MOLECULAR BEAM EPITAXIAL GROWTH AND CHARACTERIZATION OF
NITRIDE NANOWIRES

A Dissertation

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Kevin Goodman

Dr. Debdeep Jena, Director

Graduate Program in Electrical Engineering
Notre Dame, Indiana
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Currently, 21% of the world’s electrical energy is used in artificial lighting. White light LEDs, the holy grail of lighting, are currently the subject of research toward efforts to reduce this alarming percentage. One method of realizing a white light emitter is to combine red, green, and blue LEDs. The Achilles’ heel of this method is the ‘green gap’ in current LED technologies. Due to large lattice mismatch between materials with bandgaps near those needed for green emission and popular epitaxial substrates, dislocations prevent fabricating materials with high optical efficiencies.

This research focuses on growing Nitride nanowires as a potential material solution to this challenge. The nanowires grow as three dimensional pillars and therefore their lattice constants can relax more closely to their inherent values. This will allow for the growth of material free from dislocations. Specifically in this work, GaN and InGaN nanowires were successfully grown on Silicon substrates. Data on the characterization of the Molecular Beam Epitaxy grown InGaN wires, which are the first ever reported, reveal
they are of high structural quality. The InGaN nanowires show Indium concentration gradients which result in a broad optical spectrum. The internal quantum efficiency of the InGaN material was found to be 8%. Silicon/Nitride nanowire p-n junctions were grown and fabricated for the first time in Nitride MBE nanowire technology using p-type Silicon.

Further, Nitride nanowire growth by MBE on ALD oxides of precisely controlled thickness has been reported here for the first time. Success in the growth of Nitride nanowires on controlled oxides has led to the first ever reported Silicon/oxide/Nitride nanowire heterostructures. Also reported for the first time is the observation of the quantum confined Stark effect in nanowire multi quantum well structures.
Dedicated to my kids, especially the ones I never had the pleasure to meet.
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This dissertation is being written with the intent that no prior knowledge of the related material, other than what is included wherein, is required to understand its contents. With this as the goal of the author, all of the background knowledge for complete understanding of the contents of this dissertation will be included. The author believes for someone to fully understand a matter at hand, that person should be able to explain the subject to someone with no prior knowledge of the subject. That is the premise for the outline of the dissertation; to include complete relevant information so anyone could read the dissertation and walk away from it with enough knowledge to explain the contents to anyone else.

With that said, the opening of the dissertation contains motivation for the research along with background information on the subject. Following the background information, a review of relevant research conducted by others can be found. The last of the dissertation describes the research carried out by the author.
CHAPTER 1:
INTRODUCTION

At the time the author is writing this document, the modern world has thrown itself into a state of cautionary panic. The guaranteed discussion that first arises when two people start a conversation is no longer about the weather but rather can be commonly heard to start with, “what’s the price of gas where you are?”

The past few years have seen the price of gas reach well over $4.00 per gallon in the United States. This has awakened a sense of energy emergency, dictating everything from automobile sales to political positions. The United States is the most out of balance country in the world when it comes to energy used compared to energy produced. According to the Department of Energy \(^1\) the United States produced 71.71 Quadrillion BTUs of energy in 2007 while consuming 101.6 Quadrillion BTUs.

This would partly explain the high price tag on the gasoline, but the price of gas is only one part of the story. The general public is slowly starting to realize that energy doesn’t just magically come from a gas pump. The earth has only a few sources of energy for humans to capture and use. There is a certain amount of energy presently on Earth stored in geothermal heat, fossil fuels, nuclear energy, and radiated heating from previous solar rays. The other source; and only other source is solar radiation reaching us at each moment.

\(^1\)
While this solar energy is more than enough to sustain human consumption, the ability to capture this energy is not yet available to mankind. Therefore, since demand is ever increasing and production, as of now at least, is tapped out, the price of energy will continue to rise. This point brings forth the desire for a more conservatory view on energy use.

Following on the previous, an interesting fact is that 21% of the electrical energy used goes to lighting. A means to lower this percentage is to initiate the use of solid state lighting in the form of light emitting diodes, LEDs. The problem with this idea is that LED technology is not advanced enough to offer efficient lighting per used wattage.

While currently there exist LEDs which will emit ‘white’ light, the color emitted is in the eye of the beholder. As will be discussed, the term ‘white light’ is not as simple as it sounds. Since white light is a combination of colors, and human eyes perceive each color differently, there is a broad range of electromagnetic emission that could be commonly referred to as white emission.

This has led to the marketing of LEDs which are described as white, but these LEDs do not always satisfy the needs of the customer. What is currently lacking in the solid state lighting market is a material which holds two key characteristics. The first…the material needs the ability to emit energy that humans perceive as the color green. Why green? The reason will be discussed in detail in this document. The second characteristic builds on the first and that is, the material must emit green luminescence efficiently. This has been the stumbling block in the past. Many materials have been fabricated to emit green light, but their efficiencies are usually low. When these materials
are fabricated into light emitting devices, the amount of energy they use does not justify their use as replacements for current lighting technology.

This leads us to the research discussed in this dissertation. The main goal of the research has been to investigate the possibility of realizing a material in the form of Nitride nanowires which can emit green light, and do so in a more efficient manner than is currently available.
2.1 Atoms and the Source of Bandgaps

Matter as humans know it is made up of atoms. Each atom has a certain number of protons and neutrons at its center, or nucleus, and a certain number of electrons orbiting the nucleus. Granted, each of these building blocks is itself made of smaller units such as quarks and these little guys are important, but if left alone they leave physics to behave if they are not even there. For a detailed reading, the author suggests looking at the referenced book.

2.1.1 Electrons as waves

At this time it should be noted that electrons are considered to be not only matter, but also waves. Eisberg offers a detailed account along with background information of this idea. Basically, a series of experiments have shown that electrons will propagate as waves instead of particles. This is not a cause for alarm or dismay. If the reader is having a problem with this idea, imagine instead of a small marble being the electron, imagine a cloud which contains possible locations for the electrons. It doesn’t really matter. The important piece of information is that these wiggly blobs travel around the nucleus in set radial distances from the nucleus. A visual representation of an atom could be thought of
as the planets orbiting the sun. The sun representing the nucleus and the planets representing the electrons orbiting at certain distances from the sun is a schematic most are familiar with.

Now, the idea that the electrons orbit the nucleus in only certain paths is important to this dissertation. Bohr postulated that electrons can only orbit the nucleus in orbits “for which its orbital angular momentum \( L \) is an integral multiple of \( \hbar \), Planck’s constant divided by \( 2\pi \).” The author will try to bring this down to layman’s terms.

There exists this electron. It is circling around a nucleus. Louis de Broglie suggested the idea that the electron, and all matter, is actually a wave (as mentioned earlier) and has a wavelength equal to \( h \) divided by the particle’s momentum. Momentum is just a particle’s mass times its velocity, and here \( h \) represents Planck’s constant. Planck’s constant is just a number. It is equal to \( 6.63 \times 10^{-34} \) Joule seconds. Associated with this wavelength is a certain amount of energy which de Broglie found to be equal to \( h \) times the frequency of the wave. As the electron flies around the nucleus, it cannot travel wherever it pleases. Immutable laws of physics acting on the electron allow it to only occupy certain orbits.

The reason for this restriction on the electron’s path is due to the fact; a fact discovered by Max Planck, that an object can only have discrete amounts of energy. That is to say that it has been shown that a particle’s energy is quantized. What this means is that a particle is only allowed certain values of energy, and thus only certain changes in energy. This seems strange in everyday activities, but that is due to the fact that this value of energy change is extremely small. It is so small it is unnoticed in
everyday life. It could be compared to removing one grain of sand from a beach; there really is no change on the large scale.

So, if a particle’s energy is quantized, and this energy is directly proportional to its frequency, then that means the particle’s wavelength can only have certain values also. Eisberg \textsuperscript{3} shows that by comparing a particle’s angular momentum in different notations, the wavelengths that an electron can have orbiting a nucleus is \( \frac{2\pi r}{n} \) where \( r \) is the radius of the path, and \( n \) is an integer. He states it beautifully, “the allowed orbits are those in which the circumference of the orbit can contain exactly an integral number of de Broglie wavelengths.”

A model for this would be if one represented an electron waving around as a curved puzzle piece. If someone wanted to construct a circle with pieces that are all the same size or wavelength, then only certain circumference circular puzzles could be made and those sizes are dictated by the puzzle pieces or wavelength. Another way to state it is that no intermediate or partial puzzle pieces may be used to make the loop.

So each atom of a material has electrons orbiting around it. And these electrons have only certain orbits which they can move in. Now, there are lots of possible orbits for the electrons in an atom to travel in, they just keep getting bigger and bigger. Since electrons are negatively charged and protons are positively charged, the lowest energy state for the atom would be for all of the electrons to fill the closest orbits. However, nature throws another curve ball and says that there can only be one electron in a certain state, or condition \textsuperscript{3}. This is known as the Pauli Exclusion Principle. When the term state
is used, it means that there can only be one electron that has a certain set of characteristics.

For example, if an atom has a certain energy and a spin up (spin is just another trait of electrons as eye color is to humans. It is important in physics but has no major direct play in this dissertation) then there cannot be a second electron with the same energy and spin. In order for there to be a second electron with the same energy, it would have to have spin down. Thus the Pauli Exclusion Principle dictates which energy level the electrons are in. There is the Coulomb attraction between the positive protons and negative electrons, but there is energy quantization and the Pauli Exclusion rules only allowing electrons to be so close to the nucleus. This is what dictates how electrons are positioned in an atom.

If an electron gets some energy, say by absorbing some heat, it can move up energy levels. In the example, an electron in the first orbit could absorb some energy and jump to the fourth orbit. But this can only occur if the electron receives exactly the amount of energy that makes the difference between the fourth and first orbitals. The electron can’t jump to a state that is in between the allowed energy levels. Likewise, if an electron loses energy, but just the right amount of energy, then it may fall from a higher energy level to a lower energy level. Both of these scenarios can only occur if there is an empty space for the electron to move to. An electron may receive enough energy to make a jump from one orbit to another, but if the spot it wants to go to is already occupied by an electron, there can be no movement.
The reader should note that the previous discussion by no means fully explains quantum mechanics. The discussion was only intended as a basis to allow the reader to somewhat grasp the idea of how electrons interact with each other and thus set up the qualitative idea of energy transitions that the electrons may make. To fully explain electron behavior, one would have to quantify their behavior by introducing other factors, one in particular being the Schrödinger equation which can predict how electron wave functions react to applied potentials. While this is a useful tool, it goes beyond the scope of this thesis and has therefore purposely been left out.

2.1.2 Interactions of atoms

So far, the discussion has applied to only one atom. This atom has certain energy levels, or orbits, that the electron can be in. But what happens if more atoms come together and form a piece of homogeneous material? Actually, things do change as atoms join together and start communicating with each other.

Crystalline materials are defined as having a periodic structure to their atomic assembly. Most semiconductor materials have atoms arranged in a cubic pattern or in the case of III-V materials, materials made of elements from columns three and five of the periodic table, these materials also form in hexagonal patterns. Now, atomic spacing in materials is on the order of Angstroms, roughly two Angstroms separates an atom from its nearest neighbor. At this close range, the outer orbiting electrons which are not bound as tightly to the nucleus because their inner brothers and sisters are shielding them from the nucleus’s electric field, are able to jump around and move between adjacent atoms.
When this occurs, the potential that the electron sees is no longer one positive nucleus acting on it. It is a series of these nuclei lined up, each having the same potential effects on the electron. This phenomenon, and its model as mentioned below, is described by Pierret if the reader would like a more in depth investigation. Basically what happens is, and this is modeled by the Kronig-Penney Model, is that the electron sees each nucleus as a potential well. In other words, if one looked at a graph of potential energy for the electron, every place there is a nucleus, there is a square well in the potential energy graph. And since the atoms are spaced periodically in the material, the electron sees periodic quantum wells.

Not to get into the details here, the end result is that when the electron can move from atom to atom, it is allowed not only single discrete orbits that it can be in, but since there are trillions of atoms, there are trillions of orbits that get crunched together and the electron is allowed to occupy thick orbits, or what are referred to as energy bands as it circles the nucleus. There are still forbidden energy states between these allowed bands and the electron can still move up or down between bands just as in the case of discrete orbits. But still the electron must relinquish or receive the right amount of energy to transfer into an allowed band.

2.1.3 Source of emitted light

The act of an electron falling from one energy band to another is the source of emitted light by a material. As the electron falls to a lower energy, it has to give up that energy to conserve it, since energy cannot be made or destroyed, only transferred
between energy and matter. There are a few options the energy has to go to. The energy can be given to the material as heat. This means the energy can be given to the lattice as a displacement of the atoms or a phonon. Or, and this is the important one for this dissertation, the energy can be given off as a photon, or light.

The color of the light that is given off is determined by the photon’s wavelength. Photons are discrete particles of light, one can think of them as being the smallest unit of light that is possible. Associated with each photon is a frequency and a wavelength, remember that all matter including light, is actually a wave. The speed that the photon is traveling is determined by the material it is moving in. A common reference is light moving in a vacuum. Here the speed of light, $c$, is found by multiplying the photon’s frequency, $f$, with its wavelength, $\lambda$. Due to the fact that the speed of light in a vacuum is constant, this shows that frequency and wavelength are inversely proportional to each other. Further, the color of the light could be identified either by the photon’s wavelength or by its frequency because fixing one dictates the other.

When an electron makes a transition from a higher to lower energy level, the photon that it gives off will have a distinct energy. This energy is determined by the energy difference between the energy level the electron moved from minus the energy level the electron moved to. This energy actually dictates the color of the photon. The reason, as Einstein showed, is that energy is related to frequency by the equation

$$E = h \times f$$

where $h$ is Planck’s constant and $f$ is the frequency of the photon. Since energy dictates frequency, and frequency and wavelength define each other, it is actually the energy of a
photon that determines its color. Further, this energy is determined by the energy difference between the two quantum states that the electron started and finished in. Summarizing, an electron loses energy and falls down to a lower energy state in an atom. This energy is given off as light. The energy of the light dictates the wavelength which is the photon’s color.

The following sections will discuss how devices can be made in which electrons are forced to move to lower energy states and thus emit light.

2.2 Characteristics of p-n Junctions and Light Emitting Diodes

2.2.1 Electrical charges

This dissertation initially discussed atoms and how they are designed. The nucleus is located in the center of the atom with neutrons and protons, and a cloud of electrons circling the nucleus. The names of the particles are in reference to their electric charge. Neutrons are neutral while protons are positively charged and electrons are negatively charged.

But what is the relevance for the positive and negative charges? Absolutely nothing fundamental went into the naming of the charges. Considered as the discoverer of electricity, Ben Franklin just happened to designate electrons as having a ‘negative’ charge. And thus protons have a positive charge since they are attracted to the electrons. He could have just as well said ‘these electrons I will designate as having a positive charge and anything that is attracted to them will be negative’. If that were the case,
everything about physics would be the same, except voltmeters would have a ‘-’ where the ‘+’ is now and vice versa. Just calling an object something doesn’t affect how the object behaves.

Looking at a piece of material, science usually groups the material into one of three categories based on how well it conducts electricity. If the material doesn’t conduct electricity very well it is considered an insulator. If it does conduct electricity well it is considered a conductor. And if the material is somewhere in between, it is called a semiconductor.

But what dictates how a material is going to behave electrically? It all has to do with the electrons. Electricity is just electrons flowing around, moving from atom to atom in a material. Solid materials have atoms that do not move around relative to each other. That is what differentiates them from liquids or a gas. Since the protons are locked into place, they cannot move around, hence, they cannot contribute to any electrical current. The only particles left with charge are the electrons, and their ability to move around in a material is what defines how well a material will conduct electricity.

One may question why protons are immobile while electrons have the ability to move around. Doesn’t it stand that since the electrons are part of the atom which is immobile, that the electrons will also be immobile? The answer is no.

Electrons ability to move from atom to atom has to do with where it sits in an atom’s energy band and how full that band is. Electrons that are close to the nucleus are tightly bound by the Coulomb forces acting between the electron and the protons. But further out, the outer electrons are shielded by the inner electrons. These outer electrons
only ‘see’ one proton pulling them toward the nucleus since some of the field lines from the protons end on the inner electrons. Thus, the outer electrons are bounded less and it takes less energy to free them from the nucleus.

The other key characteristic determining if an electron is easily removed from an atom has to do with energy band filling. As discussed earlier, when a plethora of atoms are brought together to make up a solid material, the allowed energy levels grow together making allowed energy bands. The band that is farthest out and still has electrons in it is considered the valence band. The next band outward is considered the conduction band. These allowed energy bands can be thought to stretch across all the atoms in the material.

For an electron to move around between atoms there has to be an empty place for it to move to. Just as Streetman says in the reference, if the valence band is full, even in an applied electric field, there is no current flow even though the electrons feel the electric field, because there is no place for them to move to. This is imagined by thinking of someone stuck in traffic. Although the car has gas and the driver wants to move, he can’t get anywhere since there is no place to move to.

However, if an electron receives enough energy to jump up to the conduction band, then it sees a free and open highway since there are few electrons in the conduction band. It is as if the electron exited a congested highway and is now driving on an empty country road. He can go wherever the electric field takes him. Since the electron is not tightly bound to the nucleus and it has room to move around from atom to atom, it will contribute to current flow since it will be pulled by the applied field from high potential to low potential.
Therefore, an electron that resides in an energy band that is not completely full will contribute to current flow when an applied field is applied to the material. But what about the spot where that electron that jumped from the valence band to the conduction band started? This empty spot, or hole, will also contribute to current flow. Now, the spot itself is just an empty space, it doesn’t really exist so it can’t be part of current flow. But its neighboring electrons do.

When a field is applied, the electron beside the empty space will shift into the empty space to lower its energy. When this electron shifts into the original hole, the electron that was beside it will shift into the new hole just created. This will repeat until every electron shifts over one spot to fill the hole that was originally left. Since every electron shifted, there will be a new hole at the end of the line where the last electron shifted from. It is as if the first hole just moved over to the new position at the end of the line. This is a lot easier for book keeping saying that one hole moved down the line of electrons rather than to say that this electron shifted one space, the electron next to it also shifted over, and so on.

This gives us a new ‘particle’ which is really not physically there, but considering the idea and using it really simplifies the entire book keeping. This new particle is called just what it is, a hole. The hole is considered to have the same magnitude of charge as an electron but it is opposite in sign. Therefore, there are now two particles that contribute to current flow, electrons and holes. But just to emphasize, holes are not particles, they are actually a lack of a particle.
2.2.2 Semiconductors, Insulators, Conductors

Going back to the three categories that scientists group materials into based on their electrical conduction…insulator, semiconductor, and conductor, what are their characteristic traits that give them their conducting abilities? An insulator usually has a full valence band and a relatively large bandgap. Relatively large when talking about bandgaps is anything over 6 electron Volts or 6 eV. Aluminum Nitride which has a bandgap of 6.2 eV is sometimes considered an insulator but by many it is considered a semiconductor.

Since thermal energy at room temperature is 25.9 meV, there is a low probability that an electron in a 6 eV bandgap semiconductor could get bumped up to the conduction band just from thermal energy at room temperature. Metals on the other had have very small or even no bandgap. What happens in a metal is that there are so many electrons that the valence band is full and the conduction band is partially full of electrons even at lower temperatures. This means that there is always a partially filled band which can contribute to electricity.

But semiconductors are a little different. They have mostly filled valence bands and empty conduction bands but their bandgaps are small enough that some of the electrons from the valence band receive enough energy that they can jump up into the conduction band. This gives way to thermally dependent conduction properties, where a material may be insulating at low temperatures but conductive at higher temperatures.

A second fact that is important in semiconductor conductivity is doping. Doping a material is the act of introducing other elements into a homogeneous material. What this
does is allows for the tailoring of how many electrons are available to contribute to current flow. Here is how it works.

For this example, Silicon will be used. There is a bar of Silicon and one of the Silicon atoms is replaced with an atom of Phosphorus. Since Silicon is in column four of the periodic table, it has four electrons in its outer shell. Phosphorus however is in column five, so it has five electrons in its outer shell. Silicon wants to have a full outer shell of electrons, which is eight. So it bonds covalently, meaning it shares electrons with four of its closest neighbors. So this way each Silicon atom has eight electrons in its outer shell. These electrons are locked into the lattice and don’t want to move around.

However, when one Silicon atom is replaced with the Phosphorus atom, there are five electrons available from the Phosphorus. The Phosphorus will bond with its four neighbors and share electrons covalently, but the fifth electron is free to wander around in the conduction band. Since all of the atoms are content with full outer shells, the extra electron can easily move around from atom to atom and will move when an electric field is applied.

This type of doping is called n-type doping because an extra electron is added to the material. Instead of Phosphorus, an atom of Boron, which is in column three of the periodic table and has three electrons in its outer shell, could have been added to the Silicon. In this instance, when three Silicon atoms and the Boron atom covalently bond, there are only seven electrons available, which means there is still one electron missing to fill the outer shell. So this lack of electron, or hole as discussed earlier, is also free to move around in the valence band when an electric field is applied. This type of doping is
called p-type doping since a hole is added to the material. As can be seen, doping a material can greatly increase its conductivity changing an insulator to a conductor.

