is calculated to be 62.0° based on lattice parameters of wurtzite GaN as a=3.19Å and c=5.19Å. Both semi-polar orientations of [10\overline{1}1] and [11\overline{2}2] have an angle of about 60° respect to polar growth direction in [0001] which agrees with our measured value of 60°. Therefore, all of the results are consistent. Figure 49 is the schematic of growth direction of serrated nanowire and two possible semi-polar crystal orientations of side facets of serrations. The angle between them is about 60°.

Figure 49 – Schematic of crystal orientations of side facets of serrations and growth direction
3.5 **Electron Backscatter Diffraction analysis of non-serrated and serrated GaN nanowires**

To directly confirm the growth direction and crystal orientation of side facets for serrated or non-serrated GaN nanowires, electron backscatter diffraction (EBSD) has been carried out at National Institute of Standards and Technology (NIST). Figure 50 illustrates that growth direction of serrated GaN nanowire is along c-axis along [0001] and crystal orientation of side facets of serrations of this nanowire is in [10\(\bar{1}\)1] direction. Inset shows wurtzite structure of GaN.

![EBSD Image](image.png)

*Figure 50 – Electron backscatter diffraction confirms serrated GaN nanowire growth in [0001] and side facets have crystal orientation in [10\(\bar{1}\)1] (Image courtesy, Albert V, Davydov, NIST)*

EBSD for non-serrated GaN nanowires is illustrated in Figure 51. Growth direction of
non-serrated nanowire is non-polar in [10\bar{1}0] which is perpendicular to [0001]. Again, serrated nanowire (at right top corner) grows in [0001]. Interestingly, a bridge connecting serrated and non-serrated nanowires is shown (at right top corner). It looks like a transition growth from serrated to non-serrated nanowire (or the other way) and the serrations (without shifting side facets which do not look like regular serrations) still grow in [0001] direction.

Figure 51 – Electron backscatter diffraction of non-serrated and serrated GaN nanowires. Non-serrated nanowires have growth direction in [10\bar{1}0]. (Image courtesy, Albert V, Davydov, NIST)

Based on TEM and EBSD results, we have found crystal orientation of side facets of
serrations with two possibilities of [101̅1] and [112̅2]. Based on an analysis of the serrated wires and the lattice spacings, it appears that [101̅1] is more prevalent and the reason could be that [101̅1] is more energetically favorable than [112̅2]. This could also be related to the initial faceting of the Au catalyst that may be favoring one serrated face over another. In general, it appears that the orientation of side facets can be selected between [101̅1] and [112̅2].

Thus, in conclusion, it appears that the serrated wires have a very different crystal structure orientation when compared with regular wires. The growth direction is polar. In this direction alternate layers are made up of either Ga or N. This is consistent with the fact that there is excess Ga source in the chamber. Hence a large amount of Ga is being absorbed quickly allowing for the growth of Ga layer. This Ga layer then waits until enough N atoms are absorbed (at a slow rate) to allow for the formation of the next layer of N. Hence it appears the rate of the reaction is oscillating between a very fast Ga absorption process followed by a very slow N absorption process. This change in absorption rate combined with the changing contact angle of the Au catalyst can provide insight into the growth mechanism.

A more detailed hypothesis may be drawn based on the crystal structure analysis as shown in the schematic below Figure 52.
Figure 52 - Schematic showing the main elements of the theoretical model that relates the size and the V:III ratio to the growth morphology of the serrated nanowire (Courtesy, Moneesh Upmanyu)

(a) The evolution of the droplet-nanowire system as the size oscillates. The evolution of the size dependent droplet supersaturation and the fully faceted morphology of the droplet-nanowire interface is shown. (right) The nitrogen incorporation is assumed to occur over an exposed annular ring (thickness dR) enveloping the contact line (shaded blue), which also serves as the preferred site for GaN nucleation as illustrated. (b) The energetics at the contact line. The colored regions near the contact line represent the volume swept out by the truncating facets during each oscillatory growth cycle. The dark solid and dotted lines represent the initial and final states of the droplet and the sidewall facets, respectively. The light dotted line is an alternate concave morphology of the solid-liquid interface that is also possible the sidewalls narrow inwards.

In future experiments and with a better theoretical understanding, it would be interesting to find out what are the factors that control the orientation of the serrated faces. Since a majority of the wires have the $[10\bar{1}1]$ serrated face what are the factors that control this growth mode. In-situ TEM studies could provide further insight into such mechanisms and
could be carried out in future studies.

Additionally, it is also of interest to investigate what are the growth factors that allow for wire growth in the semi-polar direction. So far there is no report in literature where GaN wires have been shown to stabilize in the semi-polar orientation. As shown above (the nanowire ‘bridge’ between two non-serrated wires, at right top of Figure 51) there are selected nanowires where there is a transition happening between the serrated polar growth direction to the regular non-polar growth direction. The transition is marked by a short semi-polar growth region. This may indicate that the semi-polar growth direction is also a possible growth mode which could be stabilized by controlling the growth parameters.

Finally, it is also interesting to investigate the optical property dependence on crystal structure orientation and serrated face orientation. For example, Chin et al. [48] have observed crystal orientation dependent photoluminescence effects in GaN nanowires. Surface states are known to act as traps of photoexcited carriers and so by controlling the morphology of the nanowires and their growth direction, one can have tighter control of optical phenomena that can lead to better performance of lasers or LEDs based on GaN nanowires. For such studies however, one needs to avail of single wire optical measurements, for example by utilizing techniques such as near-field scanning optical microscopy. These are potential experiments that could be carried out in future studies.
Chapter 4

Synthesis and Structural Characterization of GaMnN nanowires

4.1 Introduction

Dilute magnetic semiconductors (DMS) refer to semiconductors in which magnetic iron replaces a fraction of component ions. It is of great interest due to its potential applications in spintronics devices with spin in magnetic materials along with charge of electrons in semiconductors. As magnetic doping materials in DMS, transition metals (such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu) and rare earth elements (such as Eu, Gd, Er) have been used [49]. Transition-metal-doped GaN has been extensively studied since the prediction by T. Dietl et al. [50] that GaN doped with about 5 at. % of Mn (a high concentration of holes) should exhibit a Curie temperature above room temperature.

Mn-doped GaN films have been grown by metalorganic chemical vapor deposition followed by solid state diffusion from a Mn source [51] and by molecular beam epitaxy [52]. Mn-doped GaN nanowires have also been synthesized and demonstrated [54]-[58] using many different methods. For example it has been realized by reacting chemical mixtures in presence of carbon nanotubes in work of Deepak et al. [54]; annealing manganese-gallium oxide nanowires in flowing ammonia at high temperature in work of Song Y.P. et al. [55]; nanocluster-catalyzed CVD methods in work of Radovanovic P.V. et al. [56]. The goal is to be able to grow them in large-scale for future applications in spintronic devices.

In other work the growth of GaMnN nanowires has been reported using Ni catalysts [56][59]. In initial attempts in our laboratory, also, the growth of GaMnN has been
successfully demonstrated using Ni catalysts [30]. Ni catalyst was deposited on the growing substrate before CVD process, by solution dipping method or e-beam evaporation (with metallic Ni). However, Ni catalyst is also ferromagnetic which can often get contaminated in the wires and be detected during measurements of magnetic properties of GaMnN. Since our main aim is to investigate the magnetic properties of pure GaMnN, we attempted to grow the nanowires without the use of magnetic catalysts such as Ni. Hence, we attempted to grow them using Au catalyst. A few different techniques were attempted and finally Mn has been successfully doped in GaN nanowires by introducing a newly discovered ‘Au-Mn alloy catalyst’ method.

4.2 Method 1

4.2.1 Growth conditions in CVD

Following the same growth conditions as for Ni catalyst, gallium oxide powder (white color) was used as reaction source of Ga and MnO$_2$ powder (black color) was used as doping source of Mn. Au was deposited on Si (100) substrates by e-beam evaporation before CVD process. Carrier gases of hydrogen and ammonia was flowing in horizontal quartz tube during growth at temperature of 960°C inside furnace. Gas of Ar was flowing during preheating and cooling processes in furnace. From upstream to downstream in quartz tube, MnO$_2$ powder, gallium oxide powder and Au-patterned substrates were successively placed (please see schematic diagram in Figure 53). Other growth conditions were similar to those of GaN nanowire synthesis.
As-synthesized GaMnN nanowires by this method are shown in Figure 54. A large quantity of nanowires has periodic serrations along the length of nanowires. They grow very long and straight with fewer growth disturbances compared with as-synthesized serrated GaN nanowires (in Figure 25). The percentage of serrated nanowires in this sample is also much higher than that of as-synthesized serrated GaN nanowires (for example in Figure 13). This is an interesting observation. Introduction of MnO$_2$ source appears to enhance the production and growth quality of serrated nanowires. This may imply that the growth-parameter window for the serrated morphology is enhanced upon introduction of MnO$_2$ source. Figure 55, Figure 56 and Figure 57 show individual serrated nanowires with beautiful hexagonal cross-sections. Outer diameters are around 200nm.

However, no Mn signals by using EDS were detected in this sample. Various growth conditions were controlled and yet no Mn signals were detected using EDS. It indicated that Mn was not successfully doped in GaN nanowires by using MnO$_2$ powder with Au catalyst. Though, it has exhibited enhanced growth of serrated GaN nanowires. This does imply that the growth mechanism of serrated wires still needs further investigation.
Figure 54 - Nanowires synthesized by method 1 using MnO$_2$ with Au catalyst in CVD

Figure 55 - Single nanowire synthesized by method 1 using MnO$_2$ with Au catalyst in CVD
Figure 56 - Single nanowire synthesized by method 1 using MnO$_2$ with Au catalyst in CVD

Figure 57 - Single nanowire synthesized by method 1 using MnO$_2$ with Au catalyst in CVD
4.2.2 Increasing growth temperature

Generally, increasing growth temperature will have a higher chance for better solubility. For specific conditions of alloy, phase diagram should be introduced (please see Chapter 4.3). One possibility to increase the solubility of Mn in Au is to set higher growth temperatures as revealed in the phase diagram. We therefore attempted to grow at temperature of 1100°C with Au catalysts instead of regular growth temperature of 960°C under same other conditions. Under this high growth temperature, however some other material other than GaN was found to grow (as shown in Figure 58 and Figure 59). The morphology and appearance of nanowires look very different from those of GaN nanowires. By means of EDS under TEM to confirm elements, signals including those from Si were detected. This may imply that the Si from the substrate is incorporated in the wire due to the high temperature. Also, since optimal growth temperature for GaN nanowire synthesis is reported to be 800-1000°C [31], therefore, increasing growth temperature may not be the solution to allow for Mn-doping.
Figure 58 - Materials other than GaN formed by increasing growth temperature to 1100°C

Figure 59 - Materials other than GaN formed by increasing growth temperature to 1100°C (zoomed-out view)
4.2.3 Considerations of other catalysts

Another solution is to switch from Au catalyst to other non-magnetic metal catalysts which have better solubility of Mn. Some non-magnetic metals (such as Al or Pt) can be considered for use as catalysts. From the phase diagrams (not shown) for Al and Pt, it may be possible to have Mn in the $\gamma$-phase at the growth temperature of around 1000°C indicating better solubility. However, there is no standard answer to confirm if a certain metal catalyst could enable Mn doping because the phase diagrams are complicated and specific alloy conditions are difficult to control. Also, Mn doping can be affected by many other factors, such as the solubility of Ga or N in a certain metal used as catalyst.

4.3 Method 2

Thus it is interesting to note that under the same growth conditions, with Au catalyst, GaMnN wires do not appear to grow as under the same conditions they grow with Ni catalyst. In fact, the morphology of the GaN nanowires is quite unique in that a significant percentage of the wires are now serrated. To understand the reasons for different cases with Au and Ni catalysts, the phase diagram of Au-Mn is studied (see Figure 60 taken from book of “ASM Handbook, Volume 3, Alloy Phase Diagrams” [60].
Figure 60 - Phase diagram of Au and Mn from book of “ASM Handbook, Volume 3, Alloy Phase Diagrams” [60]

Au catalyst is liquid at growth temperature of 960°C while Mn is in vapor form due to decomposition of solid MnO$_2$. Concentration of Mn in vapor phase is very low when compared with the concentration of Au in liquid phase. This is in the Au-rich region and the solubility of Mn in Au in this region may be poor revealed by phase diagram. Therefore Mn may not be doped in GaN under these conditions.

For comparison, Figure 61 shows phase diagram of Mn-Ni [60]. At growth temperature of 960°C and in Ni-rich region, Mn is in the $\gamma$-phase. This may indicate that solubility of $\gamma$Mn in Au is good or better than that of other phases of Au-Mn.
4.3.1 Introduction of Mn in the catalyst as opposed to source

Finally, a third solution was attempted, namely use of a new “Au-Mn alloy catalyst” method. To synthesize GaN nanowires, suitable growth temperature is between 800°C and 1000°C. The reason for the higher temperature is that at these temperatures, it is easier to have liquid phase of the catalyst. Therefore, growth temperature has been set at 1000°C. If we extend from Au rich region to intermediate regions (at 1000°C) in Au-Mn phase diagram (Figure 60), it may be seen that there are regions wherein the Mn is in the γMn and βMn phases. Since these could better form Au-Mn alloy phases, one solution could be to use metallic Mn (paramagnetic) as source of Mn instead of MnO₂. Then concentration of Mn in Au-Mn alloy (or metallic Mn/Au ratio) can be easily controlled by varying catalyst
deposition conditions. Mn is possible to be doped in GaN if we use both metallic Mn and Au as catalysts.

4.3.2 Growth conditions of “Au-Mn alloy catalyst” method in CVD

Before the CVD process, Au catalyst (of 7nm or 11nm thickness) was deposited on Si (100) substrates by using e-beam evaporation. Then metallic Mn was deposited on Au by using thermal evaporator.

During CVD process, gallium oxide was used as reaction source of Ga and mixture of ammonia and hydrogen was flowing in horizontal quartz tube at 30 sccm and 50sccm separately. Ar of 70sccm was flowing in quartz tube during preheating and cooling processes in CVD. Growth temperature was maintained at 1000°C. Pressure inside quartz tube was maintained at 100torrs. Growth time was typically 1 hour.

Initially, about 0.06g of metallic Mn was evaporated during thermal evaporation. Two samples (1cm by 1cm) with Au-Mn alloy catalyst were prepared for Au thickness of 7nm and 11nm separately. After CVD growth, the materials on substrates formed some continuous structures other than nanowire structures (Figure 62). Our goal was to synthesize nanowires so we needed to obtain nanowire structures first by controlling growth conditions.
The key factor to control material structures in this case could be Mn/Au ratio. Therefore we tried to reduce mass of evaporated metallic Mn for Au of 7nm and 11nm thicknesses. When mass of evaporated metallic Mn was 0.005g for Au of 7nm and 11nm thicknesses, nanowire structures were finally formed (zoomed-out view of as-synthesized GaMnN nanowires in Figure 63). Figure 64 shows an area on sample with mostly non-serrated as-synthesized GaMnN nanowires. Figure 65 shows an area on sample with serrated and non-serrated as-synthesized GaMnN nanowires.
Figure 63 – Zoomed-out view of as-synthesized GaMnN nanowires

Figure 64 - As-synthesized GaMnN nanowires (non-serrated)
4.4 Confirmation of Mn concentration in GaMnN

Since nanowire structures with “Au-Mn alloy catalyst” method have been synthesized, in the next step we need to confirm if Mn has been successfully doped in GaN and also what is the Mn concentration in nanowires. To confirm Mn existence in nanowires, EDS with SEM or TEM can be used.

For the samples removed from CVD, it was noted that metallic Mn and Au deposited by thermal evaporation or e-beam evaporation was not fully utilized as catalyst. Therefore some of it remained on the Si substrates underneath the vertically grown nanowires. So we could not confirm whether Mn signals were from nanowires or from remaining metallic Mn if EDS was carried out on the direct samples.
Therefore, we released the nanowires and checked them by using EDS either under SEM or under TEM. For releasing the nanowires, the sample is placed directly in solution of IPA with sonication of 5-8 seconds (longer sonication time will result in nanowires breaking into short pieces). Several droplets of solution (with nanowires in it) are applied onto TEM grid or other substrates successively and each of them is left to dry by itself.