Looking at the band diagram, which is just schematic plotting electron energy vs. distance, for these dopants, it can be seen that usually a dopant level will introduce an allowed energy level within the bandgap of the intrinsic material. When the intrinsic atom is replaced by an atom of a different size and charge, it changes the potential energy that the electrons see. The potential energy is no longer uniform in shape as it would be with identical atoms in the lattice but is now altered somewhat. This changes the energy levels the electrons are allowed to occupy, and usually results in an allowed energy state in the bandgap. These allowed states are usually just a few meV from either the valence or conduction band and thus are called shallow donors or acceptors since they require little energy to accept or give an electron to or from one of the bands. Thus, even at room temperature, these semiconductors with dopants, referred to as extrinsic semiconductors, will conduct at room temperature. These two types of materials can be combined and used as devices to emit light, which will now be discussed.

2.2.3 P-n junctions

Now that the idea of electricity being transferred by electrons and holes has been discussed, the focus will be turned to a device in which an n-type material is put in contact with a p-type material. Such a device is called a p-n junction. The author recommends Schubert as a great reading on p-n junctions and most of the information herein comes from that source.
A p-n junction is a semiconducting material, in which one side of the material is doped with donors making it n-type, and the other part of the material is doped with acceptors, making it p-type. These two regions are usually in direct contact with each other but don’t always have to be. There could be an intrinsic region between the two, but here the focus is on adjacent p-type and n-type materials.

Anytime there is a high concentration of one substance, it will try to diffuse and spread out evenly across the container it is in. An example would be smoke in a room. The smoke will move around from its source until it is uniformly distributed in the room. The same is true for the electrons in the n-type side of the semiconductor and for the holes in the p-type side of the semiconductor. The electrons don’t want to be confined to just the n-type part of the bar of semiconductor, they want to spread out and be evenly distributed across the bar. The same is true for the holes.

So the electrons will start to move from a high concentration in the n-side to the low electron concentration in the p-side. The holes will do the opposite, moving from the highly concentrated p-side to the low concentration in the n-side. This process would continue until the bar of semiconductor was a homogeneous mixture of holes and electrons.

However, when one electron leaves the n-side of the material, it leaves behind a nucleus (which cannot move) that is positively charged since the atom was originally charge neutral. The same is true of the p-side of the material. When a hole leaves the p-side of the semiconductor, it leaves behind a nucleus that is negatively charged since there is actually an extra electron added to the atom when the hole leaves.
Now after the electrons and holes have moved around, leaving behind positive nuclei on the n-side and negative nuclei on the p-side, an electric field will start to build up which will act to prevent the flow of electrons and holes. The electric field originates on each positive atom and ends on each negative atom so it starts in the n-type material and terminates in the p-type material. This directionality of the electric field will oppose any further diffusion of electron and holes since electrons on the n-side of the material are being pushed back to the n-side by the electric field that is set up and the same is happening to the holes on the p-side.

After the p-n junction has come to a stable configuration (which actually only takes a fraction of a second) there are still the p and n-type sides butted up against each other since the electric field that was generated prevented total diffusion of the electrons and holes. But right at the junction of the two materials, there is a region, referred to as the depletion region, in which all of the donor electrons on the n-side and all of the acceptor holes on the p-side are removed leaving charged atoms behind.

Outside of this depletion zone there is no electric field since all of the field lines of the electric field start and end on the charged particles inside the depletion zone. If there are no external forces acting on the bar of material, there will be no current flow. Inside the p-n junction there are two components of current that are at odds. There is the diffusion component of holes from the p-side wanting to diffuse to the n-side, and also the diffusion component of electrons in the opposite direction. Note that these two currents are actually in the same direction since the charge carriers have opposite signs.
Contrary to the diffusion current is drift current. This is the current that results from carriers being transported by the electric field that sets up in the depletion zone. Remember that carriers can be generated by photon excitation or thermal generation. Here, if a hole is generated in the n-side of the junction the electric field will sweep it across the junction. The same is true for an electron generated on the p-side of the junction. Note again that these currents add since once again the charges are moving in opposite directions but are of opposite sign.

There is a terminology that should be discussed. When holes are in a p-type material, they are called majority carriers since they are the majority charge carrier. Electrons in the same material would be considered as minority carriers since they are the minority charge carriers. The opposite would be the case when talking about an n-type material.

As stated, with no external forces acting on the semiconductor, there can be no current. The diffusion current is balanced with the drift current making a net current of zero. However, if a voltage is applied to the junction, things change. Consider the n-side of the device grounded and that scenarios will be discussed in which the voltages will be applied to the p-side of the material.

When a negative voltage is applied to the p-side material, this external field will support the built in field. This will increase the width of the depletion region which will lower the amount of minority carriers that can diffuse across to the material of opposite doping. If there are fewer carriers that are able to make the long trek across the widened depletion region, then there are fewer to recombine with majority carriers. This will
therefore lower the amount of photons given off of the device or at the extreme, will completely prevent any emission.

If a positive voltage is applied to the p-side material, then the external field will oppose the built in electric field. This will cause the depletion region to shrink. The majority carriers thus see a thinner barrier they must cross to make it to the opposite side of the depletion region. Therefore, more carriers will be able to successfully diffuse across the junction to the oppositely doped material. This will cause an increase in recombination which will increase the amount of photons that are emitted from the p-n junction. This is how light emitting diodes create light from biasing a voltage across a semiconducting material. Following, a look at the properties of this light will be investigated.

2.3 Properties of Light

Now that the method of making light from semiconductor materials has been discussed, attention will be moved to the properties of light. To start off, what exactly is light? Light is made of discrete elements called photons. Photons are, to the best of science’s knowledge, the smallest unit of light. Many people have carried out a plethora of experiments to determine if light is a particle or a wave. While some of these experiments show that light acts as a particle, others show that light acts as a wave.

This seems rather counterintuitive, and in all actuality what is commonly accepted is that light is both. Photons do exist; this has been proven as in the above reference. What has also been proven is that light propagates as a wave as shown in the above
reference also. Wave propagation of light is shown in objects as simple as prisms, separating the different wavelengths from each other. Based on these discoveries, it is not uncommon to hear light described as being made of particles that propagate collectively as a wave.

2.3.1 Color rendering, color temperature

White light is a complicated item. Just looking at the selection of lighting choices at the local hardware store, white light is not simply defined as ‘white light’. Since white light is made up of many different wavelengths, the ratio at which these colors are combined dictate the appearance of the final product.

One of the most important features of a white light source is its ability to render color. The idea here is how well this white light source can imitate a perfect white light source such as the sun. The casual observer may not notice a difference of how two separate light sources act on an object. When viewed side by side however, the difference becomes clear that one light source may make an object appear to be of a different color than another light source. This is the idea of color rendering.

Science tries to quantify color rendering by examining the emission of eight color samples under the light source in question and comparing the results with the samples illuminated by a black body radiator. The spectrum of light that is reflected from the eight samples is compared with the reflected light from the black body. The source in question is then given what is called a rendering index. This rendering index is a quantitative value
that indicates how closely the eight samples look when viewed under the source as compared to under the black body. 

A second quality of light that is important in lighting is a light source’s color temperature. Lighting is held to the standard of the sun, a black body radiator. It has been shown that a black body’s dominant wavelength is inversely proportional to its temperature. And for black bodies this temperature ranges from 2500 K to 10,000 K.

As discussed earlier, white light is made of many wavelengths. Sometimes the light may have a certain tint to it, which is determined by the combination of wavelengths the light is composed of. A white light source is compared to a black body and given a certain color temperature based on how it compares to different black body temperatures. This color change due to temperature is why people often associate white light with a reddish tint as a warm white, and at the opposite end, white light with a bluish tint is commonly referred to as a cool white.

2.3.2 Efficiencies of light devices

The efficiency of a light source is of utmost importance as this will determine if it can profitably be marketed. Since efficiency plays such a large role, light emitting diodes have three common measures for efficiency. These are internal efficiency, external efficiency, and extraction efficiency. The internal efficiency is what percent of the electrons that are carried by the current through the p-n junction recombine with holes and emit a photon.
Extraction efficiency is defined as the ratio of the number of photons that come out of a device to the number of photons that are created by the device. This can be enhanced or lowered by the device design, coatings, and electrical connections to the charge carrying materials.

The product of the internal and extraction efficiencies gives the ratio of photons that come out of a device to the number of electrons that flow into the device. This is also called the external efficiency. The external efficiency is the real trait of measure for a device. Since users want low power consumption and optimal lighting, the desired result is an LED which has the highest external efficiency possible.

2.3.3 Combining three colors for white light

Each wavelength of light in the visible spectrum is perceived to the human eye to have a certain color. The wavelengths that humans can see range from violet to red. This is due to the fact that humans have three types of cones in their eyes. The three are red, green, and blue cones. Each of these cone cells can depict light over a short wavelength window which peaks near the color each is referred to.

Combining two or more different wavelengths of light can become a difficult task when trying to quantify the ‘color’ of the combination. To do this, science uses what is called a chromaticity diagram. Chromaticity diagrams are constructed by calculating three tristimulus values from a light source. These three values, X Y and Z, one for each type of cone in the human eye, are found by integrating over wavelength the spectrum of the light source multiplied by the spectrum of each respective cone cell.
Once the tristimulus values (capital X, Y, and Z) are found, the chromaticity coordinates, referenced by lower case letters, are defined as the fraction of the sum of the three tristimulus values each separate tristimulus represents. Only two of these coordinates are needed since defining two sets the third. The chromaticity diagram is constructed by plotting two of the chromaticity coordinates against each other and painting in the plot with the resulting color that is obtained by the respective combination of the three chromaticity coordinates.

White light is observed as the color seen when a source gives values toward the center of the chromaticity diagram. Therefore, white light can be made of only two wavelengths. The problem with this is a source of only two wavelengths has a low rendering index of around 20°. This is acceptable for street lighting, but not for retail or indoor lighting. By increasing the number of wavelengths in the light source to three, the rendering index can be increased to the high 80s as seen in the reference by Zukauskas above.

This is why there is a big push for white LEDs made from a combination of red, green, and blue light. Not only will this combination give emission at wavelengths that are fundamental to human vision, but also they will create a source with a high rendering index which is also desirable.

2.3.4 Phosphor pumping

As was just discussed, white light can be made from combining at least two individual wavelengths. Engineers have taken advantage of this fact to make white light
sources from ultraviolet light emitting diodes which in turn are used to excite atoms which decay to emit some combination of red, green, and blue.

Ultraviolet light emitting diodes have been made which are quite efficient ¹¹. Since ultraviolet emission is of higher energy than visible, the ultraviolet LEDs are used to excite atoms which decay with longer wavelengths and emit visible light. Engineers coat the lining of the package of an ultraviolet LED with chemicals known as phosphors. These phosphors will absorb the high energy photon emitted by the LED and then through energy loss processes, the phosphor will reemit light that has been down converted to a shorter wavelength.

There are a few drawbacks to these devices as noted by Pimputkar in the above reference. If only one phosphor is used in the down conversion, then the rendering index is going to be low. If more phosphors are used, then the efficiency of the device will drop. Additionally, if any of the original ultraviolet light is not absorbed by the phosphor, then cancerous ultraviolet light is hitting whoever is under the light. A look at a few groups who have made visible light by this means will be looked at in future sections. For now, a look at materials in which visible light can be generated will be the topic of discussion.
2.4 Nitride Semiconductor Materials

2.4.1 Intrinsic physical properties

When Nitrogen bonds with metals from Group 3 of the Periodic Table, a group of semiconductors are made which are called III-V semiconductors, or Nitrides. The most common materials are Gallium Nitride, Indium Nitride, and Aluminum Nitride, or GaN, InN and AlN. Also, there can be any combination of the three metals bonded with Nitrogen to produce ternary or quaternary semiconductors such as Indium Gallium Nitride, or Indium Aluminum Gallium Nitride, or in shorthand, InGaN and InAlGaN.

These materials are still considered to be ‘new’ in research circles and still in the experimental stage of their development. There are currently many products which use their technology but when compared to Silicon, Germanium, Gallium Arsenide, and other ‘older’ semiconducting materials, there is still much to be learned from the Nitride family. A fantastic reference on Nitride materials is Wood & Jena and most of the information discussed here on Nitrides is from this literature.

One of the most promising characteristics of the Nitrides is their bandgap and the range that they span when combining the materials. Indium Nitride has a bandgap of 0.7 eV, the smallest of the Nitride materials. Aluminum Nitride is on the opposite side of the spectrum and has a bandgap of 6.2 eV, while Gallium Nitride resides in the middle at 3.4 eV.

As can be seen, these three Nitride materials span a light emission spectrum from 1772 nm to nearly 200 nm. This encapsulates the entire visible spectrum which is one of
the main reasons that the materials have drawn so much interest over the past two decades.

Most Nitride devices are created using chemical vapor deposition, CVD, techniques or by molecular beam epitaxy, MBE. Unlike Silicon which is made by pulling liquid Silicon by a solid Silicon seed crystal, most Nitride devices are grown on foreign substrates. Common growth substrates are sapphire and Gallium Nitride wafers. A drawback to these substrates is that they are very expensive. While a Silicon wafer could range around $20 for a two inch wafer, the same sized Sapphire wafer is easily ten times as much.

A second drawback to these substrates is that materials grown on them will not exactly match the native lattice constant of the substrate. When the material is grown, there will be stress in the film until a certain thickness upon which dislocations will occur in the material and introduce defects into the band gap. These defects are not desired in most electronic applications as they lower electron mobilities making devices slower.

Additionally, the defects will act as recombination sites. These sites, or traps as they are called, will lower the efficiency of a material by allowing non light emissive recombination to occur. The defect may introduce an allowed energy state within the bandgap of the material. These states can act as recombination sites for electrons and holes. If an electron is floating around and drops to an energy level in the middle of the bandgap, the photon it emits will not be of the desired wavelength inherent to the material. Also, the recombination may not result in a photon at all, as all of the energy could go to producing phonons.
A look at how Nitride materials are assembled will help to clarify why they behave as they do.

2.4.2 Polarization

Nitride materials assemble in two crystal forms. They can assemble in cubic form, or the more common form, wurtzite structure. The cubic growth is symmetric and thus there is no difference in charges throughout the material as it is viewed from the outside.

When the materials form in the wurtzite structure however, looking along the (0001) or C-direction, the electron cloud is pulled more toward the Gallium atom than the Nitrogen atom. This charge separation acts as a dipole. In the body of a solid uniform material, the net charge is neutral over the interior of the material.

At the edges of the material though, there is a layer of what appears to be a sheet charge from the electron cloud being displaced along the (0001) axis. If the material ends in a layer of Gallium (or other group III metal) atoms, then the charge polarization appears as negative sheet charge. If the material ends in a layer of Nitrogen atoms, then it appears as though there is a positive sheet charge at the face of the material. This polarization of the charges in a material is called spontaneous polarization since it is spontaneous in a material and is not due to any outside forces.

In addition to spontaneous polarization, there exists piezoelectric polarization in Nitride materials. Piezoelectric polarization occurs when one of the materials is stretched such that the c-plane atomic lattice spacing is altered from its natural distance. When this
happens, the sheet charges in the material are brought closer or farther apart which changes the electric field across the material.

The strain of the material could be due to external forces acting on the material, either compressive or tensile strain. However, a more common case is when two different metals are used and grown on top of each other. Such is the case when Gallium Nitride is grown on Aluminum Nitride or vice versa.

Since the lattice spacing of GaN is larger than that of AlN, any Aluminum Nitride films that are grown on bulk Gallium Nitride will be strained so that the lattice spacing of the Aluminum Nitride is increased to match that of the Gallium Nitride. This in-plane tensile strain will bring the top and bottom layer of the Aluminum Nitride closer than usual which is the source of the piezoelectric polarization. The piezoelectric polarization will either act in addition to or to reduce the spontaneous polarization already seen in the materials.

The major implication of the polarization of the charges in the Nitrides is the effect on the band diagrams of the materials. Since there is an electric field acting inside of the material with no applied voltages, there is an inherent band bending in the materials. This bending allows for quantum wells to be grown at material interfaces as seen in high electron mobility transistors, HEMTs. A negative effect that the band bending can have is when a quantum well is grown; the sloping of the bands will separate the electron and holes which will result in less recombination and therefore less light output from a device.
2.4.3 The ‘green gap’ in optoelectronics

A comment was just mentioned on the strain of the lattice in materials when two different materials are grown on top of each other. This is very important for this dissertation and is actually the cause of the high level of dislocations, and therefore low radiative emission efficiencies, of materials which emit in the green region. Since humans perceive the color green at wavelengths near 540 nm, a material which emits photons at an energy of around 2.30 eV must be used for LEDs emitting at this color. For direct recombination from the conduction band to the valence band, this would mean the material needs a bandgap of 2.30 eV.

Since none of the binary Nitride semiconductors have this specific bandgap, in order to achieve emission in this range, a ternary or quaternary material must be used. GaN with its bandgap of 3.4 eV and InN with its bandgap of 0.7 eV are two materials which straddle the desired value. When the two materials are combined to grow InGaN, the bandgap of the ternary material can be found by taking a linear weighted average of the bandgaps of GaN and InN. Almost anyway; research\textsuperscript{13} has shown that the InGaN system has what is known as a bowing coefficient (as do all ternary semiconductors). This means the bandgap is not a linear average, but has a slight curve and can be determined from the following quadratic equation where $x$ is the percentage of Indium…

$$E_g(x) = 3.4 (1-x) + 0.7 x -2.6 x (1-x) \text{ eV}$$

According to this, to achieve green emission at 540 nm, a material consisting of around 20% Indium will need to be used. C-plane GaN, which has an in plane lattice spacing of 3.189\textsuperscript{14} Angstroms is one of the most common growth substrates for InGaN.
InGaN composed of 20% Indium, will have an in-plane lattice spacing of roughly 3.252 Angstroms, same reference. This means that when \( \text{In}_{0.2}\text{Ga}_{0.8}\text{N} \) is grown on a GaN substrate, there will be a lattice mismatch of 1.98%. This doesn’t seem like much, however, it is enough that the \( \text{In}_{0.2}\text{Ga}_{0.8}\text{N} \) will grow stretched for a few layers until defects are formed.

When this occurs, the material’s crystal structure will alter to allow for the misfit between the two materials to be incorporated in such a way to yield the lowest energy state. This atomic altering is what is known as a defect. The defect usually is a non-radiative recombination site for electrons and holes. Therefore, the more defects, the lower the efficiency of the device which uses the material as its active area. This is the current problem with green LEDs, and it is known as the ‘green gap’ since it occurs with materials which emit in the green spectrum. Figure 2.1 demonstrates this efficiency droop at green efficiencies.

![Figure 2.1 Quantitative description of the green gap. Wetzel, RPI.](image)

2.1 Quantitative description of the green gap. Wetzel, RPI.
Since thin films of InGaN will result in a high lattice mismatch with the growth substrate, one alternative to this is the growth of InGaN nanowires. When grown under the correct conditions, InGaN will form as a three dimensional wire instead of a two dimensional film. When this happens, the wire (or nanowire if grown with dimensions on the order of nanometers) is free to expand or contract according to what its inherent lattice spacing dictates. The nanowire’s atomic spacing is no longer dictated by the substrate it is grown on. Using this technique, researchers are currently investigating the growth of InGaN nanowires and their applications to LEDs. This is the research efforts discussed in this dissertation. Before the author’s research is discussed, attention will now be focused on reviews of recent work done in other groups that have used these nanowires for making LEDs.
CHAPTER 3:
LITERARY REVIEW OF RELATED RESEARCH

3.1 Growth of Wires

Nitride nanowires have been grown by chemical vapor deposition (CVD), and also by molecular beam epitaxy (MBE). Each growth method has its advantages and disadvantages and will produce wires with different characteristics. A look at a few papers in which Nitride nanowires have been grown is now the topic for discussion.

3.1.1 VLS Growth of Nanowires

To give a brief description of VLS growth Silicon nanowires will be used as an example. A common method to grow Silicon nanowires by chemical vapor deposition is to use gold catalysts to initiate and sustain nanowire growth. The reason why this works is due to the eutectic feature of the combined gold and silicon. When two materials form a eutectic compound, it means that the combination of the materials has a lower melting point than either of the two materials by themselves. Taking advantage of this, researchers will deposit small, a few nanometers in diameter, gold droplets onto samples. These samples are then loaded into reaction chambers in which gases containing the desired growth elements are introduced. These gases are the ‘vapor’ label in the VLS name. The gases reach the gold drops and the Silicon in the precursor gases will deposit
in the gold drops making a eutectic which will melt. This is the ‘liquid’ label in VLS. This process continues until the saturation limit of the silicon in the eutectic is reached at which point the silicon will begin to precipitate out forming a solid chunk of Silicon. This is where the ‘solid’ portion of VLS comes from. This will continue, and as more silicon is precipitated out, more will be introduced to the eutectic staying right at the saturation point. More and more silicon will precipitate out on top of the previous solid Silicon.

Under the proper growth conditions, the newly precipitated Silicon will deposit on the top of the previous solid Silicon. This results in the vertical growth of a nanowire instead of a thin film. While this is commonly done for Silicon nanowires, the same process can be applied to other semiconductors. Gold is not the only element that can be used as a seed. Nickel is also a popular metal used as seeding material. Just a couple of examples are given here to introduce the reader to the method.

Using halide chemical vapor deposition, Kuykendall et al. were able to grow Nitride nanowires catalyst free with compositional ranges from pure GaN to pure InN in single growths. Carrier gases were introduced to a heated chamber by the precursors InCl₃, GaCl₃, and NH₃. The precursor gases reached the substrates (Silicon or Sapphire) at different areas and this is what allowed for the compositional fluctuations along a single substrate.