EDS measurements under TEM have been carried out for two samples: SampleA with 7nm thick Au and evaporated Mn with mass of 0.005g, SampleB with 11nm thick Au and evaporated Mn with mass of 0.005g. Thus SampleA has catalyst with relatively higher ratio of Mn/Au while SampleB has relatively lower ratio of Mn/Au.

EDS results for several nanowires in both samples (SampleA in Figure 66 and SampleB in Figure 67) contain obvious Mn signals which confirm that Mn was successfully doped in GaN for both samples. Signals of Cu and C were from amorphous film on TEM grids. Both EDS results did not show Au signals which indicated Au did not diffuse into nanowires. The explanation is that: Au was functionalized as liquid catalyst in VLS process. Au-Mn alloy phase resulted in Mn becoming soluble in Au which also absorbs Ga vapor and N vapor resulting in the growth of GaMnN.
Some quantitative analysis of Mn concentrations in two samples for several nanowires has been carried out (Table 5 for SampleA and Table 6 for SampleB). These results may not be very accurate since concentrations of light elements (N in our case) detected by EDS are not very accurate. However, it still can give us an idea of the amount of Mn doping. Mn concentration was calculated as:
\[ Mn\% = \frac{Mn}{Mn + Ga + N} \times 100\% \]

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<th>Weight%</th>
<th>Atomic%</th>
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<tr>
<td>1st NW</td>
<td>0.39%</td>
<td>0.33%</td>
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<tr>
<td>2nd NW</td>
<td>0.70%</td>
<td>0.72%</td>
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<tr>
<td>3rd NW</td>
<td>0.61%</td>
<td>0.51%</td>
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</tbody>
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Table 5 - Mn concentrations of several nanowires in SampleA

<table>
<thead>
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<th></th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td>1st NW</td>
<td>0.15%</td>
<td>0.16%</td>
</tr>
<tr>
<td>2nd NW</td>
<td>0.14%</td>
<td>0.13%</td>
</tr>
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Table 6 - Mn concentrations of several nanowires in SampleB

Based on these calculations, SampleA has a higher overall doping level than SampleB. Mn weight concentration in SampleA ranges from 0.39-0.70\% with an average about 0.57\% while Mn weight concentration in SampleB has an average about 0.15\%.

1\%, 3\% and 5\% Mn concentrations in GaMnN nanowires have been obtained in work of F.L. Deepak, et al. [54]. In work of Pavle V. Radovanovic, et al. [56], Mn-doped GaN nanowires of 2\% Mn concentration has been demonstrated.
4.5 **Structural characterization of GaMnN nanowires by TEM and XRD**

To investigate structural properties of Mn-doped GaN nanowires (GaMnN), TEM and XRD have been carried out.

4.5.1 **TEM investigation of GaMnN nanowires**

Figure 68 is a zoomed-out view in TEM of an individual GaMnN nanowire. The diameter of nanowire is about 65nm. Figure 69 shows high resolution TEM image of one GaMnN nanowire. Inset is selected-area electron diffraction pattern with hexagonal symmetry where zone axis is in [0001]. Crystal planes in TEM image shows crystal orientation of [1010] with average interplanar distance of 2.97Å. It has an angle about 30° respect to growth direction which reveals that the growth direction is [1120]. In Figure 70, average interplanar distance of growth direction for GaMnN nanowire can be directly measured which is 1.62Å also indicating [1120] direction. This nanowire is too thick in the area far from the edge so crystal orientations are only visible at the edge (since it is thin at the edge) where the measurements of interplanar distance has been taken.

As mentioned in Section 3.4, non-serrated GaN nanowires were observed to grow in [1010]. This is not the case for Mn-doped GaN nanowires where growth direction was observed to be [1120]. Both growth directions are non-polar (with 30° angle with respect to each other) and perpendicular to [0001] direction. It may be noted that GaN nanowires in both the non-polar growth directions, [1010] [61] and [1120] [20][61] have been reported using other growth techniques such as metalorganic chemical vapor deposition (MOCVD).
Figure 68 - Zoomed-out view of a GaMnN nanowire

Figure 69 - High resolution TEM of GaMnN nanowire with growth direction in [11\overline{2}0]
Figure 70 - High resolution TEM of one GaMnN nanowire with interplanar distance of 1.62Å in growth direction [11 ¯20]

Also, Mn-doped (2%) GaN nanowire with hexagonal cross-section has been reported to grow in [0001] polar direction [56] as shown in Figure 71.
Figure 71 - (a) TEM image of an ca. 2% Mn-doped GaN nanowire with a hexagonal cross section. (Inset) Electron diffraction pattern indexed for the wurtzite structure with a [0001] growth direction. (b) HRTEM image of the same nanowire. The electron diffraction and HRTEM were recorded along the [01-10] zone axis. Scale bars in a and b are 200 and 5 nm, respectively. Taken from work of Pavle V. Radovanovic, et al. [56].

Non-polar growth direction [10\bar{1}0] of Mn-doped GaN nanowires are also reported in [63] (as shown in Figure 72). The Mn concentration in GaN is 3%. Therefore, both non-polar and polar growth directions of Mn-doped GaN nanowires have been demonstrated in literatures by using different techniques.
Figure 72 - (a) SEM micrograph of high-density straight \( \text{Ga}_{0.97}\text{Mn}_{0.03}\text{N} \) NWs, homogeneously grown on the substrate. (b) The TEM image reveals that they have an average diameter of 80 nm. (c) Lattice-resolved image revealing the single-crystalline nature; the distance between the neighboring (010) planes is 2.8 Å. The FFT ED pattern confirms the [10\( \bar{1} \)0] growth direction (inset). (d) EDX line-scan profile of Ga, N, and Mn for a selected \( \text{Ga}_{0.97}\text{Mn}_{0.03}\text{N} \) NW, whose STEM image is shown in the inset.

4.5.2 XRD investigation of \( \text{GaMnN} \) nanowires

XRD pattern of \( \text{GaMnN} \) nanowire sample is shown in Figure 73. The peak positions fit very well with wurtzite GaN. The calculated lattice parameters are \( a=3.186\text{Å} \) and \( c=5.179\text{Å} \).
They are quite consistent with reported values in PDF#65-3410 and also consistent with calculated values for non-serrated and serrated GaN.

![Figure 73 - XRD of GaMnN sample with reported peak positions for wurtzite GaN and Au](image)

In G. Thaler, et al.’s work [52] Mn doping concentrations are reported varying 0 to 9 at. %. Results of XRD measurements show that c-plane lattice constant initially decreases with increasing Mn concentration, then increases when the Mn concentration increases above ~3 at. %. And optical absorption measurements show only a slight increase in the band gap for material with 3 at. % Mn compared with undoped GaN. Mn doping of below 1% in GaN nanowires has also been reported in [53].

Thus several key results are demonstrated in this chapter. First, introduction of MnO$_2$ source material in the CVD chamber does not appear to result in Mn-doping at least when the catalyst is Au. Instead, it seems to result in enhancing the production and the growth quality.
of the serrated nanowires. The role of MnO$_2$ and its interplay with Ga$_2$O$_3$ in the source boats in the CVD system needs further investigation. It appears that the growth-window for the serrated mode is enhanced with the introduction of MnO$_2$. Secondly, it has been shown that introducing Mn in the catalyst along with Au can result in Mn-doping in the GaN nanowires. This is significant since the magnetic properties of these nanowires will have minimal ferromagnetic contamination from starting materials (metallic Mn is paramagnetic). For example in the work [56]-[59] wherein they used Ni catalyst, though the authors did not eliminate effects of ferromagnetic contamination from Ni in the GaMnN, it can never be completely ruled out. Thirdly, it has been determined that Mn doping in GaMnN is of the order of a few percent, 0.1-0.7%. This is somewhat at the lower end when compared with results reported in literature where the typical doping percentages are in the range of 0.5-5%. Finally, it has also been shown that the GaMnN nanowires have growth direction in the non-polar [1120] direction. Reports in literature have demonstrated GaMnN in both polar and non-polar directions.
Chapter 5