TEM studies of the wires indeed confirm that the composition range stretches from pure GaN to InN, and the wires appear to grow defect free. Further, the only Indium compositional fluctuations seen are those in regions with Indium concentrations of 70-90%.
A 325 nm HeCd laser was used for PL excitation. Visible emission from the samples is shown in Figure 3.1. Figure 3.2 shows PL spectra along with the intensity vs. composition of the samples. The group noted that there is no drop in PL intensity near the green wavelength region making these samples good candidates for green LED devices.

3.1 PL emission of nanowires with concentrations ranging from InN to GaN. Kuykendall et al.\textsuperscript{16}

3.2 PL spectra for different compositions across the samples. Right, PL intensity shown vs. wavelength indicating no loss in the green region. Kuykendall et al.\textsuperscript{16}
Zhong et al. were able to fabricate a p-n junction from crossing p-type and n-type GaN nanowires grown by metal catalyst CVD \(^{17}\). Nickel was used as the catalyst points for reacting gases of NH\(_3\), Mg\(_3\)N\(_2\), and Gallium metal. Growths occurred on c-plane sapphire at 950 C. TEM images indicate that the wires terminate with a Nickel particle on their tips while diameters range from 20-100 nm. An SEM image is shown in Figure 3.3.

3.3 SEM images of Nickel catalyzed GaN nanowires grown by CVD. Zhong et al.\(^{17}\)

Hole mobilities for the p-type wires were found to be 12 cm\(^2\)/V s. These p-type wires were crossed with an n-type wire to make a p-n junction. The junction was rectifying showing a turn on voltage of 3.5 V. Electroluminescence measurements were
taken showing a peak at 415 nm. Figure 3.4 shows the EL emission spectrum along with I-V characteristics and an SEM of the wires.

3.1.2 MBE Growth of Nanowires

The challenge of growing high quality GaN material in the form of nanowires was the motivation for work done by Bertness et al at the National Institute of Standards at Boulder Colorado \(^{18-21}\).

The group at NIST used MBE growth to grow Nitride nanowires with no nucleating metal particles. The main reason they wanted to do away with the metal
catalyst was fear of contamination of their wires. A metal catalyst such as gold or nickel which are common catalysts, could easily unintentionally dope the pure Nitride wire or cause deep level traps which would lower the efficiency of any light emitting device made from the wires.

Substrates used for growths were (111) Silicon which were subjected to a 10% HF:H₂O dip to remove native oxides. Further oxide degassing was carried out inside the MBE growth chamber by degassing at 750 C for 15 minutes and 850 C for 10 minutes. Growths were always carried out in a high V:III ratio, which is the ratio of the Nitrogen to metal beam equivalent pressures (BEP). Typical values of the V:III ratio were 120 for the Beam Equivalent Pressures. Nitrogen cracking was done with plasma powers of 450 Watts, and Gallium BEPs were around 9.8×10⁻⁸ Torr. Substrate temperatures were kept near 830 C during growths. Typical wire dimensions were reported to be 50-150 nm in diameter and up to 2 um long.

While the group did not use any foreign metal catalyst for their nanowire growths, they did use a nucleation layer. First, 4 Angstroms of pure Aluminum was deposited at a substrate temperature of 700 C. This was followed by the growth of 50-100 nm of Aluminum Nitride while the substrate temperature was lowered to 650 C. On top of the Aluminum Nitride was grown 150 nm of Gallium Nitride.

These nucleation layers created sheets of thin films made out of hexagonal pits as can be seen in Figure 3.5. Using X-ray diffraction, the group was able to confirm that the nanowire crystallographic directions were indeed dictated by the Silicon substrate as x-ray concluded that the <11-20> GaN direction was in line with the <1-10> direction of
the Silicon. As seen in the image, the nanowires tend to grow from the center of the hexagonal pits. Interesting enough is that the group reported no nanowire growth if the nucleation layers were omitted. Instead they observed a thin amorphous layer which they attributed as Silicon Nitride.

3.5 Hexagonal pits in AlN. The centers of the pits are starting points for nanowire growth. Bertness et al.\textsuperscript{18}

The group experimented with the addition of Aluminum and Beryllium to the nanowires. The addition of Aluminum caused the wires to widen as they grew. The addition of Beryllium caused the wires to grow as ribbons. Additionally, the pressure of atomic Nitrogen was varied and this was noted to have an influence the density of the nanowires.

The group's theory of why the nanowires grew is that under high V:III ratios, the
metal atoms have a lower sticking coefficient on the sides of the nanowire crystal than at the top. This would allow the atom to diffuse up the sidewall and stick to the top.

After growths of wires, the group was able to harvest the nanowires by placing the as grown sample in a solvent and submitting it to an ultrasonic bath. The wires were then pipetted out and drop cast onto a substrate. When the wires were deposited on substrates that had prior metal patterns, the wires would tend to align to the metal pads. However, if the wire lengths were above 6 um, an applied voltage was needed to initiate wire alignment.

Calarco et al. also reported on growth of GaN nanowires on Si (111) with no metal catalyst. Although the omitting of a metal catalyst will remove the threat of impurities in the grown wires, the group notes that this growth method does not allow for precise control of nanowire positions. This is one downfall of the method, that the grower cannot initiate growth at a certain place but must let the physics work itself out at the growth interface to decide its own destiny in terms of spatial location.

Growth conditions were as follows. Gallium fluxes yielding $2.3 \times 10^{-8}$ Torr were used with a Nitrogen power of 500 Watts which kept the growth in high V:III regime. Substrate temperatures were around 785 C, which is a little lower than the Bertness group which used a substrate temperature of 830 C as stated earlier. Note however that temperatures of substrates is difficult to compare between systems but are rather a ballpark number.

Results showed that wires grew mostly perpendicular to the substrate with a few wires growing at an angle of 35 degrees from vertical. This is one difference from the
Bertness group who reported wires growing almost completely vertical. Wire densities were $10^{10}$ wires per cm$^2$. Once growth times exceeded 60 minutes, the wires began to coalesce and wire densities decreased. However, densities increased up to that point. From growth observations, the group determined that the nucleation sites were around 15 nm in diameter. Growth rates were reported to be linear at 3.2 nm/min for length and 0.4 nm/min for diameters. However they note that the vertical growth is a function of wire diameter. To obtain a more accurate measurement of the growth rate, the group grew AlN/GaN heterostructures at set time intervals. The structure consisted of GaN/AlN, 2 periods of GaN/AlN, and 2 periods of GaN/AlN with different growth times. The examination of the heterostructures yielded growth rates of 5 nm/min for GaN and 4 Angstroms/min for AlN.

In addition to the growth, the Calarco group also reported on photocurrent measurement in the wires$^{23}$. Following growth, the nanowires were removed from the Si (111) by an ultrasonic bath and dispensed onto Si (100) substrates with a 300 nm Silicon Dioxide layer. Ti/Al 20/200 nm contacts were patterned with Electron Beam Lithography.

The group investigated three wire diameters; 70 nm, 190 nm, and 500 nm. Currents were measured in the dark and under UV illumination (15 W/cm$^2$), as shown in Figure 3.6. Wires above 200 nm yielded dark currents reading maxima at 1 to 10 uA at 2.5 V in the dark. When the UV light was applied, currents increased nearly 10 fold. Interestingly, the photocurrent would not decay back to the dark level even after 5 minutes.
3.6 Dark and Photocurrent. Currents from wires ranging in diameters from 70 nm to 500 nm. Calarco et al.23

For the 190 nm wires, the photocurrent would drop off after 1-2 seconds, but still would not decay back to the dark level. The maximum current obtained for the 70 nm wire was obtained with the UV illumination and was 10 nA which equates to 2.6 uA/cm². Measurements in the dark yielded no measurable currents.

The group noted that for all of their wires, the UV current was linear ensuring their Ti/Al contacts were ohmic. At low voltages, currents would depend on voltages on
the order of $V^2$ or even $V^3$ indicating space charge limited currents. The group concluded from their results that there is a surface Fermi Level pining that occurs in GaN nanowires. From the surface of the wires, anywhere from 50-100 nm can be depleted of carriers. This results in complete pinch off for wires less than 80 nm in diameter.

Calleja et al. also demonstrated successful nanowire growth using no foreign catalysts $^{24}$. They demonstrate in the work that they could successfully grow Bragg Resonators in nanowires as discussed below.

The group put an emphasis on the fact that the V:III ratio is critical to nanowire growth over thin film and noted that metal fluxes, plasma power, and substrate temperatures can all dictate the ratios of metals to Nitrogen. The temperature needs to be kept at a level high enough to give the metal atoms enough energy to diffuse on the surface but low enough to prevent metal atoms from dissociation from the surface.

TEM studies of their wires showed that the wires were grown defect free and there was a thin layer of Silicon Nitride roughly 2 nm thick grown on the surface prior to the nanowire growth. The group determined that the layer is due to the high reactivity of Silicon with Nitrogen. It was found that if this Silicon Nitride layer becomes too thick, then the wires no longer grew parallel to each other. This could be prevented by growing a thin AlN layer prior to the nanowire growth as has been shown by other groups.

The group noted that the problem of temperature control is a delicate challenge when trying to grow Indium Nitride nanowires. Since InN dissociates at 550 C, the temperature cannot be above this ceiling. Further, if the temperature is below the
dissociation temperature but still at a level too high, the Indium will diffuse rapidly and cause mushrooming of the nanowire tops.

Concerning the growth of InGaN, the group stated that since the binding energy of Gallium with Nitrogen is 2.24 eV compared to 1.93 eV for Indium and Nitrogen, if there is a lack of Nitrogen, the Gallium will always win the battle for metal crystal sites making a material that is Indium deficient. This is another demand for high V:III ratios. The group grew three InGaN samples at 630 C, 600 C, and 580 C to compare Indium concentrations. Results showed that Indium compositions were 16%, 27%, and 31% respectively showing the Indium’s dependence on substrate temperature.

A second interesting investigation that the group carried out was dependence of metal droplet nucleation size on nanowire density. Using a flux of $1.7 \times 10^{-7}$ Torr at 560 C substrate temperature, Gallium droplets were deposited on the substrate at different time lengths allowing for varying droplet sizes.

The group discovered that droplets with diameters of 340 nm actually prevented nanowire growth. Droplets with diameters below 90 nm and even bare substrates showed no dictation of nanowire densities. The group noted that this does not follow the VLS method for wire growth which is the mechanism used when metal catalysts are used in other nanowire growths.

The group also grew heterostructures containing AlGaN and GaN layers. It was found that nanowires with GaN disks in AlGaN layers revealed stress in the GaN disks. This stress varied radially.
Using the growth abilities of heterostructures in the nanowires, the group constructed a Fabry Perot resonator by growing 5 X (3 nm GaN / 10 nm Al$_{0.28}$GaN). This structure was put into AlGaN/GaN Bragg Reflectors to finish the device. The sample was successfully grown with no cracking.

One more feat tackled by the group was to grow periodic arrays of nanowires. Silicon Dioxide layers 80 nm thick were first thermally grown on (111) Silicon substrates. The oxide was patterned with Electron Beam Lithography and 80 nm diameter holes were dry etched into the oxide. Growth of nanowires was carried out on this sample and following growth the oxide was removed with an etch. The resulting structures showed 80 nm columns of nanowires that grew and then tapered outside of the template into large diameters. The group noted that to prevent closing of the template holes, the diameter to height ratio of the template must be kept around a value of one.

Ishizawa et al. tried a method to control the growth positions of their nanowires. The method they used was to deposit a thin layer of Aluminum on Silicon substrates and use the Aluminum as ‘seeds’ for nanowire growth. This method is somewhat different from Calarco’s view in the above mentioned paper as to not being able to control the position of the nanowires. However, even though Aluminum is not a foreign metal into the MBE system, it is still not an intrinsic metal to GaN nanowires. Therefore, it could be considered a foreign catalyst to use Aluminum in GaN nanowire growth.

The group deposited 5-31 nanometers of Aluminum on n-type Silicon substrates, patterned with Electron Beam Lithography and used liftoff procedures to make 2.2-3.4 um diameter circles of Aluminum on the Silicon.
The sample was then exposed to Nitrogen for 15 minutes at a substrate temperature of 860 °C. The Aluminum reacted with the nitrogen forming Aluminum Nitride islands. Gallium Nitride nanowires were then grown at 960 °C for one hour.

Using SEM images, the group discovered that wires that grew on the Aluminum disks averaged about 1.2 um in height while nanowires that grew on the Silicon substrate averaged 0.8 um tall. Additionally, there was a ring 0.3 um around the disks where the nanowires were shorter. The group believes the Gallium that adsorbed in these rings migrated to the AlN disks and fed the growing nanowires at the disk. The group mentioned that this may be the averaged diffusion length of the Gallium on the Silicon. A trend that the group noticed was that a linear correlation was obtained between the ratios of the height of the nanowires on AlN to those on Silicon to the spacing of the AlN disks.

Meijers et al. grew Gallium Nitride nanowires on Silicon (111) substrates and investigated the optical properties as they relate to growth temperatures. Growths occurred at 500 Watts of Nitrogen plasma and Gallium BEPs of $1.6 \times 10^{-8}$ to $5 \times 10^{-8}$ Torr after the substrates had been annealed at 925 °C for 15 minutes.

Wires were grown with diameters ranging from 20 to 150 nanometers and heights of 300 to 500 nanometers. Substrate temperatures ranged from 770 °C to 810 °C. The group reported that the wires they grew that had smaller diameters were taller than those with larger diameters.

Growths were carried out and split into three different III-V ratio sections. During the middle section, the Gallium flux was increased and then held constant in the last section of growth. Increasing the Gallium flux to a high level resulted in wires that
coalesced at the tops. Reducing the Gallium flux slightly from this coalescing level resulted in wires that had crown shaped bulges on their tops. Increasing the growth substrate temperature resulted in growths that did not show any signs of wire widening or crowning.

Figure 3.7 shows results from CL measurements taken on three samples grown at different temperatures. As can be seen, increasing growth temperature resulted in nanowires that have less emission from defects. The group concluded that increasing the growth temperature results in nanowires with higher optical emission efficiencies.

3.7 CL Intensities. CL Intensities compared at different growth temperatures. Meijers et al.\textsuperscript{26}
Park et al. grew nanowires not only in Nitrogen rich conditions but also in Gallium rich conditions. Samples were grown on Si (111) which were dipped in HF and then annealed at 900 C for 30 minutes. Growths were carried out at 800 C with Gallium fluxes ranging from $2 \times 10^{-7}$ to $2 \times 10^{-6}$ Torr.

Growths initially started with columnar growth and once the columns reached a height of about 400 nm, hexagonal nanowires grew from the nanocolumns as shown in 3.8. TEM investigations showed that the columns contained defects while the nanowires grew defect free. Emissions from growths revealed the same data, as nanowire emissions peaked at 3.351 eV and only low emissions were obtained from the columns indicating high defects.

3.8 Nanowires on nanocolumns. Showing two growth states. Park et al.27

The group noted that as opposed to earlier group’s reports, they saw nanowire growth even in Gallium rich conditions. They believe that this could be possible due to
the high growth temperatures. Photoluminescence measurements were taken on samples grown with varying Gallium fluxes from $2 \times 10^{-6}$ to $2 \times 10^{-7}$ Torr. Highest signal peaks were obtained at 3.4734 eV from samples grown at fluxes of $2 \times 10^{-6}$ Torr. The group stated that the signals were three times as high as GaN film reports but also the signals FWHM was broader which they attributed to varying nanowire sizes. Nitrogen rich growths had higher peaks at 3.45 eV than those grown under Gallium rich conditions.

Songmuagn et al. 28 investigated the growth mechanism of Gallium Nitride nanowires on Silicon by varying initial growth conditions. Silicon (111) substrates that were dipped in 5% HF for 2 minutes and then outgassed. As seen in Figure 3.9, nanowire growth directions were different when wires were grown directly on Silicon vs. growth on an AlN layer at a substrate temperature of 790 C. Wires grown on the Silicon substrate are not perpendicular to the substrate as opposed to wires that do grow perpendicular to the substrate when grown on a thin AlN layer. Also shown in the image are Reflective High Energy Electron Diffraction (Rheed) patterns which show that growth of nanowires directly on Silicon substrates generate smeared out Rheed spots while growth on the AlN buffer layer offer a more ordered, spotty pattern. The group attributed the streaky pattern to nanowires not growing perpendicular to the Silicon surface.

Another difference between nanowire growth on an AlN layer vs. direct growth on Silicon is that Gallium Nitride islands formed on the AlN buffer layers after 10 minutes of growth from which the nanowires grew vertically. However, the growths directly on Silicon did not result in these island formations.
Figure 3.10 shows nanowire length, density, and actual material deposition as a function of substrate temperatures. It can be seen that with increasing temperatures, the nanowire growth lengths and density increase. However, the material deposition decreases. The group explained this by noting that at temperatures above 770 C, the Gallium was desorbing from the substrate due to the high temperatures.

3.9 Rheed and SEM images. Comparison of GaN nanowire growth on Silicon vs. growth on an AlN buffer layer. Songmuang et al.\textsuperscript{28}

With the substrate fixed at 790 C, the group varied the Gallium cell temperature from 850 to 910 C which altered the Gallium BEPs. Increasing the cell temperature resulted in a higher number of GaN growth centers, but fewer nanowires because they coalesced with this increase in Gallium deposition. An interesting fact that the group
noted was that at stoichiometric condition, the Nitrogen atoms arriving at the tip of the nanowires was the limiting growth factor.

3.10 Nanowire growth kinetics vs. substrate temperature. Nanowire growth rate and density increased with temperature while overall material deposition dropped. Songmuang et al.\textsuperscript{28}

3.1.3 Patterned Growth of Nitride Nanowires

One desired result when dealing with three dimensional growth is control over the location of the grown material. Since this area of growth is not concerned with total
coverage of the substrate as thin film growth, the ability to dictate where the vertical growth occurs would be another asset to the grower.

One group has optimized this process when discussing selective area growth of Nitride nanowires by MBE. Sekiguchi, Kishino, and Kikuchi \textsuperscript{29, 30}, working out of the University of Sophia in Japan have been able to use patterned Titanium masks to control where on the substrate nanowire growth will occur. The growths start with an MOCVD GaN substrate which has been coated with 5 nm of Titanium. The Titanium is then selectively etched by Focus Ion Beam etching to create circular holes on the order of 100 nm deep with diameters of the same dimension.

The sample is then loaded into the growth chamber where the sample, at 400 C, is exposed to Nitrogen plasma for 10 minutes. Following, the substrate temperature is ramped to 900 C where nanowire growth is initiated. The group has found that the substrate temperature is a critical parameter for the effectiveness of the Titanium to act as a growth mask. If the temperature is below 880 C, no patterning was observed. However, if the temperature is too high, the growth rate of the nanowires is decreased due to a higher desorption rate of the Gallium atoms from the surface. A temperature of 900-930 C was found to offer the best quality growths. This selective temperature range is in part due to the dependence of the Gallium diffusion on the substrate temperature. As the temperature was increased, the Gallium diffusion also increased which would remove any unwanted nanowire nucleation.

The second critical parameter to yield patterned growth was found to be the Nitrogen flow rate. The Gallium diffusion as well as the lateral growth rate were both
highly dependent on the Nitrogen over pressure in the growth chamber. As the Nitrogen pressure was lowered from 3.5 sccm to 1 sccm, the Gallium diffusion length on the surface changed from 92 nm to 187 nm. At the same time, the lateral growth rate of the nanowires decreased from 45 nm/hr to 10 nm/hr.

Using the above information, the group was able to grow patterned GaN nanowires with InGaN quantum wells at the tips of the wires as shown in Figure 3.11. By using the ratio of the PL intensity at 4K vs. 300 K, the wires were shown to give 77% internal efficiency.
3.11 SEM images of patterned growth. The quoted dimensions are the nanowire diameters. Sekiguchi et al.\textsuperscript{30}

3.2 Indium Nucleation in Indium Gallium Nitride Thin Films

When Indium Gallium Nitride thin films are grown, groups have reported that the Indium will diffuse in the material and instead of creating a uniform composition material there will be areas of high and low Indium composition dispersed throughout the
material. Since this dissertation focuses on the growth of InGaN nanowires, this phenomena is highly relative. A few of the papers published on this phenomena are reviewed below.

Ho and Stringfellow $^{31}$ calculated the binodal (solid) and spinodal (dashed) decomposition diagram for the InGaN system which is shown in Figure 3.12. This reference indicates that unless the temperature is 1200 C or greater, the InN and GaN are not miscible.

![Decomposition curves](image)

3.12 Decomposition curves. Decomposition values for the InGaN system. Ho et al.$^{31}$
Doppalapudi et al. 32 experimented and validated the accuracy of the plot presented by Ho. The group used substrates grown on C and A planes sapphire. The substrates were nitridized with RF plasma at 800 C. A buffer GaN layer 20-30 nm thick was then grown. InGaN was grown at temperatures between 650-725 C yielding thicknesses of 500 nm to one micron.

Figure 3.13 is X-ray diffraction spectra along with a SAD pattern of an In$_{37}$Ga$_{63}$N sample grown at 725 C. There exists a peak showing the InGaN, but there are also peaks revealing pure InN and GaN materials. The diffraction pattern also shows spots in addition to the InGaN material.

The group annealed two InGaN samples at temperatures up to 725 C. One sample consisted of an Indium composition of 9% and the other with a composition of 35%. The two samples were annealed and the resulting X-ray diffraction patterns are shown in
Figure 3.14. The In$_{0.9}$Ga$_{0.1}$N sample shows no indications of Indium diffusion from the anneal. However, the In$_{0.35}$Ga$_{0.65}$N Indium sample shows increasing peaks of pure GaN.

These results were noted by the group to be in agreement with the proposed findings of Ho and Stringfellow. The sample is stable at 725 C with an Indium concentration of 9%, but at 37%, the Indium will show signs of diffusing and clustering. The group also addressed the lack of an InN peak after the annealing of the In$_{0.37}$Ga$_{0.63}$N. This was attributed to evaporation of the InN by the group and reportedly confirmed with SEM imaging.

The group also saw indications of Indium ordering in the samples they examined. They noted that for (000k) planes where k is odd, there should be a zero structure factor given in a random InGaN film. If ordering along the basal plane of Indium occurs, this will give a nonzero term for that structure factor. Figure 3.15 shows a X-ray spectrum from a In$_{0.9}$Ga$_{0.1}$N sample showing spots for the (0001) plane. The group explains this is indicative of the Indium ordering along the basal plane.
3.14 X-ray diffraction patterns. Diffraction patterns of In$_{0.9}$Ga$_{0.1}$N & In$_{0.35}$Ga$_{0.65}$N left and right respectively. The In$_{0.9}$Ga$_{0.1}$N sample shows no effect from annealing up to 725 °C while the In$_{0.35}$Ga$_{0.65}$N sample is showing an increasing peak in GaN concentration and lower InGaN. Doppalapudi et al.$^{32}$

3.15 X-ray intensity peaks. X-ray diffraction spectrum from an In$_{0.9}$Ga$_{0.1}$N sample. The (0001) peak is showing that Indium ordering is occurring in the sample. Doppalapudi et al.$^{32}$
Smeeton et al. investigated damage to specimen caused by TEM beam irradiation. Starting off, the report noted that excitons in InGaN materials are localized and do not seem to be affected by the high number of defects that occur in InGaN materials when grown on Gallium Nitride substrates.

The group investigated if TEM beam irradiation on the specimen is cause for local Indium clustering by irradiating a sample with a 200 keV beam using a 2.5 Angstrom spot size. The sample was grown by MOCVD on c-plane sapphire in the following manner. A 30 nm GaN nucleation layer started the growth followed by a two micrometer GaN layer. A ten period In_{0.22}Ga_{0.78}N/GaN 2.8/7.2 nm quantum well series was grown last.

The sample was wedge polished and then ion milled using a 3.2 keV accelerating voltage for ten minutes at 4 degrees incident angle. Lattice parameter maps revealed localization effects in spot sizes of about 2 nm.

Figure 3.16 shows time progressed images of the sample during irradiation by the 200 kV beam which has a current density of 35 Amps per square centimeter. Clearly as time progressed the sample was affected by the electron beam radiation. Figure 3.17 shows a time progressed TEM sampling along with local lattice parameter mapping. Indicated is the Indium concentration that would be represented by the lattice spacing revealed by the TEM images. Indium mole fractions from 0% to 70% are observed.

The question arises if the inclusion of the ion milling was responsible for the changing in the position of the metal atoms. The group decided to capture TEM images of a sample that was not ion milled to remove any uncertainty. Figure 3.18 shows TEM
images of the non ion milled sample. As can be seen by comparing the two images in the figure, once again there is notable atomic manipulation by the incident beam even without ion milling.

3.16 Progressive TEM images. TEM images shown over time during irradiation by a 200 kV beam incident on InGaN/GaN quantum wells. The images clearly show the shift in the composition during the beam irradiation. Smeeton et al. 33
The group indicates that there are two possible methods by which the incident electron beam could cause manipulation of the lattice atoms. Radiolysis, in which an ionized atom receives kinetic energy when it relaxes and is thus jolted from its lattice site is the first possibility. Second is knock on lattice manipulation in which the beam directly

3.17 TEM & LPM data. TEM images along with lattice parameter mapping of the InGaN/GaN materials recorded over time. The white line traces drift of the sample. Smeeton et al.\textsuperscript{33}
3.18 TEM images. TEM images of a sample which was prepared without ion milling. The sample on the right was taken after several minutes of beam irradiation. Obvious changes in the images reveal that the ion milling was not the cause for the lattice disturbances seen in earlier images. Smeeton et al.\textsuperscript{33}

imparts enough kinetic energy to the atom to move it from a lattice site. Noted by the group is the fact that the heavier Gallium and Indium atoms are less affected by knock on than the lighter Nitrogen atoms. Thus, defects in this manner are most likely due from Nitrogen shifting. From this, the group indicates that there are two possible causes for the change in the lattice images revealed by the TEM images over time. First, the beam could be inducing Nitrogen vacancies which could cause local strain. This strain would then be perceived as a change in Indium concentration.

Second, the beam could be imparting Joule heating to the substrate in which the material would have enough energy to overcome barriers and relax to a more stable state by shifting of Indium atoms throughout the material. The group states that this is unlikely however due to the fact that under the conditions of their electron beam, there is only

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enough energy being imparted to the specimen to increase its temperature by a few degrees Kelvin.

The group does admit that there is no proof either way of what is causing the change in the TEM images, either the Indium concentration shifting or vacancy generation. They do however continue to probe the reason for the localization seen in photoluminescence measurements. The group presents two theories into answering this question.

First, the group notes that a slight change in the Indium concentration would indeed induce a large change in the bandgap of a material. Stated is that a one atomic percent change in Indium concentration would change the bandgap by well over one kT thus making a local quantum well. Second, the quantum well thicknesses could play a role in the localization due to the fact that a one monolayer addition to a material would drastically change the separation of the electron hole pair due to band bending effects.

The group leaves off stating that TEM beam irradiation does alter the atomic structure of InGaN materials. However, they are not sure if this alteration is due to Indium migration or to defect induced strain.

Galtrey et al. conducted another experiment investigating TEM beam damage on InGaN substrates. They used three dimensional atomic probe studies (3DAP) to ascertain the positions of different atoms in an InGaN/GaN multi quantum well. 3DAP as explained by the paper, is a technique where a sample is sharpened to a pin like condition. Then a voltage is pulsed across the sample exciting it to give off atoms. These atoms are then detected and the atomic number and initial position can be inferred.
The reason for use of the 3DAP technique is that they wanted to investigate the structure of the multi quantum well without submitting it to TEM irradiation. It is believed following the work by Smeeton above that the electrons from the TEM beam are causing the displacement of Indium and it is not a self contrived diffusion.

The sample that was used for this experiment was grown by MOCVD at a temperature of 740 C. The sample consisted of InGaN/GaN multi quantum well structures. X-ray diffraction revealed GaN layers with thicknesses of 6.95 nm and InGaN thicknesses of 2.38 nm where the Indium content was 18%.

The sample was ion milled to less than 100 nm at the tip and a ratio of 10:1. To protect the quantum well regions, 30 nm Au and 500 nm Pt were deposited on top of the sample to protect the wells from ion beam damage. Results of the 3DAP are shown in Figure 3.19.
3.19 3DAP image. Three dimensional atomic positioning image showing concentrations of different elements. Top: Gallium atoms are colored blue, and Indium atoms are colored orange. Bottom: Gold atoms are blue while Indium atoms are orange. Clearly, the quantum wells at the right did not undergo any Indium displacement. Galtrey et al.\textsuperscript{34}

The figure shows that the Indium is confined to the quantum well regions and there appears to be no diffusion of the Indium. The Indium concentration revealed by the 3DAP was 19% which is well in agreement with the 18% value obtained by X-ray diffraction. There is no evidence anywhere in the sample of an Indium concentration of over 33% which is well below that seen in samples viewed by TEM.
From these results, the group concluded that the Indium clustering which has been seen by many groups was not seen in their sample and they suggest that strain seen is due to TEM damage.

Shifting from examining the materials that LEDs can be made from, focus will be turned now to groups that have fabricated LEDs either from phosphor excitation or nanowire structures.

3.3 Light Emitting Diodes

Earlier sections discussed the works that groups have been obtaining growing Nitride nanowires by Molecular Beam Epitaxy. As stated, many of those works were carried out with the goal of lowering the defects in the Nitride material to increase the optical efficiency of the material. Attention will now focus on reviewing works that groups have produced using nanowires to make light emitting diodes. In addition a few reviews will also be included on another method of producing light emitting diodes which emit in the visible spectrum. This method utilizes ultra violet emission from solid state materials which excites phosphors which in turn red shift the energy to visible emission.

3.3.1 Phosphor LEDs

Shue et al. 35 fabricated UV light emitting diodes that pumped red, green and blue phosphors. This opposes traditional techniques of UV or blue LEDs pumping only yellow and blue phosphors.
The material was grown using organometallic CVD on c-plane Sapphire substrates. The growth layers were 30 nm Gallium Nitride grown at 560 C, four microns of Gallium Nitride doped n-type with Silicon. The five period Al$_{0.1}$Ga$_{0.9}$N/In$_{0.1}$Ga$_{0.9}$N active region was next. The p-side was made of fifty nanometers of Al$_{0.15}$Ga$_{0.85}$N used as an electron blocking layer followed by 250 nm Magnesium doped GaN followed by a Silicon doped In$_{0.23}$Ga$_{0.77}$N/GaN superlattice. Contacts were made by etching to the GaN and depositing Ni/Au on the p-type GaN and Ti/Al/Ti/Au on the n-type GaN.

The diode showed emission peaks near 400 nm. The group used Rubidium doped phosphors, NANTEX-RU-B403, G502, R603 phosphors on the package of the LED. Figure 3.20 shows the emission spectrum from the device when pumped with 20 mA of current. From the plot, the group noted that some of the UV light is escaping which they attributed to either non uniform coating of the phosphors or less than 100 % capturing by the phosphors.
3.20 Emission spectrum. Emission spectrum from a UV diode pumping red, green, and blue phosphors. Schematic growth structure. Sheu et al.\textsuperscript{35}

The group stated that current pumping can cause emission changes from LEDs and that if the generated light is visible, this can cause a change in the emission spectrum that is seen by the total package. However, they saw no change in emission with their UV diode when the current level was increased as can be seen in Figure 3.21.

The efficiency of the lighting device was seen to be 10 lumens per Watt which the group reports as lower than other phosphor pumped white LEDs at 20 lumens per Watt. The color temperature of the device was seen to be 5900 K and the color rendering index was 75. With current values ranging from 20-60 mA, there was no change in these values.
3.21 Emission spectrum. Emission spectrum from UV pumped phosphor LED showing no emission change from 20 mA to 60 mA current pumping. Sheu et al. 35

3.3.2 LEDs from Nitride Wires

Kikuchi et al. 36 fabricated a light emitting diode out of GaN nanowires with InGaN wells embedded in the Gallium Nitride. Growths occurred on Sb doped Silicon (111) substrates which were dipped in HF for 3 minutes and outgassed at 830 C for 10 minutes. Titanium was deposited on the back of the wafer for heat transfer and the substrate was mounted Indium free into the growth chamber.

Growth methods included initial deposition included Gallium for 25 seconds followed by Nitrogen plasma irradiation for one minute. This occurred at 530 C
depositing Gallium Nitride islands on the Silicon. Following this growth, the substrate was ramped to 870-890 °C and GaN was grown for 1 hour.

This light emitting diode fabrication was carried out following the aforementioned nanowire growth method. The layers grown were 750 nm of Silicon doped GaN / 10 nm of UID GaN / eight periods of (2 nm InGaN / 3 nm GaN) / 10 nm UID GaN / 600 nm Mg doped GaN. The resulting structure is shown in Figure 3.22. It can be seen that the p-type layer was grown at a lower temperature, 640-680 °C as opposed to 890 °C for the UID and n-type layers, allowing for the wires to grow together into a film.
3.22 SEM of grown structure. Substrate temperature control was used to allow for the nanowires to coalesce into a film for contacts. Kikuchi et al.\textsuperscript{36}

Ni/Au 2/3 nm contacts were deposited on the p-type layers and the original silicon substrate was coated with InGa metal and attached to a Copper heat sink. Current results from the device can be seen in Figure 3.23. The device had a turn on voltage of 2.5-3 V, and at a forward bias of 5 Volts the device yielded 10 mA while at -5 Volts bias only -400 uA were extracted. Electroluminescence measurements for three devices grown...
in this manner with slight growth changes yielded peak emissions at 530 nm, 580 nm, and 645 nm, as shown in Figure 3.23.

3.23 I-V results & EL intensity. Rectification current obtained from GaN/InGaN/GaN nanowire LED. Kikuchi et al.\textsuperscript{36}

Guo, Zhang, and Bhattacharya out of the University of Michigan have successfully fabricated a LED from InGaN nanowires\textsuperscript{37}. Using both (001) and (111) Silicon substrates they deposited a few monolayers of Gallium metal at 800 C before nanowire growth. Nanowires were then grown at 550 C yielding Indium compositions near 25% as shown by selective area diffraction TEM images. Photoluminescence measurements revealed that at an emission wavelength of 550 nm the nanowires have an internal efficiency of 30% assuming a 100% efficiency at 10K.

The group fabricated LEDs by coating the grown nanowires with a spin on dielectric and etching back planarizing the surface to make top contacts as shown in the image below. By incorporating wells with different Indium compositions, the LEDs
would emit light across the visible spectrum thus offering white emission.

3.24 Left: Schematic showing fabrication of LEDs from nanowires. Right: I-V and photo of biased structure. Guo, Zhang, & Bhattacharya.37

From the discussions in this chapter on nanowire research it is now an appropriate time to summarize the results of researchers worldwide and identify the uncharted territories that still exist in nanowire technology. Looking at the work carried out by others, it appears the largest piece of information to use as a stepping stone is the actual methods for producing nanowire growth as opposed to thin films. This information is indeed valuable and will be used by the author in the next chapter as a starting point for the growths discussed herein. The first obstacle in this research is obtaining growth conditions which actually yield the desired materials in nanowire format.

A notable observation in the field of nanowire research already carried out by other groups is that there have been groups who grow GaN nanowires, InN nanowires, or InGaN quantum wells within wires. These groups have done extensive research on characterizing the wires they have grown. However, a window of opportunity exists in MBE growth at the InGaN regime. There have only been two reports24,38 on the growth
and characterization of bulk InGaN nanowires by MBE, with one of these (which was concurrent with this research) discussing characterization of the wires. This material system specifically is where the research in this dissertation attempts to push the boundaries on current knowledge of Nitride nanowire technology. By successfully realizing the growth conditions to obtain bulk InGaN nanowires, much knowledge can be obtained in filling in the missing link between GaN and InN material growth.

Following, further characterization of the InGaN nanowires will help to decide if they can indeed be grown without the threading dislocations that plague thin film InGaN materials and to attempt to quantify the wire’s efficiency. Finally, by fabrication of a device from these nanowires which utilizes a p-type Silicon substrate as opposed to an n-type substrate as done by others, experimentation will reveal if it is possible to inject holes from Silicon into the nanowires. Such an experiment would be the first of its kind and reveal the possibility of using the easily p-type doped Silicon in conjunction with the n-type Nitride nanowires.
CHAPTER 4:  
MBE GROWTH OF NITRIDE NANOWIRES

Moving forward from the results that others have obtained, attention will now be focused on research carried out by the author. The first step in this journey was to find appropriate growth settings which allow for nanowire growth by Molecular Beam Epitaxy. This naturally leads to the need for a description of how the semiconductor materials were grown.

Material growth took place in a Veeco Gen930 Molecular Beam Epitaxy system as seen in Figure 4.1 The system is broken down into three separate chambers. The load-lock chamber, used for loading substrates contains radiative heating elements which allow for baking of the chamber each time samples are loaded or unloaded. The standard bake used is a 200 C bake for 7 hours. The main purpose of this bake is to remove as much water vapor and adsorbed oxygen as possible.

The second chamber separates the intro chamber from the growth chamber and is thus called the buffer chamber. This chamber contains a substrate heater for baking samples immediately before growth to further remove any contaminants. While this heater is not water cooled, the maximum bake temperature for this heater is 450 C. Once substrates are baked in the buffer chamber, they are ready to be loaded into the growth chamber.
4.1 Photo of MBE growth system used.

The growth chamber of this particular Nitride system uses a Veeco RF plasma generator to split Nitrogen into $N_1$ atoms for the Nitrogen source. Solid sources of Aluminum, Indium, and Gallium are loaded into pyrolytic boron nitride (PBN) effusion cells (shown in Figure 4.2) for metal deposition. Doping comes about from solid Silicon and Magnesium sources also loaded into PBN cells.
4.2 Crucibles which hold source materials for growths.

Each chamber is kept under vacuum by a separate pump. The load-lock chamber is pumped by a turbo pump which is roughed by a scroll pump. The buffer chamber and growth chambers are first roughed with the intro chamber’s turbo pump. Once pressure reaches the range of $10^{-5}$ Torr in the buffer chamber an ion pump can take over and pump on the buffer chamber taking it into the range of $10^{-10}$ Torr background pressure. The growth chamber is also roughed by the intro chamber’s turbo pump, and once pressure reaches $10^{-4}$ Torr a CTI8 cryogenic pump takes over to pump this chamber. In addition to the cryo pump, a liquid nitrogen jacket is embedded around the outer shell of the growth chamber which also helps to lower the pressure of the growth chamber to pressures ranging from $10^{-9}$ to $10^{-12}$ Torr.
4.3 Showing the Load-lock, Buffer, and Growth chambers of the MBE.

Another measure which is undertaken is a complete exterior bake of the entire system anytime it is opened to atmosphere. When this is done, a shell which has heating elements inside is placed around the system. The whole shell is then baked at 200 C until a time when the background partial pressure of Oxygen is below $\times 10^{-10}$ Torr. This is crucial due to Oxygen being an unintentional n-type donor in Nitride Semiconductors.

At the low pressures of the growth chamber, as the source materials are heated in their cells, they will either melt and evaporate or sublime. Substrates for growth are mounted onto a heated stage which is in the line of sight of the source materials. As the sources evaporate, the atoms have a large enough mean free path that they will arrive at the substrate. The atoms will have a finite diffusion length on the surface upon which
they will finally bond with the substrate and other growth materials to form a semiconductor material.

Deposition rates are measured by using a nude ion gauge which can be rotated into the substrate position. An artificial pressure is measured as the ion gauge pressure reading changes as a result of the incident metal atoms. This pressure reading is referred to as a Beam Equivalent Pressure, or BEP. While it is not a real pressure, and not even a real partial pressure, it does give a reference point of the amount of metal flux hitting the substrate. This allows for the changing the relative amount of metal flux arriving at the surface of the substrate from growth to growth.

Control of specific material growth is obtained by opening and closing shutters which can blank the flux coming from each cell. By changing which shutters are opened and closed, heterostructure materials can be grown layer by layer on the substrate. Additionally, since the plasma power is controlled by a RF source, the amount of atomic Nitrogen which is hitting the substrate can be controlled by changing the plasma power of Nitrogen.

Therefore, the variables which can be dictated during a growth by the grower are as follow. The amount of flux from each cell which reaches the substrate, the background Nitrogen pressure, the substrate temperature, the Nitrogen plasma power, and the species of elements which arrive at the substrate are all controlled by the grower. Now that the growth variables have been established, a closer look at the conditions used for this research will be discussed. As mentioned in the previous chapter, the successful results
other groups have seen in realizing nanowire growth will be a stepping stone for the start of this research.

All nanowire growths used a Nitrogen plasma power of 450 Watts unless otherwise mentioned. Also, all of the growths were performed on Silicon (111) substrates unless otherwise noted. The Silicon was dipped in 10 % HF acid for 90 seconds and loaded into the MBE system. Before transferring into the growth chamber, the substrates were outgassed for 4 hours at 200 C in the MBE intro chamber. Following, a buffer bake of 400 C for 2 hours occurred before growth. Immediately before growth, the substrate was further outgassed at 750 C for 15 minutes and then 850 C for 10 minutes in the growth chamber. The last high temperature bakes were in efforts to remove any native oxides that formed on the Silicon surface between HF dipping and loading into vacuum. A representative RHEED pattern taken after outgassing can be seen in Figure 4.4. While 7X7 reconstruction which is characteristic of an oxide free Silicon (111) surface is not visible here, the streakiness of the pattern reveals a smooth surface.
For any growth method, nanowires will only occur in a regime where certain factors combine to yield the three quasi 1-dimensional structures rather than a thin film. The factors for nitride nanowires by MBE are substrate temperature, Nitrogen plasma power, and metal fluxes. The first step in the research was to determine the windows for these variables to yield the best nanowire growth.

4.1 Nanowire growth using Aluminum Nitride Buffer layer.

Initial growth attempts followed the growth method used by Bertness et al. as discussed in the previous chapter. Recalling, the method started with a layer of
Aluminum deposited on a Silicon (111) substrate upon which Aluminum Nitride was grown. It was upon this layer that the nanowires stemmed. This method was used as a starting point for the research carried out by the author.

The growth conditions for an early sample, 070704b, were as follows. The Aluminum cell was opened for 6 seconds while the substrate temperature ($T_{\text{sub}}$) was at 630 C. Following Aluminum deposition, AlN was grown for six minutes (~30 nm) at 630 C using an Aluminum BEP ($F_{\text{Al}}$) was $9.11 \times 10^{-8}$ Torr. $T_{\text{sub}}$ was then raised to 820 C and GaN was grown for one hour using a Gallium BEP ($F_{\text{Ga}}$) was $7.6 \times 10^{-8}$ Torr. The Nitrogen plasma power ($P_{\text{N}}$) was 400 W throughout. The Aluminum cell was closed after the growth of the AlN layer.