Investigation of magnetic properties of GaMnN nanowires

5.1 Introduction

GaN is a promising candidate for achieving ferromagnetic ordering with Curie temperatures at room temperatures and beyond [50]. It is also a wide band-gap semiconductor with interesting optical and electrical properties, hence, doping magnetic entities such as Mn can lead to multifunctional materials that exhibit optical, electrical and magnetic properties. For GaMnN films several reports indicate ferromagnetism at room temperatures and above [51]. Very few reports exist for the GaMnN nanowires [54][57][58]. These reports also show ferromagnetism in nanowires at room temperature. In the previous chapter, we showed a simple method for the large-scale synthesis of Mn-doped GaN nanowires. For investigation of their magnetic properties, we carried out magnetization studies in a SQUID magnetometer. Magnetization versus field measurements were obtained at room temperature and at low temperatures down to 10K in field values ranging from 0-5.5T. Magnetization versus temperature measurements in the range 4.2-300K were also carried out in applied fields of the order of 1T. Room temperature magnetic force microscopy measurements have also been obtained using a Nanomagnetics Instruments Magnetic Force Microscopy (MFM).
5.2 Magnetization versus field measurements

5.2.1 GaMnN nanowires

GaN nanowires with around 0.5% Mn doping were used in this study. A 5mmx6.5mm sample was used. The sample was positioned perpendicular to the applied magnetic field direction inside the SQUID magnetometer. Though the general wire growth direction is vertical to the substrate, with respect to the magnetic field, the wire alignment is expected to be random. The magnetic signals may include those from GaMnN, metallic Mn (paramagnetic) and Si background (diamagnetic).

![Figure 74 - M-H for Mn-doped (~0.5%) GaN sample at 300K](image)

Figure 74 shows magnetization versus field curves at room temperature for Mn-doped (~0.5%) GaN sample. This is the data obtained after subtraction of the background Si signal. The signal is very small due to the small mass of nanowires and hence it is noisy. The curve has a weak hysteresis type of behavior. Coercivity is negligible. The saturation magnetization, $M_s$, value is around $4 \times 10^{-6}$ emu. For comparing this value with literatures, we consider a
simple case. Assuming that for every 1µm by 1µm area of sample, there are approximately 10 wires, we can estimate that there are approximately $25 \times 10^7$ wires in the total sample area. This is a reasonable approximation after considering the catalyst distribution density as in Figure 20. Assuming that each wire has a diameter of around 100nm and length of the order of 10µm, we can estimate the mass of the GaMnN nanowires to be around $12 \times 10^{-5}$ grams (density is assumed to be 6.15g/cm$^3$). This means that $M_s$ is about 0.03 emu/gram.

Also since the doping is 0.5%, it means 1 molecule has 0.005Mn or for every 200 molecules there is 1 Mn atom. From the formula weight of Ga$_{0.995}$Mn$_{0.005}$N (~84u), we have 1 mole ($6.023 \times 10^{23}$) of Ga$_{0.995}$Mn$_{0.005}$N has a mass of 84grams. From this it can be shown that every 200 molecules has a mass of $3 \times 10^{-20}$ grams which amounts to $M_s \sim 10^{-21}$ emu (that is 0.1 µB). Hence the $M_s$ per Mn atom can be estimated to be around 0.1 µB. These results agree well with reports in literature [55] where the $M_s$ per Mn atom is estimated to be around 0.032 µB.

![Figure 75 - M-H for Mn-doped (~0.5%) GaN sample at 40K](image-url)
At 40K, the M-H behavior (Figure 75) demonstrated similar hysteretic behavior as at room temperature. At low temperature ~ 10K, the hysteresis behavior (Figure 76) is not as evident. The M-H behavior is less square in comparison with the room temperature and the 40K behavior. In fact the behavior is more paramagnetic rather than ferromagnetic indicating there may be a transition from ferromagnetic to paramagnetic or antiferromagnetic in the temperature interval 10-40K. Further M-T measurements at intermediate temperatures confirm a transition at or below 20K. Figure 77 shows M-H behaviors at low temperatures 26K, 24K, 20K and 10K. It shows the transition from more square shape (ferromagnetic) to less square shape (paramagnetic or antiferromagnetic) as temperature decreases.

![Figure 76 - M-H for Mn-doped (~0.5%) GaN sample at 10K](image.png)
5.2.2 GaN nanowires

Figure 77 - M versus H at low temperatures

Figure 78 - M-H for GaN sample at 300K and 10K

In order to compare with undoped GaN, we measured the M-H behavior of GaN at room temperature and at low temperature (Figure 78). From the plots one sees that the signals are
extremely noisy and only of the $\sim 2 \times 10^{-6}$ emu. Though there appears to be some hysteresis, it is most probably due to presence of impurities or defects.

### 5.3 Magnetization versus temperature measurements

Figure 79 - $M$ versus $T$ at $H=1T$

Figure 79 shows the $M$-$T$ behavior at low fields of the order of 1T. The magnetization is seen to increase steadily down to low temperatures and has a concave shape. The $M$-$T$ results do not appear to be consistent with ferromagnetism in the material since for a ferromagnetic material, one expects the $M$-$T$ curve to have a convex shape (please see Chapter 5.5 for detailed discussion). Figure 80 shows $1/M$ vs. $T$, which has a linear trendline. Fitting the curve to Curie law, the transition temperature $T_{AF}$ has been determined to be around 5K.
5.4 Magnetic Force Microscopy

To further analyze the magnetic properties, MFM measurements were obtained at the single nanowire level. Figure 81 show results on the magnetic force imaging of the GaMnN nanowires. The left images are the RMS value and provide topographic information. The right images are the phase image providing the magnetic information. The lift height is around 100 nm. The measured value of the phase change is of the order of 1 degree. Because this is a dilute magnetic material, the phase change may be small. In the image one can see that there are some regions with magnetic gradient spread over the nanowire. It is not clear whether this is indeed due to Mn-doping or due to stray magnetic effects or even topographic artefacts.
We also obtained MFM images of nanowires synthesized using MnO$_2$ in the source. Note that for these samples, we showed in Chapter 4.2.1 that the EDS did not indicate Mn-doping. However, MFM images of such samples seemed to indicate the presence of some magnetic material in some of the nanowires as seen in Figure 82. It must be noted however that the lift height for the MFM imaging is different for the two samples. At the lower lift height of 40nm it may still be providing some topographic information instead of magnetic phase information in the top image. While at higher lift height of 120nm it may be providing more reliable magnetic phase information and it does not show magnetic phase transition indicating non-magnetic materials.

Figure 81 - MFM images (left) RMS and (right) Phase image
Figure 82 - MFM images (top) show some trace of magnetic entities; MFM images (bottom) show no trace of magnetic entities.

5.5 Discussion and analysis

Several models have been proposed to explain ferromagnetism in DMS systems, for example the bound-hole model [64] based on mean-field theory, carrier-mediated model [65] based on the formation of an impurity band, etc. In the carrier-mediated model, it is thought that an exchange coupling between the carrier and the local spin is responsible for ferromagnetic ordering. The carriers in Mn-doped GaN are holes. The exchange coupling between the holes and the Mn spins leads to strong binding between them resulting in ferromagnetic ordering in the sample. This hole-spin exchange coupling also competes with a superexchange-mediated antiferromagnetic interaction between neighboring spins.
Our magnetic results indicate that above 20K the ferromagnetic exchange coupling between hole and spin may be dominating while below 20K the superexchange-mediated antiferromagnetic interaction may be dominant resulting in the linear M-H behavior. This result must now be reconciled with the M-T behavior. This may be understood if we consider the dependence of the transition temperature as a function of the hole concentration and the dopant concentration.

The transition temperature to ferromagnetism has been shown to be a function of both the hole concentration and the dopant concentration. Figure 83 shows the dependence of transition temperature on the hole concentration for GaN with 5% Mn doping (as calculated by Song et al. [55]).