A scanning electron microscope (SEM) image of one of the first trials for nanowire growth using this method is shown in Figure 4.5. From the images, it can be seen that the growth did not produce a thin film yet did not produce nanowires either. Instead, the growth resembled what appears to be a grassy like material.

4.5 Sample 070704b. SEM images, top view on left and side view on right. The growth resulted in a grassy material. Not a film, yet not nanowires.
The very next growth, 070713a, used the same growth procedure, \([F_{Ga} \approx 3.9 \times 10^{-8}, \quad F_{Al} \approx 9.1 \times 10^{-8}, \quad P_N \approx 400 \, W, \quad T_{sub} \approx 630/630/820]\). Except here, note the Gallium BEP was roughly halved. Images of the growth are shown in Figure 4.6.

4.6 Sample 070713a. From top left clockwise. 3D image showing pitted surface. Side view revealing compact wire growth. Top view showing pitted surface. Zoomed in top view showing hexagonal wire top growing from the pit in the film.

From the images, it can be seen that lowering the Gallium flux and increasing the growth time resulted in a pitted film. In the middle of the film there are wires growing vertically from the surface. Looking at the side view images, it appears that the film is...
actually made up of these nanowires, they have coalesced resulting in a film. It is suspected that eventually the film would grow together and the pits would be eliminated. However, this growth shows that although the nanowires coalesced into a film, growth is occurring in a regime where wire growth is possible.

The next few growths were carried out with $F_{Ga}$ at $4\times10^{-8}$ Torr, $F_{Al}$ at $9\times10^{-8}$ Torr and $P_N=450$ W. $T_{sub}$ during the Gallium Nitride growths was 650, 750 and 850 C. Other conditions were held as before, but increasing the AlN growth time. Aluminum was deposited for 6 seconds at 630 C substrate temperature. This was followed by sixteen minutes of AlN growth at a substrate temperature of 630 C. All three of the Gallium Nitride depositions occurred for two hours. Top and side view SEM images are shown in Figure 4.7.

4.7 Top and side view SEM images. Left to right; 070807a, 070810a, 070814a. Substrate temperatures respectively; 650 C, 750 C, 830 C. The red lines indicate the Silicon-Nitride interface.
The images show that growth at 650 C yielded nanowires that were not grown on the hexagonal pitted surface as seen by Bertness et al. Growth at 750 C once again yielded more of a thin film than wires as they coalesced. Growth at 830 C produced the pitted surface as seen by Bertness et al. when the thin AlN buffer was used. However, this growth arrangement yielded low to zero nanowire density.

Looking at the growth of 070814a, which produced the pitted surface that other groups have reported, a following growth was carried out under the same settings but with a higher $F_{Ga}$. Reasoning that the low nanowire density of the previous growth could be due to too low of a Gallium flux, $F_{Ga}$ was increased from $4 \times 10^{-8}$ to $1.9 \times 10^{-7}$ Torr. Optical and SEM images of this growth are shown in Figure 4.8.

![Optical Image Plan View SEM Image](image)

4.8 Sample 070817b. Optical image magnified 100 X showing cracks (highlighted by arrows) at roughly 60 degrees. Top view SEM shows rough surface.

Figure 4.8 shows an optical image of the as grown substrate. Cracks are clearly visible in the image indicating that growth occurred in the thin film regime. This could be due to the increase in the Gallium flux which switched growth conditions from Nitrogen
rich to metal rich. When this happens, instead of nanowire growth, thin films will be deposited. Since the GaN and Silicon have such a large lattice mismatch, the thin GaN film will crack to relieve any stress. The difference in $F_{Ga}$ between the two regimes was $4 \times 10^{-8}$ Torr increasing to $1.9 \times 10^{-7}$ Torr. This information is vital to keeping growths in Nitrogen rich regimes which would allow for nanowire growth as opposed to thin film growth.

Knowing roughly the upper limit of the flux in the Nitrogen rich regime, growths were then carried out with a slightly lower Gallium BEP. Since a $F_{Ga}$ of $1.9 \times 10^{-7}$ Torr resulted in more of a film than nanowires, the Gallium BEP was lowered to $1.1 \times 10^{-7}$ Torr for two growths. The substrate temperatures for the two were 830 C and 750 C during the Gallium Nitride deposition. SEM images of the growths are shown in Figure 4.9.
4.9 Side and top view SEM images. Top row, sample 070821A grown at 830 C. Bottom row, sample 070824a, grown at 750 C. The red lines indicate the Silicon-Nitride interface.

The images show that growth is still occurring as a film. From the side view SEMs, it appears that the film is made of separated columnar structures, but the columns are not separated into single wires. Based on the fact that other groups reported the growths of films at high metal fluxes, the Gallium BEP was lowered even more.

Sample 070829c was grown in the same manner as previous growths utilizing a thin six second Aluminum flux followed by sixteen minute Aluminum Nitride buffer layer. T_{sub} for the Aluminum and Aluminum Nitride depositions was at 630 C and 830 C.
for wire growth. Other conditions were $[F_{_{\text{Al}~9}} \times 10^{-8} \text{ Torr}, F_{_{\text{Ga}~2}} \times 10^{-8} \text{ Torr}, P_{_{\text{N}}~450 \text{ W}}]$. SEM images are shown in Figure 4.10.


It can be seen in the images that by lowering the Gallium flux individual wires were able to grow without coalescing together into a film. The top view images indicate that wire growth seems to nucleate at the center of the pits in the surface just as seen by previous groups using the Aluminum Nitride buffer layer. The side view images indicate that wire growth is mostly parallel from wire to wire and an average height of roughly
150 nm. Since the GaN was grown for two hours this equates to a growth rate of approximately 75 nm per hour under these conditions.

An attempt was made to add Silicon dopants to a Gallium Nitride nanowire growth. Once again, the Aluminum-Aluminum Nitride buffer layer was used under the same growth conditions. $F_{Ga} \sim 2 \times 10^{-8}$ Torr was used which is what yielded good nanowire growth earlier. $F_{Al}$ was set to $2.4 \times 10^{-8}$ Torr which is a little lower than the $9 \times 10^{-8}$ Torr used earlier. The substrate temperature during the Gallium Nitride deposition was held at 830 °C. The Silicon cell temperature was set at 1120 °C, which gave $F_{Si} \sim 2.2 \times 10^{-12}$ Torr.

SEM images of the growth can be seen in Figure 4.11. From the figure, notice how the Aluminum Nitride layer looks pitted as is expected under these growth conditions. However, the nanowire density is low to none. These results indicate that the addition of Silicon to the growth has lowered the nanowire density.

![SEM images of sample 071026a. High and low magnifications of the surface. Nanowire density is low to nonexistent.](image)

4.11 SEM images of sample 071026a. High and low magnifications of the surface. Nanowire density is low to nonexistent.

At this point, once unintentionally doped Gallium Nitride nanowire growth was yielding good results, the addition of Indium into the Gallium Nitride was investigated.
Growth results show that nanowire density is far below that of pure Gallium Nitride grown under the same conditions during the InGaN growth. Since the only other factor changed was the Aluminum flux being lowered, but the Aluminum Nitride film still looks
complete, the lower density is possibly a result of the Indium evaporating from the surface and leaving less metal on the surface to yield material growth.

A growth of InGaN was carried out on an Aluminum Nitride substrate instead of the typical Silicon (111) substrate. Perhaps a more uniform Aluminum Nitride surface would yield better wires, or even a higher density. Indium and Gallium BEPs were held at $1 \times 10^{-8}$ Torr as in the previous InGaN growths. The Aluminum and Aluminum Nitride depositions were skipped since there was a preexisting layer on the substrate. The growth temperature was set to 575°C since this temperature did result in the growth of some wires in the previous InGaN samples. SEM images of the growth are shown in Figure 4.13.

![SEM images of InGaN growth on AlN substrate](image)

4.13 SEM top view images. Sample 071019b top view images. Left is a wide view showing low wire density. Right, single hexagonal wire only about 40 nm tall.

Using the Aluminum Nitride substrate instead of the Silicon substrate seemed not to have an effect on the growth. From the figure, it is clear that there is hardly any nanowire growth. The right image shows a single wire not more than roughly 40 nm in
height which would equate to a growth rate of 20 nm/hr since the deposition was two 
hours.

Interesting to note is how the surface is still rough even though it was a smooth 
AlN substrate. This indicates that some of the InGaN deposited on the substrate creating 
the features that resemble hillocks. These features have been seen in the Silicon (111) 
growths as well.

Two growths, one of InGaN and one of GaN, were carried out using a Nitrogen 
plasma power of 350 W instead of 450 W as in the previous growths. The growths were 
on Silicon (111) so the standard Aluminum-Aluminum Nitride buffer layers were 
deposited. The InGaN growth used BEPs for metals of $1\times10^{-8}$ Torr for Gallium and 
Indium, and $1.5\times10^{-8}$ Torr for Aluminum. The GaN growth replaced all of the Indium 
flux with Gallium flux for a BEP of $2\times10^{-8}$ Torr and a similar Aluminum flux of $1\times10^{-8}$ 
Torr. Substrate temperatures for the two were 675 C for the InGaN and 830 for the GaN. 
The growth results are shown in Figure 4.14.
The SEM images reveal that there is little to no change in the growth results when growing at a Nitrogen plasma of 350 W versus 450 W under these growth conditions. Neither the InGaN nor GaN sample had a very high nanowire density. Once again the pitted mountain range growth did occur.

After gathering these results, another method for growth was examined. Here, the initial Aluminum Nitride layers were skipped. This method resulted in more dense nanowire growth results as shown below. The following discussion will also start to introduce experimental results which are the first of their kind ever produced. Specifically, these would be honed in growth temperatures, fluxes, and plasma powers which produce high Indium concentration InGaN nanowires.
4.2 Nanowire growth by Gallium Droplet Method

Another method for nanowire growth as discussed in the section reviewing the works of others is the method used by Kikuchi et al. to grow nanowire light emitting diodes. Here, there is no Aluminum Nitride buffer layer. Additionally there are no outside catalysts. This method has been described as catalyst free, although there is a catalyst used sometimes. Since the catalyst is Gallium, no foreign metal particles are used.

The Gallium droplet method is described here, and a schematic diagram is shown in Figure 4.15. The same substrate is used at before, namely a Silicon (111) wafer. The substrate is outgassed in the same fashion as before. There is the initial 10% HF dip followed by Indium mounting onto Silicon wafers for loading into the MBE.

The intro bake is set at 200 C for four hours followed by a buffer bake at 400 C for 2 hours. As before, immediately before growth, the sample is outgassed at 750 C for 15 minutes and then at 850 C for 10 minutes in the growth chamber.

After outgassing the sample, the growth can begin. Once the substrate is lowered to the desired growth temperature, usually in the range of 650 C, the substrate is exposed to a Gallium flux for a set amount of time. The time ranges from zero to 1-2 minutes. Following this, the Gallium cell is closed and the Nitrogen plasma is opened allowing for Nitrogen radicals to bombard the substrate.

When the Nitrogen hits the surface, it reacts with the Gallium which has formed nanoscale droplets on the Silicon surface. This produces GaN islands on the Silicon. Following the N$_1$ bombardment, the cell is closed and the substrate temperature can be
adjusted for wire growth. This usually means an increase in the substrate temperature but not always. Substrate growth temperature depends on what material the wires are to be made out of since each metal has its own evaporation temperature.

Once the substrate temperature reaches the desired growth temperature, the Nitrogen cell along with the cells of any desired metals are opened simultaneously. Although not yet confirmed, a few groups have noted as mentioned earlier, that the GaN islands act as nucleation sites for nanowire growth. The proposed theory as mentioned in the research by others in Chapter 3, is that the diffusion length of the metal atoms is higher on the m-plane of the Nitride which is the sidewalls of the wires. Once the metal atoms diffuse to the top of the wire, they incorporate into the structure because their diffusion length is lower at the top of the wire, on the (0001) face.\textsuperscript{18}
A critical factor in this method of nanowire growth is the substrate temperature. The metal atoms need enough kinetic energy to diffuse to the top of the wires, but the temperature cannot be too high or the metal atoms will evaporate from the surface.

All of the growths carried out using this method used a substrate temperature of 530 C for the initial metal deposition along with the exposure to the Nitrogen plasma.
unless otherwise mentioned. Also, the standard time and power for the Nitrogen plasma bombardment is one minute at 450 W.

Initial growths were in pursuit of finding growth conditions that yielded good GaN nanowire growth. The Gallium cell shutter was held opened for either 25 or 40 seconds depositing with $F_{\text{Ga}} \approx 2 \times 10^{-8}$ Torr or $3.2 \times 10^{-8}$ Torr. Once the sample was exposed to the Nitrogen flux, the temperature was raised to 830 C, which is the temperature which yielded the best wire growths using the Aluminum Nitride buffer layer. Figure 4.16 shows the results of four growths comparing the changes in Gallium deposition times and also Gallium BEP levels.

The top two images used a $F_{\text{Ga}}$ of $2 \times 10^{-8}$ Torr. However, the Gallium cell was open for 25 seconds for the image on the left and for 40 seconds for the image on the right. The bottom right image used a $F_{\text{Ga}}$ of $2 \times 10^{-8}$ and deposition time of 40
4.16 Top view SEM images. Clockwise from top left: samples 071030a, 071102a, 071107a, 071106a. Gallium BEP (Torr) and deposition times respectively: $2 \times 10^{-8}$ & 25 seconds; $2 \times 10^{-8}$ & 40 seconds; $2 \times 10^{-8}$ & 40 seconds; $3.2 \times 10^{-8}$ & 25 seconds.

seconds also, however the growth time was increased from two hours to 3 hours. The bottom left image used a $F_{Ga}$ of $3.2 \times 10^{-8}$ and a Gallium deposition time of 25 seconds along with a growth time of two hours.

Looking at the images, it can be seen that by increasing the Gallium deposition time results in a higher density of wire growth. Also, there is a slight increase in wire density when the nanowire growth time is increased. This is interesting because it
indicates that nanowire nucleation sites are continuously created during the growth when both metal and Nitrogen cells are open.

Increasing the Gallium flux also resulted in an increase of the nanowire density. It appears that the wire density is more sensitive to the metal flux than the metal deposition time. Another interesting fact that the images show is that the wires are not parallel to each other as was seen for the Aluminum Nitride buffer layer growths. This is the same result that was seen from other groups as mentioned in Chapter 3 Section 1.

$F_{Ga}$ was raised from a BEP of $2 \times 10^{-8}$ or $3.2 \times 10^{-8}$ Torr from the earlier growths to $5 \times 10^{-8}$ Torr. The deposition time for the initial Gallium droplets was held at sixteen seconds and the Gallium Nitride growth time was set to two hours. Figure 4.17 shows SEM images of three samples, one grown with a Gallium BEP of $2 \times 10^{-8}$ Torr, one with $3.2 \times 10^{-8}$ Torr, and one with $5 \times 10^{-8}$ Torr for comparison. The deposition times were 40 seconds, 25 seconds and 16 seconds respectively.

![Ga flux & Time](image)

4.17 SEM images of samples 071102a, 071107a, and 080116a. Top view SEM images showing the increase in the density of nanowires vs. Gallium flux and deposition time.

The images show plan view SEMs of the growths. Note that if the deposition time of each sample is multiplied by the BEP of the Gallium, the values are roughly the same.
Theoretically, this would mean that the same amount of Gallium is deposited on the substrate. However, from the images, it can be seen that the higher the Gallium BEP has more of a profound effect on the density of wires than the Gallium droplet deposition time.

Since a high density of wires is desired, a few growths were carried out changing the Gallium flux between the droplets and the actual Gallium Nitride wire growth. Two growths were carried out, both with a BEP of $2 \times 10^{-8}$ Torr for the droplets and a time of 40 seconds. For growing the wires after the droplet deposition, the first Gallium Nitride flux was $5 \times 10^{-8}$, and the second was doubled to $1 \times 10^{-7}$. Both samples were grown for two hours. Figure 4.18 shows the growth results.
4.18 Top and side view SEM images. Top: 080122a with a Gallium BEP of $5 \times 10^{-8}$ Torr for Gallium Nitride deposition. Bottom: 080123a with a Gallium BEP of $1 \times 10^{-7}$ Torr.

Looking at the images, it appears that increasing the Gallium flux did not have a substantial increase on the height of the nanowires, as it appears the median height of the samples are 400 and 500 nm. Since the metal flux was doubled, it does not seem all of the extra metal went into making the wires taller. However, looking at the nanowire density, it appears that the extra metal flux had an impact on the nanowire density. It could be contemplated that the extra flux went into making new nucleation sites even after the initial Gallium droplet deposition since that flux and time was the same for both samples.
Two growths were carried out investigating the growth of pure Indium Nitride nanowires. Indium metal droplets were first deposited using $F_{\text{In}} \sim 5 \times 10^{-8}$ Torr and $2 \times 10^{-8}$ Torr for 40 seconds followed by a one minute 450 Watt Nitrogen plasma shower. The Indium BEP for the second sample was raised to $5 \times 10^{-8}$ Torr during the Indium Nitride nanowire growth to match that of the first sample.

Since Indium will evaporate at a lower temperature than Gallium and Indium Nitride will dissociate at a lower temperature than Gallium Nitride, substrate temperatures could not be set at the same values as growths for Gallium Nitride. The first sample was grown with a substrate temperature of 475 C while the second was grown at 530 C. Figure 4.19 shows SEM images of side views of the two samples.

The sample grown at 475 C reveals relatively large islands of what appear to be Indium metal, or Indium Nitride, on the substrate that occur in hemispherical shapes. This indicates that there was not enough kinetic energy for the metal atoms to diffuse up the sidewalls of the wires but instead the metal clumped up to form the islands. The sample grown at 530 C shows that there is no material left on the Silicon substrate. This indicates a temperature at which the Indium Nitride would dissociate and even the Indium itself would also evaporate from the surface. If future growths of pure Indium Nitride are needed, a sampling of growths comparing substrate temperature would be needed to find the exact temperature that allows for nanowire growth. However, attention was focused back to Gallium inclusion in the growths.
4.19 Side view SEM images. Side view SEM images of samples 080130a & 080210a. Both samples were attempts at growing InN nanowires at 475 C and 530 C respectively.

A quick interest in doping motivated growths using Silicon and Magnesium dopants. Concerning Silicon, an earlier growth that produced a dense and well defined group of Gallium Nitride nanowires was repeated. This growth however was performed with the Silicon cell opened with a temperature of 1120 C. Figure 4.20 shows top and side view images of the two wires for comparison.

Top view SEM images indicate that the nanowire densities are comparable and the inclusion of Silicon had little effect. The same is true for the side view images. The growth times were four hours for both samples using the same metal fluxes and Nitrogen power. This should equate to an equal nanowire height. As is indicated by the images, this is true as both samples yielded nanowire heights roughly one micron in length. This leads one to believe that the inclusion of Silicon into growths using parameters near the ones used for these two growths will lead to no altering of the nanowire growth from UID samples.
4.20 SEM top and side view images. Top: sample 080127a, UID top and side views. Bottom: sample 080217a, Silicon doped top and side views. Note density and heights are comparable.

A sample was also grown testing the results of adding Magnesium as a dopant into Gallium Nitride nanowires. Growth conditions were the same as the previous sample doped with Silicon except that the Silicon was replaced with Magnesium at a cell temperature of 340 C. This cell temperature equates to $F_{\text{Mg}} \approx 1.3 \times 10^{-10} \text{ Torr}$.

Figure 4.21 shows SEM top and side views of the sample which was grown for four hours, the same as the Silicon doped sample. The nanowires in the images appear to have about the same height as the Silicon doped wires and roughly the same density. However, the Magnesium doping appears to have made the wires coalesce into groups of
wires. The side view image indicates that the wires are still growing as individuals but they seem to push together. An analogy might be a fistful of straws gripped together. This indicates that when using Magnesium in Gallium Nitride nanowires, coalescence of wires should be monitored.

4.21 SEM images. Side and top views of sample 080203a; Gallium nitride doped with Mg. Top view indicates that coalescing occurred in the wires.

The growths using the Gallium droplet method seemed to yield higher densities of nanowires and longer wires than growths performed on AlN buffer layers. Since success was seen using this method for GaN nanowires, interest was turned to try to reproduce the same success for InGaN nanowires.

As stated earlier, since InN and GaN react differently at different temperatures, it was necessary to find suitable growth temperatures for the InGaN nanowires. Since it is known that the substrate temperature must be lower than that of GaN growths to prevent InGaN dissociation and evaporation of Indium, growths were tested at temperatures lower than the substrate temperature used for growing GaN, namely 830 C.
A series of growths were carried out over a range of temperatures from 400 C to 750 C testing how well the Indium Gallium Nitride nanowires would react to the substrate temperatures. Growths were performed in two steps. The first step was the usual forty second Gallium droplet deposition at 530 C followed by a one minute Nitridation.

Following, pure GaN wires were grown at a substrate temperature of 830 C as was seen before. After thirty minutes of GaN growth, the substrate temperature was lowered to the respective value for each test. Once the desired substrate temperature was reached, the Indium cell was opened along with the Gallium cell to incorporate both metals into the growth.

Conditions for the growths were as follows. F_{In} was held at 7.5 \times 10^{-8} Torr for all growths. The Gallium cell BEP was the same for all growths but was varied in three stages during each growth. The Gallium droplet deposition used F_{Ga} of 2 \times 10^{-8} Torr while the GaN nanowire growth used F_{Ga} of 1 \times 10^{-7} Torr. During the InGaN nanowire growth, F_{Ga} was set to 2.25 \times 10^{-8} Torr. The hope was that since Gallium would stick to the substrate and growing material more, then the developing InGaN should be about a 50% metal mixture.