To compare our results with this plot, we need to estimate the dopant concentration. Since we have a hexagonal wurtzite lattice, we can estimate the unit cell volume to be around 137nm$^3$ with each cell containing 6 $\text{Ga}_{0.995}\text{Mn}_{0.005}\text{N}$ molecules. Hence the volume occupied by 200 molecules (or 1 Mn dopant atom) is 4570nm$^3$. From this the Mn dopant concentration can be calculated to be around $0.002 \times 10^{20}$ Mn/cm$^3$. If all of these dopants contributed to holes, the hole concentration would be exactly equal to the Mn dopant concentration. On the plot one can see that for this value of hole concentration, the $T_C$ is small < 50K. (Note: In the plot the dopant concentration is 5% while in our sample the dopant concentration is 10 times smaller so that the theoretical value of $T_C$ will be even smaller, consistent with the low value of ~20K as seen in our sample.) Yet, there is no real ferromagnetism demonstrated in our sample. This is because in reality the hole concentration is often much smaller than the dopant concentration, $n_C << n_i$, that DMS is a heavily compensated system.
Based on the carrier-mediated exchange coupling model and also considering the superexchange-mediated antiferromagnetic interaction, Song et al. [55] have calculated the magnetization of GaMnN as a function temperature for various values of $n_C/n_i$. This is shown
in Figure 84. Depending on the ratio of \( n_C/n_i \), one notes that the shape of the curve changes from highly concave to convex. Only at high ratios ~0.8 the shape of the curve is convex and assumes the classical brillouin shape. So it seems that in our system in addition to the fact that we have low concentration of Mn dopants, we have a highly compensated system, resulting in a much lower concentration of holes. In fact \( n_C \sim 0.01 \, n_i \) or smaller. The reason for the large compensation may be due to presence of defects or vacancies in the material. This is not unusual since as mentioned earlier, the solubility of N in Au is small, hence, there is a strong possibility of having N-vacancies in the material. This may further explain why other groups have observed enhancement in ferromagnetism with N-annealing/plasma treatment [55][66]. The higher concentration of N will reduce the vacancies and hence the hole-compensation will also be reduced thus increasing \( n_C/n_i \).

Thus in conclusion, GaN with ~0.5% Mn doping demonstrates a weak ferromagnetic behavior as revealed in M-H, M-T and MFM measurements. The transition temperature is in the range of 20K. The low \( T_C \) is due to the low dopant concentration and the weak ferromagnetism is due to the heavy compensation of holes due to defects and vacancies in the system.
Chapter 6

Investigation of transport properties of GaN and GaMnN nanowires

6.1 Introduction

Electrical transport of semiconductor nanowires is an important area of investigation mainly because of their applications in nanoelectronics and optoelectronics, logic devices, etc. As promising III-V compound material, GaN has been widely investigated for applications in short-wavelength photonic devices, high-power and high-temperature electronic devices [67] and room-temperature spintronic devices. Typically, one can obtain significant information from current-voltage measurements on bulk arrays of nanowires or on single nanowires. Transistor characterization studies such as measurement of the output and transfer characteristics can provide key information such as mobility of the charge carriers. There are reports in literature which describe the current-voltage characteristics and transistor characteristics of single GaN nanowires produced using different growth techniques and field effect transistors (FET) have been fabricated [68]-[76]. In this work we have investigated the electrical properties of serrated GaN due to their immense potential for device applications by virtue of their large effective surface areas; and also those of non-serrated GaN, Mn-doped GaN due to many potential advanced applications.

6.2 Fabrication of single nanowire transport measurement device

Fabrication of device for single nanowire transport measurements involves a series of
steps where cleanroom work is needed (schematic of fabrication procedures is shown in Figure 85).

![Fabrication Procedure Steps]

Figure 85 – Schematic of fabrication procedures of single nanowire transport measurement device, taken from [30].

The details of fabrication procedure are as follows:

6.2.1 Prepare for alignment markers for accurate nanowire relocation

For transport (I-V) measurements, isolating the substrate is important. Here, we use SiO$_2$ (300nm thick) coated Si substrate (SiO$_2$/Si). Alignment markers need to be written (by using E-beam Lithography) on substrates before releasing the nanowires. Their function is to accurately relocate individual nanowires during e-beam lithography process. The design of alignment markers was similar to that used in previous work [76] as shown in Figure 86.
Figure 86 - Design of alignment marker for accurate relocation of nanowires during e-beam lithography process, taken from [76].

In this work, the alignment markers were deposited with Cr/Au. It has good contrast under SEM with respect to the background on substrate. It is transparent through PMMA layer and is therefore easy to locate. The square feature of alignment markers is 50microns by 50microns. And the thickness of x and y are 2microns. For each SiO$_2$/Si substrates (10mm by 10mm), alignment markers were placed at each corner with 1mm distance to the edges of substrates.

To prepare substrates, alignment markers were first written on 2-inch diameter SiO$_2$/Si wafer and then the wafer was diced into 10mm by 10mm pieces. Wafer was first coated with a uniform layer of PMMA (950, 7%) by using Laurell Spinner. Using dicing saw, two alignment lines (blue lines in Figure 87) were “drawn” with very thin depth dicing. They were perpendicular to each other and formed a coordinate system for writing alignments markers with e-beam lithography.
Alignment markers with the square feature as in Figure 86 were then written on PMMA coated SiO$_2$/Si wafer which was followed by developing wafer in solution of “MIBK + IPA (1:3)” for 90 seconds and cleaning wafer with IPA for 20 seconds. Then the wafer was checked under the microscope to see if the marker patterns were well developed.

Then, 5nm Cr and 40nm Au was deposited on wafer successively using E-beam Evaporation. Finally, Cr/Au deposited wafer was placed in acetone with sonication for minutes (acetone helps strip the PMMA and unneeded Cr/Au from the wafer). The wafer is checked under SEM to see if Au patterns of alignment markers are well-formed. Next, wafer with Au alignment markers was diced into pieces (10mm by 10mm) by using dicing saw (illustrated in Figure 87).

6.2.2 Release nanowires onto substrates

With the samples of nanowires synthesized in CVD, the first step is to release nanowires onto SiO$_2$/Si substrates so the individual nanowires could be separated. This allows for
writing device pattern on a single nanowire.

Nanowires are often covered by a thin amorphous layer after synthesis which may affect transport measurements. To remove the amorphous layer, one can dip the sample of nanowires in solution of 5% vol. HF for 5 seconds (followed by IPA cleaning). Then, the sample is placed in IPA for sonication for 5-8 seconds. This results in some of the nanowire releasing as single tubes in the IPA.

One droplet of IPA solution is applied onto SiO$_2$/Si substrates. After several minutes it is allowed to dry. Then the second droplet is applied and allowed to dry. The density of nanowires dispersed on substrates can be controlled by the number of droplets. The density should be well controlled. It is challenging to find good nanowires if the density is too low while it is impossible to write device pattern on isolated nanowires if the density is too high. Generally, 4-8 droplets are found to be optimal in our case.

6.2.3 Identify nanowires for patterning under SEM and calculate coordinates with respect to alignment markers

Sample is checked under SEM after releasing nanowires to find several “good” nanowires for pattern writing. Since the nanowires are randomly dispersed on the substrate with a specific density (in Figure 88) the goal is to find some good nanowire which are not deformed in some manner, for example bent or broken wires are avoided. Also the wires must be long enough, also it is ideal if they are not surrounded by other nanowires that is, the neighborhood must be relatively clear. Figure 89 is an example of “good” serrated nanowire. For non-serrated GaN nanowires and GaMnN nanowires (mostly non-serrated), it is easier to find some long nanowires because they have thinner diameters compared with serrated GaN nanowires. The length can be up to 15micron or even 20microns. For serrated GaN nanowires, they are typically 8-12 microns long.
Figure 88 – Randomly dispersed nanowires on substrate

Figure 89 – An example of “good” nanowire
Once the nanowire is identified for pattern writing, one must record the x and y coordinates (in SEM system with units of mm) of the center of the nanowire. The coordinates of center of alignment markers must also be recorded. The alignment marker looks like Figure 90. For each substrate, there are four designed markers in total with one marker at each corner. Two alignment markers at bottom on the substrate are used as references during e-beam lithography. The straight line connecting two reference points is automatically defined as x axis for pattern writing and left bottom alignment marker is defined as origin of the coordinate system. The straight line perpendicular to the line connecting two reference points which also goes through origin will be defined as y axis correspondingly.

By using the triangle made by nanowire and two bottom alignment markers, the new x and y coordinates of center of nanowire in newly defined coordinate system are calculated (please see Appendix A for details). This information is important for accurate nanowire relocating during e-beam lithography writing.