Six different growth substrate temperatures were used for the InGaN nanowire growths. Four of those samples are shown below in Figure 4.22. Starting from the top, temperatures of growths pictured are 450 C, 550 C, 600 C, and 650 C.

The images show that at temperatures below 600 C, there is not enough kinetic energy for the metal atoms to diffuse up the sidewalls of the nanowires. When this is the
case, the wires clump up, and form mounds of material on top of the short GaN nanowires.

4.22 SEM images. Side and top view images comparing substrate temperature on InGaN nanowire growth results. Top to bottom: samples 080222a, 080220a, 080303a, and 080218a. Substrate growth temperatures respectively: 450 C, 550 C, 600 C, and 650 C.
Once the temperature reaches 600 C, the metal atoms have enough energy to diffuse partially up the nanowire columns, but as can be seen, as the metal migrates to the top of the wire it spreads out laterally instead of growing vertically. This results in a golf tee shaped structure. When the substrate temperature is set to 650 C, there is enough kinetic energy transferred to the metal atoms that they can diffuse up the sidewall completely and provide vertical growth to the nanowires instead of lateral expansion. Thus it was found that under these flux conditions, it is necessary to keep the substrate temperature at least 650 C to maintain nanowire regime growth.

Once a suitable substrate temperature was determined, the Indium flux was varied over a small window to see if there would be any dramatic differences between the growths. This was done in conjunction with photoluminescence measurements (discussed in detail under the optical properties section) on the samples to determine if the emission of the samples could be shifted with slight adjustments of the Indium flux.

Gallium droplets were deposited for forty seconds with $T_{\text{sub}}$ at 530 C and subject to a 450 Watt Nitrogen plasma for one minute. Gallium BEPs remained the same and were varied for the three stages of growth; $2\times10^{-8}$ Torr, $1\times10^{-7}$ Torr, and $2.25\times10^{-8}$ Torr, for droplets, GaN and InGaN respectively. The $F_{\text{In}}$ varied from $7.75\times10^{-8}$ Torr to $8.5\times10^{-8}$ Torr. The flux-time diagram in Figure 4.23 schematically shows the flux values. SEM images of the growths are shown in Figure 4.24. It can be seen that these slight adjustments of the Indium flux reveal no significant manipulation of the growth results. The nanowires are still growing with diameters ranging from 50-100 nm. There are still
two nanowire shapes present, short and thick along with tall and thin. The mushrooming shape seen at lower temperatures does not occur at any of the fluxes used.

4.23 Flux vs. Time for samples in Figure 4.24.

Upon electrical characterization of some of the wires, discussed in more detail in later sections, there arose a concern about the GaN layer that forms from the Gallium droplets reacting with the Nitrogen plasma at the start of all the growths that
4.24 SEM top and side views. Top to bottom; samples 080310a, 080310b, 080311a, 080311b. Respectively, Indium BEPs were $7.75 \times 10^{-8}$, $8 \times 10^{-8}$, $8.25 \times 10^{-8}$, and $8.5 \times 10^{-8}$ Torr. There seems to be no apparent change in the structural nature of the wires between flux alterations.
use the Gallium droplet method. The concern is the wider bandgap GaN separating the Silicon substrate from the InGaN material for purposes of current injection between the two materials.

Therefore, growths were carried out testing if the Gallium nucleation and Nitrogen plasma steps could be skipped and still result in quality InGaN nanowire growth. As such, the growth method was to skip these initial steps, and start depositing materials for InGaN growth at a substrate temperature of 650 C. The first growth in which this was tried was one hour of UID InGaN followed by one and a half hours of Gallium Nitride doped with Silicon. The Silicon cell was held at 1120 C and $F_{Ga}$ was $2.25\times10^{-8}$ Torr while $F_{In}$ was $8\times10^{-8}$ Torr. These conditions are the same as those used for InGaN growths earlier.

SEM images of the growth are seen in Figure 4.25. The top and side view images show that skipping the droplet deposition had little effect on the growth. Nanowires still formed in a dense pattern. This result is promising in such that the GaN layer is not necessary for wire growth allowing for InGaN growth directly on Silicon.

A growth was carried out to see what would result from a longer growth time. GaN was grown using droplets deposited with $T_{sub}$ at 530 C and $F_{Ga}$ at $2\times10^{-8}$ Torr. The drops were bombarded with Nitrogen plasma and then a twenty four growth of GaN preceded using $T_{sub}$ of 830 C and $F_{Ga}$ of $1\times10^{-7}$. The resulting growth is shown in Figure 4.26.

The images show that the growth yielded wires six microns in length which equates to a growth rate of 250 nm per hour at this metal flux setting. Top view SEM
images indicate that many of the wires coalesced into islands but there remain many wires that are still individual rods.

![InGaN/GaN NW on Silicon Sub.](image)

4.25 Top and side view SEM images. Sample 081118a. One hour of InGaN growth followed by 1.5 hours of GaN (Si) growth. Sample confirms the Gallium droplet step is not necessary for wire growth.
4.26 SEM top and side view images. Twenty four hour growth, sample 080508a. Top view indicates that many of the wires coalesced into islands however there are still wires that are separated. Side view indicates that the growth yielded wires six microns in length.

After successfully growing InGaN nanowires on Silicon substrates, another idea was tested. As Kikuchi et al. 29 have shown, patterned growth is possible for nanowire growth.

4.3 Patterned Nanowire Growth

Following the works of Kishino and Kikuchi 29, the author also searched for controlled placement of nanowire growth on substrates. The Kishino results offer a good method and starting point for the correct growth settings to yield patterned growth. However, every MBE system will behave slightly differently. Therefore growth settings had to be tweaked to yield the desired results.
Looking back at Kishino’s patterned growth methods, the following sample preparations were undertaken prior to growth. Growths were carried out on commercially grown epi-polished semi-insulating GaN layers which were grown by MOCVD on sapphire substrates. 1×1 cm² samples were cleaned in three steps composed of Acetone/Methanol/Isopropyl for 20/10/10 minutes in an ultrasonic bath. Five nanometers of Titanium were then E-beam evaporated onto the epi-polished side using a background pressure of 2×10⁻⁶ Torr, and a material tooling factor of 75 at a deposition rate of a few Angstroms per second. This Ti layer would become the growth surface.

The samples were then patterned by using a FEI Helios Focused Ion Beam (FIB) system. A schematic process flow is shown in Figure 4.27. A quick introduction to FIBs is appropriate. Focused Ion Beams are just what the name implies. Samples are placed in a vacuum chamber which has two high voltage guns attached. The first is a standard SEM for viewing the sample. The second gun uses melted Gallium as an ion source. The Gallium ions are pulled from the source with a high voltage and accelerated toward the sample. By using magnets just as in an SEM, the beam of ions can be focused and directed to impact the sample at desired positions. When the beam strikes the sample, the impact force will physically etch the sample. In this manner, the beam can be used to cut and pattern desired shapes into the specimen.
Patterned growth process.

Patterning using the FIB was accomplished using what are known as scripts. Note that this work represents the first use of scripts for FIB patterning at the University of Notre Dame, a development which should prove useful to future users here. Scripts are programs which control where the beam is scanned and what patterns are written. For this research, arrays of holes were drilled into the substrate. There were a few variables which needed to be tested which include the ion beam current, the acceleration voltage, the hole diameter, and the hole depth. For a starting point, 30 kV was used as the accelerating voltage of the ion beam. This value was kept stable over the course of all the FIB patterning. The first item tested was the ion beam current. This was done by patterning the same pattern on one sample twice; once at a beam current of 28pA and once at 9.7pA.
The first patterned sample was grown under the following conditions \([T_{\text{sub}}: 830 \, \text{C}; F_{\text{Ga}}: 2.25 \times 10^{-8}; N_1 \text{ pressure; } 2 \times 10^{-5}]\). As stated, there were two patterns generated on the sample, one using 9.7pA and one using 28pA. A representative image of a pattern is shown in Figure 4.28. Each square represents a 15 x 15 array of holes drilled with the noted diameters. The spacing indicates the spacing between holes from center to center. The individual dots between the squares are single holes drilled. The bottom row is of donut shapes with the inner and outer diameters indicated as ‘i’ and ‘o’ respectively.

Figure 4.29 shows an SEM image of the growth over the patterned area with the 50 nm diameter row left off the top of the image. The image shows that outside of the patterned areas, growth was indeed suppressed to zero. A closer look at the structures reveals more information.
4.28 Schematic showing the pattern used on the growth samples. Each square is a 15 x 15 array of holes.
4.29 SEM image of patterned area of growth 090929a. The 50 nm row has been left off.

While from a zoomed out perspective it appeared that the growth only occurred in the patterned region, the images below in Figure 4.30 show otherwise. Here it can be seen that the material grew in the hole regions but also in the areas around the holes. Further, the growth that occurred in the desired regions was not composed of solid material. Rather, the growth appears to be of nanowires that have coalesced together.
4.30 Close up SEM images of sample 090929a. Note that the material did not grow only in the patterned holes but in the spaces between them.

To compare the results of the two different currents, images were taken of the 100 nm diameter holes with the 795 nm spacing of both the 9.7pA and 28pA patterns. The images are shown side by side in Figure 4.31.

4.31 090929a SEM images of the 100 nm diameter, 795 nm spacing hole arrays for both the 28pA(left) & 9.7pA(right) currents. The images look to be almost identical.

At this point a note on how the FIB determines how it etches the patterns is fitting. The material to be etched is chosen in the program. If the desired depth of the hole
is also indicated in the program, along with the current, then the FIB will automatically
determine the appropriate dwell time to yield results close to the user’s request. Thus, the
difference between two currents is how fast the material is etched away. There is
something to be considered in this. As the material is etched away, it needs to go
somewhere. This ‘somewhere’ is usually off of the sample by means of the vacuum pump. However, if the etch rate is too high, there is not enough time for the material to be removed and it will collect near the etched area. When picking currents to use, this must be taken into account. While one wants patterns to be written quickly, there is such a thing as too quick. Since the images of the 28pA and 9.7pA look to be almost identical, it appears that either of these currents will yield close matching results. Since the 28pA current etches faster, this value was used on future patterns.

The initial patterned growths were carried out by mounting growth samples onto Silicon carrier wafers for growth. Indium was melted onto the Silicon wafers and the surface tension is enough to hold the samples in place. However, at the high growth temperatures used for these patterned growths, namely around 900 C, the Indium would dissociate from between the sample and carrier wafer rather quickly. This led to a high percentage of samples dropping from the carrier wafers.

To circumvent this occurrence, Molybdenum plates were used in place of the Silicon carrier wafers. Using this mounting technique, the growth samples were sandwiched between two plates which had cm² openings in them so that the surfaces of the samples were not covered. Small clips held the samples in place. This was the
mounting procedure of choice for the rest of the patterned growths. Once this system was used, the sample drop rate declined greatly.

A second addition to the sample preparation was also made at this point. Since the Molybdenum plates do not offer the same thermal transfer as Indium mounting, 200 nm of Titanium was evaporated onto the backs of the samples to help facilitate a uniform thermal condition. This evaporation occurred prior to the FIB patterning in the sample preparation. With these changes, to obtain the same sample temperature as with Indium mounting, the thermocouple setting had to be increased. This will be reflected in slightly higher growth temperatures for the samples using the Molybdenum plates.

Many growths were carried out varying the growth temperature between 900-920 C and Gallium fluxes between $5 \times 10^{-8}$ & $5 \times 10^{-7}$ with no substantial changes in growth results until sample 091124A was grown with the following settings $[T_{\text{sub}}: 920 \text{ C}, F_{\text{Ga}}: 1 \times 10^{-7}, N_{\text{press}}: 1 \times 10^{-5}]$. SEM images of the growth are shown below in Figure 4.32.

The images show that growth of hexagonal shaped nanowires with six-faced pyramidal caps was accomplished in the desired areas. The rows of nanowires can be seen to run diagonal from bottom left to top right in the upper images of the figure. The upper right image shows an area that was patterned on the right, but not on the left. It can be seen that the rows of nanowires end at this interface indicating further that the growths are only occurring in the patterned holes.

The lower images; which are at higher magnifications show further features of the nanowires. The wires are growing solid, uniform, and as hexagonal rods with pyramidal shaped tops. There is still unwanted growth between the wires in what appears
as not only thinner wires, but also triangular shaped facets of which horizontal growth appears to be occurring at 120° directions from their concentric center. It should be noted that these images were taken of areas patterned with holes of 200 nm diameters. While the 100 & 200 nm diameter holes show results with these characteristics, the 50 nm and spot (0 nm) patterns did not show any patterned growth. Also, while usual semi-insulating GaN substrates are from IQE, this growth was on a substrate purchased from Lumilog.

4.32 SEM images of sample 091124a. Note pyramidal shape on the single wire image. Further, still unwanted growth between the desired wires.
Since Kikuchi had published that a higher substrate temperature would allow for a higher Gallium mobility on the surface, a growth was carried out under the same conditions but at 930 C instead of 920 C. The hope was to eliminate the unwanted growth between the patterned holes. SEM images for this sample can be seen in Figure 4.33 below.

4.33 SEM images of sample 091210a. Grown at Tsub: 930. Increase in temperature eliminated unwanted growth but nanowires are not solid. These wires were from 200 nm holes.

While the images in Figure 4.33 reveal that the unwanted growth was suppressed, the nanowires do not look as clean as was seen in sample 091124a. The increase in the growth temperature seemed to create nanowires which are not solid and hexagonal as seen before, but rather they appear to be made of smaller nanowires which have grouped together. A possible cause of this occurrence is that the increase in the substrate temperature has increased the evaporation rate of the Gallium from the surface.

To test this hypothesis, a sample was grown under the same conditions as 091210a, but the Gallium flux was increased from $1 \times 10^{-7}$ to $1.55 \times 10^{-7}$. This is double the
amount of Gallium arriving at the surface of the substrate as before. SEM images of the results are shown below in Figure 4.34.

**Patterned NW Growth**

4.34 SEM images of sample 091211b. Note that the increase in the substrate temperature has eliminated the unwanted growth. Also, the increase in the Gallium flux has created solid hexagonal shaped nanowires.

The SEM images show that the increase in the substrate temperature from 920 C to 930 C has eliminated the unwanted nanowire growth between the patterned areas. Also, the increase in the Gallium flux from $1 \times 10^{-7}$ to $1.55 \times 10^{-7}$ has resulted in solid hexagonal shaped nanowires as opposed to the thinner coalesced wires that were seen
with the lower Gallium flux. Concluding this section, patterned GaN nanowires were successfully realized. While similar studies have recently been reported by the Kikuchi group\textsuperscript{29,30}, these are the first of their kind at Notre Dame and open the door for future work using patterned growth substrates. This would allow for controlled placement of growth materials.

Another interesting growth scheme investigated was the growth of nanowires with altering material compositions along the wire axis. With this in mind, growths were carried out with AlN/GaN heterostructures created in the wires.

4.4 AlN/GaN Heterostructures

Growths were carried out to see if it were possible to grow quantum wells or heterostructures within the nanowires. Two growths were carried out under the same growth conditions, only the thickness of the quantum wells was changed between the two samples. $F_{Ga}$ was $2 \times 10^{-8}$ Torr for a forty second droplet formation and $1 \times 10^{-7}$ Torr for the wire growth. $F_{Al}$ was $6 \times 10^{-8}$ Torr, and $T_{sub}$ was 830 C.

Roughly one and one half hours of GaN growth started the nanowires and then a seven period heterostructure between AlGaN and GaN was made. The Gallium shutter was held open the entire growth, but to make the AlGaN regions the Aluminum shutter was opened for one minute between ninety second closure periods. A Gallium Nitride cap layer was grown on top of the heterostructure for sixteen minutes.

Figure 4.35 shows a TEM image of the growth still attached to the Silicon substrate along with a close up of the heterostructure region. The top images shows a Nitrogen mapping
of the wires still attached to the Silicon substrate. The AlGaN/GaN heterostructures are clearly visible in the image. Heavier atoms appear lighter in the image making the AlGaN appear darker than the GaN regions.

From the images, an estimate of the growth rate can be extracted. The growth time for one GaN layer was set to 90 seconds and yielded a material thickness of five nanometers, which equates to a growth rate of 3.33 nm/min. The growth time for the AlGaN layer was 60 seconds and yielded a material thickness of eight nanometers, which equates to 8 nm/min. EELS measurements were carried out on these samples and revealed an AlGaN compositional makeup of $\text{Al}_{0.9}\text{Ga}_{0.1}\text{N}$. While EELS can be a very useful tool for identifying species, this measurement should be taken with a grain of salt as the statistical sampling was relatively low for a more accurate quantitative analysis.

Once the nanowires were formed, characterization of them needed to be carried out. The first step in this was characterizing their optical properties. This is the topic of the next chapter.
CHAPTER 5:

OPTICAL PROPERTIES OF NITRIDE NANOWIRES GROWN BY MBE

Initial optical investigations into Nitride nanowires that had been grown include photoluminescence measurements to investigate the optical bandgap and emission properties by optical pumping. A 325 nm He-Cd laser was used to optically pump the as grown materials and photoluminescence (PL) measurements were taken from 4 K up to 300 K.

5.1 Optical properties of GaN and InGaN nanowires

Both InGaN and GaN films have been investigated using photoluminescence measurements yielding expected results. AlGaN/GaN heterostructures were also investigated which revealed some interesting characteristics. Samples were also tested by varying the laser power, and tests of quantum efficiencies were also carried out. The results have been interesting to say the least; discussion now focuses on these results.

Since growths started with using an AlN buffer layer, the first PL measurements discussed will be of an InGaN sample grown using an AlN buffer layer. The results are shown in Figure 5.1. The Aluminum Nitride buffer was grown for sixteen minutes at 630 C. The InGaN was grown for two hours with T_{sub} at 475 C. The metal fluxes were balanced at $1 \times 10^{-8}$ Torr for each.
The data in the figure shows that the maximum optically generated emission is at 600 nm which equates to a bandgap energy of 2.08 eV. This energy gap would result from a material with an Indium concentration of 49% if no band bowing is considered. However, research\(^\text{13}\) has shown that InGaN has a significant bowing parameter equal to 2.6 eV. This means that it takes less Indium to achieve a red shift from pure GaN than if there were no band bending. Taking this into account, a PL peak of 600 nm would imply an Indium concentration of 29%.

PL data was taken from a sample of GaN nanowires grown using the Gallium droplet method. The sample was grown at 830°C for two hours with \(F_{\text{Ga}}\) at \(1 \times 10^{-7}\) Torr. Figure 5.2 shows the PL data from the sample. At room temperature the peak emission is...
at 363 nm which is in excellent correlation with the band gap of Gallium Nitride of 3.4 eV. At 80 K, it can be seen that the emission blue shifts to 357 nm. This quality is attributed to lattice cooling and bandgap widening from the shrinking of the atomic spacing.

Two InGaN samples were grown using the same conditions except for the substrate temperature in an effort to discover roughly where the substrate temperature had to be in order to allow for Indium to successfully incorporate into the material without InGaN dissociating from the substrate.

5.2 PL data. PL data for a Gallium Nitride nanowire growth using the Gallium droplet method. The peak shifts from 357 nm at 80 K to 363.3 nm
at room temperature. This is attributed to lattice cooling and band gap shrinking.

Figure 5.3 shows PL data from these two samples. This data represents the first ever reported PL data from bulk InGaN nanowires grown by MBE. The plot on the top shows data from a sample grown at 750 C and the plot on the bottom shows data from a sample grown at 650 C. The sample grown at 750 C shows peak emission at 362.6 nm with a smaller peak at 369 nm. The 362.6 nm emission corresponds to pure GaN material in which all of the Indium was not incorporated into the nanowires. The 369 nm peak could be generated by material in which still a small amount of Indium is present.
5.3 PL data. PL data from two InGaN samples grown under the same conditions except for substrate temperature. Top: 080211a, grown at 750 C shows no InGaN emission. Bottom: 080218a, grown at 650 C shows a red shift indicating Indium inclusion into the material.

The sample shown on the bottom, which was grown at 650 C shows a definite red shift in emission when compared to the 750 C sample. The main peak has shifted from 363 nm to around 517.4 nm. The Indium composition that equates to this emission would be 21%. There is also a peak shown around 404.9 nm indicating there are areas with Indium concentrations of 6.5%. This secondary peak in the blue-green region is seen in most of the InGaN samples grown. The reason for this extra peak was discovered and will be discussed in future chapters.

The important piece of information from these two samples is that 750 C is too high of a growth temperature to allow Indium incorporation into the material. If the
temperature is lowered to 650 C, Indium will incorporate into the growth which will allow for material which emits in the green spectrum.

Four samples were grown to monitor how much of an extent slight variations of the Indium cell temperature would change the emission of the materials. Four samples were grown at 650 C with F_{In} at 7.75\times10^{-8}, 8\times10^{-8}, 8.25\times10^{-8}, and 8.5\times10^{-8} Torr. The emission spectra for the four samples are shown in Figure 5.4.