Figure 90 - Alignment marker under SEM
6.2.4 PMMA coating

After this the substrate needs to be coated with a layer of PMMA. The thickness of PMMA generally should be at least three times the thickness of Au deposition of the device pattern. Typically, Au thickness of 200nm or below is deposited. Therefore, thickness of PMMA needs to be at least 600nm.

PMMA (950, 7%) is used. Spinning conditions of 5000rpm for 1 minute generates 600-650nm thick PMMA while spinning conditions of 3000rpm for 1 minute generates 800-900nm thick PMMA. The thickness of polymer is affected by the molecular weight of polymer, the percentage and the rpm. 1-minute spinning is sufficient to generate uniform polymer layer.

6.2.5 E-beam lithography for writing device patterns

During e-beam lithography, the electron beams of SEM interact with PMMA resulting in chemical modification of the PMMA layer which can then be lifted off later. The electron beam is controlled such that it is switched on and off in the designated area by means of a software called Nanometer Pattern Generation System (NPGS). Patterns are designed in “DesignCAD”.

Diamond scriber is used to scratch four corners on PMMA so SiO$_2$/Si is exposed for focus purpose since it is difficult to focus directly on PMMA. The e-beam lithography patterning voltage is 30KV. Working distance is around 8mm. Smallest features in our patterns have resolution of 1μm, so aperture size of 30μm is found to be sufficient. (Smaller aperture size results in higher resolution but needs longer writing time.) Linear area dose of 500 is used for 600nm thick PMMA and linear area dose of 600 is used for 900nm thick PMMA. Higher dose takes longer writing time while lower dose may not be enough for full interaction between electron beams and PMMA.
Before e-beam lithography writing starts, one can choose two references successively (two horizontal bottom alignment markers on substrate) by enabling global rotation function. Then the four corners of substrate are brought into focus and the system will record these data for calculation of focusing parameters at each place on the pattern. Electron beams will move to the specific nanowire (with defined coordinates) and generate device pattern. Figure 91 is the pattern for nanowire transport measurement device.

It is challenging to locate the device patterns exactly on the specific nanowires. Some shift may occur and that is generally acceptable. The design of device pattern also allows for some shift both in x and y directions. However, it is still a challenge to locate the pattern on the specific nanowire within small acceptable shifts. After several attempts, we have successfully controlled the patterns within very small shifts that are repeatable and easy to operate.

Figure 91 - Pattern for nanowire transport measurement device
6.2.6 Lift-off

After e-beam lithography, solution of MIBK + IPA (1:3) is used for developing the sample so PMMA at patterned areas will be removed. The sample is dipped in MIBK + IPA solution for 90 seconds which is followed by IPA spray cleaning for 20 seconds. The sample is dried using nitrogen gas. The pattern is checked under microscope for lift-off quality and nanowire position with respect to device pattern. 2-probe and 4-probe measurements are most common for transport measurements. To carry out 2-probe measurements, the nanowire should connect with at least 2 contact pads; while for 4-probe measurements, the nanowire should connect with at least 4 contact pads. These can also be checked under microscope.

6.2.7 Ti/Au or Cr/Au deposition

E-beam evaporation is used for deposition of device patterns. Au has excellent conductivity which is good for transport measurements. A thin layer of Ti or Cr improves bonding between Au and SiO₂ surface. A layer of 5nm thick Cr or Ti is deposited on SiO₂/Si substrate (attached on a 3-inch Si wafer with Kapton tape for e-beam deposition) which is followed by 100-200nm thick Au deposition.

Figure 92 – Non-conformal Au across nanowires
However, tilted SEM images reveal that Au contact is not conformal across the nanowires (Figure 92 for serrated GaN nanowires with about 200-300nm outer diameters). The first reason is that e-beam evaporation is a directional deposition method resulting in disconnection of Au at the side of nanowires. The second reason is that nanowires in our work generally have large diameter. Two solutions to this issue are a) “tilted angle deposition” method (illustrated in [76], Figure 93) or b) sputtering deposition.

![Figure 93 - Tilted angle deposition method for resolving problem of non-conformal Au, taken from [76].](image)

In tilted angle deposition method, Cr/Au is deposited on sample at an incident angle
about 45° from one side of nanowire and Cr/Au is deposited on sample at an incident angle about 45° from the other side of nanowire. This kind of tilted deposition can fill the gap with additional Au. Figure 94 is an SEM image of a non-serrated GaN nanowire with good conformal coating of Au by using tilted angle deposition method. Gently annealing the sample may also result in better coverage of Au.

Sputtering deposition is not a directional deposition. Instead the beam is scattering in all directions. Hence it can result in better Au coverage around the nanowire. Figure 95 shows a GaMnN nanowire with good Au coverage by using sputtering deposition with 5nm Ti and 150nm Au. This is very different from directional deposition methods such as e-beam evaporation.

However, the advantage of directional deposition methods such as e-beam evaporation is
that it is very easy for lift-off. And here the disadvantage of sputtering deposition is that it can cause lift-off problems in some cases. Figure 96 shows a lift-off problem with sputtering deposition. The unnecessary Au and PMMA between two contact pads have not been fully lifted off so these two contact pads were connected. To solve this problem, two layers of PMMA can be coated where the bottom layer of PMMA has lighter molecular weight and the top layer of PMMA has heavier molecular weight to generate an undercut.

Figure 95 - Good Au coverage of GaMnN nanowire using sputtering deposition with 5nm Ti and 150nm Au
6.2.8 Lift-off

The final step of fabrication procedures is lift-off of unneeded PMMA and Au. The sample deposited with Au is placed in acetone overnight. Acetone has a function of stripping PMMA. Acetone is then gently sprayed on sample and the unnecessary PMMA and Au will be completely removed from the sample without removing the nanowires under Au patterns. Sonication or strong shaking should be avoided which will remove the nanowires from the sample.

Figure 97 and Figure 98 show SEM images of transport measurement device of a single serrated and single non-serrated GaN nanowire. For both cases, 4 contact pads cover the nanowires which can be used for 4-probe I-V measurements. Figure 99 shows four transport measurement devices designed on one substrate. Au contact pads have very good contrast under SEM respect to SiO$_2$/Si.
Figure 97 – Transport measurement device of a single serrated GaN nanowire

Figure 98 – Transport measurement device of a single non-serrated GaN nanowire
Figure 99 - Four devices on one substrate

Figure 100 shows a nanowire removed from substrate due to strong shaking when lifting off. In this case, the Au contact pads have not completely overlapped. To solve this issue, the device pattern is designed with contact pads (lines) either parallel to or perpendicular to x axis defined by two bottom alignment markers on substrate.
6.3 Electrostatic discharge

Electrostatic discharge problem on device when measuring I-V data needs to be seriously considered and carefully avoided. It can easily destroy sensitive devices. Even upon careful grounding of the meters and probe station, several devices failed. This may imply that there may be electrostatic discharge in the air which is difficult to get rid of.

Figure 101 and Figure 102 show two nanowires burnt during I-V measurements due to electrostatic discharge problem. Figure 103 shows Au contact pads of one device burnt over large areas which happened immediately after the probes were placed on Au contact pads, even before any voltage or current was applied. This clearly indicates that it is due to electrostatic discharge in air or on probe station.

Electrostatic discharge problem was eventually resolved by using Janis Probe Station and placing sample in sealed grounded chamber with high vacuum. The electrostatic discharge is greatly reduced in this method.
Figure 101 - Nanowire burnt during I-V measurement due to electrostatic discharge

Figure 102 – Nanowire burnt during I-V measurement due to electrostatic discharge
6.4 2-probe and 4-probe measurement methods

4-probe method is illustrated in Figure 104: current or voltage sources is applied between A and D therefore there is current going through A, B, C and D. Voltmeter measures the voltage between B and C. Plot of I vs. V can be generated from them. 4-probe method has advantage of reducing effect of contact resistances between Au contact pads and the semiconductor, compared with 2-probe method.

Figure 104 – Schematic of 4-probe measurement setup, taken from [30].