The data reveals that changing the Indium BEP over this small window has little noticeable effect on the bandgap of the material grown. Once again the smaller peak shows up around 400 nm which results from the ~6% InGaN material as discussed earlier.
Three samples were grown varying the Indium flux in a more dramatic fashion than before. $T_{\text{sub}}$ set to 615 C for all three samples and $F_{\text{In}}$ was varied from $7.5 \times 10^{-8}$, $1 \times 10^{-7}$, and $3 \times 10^{-7}$ Torr. PL data for the growths can be seen in Figure 5.5. The plots show peaks near 490 nm for each sample. However, for the lower two Indium fluxes, there is a smaller peak at around 430 nm. As the Indium BEP is increased, this peak
seems to disappear as it merges with the larger peak at 490 nm. This could be indicative that at a growth temperature of 615°C with $F_{Ga}$ at $1 \times 10^{-8}$ Torr, there will still be material that is Indium lean until $F_{In}$ of $3 \times 10^{-7}$ Torr is reached. Once this point is reached, the PL data is indicating that on an area having the dimensions of the laser spot, ~2mm in diameter, all of the material is uniform in composition.

5.5 PL data. The plots show that up until a BEP of $3 \times 10^{-7}$ Torr there is still some low Indium content material being grown.
Two samples were grown with the same metal fluxes but the substrate temperature was altered to see its effect on the Indium concentration. Using $F_{Ga}$ of $1 \times 10^{-8}$ Torr and $F_{In}$ of $3 \times 10^{-7}$ Torr, two samples were grown at $T_{sub}$ equal to 615 C and the other at 650 C. The PL spectra from the two samples can be seen in Figure 5.6. Remembering, the sample at 615 C had just started yielding uniform Indium compositions as compared to growths with lower Indium fluxes. When compared, the PL plots show that at 650 C at these metal fluxes, there is a red shift of the emission. The 650 C growth still shows a peak near 490 nm as the 615 C sample does. However, there is a larger peak positioned near 425 nm.

This blue shifted peak is due to the fact that at a $T_{sub}$ of 650 C, the Indium will not stick at these metal fluxes. Therefore, the sample becomes Indium lean, and a blue shift to a more Gallium rich material is obtained. This shows that at a BEP of $3 \times 10^{-7}$ Torr, total Indium flux will not stick at substrate temperature of 650 C.
5.6 PL Data. PL data from two samples grown with the same fluxes but different substrate temperatures. Top: grown at 615 C peaks near 490 nm. Bottom: grown at 650 C is blue shifted near 425 nm.
Two samples, 081205a and 090130a, were grown as InGaN material with and without Silicon doping. The doped sample was grown with a Silicon cell temperature of 1120 C. The metal fluxes were held constant over the entirety of the growths and were the same for the two growths. The growth conditions were \([F_{Ga}: 2.25 \times 10^{-8}, F_{In}: 8 \times 10^{-8}, P_N: 450 \text{ W}, T_{\text{sub}}: 650 \text{ C}]\). PL data for the two samples are shown in Figure 5.7.
5.7 PL data. PL data for two InGaN samples. Top: Silicon doped at a cell temperature of 1120°C. Bottom: UID sample. Note that both samples are showing peaks near 425 nm and a larger peak near 550 nm. Indium clustering is a possibility for the two peaks.
Even though these two samples were grown with constant metal fluxes, there are two peaks in the PL emission spectrum. A lower peak is seen near 425 nm while a larger peak resides near 550 nm. There is a peak near 360 nm which is indicating a nearly pure GaN content of the material. The 425 nm peak would equate to an Indium concentration of around 9.5%, while the 550 nm peak is from an Indium concentration of 25%.

The emission intensity of the wires was collected over a variety of PL sample temperatures for both GaN and InGaN samples. This data was integrated to yield the internal efficiency of the wires as was carried out by Narukawa et al. The method referenced suggests that at low temperatures, all of the non-radiative recombination is eliminated since there is little kinetic energy given to the sample to allow for momentum transfer often associated with non-radiative emission. Therefore the model assumes near a 100% recombination rate at low temperatures. By taking the ratio of the integrated intensities at 300K vs. 4K, one could have a quantitative value for the efficiency of the material. This is shown in Figure 5.8.

Revealed in the data is an efficiency at room temperature of near 2% for GaN nanowires and 8% for InGaN nanowires. The values for the InGaN nanowires match or exceed quoted values of 2% for bulk thin film InGaN films as shown in the lower portion of Figure 5.8. However, as can be seen, there are materials which offer a higher internal efficiency over the InGaN nanowires. These materials are composed of InGaN quantum wells (represented by the open circle plots) which allow for electron and hole confinement to a 2D plane in which they are more apt to recombine since they are held closer to each other.
Based on these findings, unless further enhancement of the InGaN nanowire efficiency is discovered, the author cannot at this time recommend them as candidates for green emitters in solid state lighting. However, the InGaN nanowires do exhibit some strong positive characteristics, namely a structural make up free of threading dislocations and the capability for growth on Silicon substrates.

In light of these traits, the author suggests the pursuit of further efforts to improve the efficiencies of the InGaN nanowires such as those that have been pursued for thin films. Suggestions for improvement to the internal efficiencies of the wires are the use of quantum well structures, as has been implemented by other groups\textsuperscript{36, 37}, combined with surface passivation of the wires to remove any possible dangling bonds.
5.8 PL data. Emission intensity vs. substrate temperature and internal efficiencies of the nanowires. InGaN wires have an internal efficiency of 8%.

The lower plot shows comparative efficiencies of different materials with the InGaN nanowires grown by the author plotted with a star. Plot from Chichibu (40).

PL studies were also carried out to characterize the spectrum from single nanowires. Nanowires were harvested in isopropyl alcohol using ultrasonic agitation and deposited onto quartz slips. AFM scans shown in Figure 5.9 reveal the dimensions of the nanowires, which appear to be a couple of wires which have coalesced. The plots in the
right of Figure 5.9 show the PL spectrum given by the nanowires. Note that these are InGaN nanowires harvested from the same growth sample. In spite of this, the two wires show different spectra. While the top wire shows just one peak, the bottom wire is giving off emission at three to four wavelengths.

This is very interesting indeed. While these wires are from the same growth, it is expected that the material makeup would be consistent from wire to wire across the growth. Further, it is interesting that a single wire would yield multiple peaks. This phenomenon was hypothesized to be contributed to compositional changes in the material. To test this hypothesis, experiments using EDX capabilities of the TEM were used to identify the material makeup of the wires. The results of these experiments are documented in the following chapter.
5.9 Left: AFM images of harvested nanowires. Right: PL spectra of the represented nanowires. Note the difference in the emission even though the wires are from the same growth. Figure courtesy of Vlad Protasenko.

5.2 Optical studies of AlN/GaN Heterostructures

PL measurements were taken on samples 080128a and 080129a, which are the GaN nanowires grown with seven periods of Al$_{0.9}$Ga$_{0.1}$N (composition roughly measured by EELS) material separated by GaN. PL data from the samples is shown in Figure 5.10.
Both samples were grown with roughly one and a half hours growth of GaN initially then the heterostructures were grown. Sample 080128a was grown with the GaN quantum wells grown for three minutes and the Al$_{0.9}$Ga$_{0.1}$N wells grown for 1.5 minutes. Sample 080129a was grown with the GaN quantum wells grown for 1.5 minutes and the Al$_{0.9}$Ga$_{0.1}$N wells for 1 minute. Sample 080129a was capped with a sixteen minute growth of GaN as opposed to no cap for sample 080128a.

The PL data shown reveals that there are peaks around 360 nm for both samples. This corresponds to the GaN material. The second interesting result from comparing the two plots is the distinct red shift in the sample with the thinner quantum wells. The wider well sample is peaking at around 370 nm while the thinner well sample is peaking around 390 nm. A plot comparing sample 080128a with a pure GaN sample is also shown. The red shift due to polarization is distinctly shown here. It should be noted that this is the first report of the quantum confined Stark effect in AlGaN/GaN MBE grown nanowires.
5.10 PL data. Photoluminescence data from AlGaN/GaN heterostructures. Top left: sample 080128a grown as AlGaN/GaN 1.5/3 min. Top right: sample 080129a grown as AlGaN/GaN 1/1.5 min. The data shows that the thinner quantum wells resulted in a red shift in emission peak. Bottom: Comparing a heterostructure with GaN sample.
Two more measurements were taken on sample 080129a. Figure 5.11 shows emission intensity vs. wavelength for different laser intensities. Figure 5.12 shows the energy of the emitted light vs. laser intensity for different sample PL temperatures.

5.11 Emission intensity vs. Wavelength. Plot of PL data from sample 080129a. As the laser intensity is increased, the emission is blue shifted. This could be explained by band filling in the quantum wells. Courtesy Kejia Wang.
5.12 PL data. Energy of emitted light vs. laser intensity for different PL sample temperatures, sample 080129a. As the laser intensity is increased, there is a blue shift in the emission. Also, as the substrate temperature is lowered, there is a blue shift in emission. Courtesy Kejia Wang.

Figure 5.12 shows that lowering the substrate temperature yields a blue shift in the emitted light. This can be explained by the lower temperatures shrinking the atomic spacing of the material resulting in a wider bandgap as the atomic spacing shrinks.

Both plots show that when the laser intensity is increased, a blue shift in the emission spectra is observed. The band diagram of the sample shown in Figure 5.13 along with a schematic plot can be used to help explain what is going on here.
5.13 Top: Band diagram\textsuperscript{41} of sample 080129a. Piezoelectric polarization is shown in the band bending. Bottom: Schematic diagram showing increasing the carrier concentration in the wells will result in a flat band condition as seen in the PL data.
As seen in the band diagram, the polarization effects of the \( \text{Al}_{0.9}\text{Ga}_{0.1}\text{N}/\text{GaN} \) interfaces result in a bending of the bands due to sheet charges at the interfaces. As the incident light creates electron hole pairs, the carriers are swept to opposite sides of the quantum wells as a result of the built in piezoelectric field. When the intensity of the laser is increased, more and more carriers are generated and separated by the field.

As this happens, the carriers begin to generate a secondary electric field which screens the built in piezoelectric field. The competing fields result in a band flattening. The flattening of the bands separates the electrons and holes in energy and as they recombine, the photon is of higher energy than when the bands were bent.

Following on the above discussion of optical properties, momentum naturally is carried to investigating the structural characteristics of the nanowires. This will be discussed in the following chapter.
6.1 GaN Nanowire Structural Characterization

Structural analysis was determined by TEM examination of the grown materials. For this purpose a Jeol 2010 transmission electron microscope using a 200 kV beam along with a FEI Titan transmission electron microscope using a 300 kV beam were used. To acquire images of grown wires, samples were placed in vials of isopropyl and agitated with ultrasonic vibrations. The liquid was then dropped onto copper grids and allowed to dry leaving behind the nanowire specimens. There will always be a copper peak in the EDX spectra of the samples which is attributed to the grids however, and not the specimen themselves.

Figure 6.1 shows a high resolution TEM image of a GaN nanowire. The insert shows a zoomed out image of the wire. The red square on the insert refers to an approximate area of the higher resolution image. Note the image shows the nanowire to be free of defects. The light and dark regions easily visible in the zoomed out image are due to beam damage from the 300 kV electron beam. At high magnifications, damage to the material would occur in only a few seconds of viewing.

The next image, Figure 6.2 is an EDX spectrum of the nanowires. Note the copper peaks are accredited to the copper grid as mentioned before. Here, the Gallium peak is
easily visible. The Nitrogen peak appears to be over shadowed by the Carbon peak which could be intense due to the Carbon on the grid. The insert in Figure 6.2 is a selective area diffraction pattern of the GaN nanowire around the region of the HRTEM image. Note the pattern suggests single crystal material forming wurtzite construction which is expected from GaN material. Immediately following is a HRTEM image in which the (0001) directional lattice spacing is measured to be 5.13 Angstroms.

6.1 HRTEM image of a GaN nanowire. Note the perfect crystalline material showing lattice fringes running diagonal toward upper left.
6.2 EDX spectrum of a GaN nanowire. Insert shows a SAD pattern of the lattice image in Figure 6.1.
6.3 HRTEM image showing lattice spacing along C-direction. Courtesy Kejia Wang.

A characteristic which was seen in all growths on Silicon substrates is the existence of a thin film of Silicon Nitride between the nanowire growth and the Silicon substrate. While this film was not intentionally grown, with the clean Silicon surface of the substrate in a Nitrogen ambient at high temperatures it is inevitable for this film to form. Figure 6.4 shows a Nitrogen mapping of a cross view section right at the nanowire-substrate interface. The high level of Nitrogen identifies the Silicon Nitride thin film. The thickness of the film varied from zero to 3 nm across the surface. While the film shows no atomic dictation from the substrate, the nanowires grown on top of it show crystalline construction.
6.4 Nitrogen map showing the 2-3 nm thick Silicon Nitride film which is formed on the top of the Silicon surface. Courtesy Tom Kosel.

6.2 InGaN Nanowire Structural Characterization

Investigation of the InGaN nanowires has revealed some interesting results. While the GaN nanowires showed perfect lattice formation, the InGaN nanowire structures
showed a more charismatic structural make up. First off, the InGaN nanowires structural
design was not consistent from nanowire to nanowire, even when comparing wires from
the same growth. Second, the compositional makeup of the nanowires varied *within* the
wires. Discussion will now focus on these two topics.

Figure 6.5 shows a high resolution TEM lattice image of an InGaN nanowire. The
image reveals perfect lattice formation with no threading dislocations which was the goal
of the InGaN nanowire growth. This is the first ever reported demonstration of the
structural characterization of MBE grown bulk InGaN nanowires. The inset in the image
shows another interesting characteristic these InGaN nanowires have. The inset is an
atomic contrast image from scanning transmission electron microscopy (STEM) image of
another wire from the same growth. What is revealed is that along the c-axis of the
nanowires, there are regions of both wurtzite and zinc blende structural formation. Along
the growth direction, there are horizontal light and dark stripes of different thicknesses
along the wire’s axis as shown in the inset. While a Z-contrast image cannot reveal lattice
images, these light and dark striations do resemble the mixing of wurtzite and zinc blende
material along the growth of the wire that was seen in HRTEM images. These stripes are
labeled as ‘twins’ and are the different sections of the two structural formations. When a
material exhibits this change of structure, it is referred to as polytypism.
6.5 High resolution TEM image showing InGaN nanowire free of threading dislocations. Insert shows an InGaN nanowire Z-contrast image revealing both wurtzite & zinc blende material formation. Courtesy Tom Kosel.

While some InGaN nanowires showed this behavior, not all of the wires demonstrated such a phenomena. Some of the wires were completely grown without the structural changes along the growth axis. Further, the wires which showed the structural changes usually did not show this result along the complete length of the wire. When this did occur, it was usually seen in sections along the wire instead of along the whole length.

The question arises then, what is the cause of the polytypism of the materials. What is physically happening is that as the nanowire grows, it has planes of atoms
coming together to form its crystal structure. Conditions may force the material to omit a plane, or add an extra plane, of atoms which are shifted out of symmetry from the underlying material. This results in the material shifting from growing with a wurtzite construction to one with a zinc blende pattern.

Digging deeper, what causes the change in the first place? Caroff et al. explain that in bulk, the determining factor determining if a material will grow in wurtzite or zinc blende form depends on the atom’s ionicity. He states that since third nearest neighbors are closer in wurtzite formation, atoms with a high ionicity favor wurtzite formation and atoms with lower ionicities favor zinc blende formation. Caroff goes on to reference the work done by Johansson et al. in which they state that if indeed nanowire growth occurs layer by layer, then the starting atom of the next layer will determine if the structure is continued or if a switching of the atomic structure, known as a ‘twin or twin boundary’ will occur. Since the energy difference for the atom to form a twin or not to form a twin is small, the likelihood is increased of the material having a twin.

Taking a look at the ionicity values for GaN and InN, which from Akiyama et al. are 0.74 & 0.83 respectively with energy differences (meV/atom) between wurtzite and zinc blende for the two being -12.7 & -15.5 also respectively, the theory by Johansson seems plausible. With an energy difference that is smaller than room temperature thermal energy, the chances of a twin forming are probable. Along the same line is the fact that Akiyama’s research predicted that by themselves GaN, InN, and AlN nanowires would grow without twins and thus be completely composed of wurtzite material. This is in agreement with the GaN nanowires grown here. The difference then must lay in the fact
of the combination of the GaN and InN in the growth of InGaN which allows for the formation of twins in the nanowire material.

6.3 Indium Segregation in InGaN Nanowires

Another interesting feature of the InGaN nanowires that was seen was that the compositional make up of the nanowires is not uniform along the wire’s length. In other words, the Gallium to Indium ratio along the wire is not uniform. This is due to what is known as Indium segregation where the Indium atoms will tend to move around and create areas of high and low Indium concentrations. This phenomenon has been seen in InGaN thin films as discussed in previous chapters.

Since the PL of the as grown nanowires was yielding optical emission over a broad spectrum, it was thought that the cause could be a non uniform material makeup. To test this hypothesis, the nanowires were harvested onto copper grids and EDX measurements were taken along their lengths. The Gallium (k) and Indium (l) peaks were compared between the nanowires and a sample of known composition. Using this data, the Indium concentration of the nanowires can be determined by using the Cliff-Lorimer method of comparing peak intensities between the two samples.

Figure 6.6 shows a STEM image of a nanowire upon which EDX data was taken. The blue points represent where the beam was positioned for each acquisition. The Indium concentration found at each point is plotted below in image B. As can be seen, the Indium concentration varied from 0% to upwards of 35% along the length of this one wire. Converting this concentration to bandgaps using a bowing factor of 2.6 eV, a
schematic band diagram of the energy gap along the length of the wire is shown in image C. This experimental data has been the first ever reported on the Indium segregation within a Nitride nanowire grown by MBE.

From the wide variation in Indium content along the length of the wire, the source of the broad emission spectrum can be seen. As the band diagram shows, there are areas with Indium concentrations that would allow for emission ranging from red, to green, to blue. This data is in agreement with the broad spectrum seen in the ensemble PL measurements. This is not the first time Indium segregation has been reported in nanowires. Jabeen et al. reported the same occurrence in InGaAs nanowires.

While this data reveals that the Indium concentration along the nanowires is not uniform, this may not always be a bad characteristic. Since the materials offer bandgaps ranging from red to UV emission, it could be possible to incorporate these nanowires into broad spectrum emitters. However, for use as green emitters, the Indium fluctuation needs to be controlled. Suggestions for controlling the Indium segregation in the nanowires are a constant Nitrogen over pressure in the system. This could be obtained by incorporating a mass flow meter on the Nitrogen line on the MBE system. Second, the introduction of growth interruptions in which the cells are closed periodically during growth to allow for complete adatom incorporation into the growth specimen may help to reduce the movement of the Indium atoms in the grown material.
6.6 A.) STEM image showing beam positions for data acquisition. B.) Indium percentage plotted along the length of the wire. C.) Schematic band diagram calculated from Figure B.
This chapter discussed the structural make up of the wires and has shown that the nanowires grown were free of threading dislocations. However, the PL data captured suggest that growth of material without threading dislocations has shown not to be enough to yield a high internal efficiency. The next chapter discusses the electrical characterization of the nanowires.
CHAPTER 7:

ELECTRICAL PROPERTIES OF NITRIDE NANOWIRES GROWN BY MBE

A discussion of the electrical properties of grown nanowires seems appropriate. There are two main categories that the nanowires were tested in. Wires were harvested from the substrate after growth by ultrasonic agitation and then drop cast onto substrates for making electrical contacts to individual wires. These experiments have been carried out by other groups in testing their nanowires\textsuperscript{23}, but warranted attention in this work to quantitatively characterize the wires grown here.

Second, wires were left on heavily doped p-Silicon substrates and contacts were made from the back of the Silicon and from the tops of the as grown wires. Thus, electrical characteristics from the Nitride nanowire/Silicon substrate heterojunction were investigated. This method of constructing a p-n junction by injecting holes into the nanowires from the Silicon substrate are the first ever reported using Nitride MBE wires. Each method will be discussed in detail below.

7.1 Single wire electrical properties

As mentioned earlier, electrical properties were extracted from individual nanowires. Following growth, the samples were placed in a solvent solution and agitated
in an ultrasonic bath. The suspended wires were then drop cast onto substrates using pipettes as per Bertness \(^{20}\).

The substrates that the wires were drop cast onto were highly doped Silicon substrates with a 90 nanometer oxide thermally grown on the Silicon for insulation. Optical lithography was used to pattern alignment marks on the samples and Ti/Au 20/200 nm contacts were evaporated with standard liftoff techniques were used to pattern the metal. At this stage the wires were dropped onto the substrates and the solvent was allowed to dry.

The sample was then loaded into the Elionix Electron Beam Lithography system using a 75 kV beam acceleration voltage. The alignment marks were located and the position recorded. Following, the sample was combed and nanowires were located. The positions of the wires were located with respect to the alignment marks on the sample. This method allowed for pattern generation to make contacts to the wires.

Following pattern generation, the sample was coated with two layer Electron beam resist, namely MMA followed by PMMA. The spin conditions for the resist were thirty seconds at 4000 rpm followed by soft bakes of two minutes for the MMA and three minutes for the PMMA. The sample was then exposed in the Elionix using a dose of 50 pA for small features and 2 nA for larger features such as probing pads.

Once exposed, the resist was developed in MIBK:IPA:MIK mixture for one minute and then followed by a one minute rinse in IPA to stop development. Evaporation of the desired metals was then carried out at thicknesses of 20 nm Ti as a sticking layer followed by a 200 nm layer Al. These values varied from sample to sample though.
Liftoff occurred in Acetone over night and if metal was still sticking it was removed with a squeeze bottle spray of acetone.

One of the first samples made in this manner was 080508a. This sample was composed of Gallium Nitride UID nanowires grown for twenty four hours. The sample was prepared in the manner just discussed utilizing E-beam patterning and liftoff. Additional steps were included in this sample preparation. A Ti/Au 20/200 nm back gate was deposited on the Silicon substrate after a HF dip to remove native oxide. Also, when the optical lithography alignment marks were deposited, Ti/Au 5/20 nm metal contacts were deposited for contacts to the E-beam pattern. Then a second Ti/Au 20/200 nm contact layer was made for probing pads.