6.5 GaN-metal contacts

In general, metal electrodes to GaN nanowires must be carefully selected to allow for Ohmic contacts. Typically, Al is found to make Ohmic contacts to n-type GaN while Au makes a Schottky contact with n-type GaN [77][78]. This may be understood if we compare the work function of various metals Au (5.1 eV), Cr (4.5 eV), Ti (4.3eV) and Al (4.3 eV) with the electron affinity of GaN (4.1 eV). If the work function of the metal is higher than the electron affinity of the semiconductor, they form a Schottky contact. Hence Al or Ti are suitable materials for GaN device fabrication. There are other factors to be considered. For example, making a direct contact of Al or Au with GaN can lead to Al/Au diffusing into the nanowire. The local properties of GaN will then be modified. To avoid this, a thin layer (~5nm) of Cr or Ti is first deposited as in Cr/Au or Ti/Al contact electrodes. Additionally, the Ti and Cr provide better bonding between the SiO$_2$ and the Au.

On the other hand for p-type GaN, a Schottky contact forms when the work function of the metal is smaller than the electron affinity of GaN and an Ohmic contact forms when the work function of the metal is higher than the electron affinity of GaN. Hence in this case, Au is the preferred contact material. Mn-doped GaN is a p-type material hence Cr/Au or Ti/Au is a suitable choice for the electrode. In the work described below, all of Cr/Au, Ti/Au and Ti/Al/Au electrodes have been used.

6.6 I-V results and analysis

6.6.1 Non-serrated GaN nanowires

The device pattern was twice deposited by using “tilted angle deposition method”, each run of 10nm thick Cr followed by 130nm thick Au. Total effective thickness is about 200nm. And all the I-V data were taken by using Janis Probe Station (in Kostas Center, Northeastern
University) at room temperature.

Some 2-probe measurements of I-V data for non-serrated GaN nanowire have been carried out (as shown in Figure 105). Several curves are corresponding to different pairs of Cr/Au contact pads (between 2 and 3, 2 and 4, 3 and 4). The I-V behavior is clearly non-ohmic in all cases which is due to the Schottky contact between the GaN and the Cr/Au contact. Also, since this is a 2-probe measurement, the contact resistance cannot be avoided. Schottky barrier of Au on n-type GaN is reported to be 0.88eV; contacts of Ti or Cr exhibited only slightly rectifying characteristics [78]. An estimate of the resistance can be obtained from the linear portion of the curve and is around 2.5e4 Ω. By exponential fitting of non-ohmic I-V curves, threshold voltage of Schottky barrier for non-serrated wires are determined to be 0.74V, 0.72V, 0.71V and 0.70V respectively.

Figure 105 – 2-probe I-V results for non-serrated GaN nanowire
The non-ohmic I-V behavior may be compared with previous I-V measurements on GaN nanowires synthesized using Ni catalyst (Figure 106 in Zhen Wu’s work [30]). This is results of measurements of a 10microns length regular nanowire with Cr/Au contact pads. It may be noted that in that work the I-V exhibits a linear behavior. This difference is due to the fact that our nanowires have a larger concentration of n-type carriers (or electrons). This is due to the fact that we used Au catalyst which as mentioned earlier is less soluble to N. This means there are more N vacancies in our sample. In contrast in previous work, Ni catalyst is more soluble to N which resulted in less N vacancies and hence, there is a lower concentration of n-type carriers (less n-type or more p-type than nanowires with Au catalyst). Therefore, Schottky contact is less likely to form in case of Ni catalyst than that of Au catalyst. This explains why I-V in previous results is ohmic while I-V in our results with Au catalyst is non-ohmic. This “Ni catalyst vs. Au catalyst” reasoning also ties in with the observation of the weak ferromagnetism in our Mn-doped sample. Because the as-synthesized GaN in our work already has a large number of n-type carriers, many of these n-type carriers will compensate with the holes generated due to Mn doping.

Figure 106 – I-V curve for a single non-serrated GaN nanowire, taken from [30].
Figure 107 and Figure 108 are 2-probe I-V results for non-serrated GaN nanowires using Ti/Al/Au contact pads which were done by Adam Friedman at US Naval Research Laboratory. Here the I-V behavior is more linear in comparison to Cr/Au as expected.
6.6.2 Serrated GaN nanowires

Figure 109 is 2-probe I-V results of a serrated GaN nanowire (with different pairs of electrodes). The curves are not smooth due to fewer acquired points of data. The I-V behavior is again non-ohmic due to the Schottky contact between the GaN and the Cr/Au contact.

![Figure 109 - 2-probe I-V results for serrated GaN nanowire](image)

Figure 110 shows I-V result for a serrated GaN nanowire. At high negative voltage (close to -2V), the curve has a linear trendline and has been fitted with a linear function which has a value of -1.21V for V-intercept. That indicates threshold voltage of Schottky barrier is 1.21V. On the positive-V side, current is non-zero after V reaches 0.86V. That indicates threshold voltage of Schottky barrier is 0.86V which is consistent with the value for Schottky contact.
between Au and n-type GaN. From the linear portion of the curve the resistance of the wire was estimated to be around $2.24 \times 10^7 \, \Omega$. The resistance is quite large when compared with the value for the non-serrated wires. This is interesting since the serrated nanowires have large diameters so that one would expect a lower resistance. Instead the larger resistance may be arising due to factors such as the anisotropic polar growth directions and enhanced scattering at surfaces. Here the surface effect is particularly significant considering the repeated change in morphology and also considering the increased effective surface area of the nanowires.

![Graph](image)

**Figure 110 - 2-probe I-V results for serrated GaN nanowire (pins62)**

In Figure 111, on the V-positive side the linear portion of the curve has been fit into a linear function which has a value of 1.07V for V-intercept; on the V-negative side, the linear fitting function has a value of -1.16V for V-intercept. Those indicate threshold voltage of
Schottky barrier is 1.07V and 1.16V based on analysis from different sides respectively. The slopes of linear portions result in resistances of 1.2e6 ohms and 4.62e6 ohms respectively. By exponential fitting of these two I-V curves for both positive-V and negative-V sides, threshold voltage is determined to be 0.48V, 0.42V, 0.33V and 0.35V respectively. Since due to the morphology, electrode contact for serrated wires may not be as well conformal as the one for non-serrated wires, the calculation of area of Schottky contact can affect calculated threshold values. Also, both Cr and Au may have contact with nanowires.

Figure 111 - 2-probe IV results for serrated GaN nanowire (pins61)

Figure 112 (first measurement) and Figure 113 (after repeating for several measurements) are both results for I-V of serrated nanowire across pins 6 and 3. As times of measurements on same part of nanowire increases, the current increases dramatically (approximately by
order of $10^4$). Such effects are not uncommon in nanoscale systems due to phenomena such as hot electrons [79]. Over repeated measurements, the electrons may be gaining in energy resulting in enhanced current values. One cannot also rule out the possibility that there may be other optical effects due to the generation of photon-absorbed electron-hole pairs which can further enhance the current values. Another possibility is that the contact resistance may be higher in the serrated wires. Due to the serrated morphology, the contact with the Cr/Au electrode may not be as intimate at first when compared with the contact between the non-serrated GaN and Cr/Au. And contact resistances may be reduced after several measurements due to better conformal Au with nanowire.

![Graph](image.png)

**Figure 112 - 2-probe I-V results for serrated GaN nanowire (pins63, the first measurement)**
Figure 113 - 2-probe I-V results for serrated GaN nanowire (pins63, after measurement several times, current increasing of nearly 4 orders)

Figure 114 shows the case of burnt serrated nanowire after I-V measurements.

Figure 114 - SEM images after I-V measurements, serrated nanowire was burnt.
Figure 115 shows a burnt nanowire after several repeated measurements across pins 1 and 2. The current through the wire should be less than the maximum since the heat generated by current has already been accumulated during previous measurements.

6.6.3 GaMnN nanowires

Transport measurement devices for GaMnN nanowires are 5nm thick Ti and 150nm thick Au using sputtering deposition. Figure 116 shows I-V results for GaMnN nanowire which has linear behavior with resistance of 9.53k Ω.
Figure 116 - 2-probe I-V measurements for Mn-doped GaN nanowire

Figure 117 shows a second pair of electrodes on the same nanowire as in Figure 116. It also has linear behavior. The data is not smooth and it may be due to the poor contact between probes and Au pads. It is very tricky to have good connection between probes and Au pads. From the slope, the resistance is calculated to be 116 Ω.

Figure 117 - 2-probe I-V measurements for Mn-doped GaN nanowire
Figure 118 shows I-V results for a different GaMnN nanowire. However, it has non-ohmic behavior which is different from that of the first nanowire. This may be a result of Schottky contact due to lower Mn doping. When current is 0, voltage is non-zero in the circuit due to in-built potential at the junction.

Figure 118 - 2-probe I-V measurements for Mn-doped GaN nanowire

Figure 119 - 2-probe I-V results of a second GaMnN nanowire
We also tried to measure the maximum current through nanowire after which the wire is burnt out. We found at 5.71V the nanowire was burnt out with the maximum current of 47.1μA as shown in Figure 119. The burnt nanowire is shown in Figure 120.

![GaMnN nanowire burnt out after 5.71V with the maximum current of 47.1μA](image)

In conclusion, two-probe measurements have been carried out for single nanowires of the serrated, non-serrated GaN and GaMnN nanowires. The contact resistances play a large role in influencing the I-V behavior. Very large resistance values are noted for the serrated wires in comparison with the non-serrated and the Mn-doped wires. The large resistance may be attributed to the large surface effects resulting in enhanced scattering effects. The Mn-doped wires have significantly low resistances potentially due to the enhanced charge carriers in the system.
Chapter 7

Summary and Future Outlook

The key results described in this thesis may be outlined as follows:

1. Demonstration of a new GaN morphology in which the wires have a periodic serrated morphology. The wires are single crystalline with growth direction in the polar [0001] direction and serration side faces in the [10\overline{1}1] or [11\overline{2}2] orientations.

2. The serrated wires grow when the catalyst used is Au as opposed to say Ni. Also the catalyst size must be somewhat large and the ratio of Ga:N must be large. Interestingly, what we have shown is that only the initial conditions need to be controlled, that is before the initiation of the CVD process. Other reports have tried to obtain wavy and varying diameter morphologies but they typically vary the growth conditions such as the gas flow during the process. In our process, no further control is necessary.

3. Interestingly, the percentage of serrated wires is found to increase when some instability is introduced. For example, when MnO$_2$ source is introduced in the CVD chamber as source along with Ga$_2$O$_3$, then a higher percentage of the GaN wires appear to be serrated. This implies that introduction of MnO$_2$ increases the growth-window for the production of serrated wires.

4. Mn-introduction into GaN nanowires can be achieved by using Au-Mn alloy catalyst method. Successful doping of Mn has been demonstrated by means of energy dispersive characterization studies. Doping concentration has been estimated to be in the range of $\sim$0.5%.

5. GaMnN nanowires have been demonstrated to have growth directions in the non-polar [11\overline{2}0] direction. This is distinct from the non-polar [10\overline{1}0] growth direction observed
for the regular, non-serrated GaN nanowires.

6. Magnetic property measurements on Mn-doped GaN (~0.5% doping concentration) exhibit weak ferromagnetism. The behavior may be explained in terms of hole-local spin ferromagnetic exchange and a competing antiferromagnetic interaction between the spins via superexchange mechanism.

7. Electrical transport investigations on the new serrated GaN nanowires shows enhanced resistivity when compared with the regular wires. Though the wire diameter is larger than the regular wires, the resistivity appears to be higher. This is consistent with the fact that the serrated wires are expected to have surface scattering effects. Resistance of Mn-doped GaN (~0.5% doping concentration) is even lower potentially due to the enhanced charge carriers in the system by hole doping.

**Insights for future studies:**

Based on extensive work in the lab, we have already demonstrated the growth of epitaxial nanowires which are horizontally aligned. The wires appear to have cubic zinc blende structure. This work has gone one step further to demonstrate yet another morphology, namely, the serrated wires. Also, the work indicates the potential for the discovery of new growth modes hitherto unexplored, such as semi-polar growth modes. We have already initiated preliminary work in this area. Figure 121 (work in this thesis) and Figure 122 (work done by Dillon McDowell in our laboratory) show some serrated nanowires not growing in regular serration morphologies due to instability. And some portions of nanowires seem to grow in semi-polar directions (with an acute angle respect to regular polar growth direction of serrated nanowires). Generally, the semi-polar portions of nanowires seem to grow more or less in the direction parallel to one of the side faces of serrations. Further crystal orientation information needs to be confirmed by using TEM, EBSD, etc.. It is very interesting of these
semi-polar growth directions of GaN nanowires since no GaN nanowires have been reported in literatures by now to grow in semi-polar directions.

Figure 121 – GaN nanowires with semi-polar growth direction in our work, synthesized by using MnO₂ and Ga₂O₃

Figure 122 – GaN nanowires with semi-polar growth direction, work done by Dillon McDowell.

The work also has gone one step further in the demonstration of Mn-doped GaN nanowires. Previous work showed that such wires can be grown using Ni catalyst. However, the ferromagnetism in such GaMnN nanowires is difficult to confirm since Ni could be embedded in the nanowires as an impurity. This work has done away with the use of Ni
catalyst for the growth of GaMnN. In spite of the poor solubility of Mn in Au, a new alloy catalyst technique has resulted in the growth of GaMnN nanowires. In further work, it is of interest to control the doping concentration of Mn and to investigate its influence on the magnetic properties.

Further investigation is needed to understand the interplay between Au, Mn and Ga and how they control the growth mechanism. It may be recalled that the growth of serrated nanowires is enhanced by introducing MnO₂ in the reaction source. It may also be noted that the GaMnN nanowires grow in the [1120] non-polar mode, yet distinct from the regular non-serrated GaN wires which grow in the [10\(\bar{1}\)0] non-polar mode. These new results point to the importance of further investigation that needs to be carried out on the growth of GaN nanowires. A combined theoretical and experimental investigation will be very useful to obtain a better understanding of growth mechanism. Advanced techniques such as in-situ TEM could provide significant insight into the growth mechanisms.
References


[18] Song Han, Wu Jin, Tao Tang, Chao Li, Daihua Zhang, and Xiaolei Liu, Controlled growth of gallium nitride single-crystal nanowires using a chemical vapor deposition method, J. Mater. Res., 18 (2), 245-249, 2003


[63] Seon Oh Hwang, Han Sung Kim, Seong-Hun Park, Jeunghee Park, Seung Yong Bae, Bongsoo Kim, Ja Young Park and Gangho Lee, Selective Growth of Straight and Zigzagged Ga1-xMnxN (0 ≤ x ≤ 0.05) Nanowires and Dependence of Their Electronic Structure and Magnetization on the Mn Content, J. Phys. Chem. C 2008, 112, 2934-2942


[66] Jeong Min Baik, Yoon Shon, Tae Won Kang, Jong-Lam Lee, Fabrication of (Ga,Mn)N nanowires with room temperature ferromagnetism using nitrogen plasma, APPLIED PHYSICS LETTERS, 87, 042105 (2005)


[72] Lorenzo Rigutti, Gwenole Jacopin, Andres De Luna Bugallo, Maria Tchernycheva, Elias Warde, Francois H Julien, Rudeesun Songmuang, Elisabeth Galopin, Ludovic


Appendix A

Methods of calculations for accurate nanowire relocating during E-beam Lithography

Figure 123 – Schematic of calculations of coordinates of nanowire in the newly defined coordinate system based on two alignment markers as references
For accurate relocating of one specific nanowire during e-beam lithography for device writing purpose, some calculations need to be carried out (as shown in Figure 123). In the step of identifying “good” nanowire under SEM, coordinates (in SEM system) of nanowire (Xn, Yn) and those of two alignment markers (X1, Y1) (X2, Y2) are recorded. During e-beam lithography two alignment markers will be chosen as first and second references by using global rotation function. Then the pattern writing location is at the coordinates of nanowire (Xn’, Yn’) in newly defined coordinate system based on locations of two references. Following steps are for calculating (Xn’, Yn’).

\[
\theta_1 = \arctan\left(\frac{Y1 - Y2}{X2 - X1}\right)
\]

\[
\theta_2 = \arctan\left(\frac{Yn - Y1}{Xn - X1}\right)
\]

\[
R = \sqrt{(Xn - X1)^2 + (Yn - Y1)^2}
\]

\[
Xn' = R\cos(\theta_1 + \theta_2)
\]

\[
Yn' = R\sin(\theta_1 + \theta_2)
\]

Then calculated values of Xn’ and Yn’ can be used for identifying the nanowire location respect to two alignment markers.