Wires were dispensed from isopropyl to the substrate by pipette. The E-beam metal was patterned connecting the wires to the 5/20 nm optically patterned metal lines. The metal E-beam contacts were deposited as Ti/Al/Au 30/50/140 nm. Following liftoff, the sample I-V characterizes were tested after annealing at 663 C for one minute under Nitrogen backfill. A schematic diagram of the finished sample is shown in Figure 7.1.

![Schematic diagram of contacts to a single nanowire.](image-url)

7.1 Schematic of contacts to a single nanowire.
Current was measured with the sample sitting on a glass slide to prevent any current from flowing through the chuck of the probe station. However, this does not guarantee that there was no current flow in the Silicon substrate if the eighty nanometers of oxide is leaky. Measurements were taken with the sample in the dark and also with a 325 nm laser incident on the sample in the area of the nanowire.

Figure 7.2 shows a SEM image of successful contacts to each end of the nanowires. Also pictured are the I-V results for the nanowires biased up to 20 Volts biased both directions across the wire. Resulting currents only reach the range of tens of pA even at voltages up to twenty Volts. This result is indifferent from dark measurements or measurements taken with the wires excited by the 325 nm laser.
7.2 SEM & I-V characteristics. Sample 080508a single nanowire UID Gallium Nitride. SEM images show successful contact to each end of the wires. I-V characteristics show no extremely low currents only reaching tens of pA at voltages up to 20 Volts.

Figure 7.3 shows an SEM image and I-V measurements taken on a wire from the same sample. Here however, there seems to be a difference from the previous two nanowires. Here, the current is much higher at the same bias. The current increased from the pA range to the uA range. Also, there is a definite difference between the dark and excited measurements, a signature which was not seen in the two previous wires from the
same sample. The question arises, how is it that the I-V characteristics can be so different from wires from the same sample?

7.3 SEM image & I-V results. Top left: SEM images showing wire diameter of 190 nm. Top right: I-V results showing currents reaching 40 µA at biases of 20 V. Note the 325 nm excited measurements yield higher currents. Bottom: I-V showing pulsing behavior of nanowire current between pulses from 325 nm laser.
The answer may lay in the nanowire diameters. Looking at the SEM images of the first two nanowires, it can be seen that the diameters are roughly 40 nm and 80 nm, certainly less than 100 nm. The third nanowire, the wire which yielded the higher currents, shows a diameter of nearly 190 nm.

Going back to the paper by Calarco in Chapter 3 Section 1, the difference in the nanowire currents could be due to Fermi level pinning in the Gallium Nitride. Referring to the paper, it was noted that for Gallium Nitride, there is an inherent characteristic of the material in which the conduction band will bend up at the edge of the wires thus removing all carriers along the radial edge of the nanowires. If the diameter of the wire is below a critical value, this would lead to total pinch off of the wire. The paper quoted the critical thickness to be around 80 nm.

This data fits perfectly with what is seen from these three individual nanowires. The wires are UID Gallium Nitride which could be venerable to the pinch off characteristic. Also, the diameters of the two wires which show low current values are under the critical diameter. However, the nanowire which yielded higher current is well above the critical diameter. This puts this data in agreement with the referenced paper. However, this current could be due to leakage through the Silicon substrate. Photocurrent measurements could help determine if the current path is through the nanowire, or the Silicon substrate.

Wires were harvested from sample 080902a and contacts were made to single wires. This sample was grown for five hours and made of Silicon doped Gallium Nitride nanowires. The Silicon cell was at 1120 C for the growth.
The harvested wires were deposited onto the oxidized Silicon substrates that had a 20/200 nm thick Ti/Au back gate metal evaporated on the underside of the Silicon to allow for back gating the sample. Electron beam lithography was used to pattern the metal contacts and a metal stack of Ti/Al/Ni/Au 20/100/20/80 nm was deposited making probe pads for the nanowires. A schematic diagram of the sample is shown in Figure 7.4.

![Schematic diagram of preparation of sample 080902a.](image)

Prior to annealing, the sample was measured in the dark by applying a voltage across the wire and also changing the voltage on the back of the sample. Figure 7.6 shows SEM images of the single wires after contacts had been made and also corresponding I-V measurement results.
7.5 SEM & I-V measurements. SEM images of single wires. Corresponding I-V data showing current in the wire matching current out.
7.6 (Continuation of image) SEM & I-V measurements. SEM images of single wires. Corresponding I-V data showing current in the wire matching current out.

These four nanowires are all about 80 nm or greater meaning they should not show any signs of the pinch off problem that thin wires have. The I-Vs show this is the case as the wires are showing currents reaching into the nA regime at a bias of 5 Volts.

Figure 7.7 shows an SEM image and corresponding I-V data from a wire that obviously is not in good contact. This is a good reference to make sure that the wires are indeed the pipeline for the current flow seen, as opposed to the Silicon substrate carrying
the current. As can be seen, the current from the device is only in the fA range and the current through the two probes is not matching. This shows that noise current would be less than the values obtained for the four devices pictured above indicating the current is indeed courtesy of the nanowires.

![SEM image & I-V data](image)

7.7 SEM image & I-V data. Top view SEM image showing obvious misalignment of metal and wire. I-V data shows only fA range and also that the current through the two probes is not matching.

An anomaly of the group is pictured in Figure 7.8. This nanowire appears to be large enough in diameter to not be suspect to the pinch off problem arising from radial edge depletion. However, the currents that it yields are low in comparison to the other wires of the same dimensions. The low current levels could be due to contact problems such as broken metal lines.
7.8 SEM image & I-V data. SEM image showing good metal contact to wire. However, current measurement is showing no significant current flow.

Summarizing the GaN nanowire transport, the wires show good conductivity when their diameters are larger than 80 nm. Below this diameter, the wires show little current flow. This agrees with reports of GaN nanowires pinching off due to Fermi level pinning at their edges thus depleting the wires.

Three InGaN samples were grown with varying Silicon fluxes to examine the effect of doping density between the samples. The samples were grown under identical conditions except for a variation of the Silicon cell temperature. The growth conditions were \([F_{\text{Ga}}\sim2.25\times10^{-8}, F_{\text{In}}\sim8\times10^{-8}, P_{\text{N}}\sim450 \text{ W}, T_{\text{sub}}\sim650 \text{ C}]\) for 7 hours of growth. The Silicon was closed for one growth and set to 1030 C and 1120 C for the other two growths.

Figure 7.9 shows SEM images of the as grown wires along with PL data from the samples. The PL data reveals three peaks as seen before in InGaN samples. There is the high energy peak at 360 nm from GaN, a peak at 420 nm, and one at 550 nm. Interesting
enough, as the Silicon flux is increased, the relative height of the 360 nm peak with the other two peaks lessens.

Figure 7.10 shows SEM images and I-V data for contacts made to the single nanowires. Note that for the UID and low Silicon doped wires the current is measured in the fA range. However, at a Silicon cell temperature of 1120 C, the current jumps to the uA range.

It was noticed that the diameter of the wire, or group of wires, in the SEM image for the 1120 C sample is larger than the wires of the other two dopings. This raised a concern that maybe Fermi Level pinning instead of doping effects was the cause in the increased current.

As it were, another wire from the highly Silicon doped sample was examined with a diameter of near 80 nm. This wire gave currents of up to 300 uA at 5 V, yielding a current density on the order of nearly 6MA/cm². The current from this wire indicates that it is indeed the doping and not the fact that the cluster of wires is larger in the highly doped sample and not in the other two samples.
7.9 SEM images and PL data from three different InGaN samples grown with different Silicon fluxes.
7.10 SEM images and I-V plots for three samples with varying Silicon doping. Note only at a Silicon cell temperature of 1120 C does the wire show a substantial current.
These results of currents through single wires reveal interesting information. First off, it is possible to make contacts to the small nanometer features of the wires. Second, the wires will yield high currents in spite of their small size. This is due to a very high current density in the wires. Attention now is turned to combining the Silicon doped wires with p-Silicon substrates in attempts to make heterostructures.

7.2 Electrical Properties from Nitride Nanowire / Silicon heterostructures

Published research concerning p-type doping of Nitride materials has shown that this is a difficult challenge to address. Since the acceptor dopant levels are deep within the bandgap in GaN, they are hard to activate in the materials, leaving the material intrinsic. Silicon however, is easily doped with a plethora of p-type dopants most of which are activated at room temperature.

Due to need for the wide bandgap of the Nitride materials for light emission from the visible spectrum along with the ease of the p-type doping of Silicon, a heterostructure of the two materials seems beneficial. This attempt is the first ever at creating a p-n junction using the p-type Silicon substrate as the p-type material with MBE grown InGaN nanowires.

The method in this dissertation of growing Nitride nanowires on Silicon substrate which yields perfect crystalline Nitride materials is a way to realize the combination of the Nitride materials with Silicon. The nanowires have been shown to be free of defects and to have optical bandgaps in the visible spectrum. Following on this, electronic signals
have been tried to couple holes in p-type Silicon substrates with n-type Nitride nanowires to make p-n junctions between the two materials.

As seen from the TEM studies shown in Chapter 6.1 Figure 6.4, there is a thin, roughly two nanometer layer of Silicon Nitride that exists on the Silicon substrate after a growth. Following the work of Zimmler et al. this thin insulating layer, in theory, can be used in transferring charge from the Silicon to the nanowires. Since the layer is only a few nanometers thick, charge is able to tunnel through the layer when a voltage is dropped across it. A representative band diagram of the Nitride Nanowire/SiN/Silicon heterostructure is shown in Figure 7.11.
7.11 Band diagram\textsuperscript{41} of the InGaN/SiN/Si heterostructure. The SiN layer was modeled to be 2 nm thick here.

Following Zimmler’s work, the idea of coupling the nanowires with the substrate was taken from Sun et al. \textsuperscript{48}. By depositing a layer of spin on dielectric between the wires, contacts can be applied to the tips of the wires and also on the back of the substrate. These two contacts complete a circuit which allows current flow from the nanowires through the Silicon. The process is described below, along with a sketch of the finished device following.
Nanowire growths were grown on highly doped p-type (111) Silicon. Following growth, a 200 nm Aluminum back contact was evaporated on the underside of the Silicon substrate. The contact was annealed at 450 C for 10 minutes.

To isolate the top contacts from the Silicon, BCB is applied between the nanowires. Adhesion promoter AP3000 is spun on the sample for 20 seconds at 2000 rpm. BCB is drop cast onto the sample and spun in three stages. The BCB is spun at 50 rpm for thirty seconds, 750 rpm for seven seconds, and 5000 rpm for one minute. The sample is then soft baked at 100 C for one minute. The BCB is then annealed at 250 C.

Once the BCB is spun on, it covers the entirety of the nanowires so it must be etched back revealing the tips of the wires. A reactive ion etch is carried out using SF$_6$ :O$_2$ 3.3:30 sccm giving 300 mT at 60 Watts. The etch is done in steps of one or two minutes and checked by SEM identification to ensure the etch has gone far enough but not all the way through the BCB. If the etch goes too far, the Silicon Nitride layer will be etched away and all of the Nitride material will flake off of the Silicon.

Top contacts are evaporated on top of the BCB using electron beam evaporation. Optical lithography is used to pattern negative resist for lift off of the 20/200 nm Ti/Al layer. Once the metal is lifted off, the sample is ready for I-V testing. A schematic diagram of a completed sample is shown in Figure 7.11. The results of some of these devices are now discussed.
The first sample prepared in this way was grown as InGaN with Silicon doping at a cell temperature of 1120°C. The processing was carried out as described above. Figure 7.12 shows images of the BCB etch back revealing the tops of the nanowires.
7.13 SEM images. SEM images showing progress of BCB etching. From top left to right, bottom left to right: 4 min, 6 min, 8 min, and 10 min.

The images show that the wires can just be seen after four minutes of etching and as the time is increased, the wires protrude through the BCB. Figure 7.13 shows SEM images of the sample after the Ti/Al liftoff.
7.14 SEM images. SEM images taken after liftoff of the Ti/Al top contacts.

The images reveal good coverage of the wires even though the evaporation is a vertical deposition technique. Following the metal liftoff, the device is ready for testing.

Figure 7.14 shows I-V results from this sample along with the other two samples involved with the testing of the Silicon doping. Recalling, the Silicon cell temperatures were UID, 1030°C, and 1120°C. Growth conditions were the same otherwise and are noted here [F_Ga~2.25×10^{-8}, F_In~8×10^{-8}, P_N~450 W, T_{sub}~650 C].

The samples were measured by biasing the chuck which is in direct contact with the Aluminum back metal. A probe tip was placed in contact with the Aluminum contact on top of the sample which was in direct contact with the nanowire tips and held them at zero voltage relative to the chuck. Current compliance was set to 100 mA and can see is a limiting factor for two of the samples.
7.15 I-V data. I-V curves taken from samples 090130a, 090206a, & 081205a. The chuck was biased with the Silicon substrate and the patterned top contacts were grounded on the nanowire tips.
These samples were tested for electroluminescence however none was successfully generated. While no light was seen from these devices, they represent the first reports of successful injection of holes from a p-type Silicon substrate into MBE grown Nitride nanowires. Such a demonstration opens the door for the possibility of using the easily doped Silicon as the p-type material in conjunction with Nitride nanowire devices.

Looking at the topic of the lack of emission from these devices, the following theories arise. First, since the metal contacts to the Nitride material are thick, 220 nm, any light produced would not escape from the top. Using a absorption index of 6.749 at 550 nm for Aluminum, this gives an adsorption coefficient of 0.15/nm. Therefore, the amount of light that would escape from 200 nm of Aluminum alone (not to mention the additional thin layer of Titanium) would be only 9.4x10^{-14} of the original light generated. Clearly an alternative contact is needed such as a thin ~5nm Ti/Al stack.

Second, the Silicon Nitride layer is not resistive enough to provide a voltage drop across itself. This scenario was seen by Zimmler 47. In his paper, Zimmler made LEDs from Zinc Oxide nanowires and p-Silicon substrate heterojunctions and noticed he needed a resistive layer between the doped materials to achieve emission.

Zimmler notes that samples with the Zinc Oxide in direct contact with the Silicon that high currents are obtained but no light emission was seen. However, when a thin oxide was deposited between the Zinc Oxide and the Silicon, light emission occurred. Zimmer attributes the change to the fact that without the oxide, the band offsets of the two materials are locked in place relative to each other. When the oxide is sandwiched
between them, it allows for a substantial voltage drop across itself as shown in Figure 7.15, Zimmler et al. This voltage drop allows for a shifting of the band edges and charge carriers may then be injected into the proper bands.

7.16 Schematic diagram of the band structures with and without a separating oxide. Zimmler. 47

A test of the Silicon Nitride layer seen on the nanowires grown by the author was undertaken to evaluate its electrical properties. A sample was needed with just the Silicon Nitride layer and no other Nitride growth. To obtain this, a p-Silicon substrate was degassed and loaded in the MBE as before. The sample was taken through the same stages as those that would occur for a normal nanowire growth. Nitrogen was vented into
the chamber with the substrate at 650 C. A plasma was struck at a back pressure of N\textsubscript{2} of \(3 \times 10^{-5}\) Torr. Right before the time when the cells would be opened, the growth was stopped.

Processing of the sample was the same as before except the BCB was left off. A 200 nm Aluminum layer was deposited on the back of the Silicon. For top contacts Ti/Al 20/200 nm contacts were patterned with liftoff as before. The resulting structure is shown schematically in Figure 7.16.

7.17 Schematic diagram of Silicon Nitride junction with Silicon.

I-V characteristics were tested in the same manner as before. The back gate of the sample was biased with the chuck and the metal pads connected to the Nitride were probed. The results are shown in Figure 7.17 along with the current from a reference sample. The reference sample was a Silicon substrate with 200 nm Aluminum deposited on both sides of it. The current was measured in the same manner for both samples.
7.18 I-V characteristics from sample with SiN layer grown on Silicon and an Al/Si/Al reference sample.

This result shows that the Silicon Nitride layer is thin enough to allow current to tunnel through it, without much impedance. This leads to the claim that there is not enough of a voltage drop across the layer to allow for any manipulation of the band edges.

To include a thin insulating layer as Zimmler did, experiments were carried out involving depositing 5-7 nm of Aluminum Oxide by Atomic Layer Deposition onto highly doped p-type Silicon substrates. Nitride nanowires of both GaN and InGaN compositions have been successfully grown on the Al₂O₃ layers. These successful MBE Nitride nanowire growths on controlled Aluminum Oxide are the first ever demonstrated. This is an important step in nanowire technology not only because these results show that growth is possible on Aluminum Oxide, but further, the growth substrate need not be a
crystalline material to obtain crystalline nanowires. SEM images and PL data from the samples are shown in Figure 7.18.

A sample was processed to test the hypothesis that the lack of emission is due to the need of a resistive material between the p-Silicon and the n-type nanowires. 7 nm of Aluminum Oxide, Al₂O₃ was deposited by atomic layer deposition (ALD) onto a p-type Silicon substrate. The growth was run with standard conditions which yield InGaN nanowire growth using a substrate temperature of 650 C, F_Ga: 2.25×10⁻⁸, F_In: 8×10⁻⁸ and a plasma power of 450 W. A SEM image along with a corresponding PL measurement of the growth is shown in Figure 7.19.

7.19 SEM images and PL data from GaN & InGaN samples grown on thin films of Al₂O₃.
Following growth, a 200 nm back contact of Aluminum was evaporated onto the sample and annealed at 450 °C for 10 minutes. BCB was spun onto the sample, hard baked, and etched using a SF6:O₂ RIE dry etch for 10 minutes. A lift off was carried out to pattern top contacts of evaporated 20/200 nm of Ti/Au. The sample was then tested for I-V characteristics. A schematic diagram along with the I-V characteristics for one of the contact points of the sample are shown in Figure 7.20. This demonstrates the first ever fabrication of a p-n junction composed of n-type MBE grown Nitride nanowires combined with p-type Silicon with a controlled ALD Al₂O₃ layer between the semiconductors.

While the device yields a rectifying I-V curve, no emission was seen from the device. A strong possibility is the Silicon-oxide-Nitride interfaces which would be the active region of the devices. The high probability of surface states, along with pinholes in the Al₂O₃, could be the cause of lack of emission. A remedy to these possibilities would
be to make the active region in a Nitride-Nitride homojunction, along with thinner top contacts on the probing pads. This design is discussed in the next chapter.

7.21 I-V characteristics from a device on sample 090428a. Inset is a schematic of the processed sample.
CHAPTER 8:
SUGGESTED APPLICATIONS SUITABLE TO THE NANOWIRES

8.1 Light emitting diodes

While the Nitride/Silicon heterostructures in the previous chapter did not yield any electroluminescence, their PL properties show that the optical possibilities for the nanowires are numerous. Since the characterization of the wires has revealed they are free of defects, are optically active in the green spectrum as shown in Figure 8.1, and are capable of carrying high current densities, they offer prime candidates for solid state lighting in the visible spectrum if a way could be developed to increase their internal efficiency.

8.1 PL showing green emission. Insert is a photo of a 325 nm wavelength laser incident upon the substrate yielding green color to the eye.
The first suggestion for future work toward increasing the efficiency of the wires is the introduction of quantum wells. Other groups as shown in Chapter 3, Kikuchi\textsuperscript{36} & Guo\textsuperscript{37} for example, have incorporated quantum wells into their nanowire structures. The benefit of quantum well structures is that the electrons and holes are confined to a 2D area of space and thus are more likely to recombine inside the well.

The second suggestion for increasing the quantum efficiency of the nanowires is to push toward passivation of surface states that the nanowires have a high probability of containing. Since the wires have a high surface area to volume ratio, there is a large percentage of atoms at the edge of the nanowire which are not bonded to neighboring atoms. These broken or irregular bonds often introduce midgap states in the bandgap of the material which can have unwanted effects on the optical properties of the material.

A means to passivate these dangling bonds is to cover the nanowires with a conformal coating or even a thin film of more Nitride material. As long as the covering material was of a wider bandgap then the active region, the light emitted from the active region should pass through the coating material and successfully escape the device. A couple of devices using this technique will be discussed shortly.

The most important area in a LED is the active region of the device. Suggestions toward future endeavors into light emission using these nanowires are focused on optimizing this area. While the devices discussed in previous chapters used a Nitride nanowire-Silicon substrate heterojunctions, the author suggests for future research that focus be turned to using a homojunction active region. Doing this would eliminate the interfaces between the Silicon, Nitride material, and any oxide between them. These
areas have a high probability of dangling bonds at the surface and as such have a high probability of hosting non radiative emission sites.

A possible solution to this problem would be to grow n-type Nitride wires on a n-type Silicon substrate. The Bertness & Davydov groups at NIST have carried out experiments such as this using GaN nanowires and GaN CVD coatings. After growth, the nanowires could be coated with a conformal insulating layer. If the insulation were etched from a portion of the tops of the wires this would reveal an area where a conformal p-type GaN film could make contact forming the needed p-n junction. While most MBE growths are not conformal, CVD depositions are. Therefore, this could be used as a conformal coating to the nanowires. Following, a transparent conformal metal coating could be applied to the top of the sample as a top contact. Probe pads could be patterned with thicker metal in regions to allow for ease of I-V testing. Back contacts could be made simply by evaporation of metals onto the underside of the Silicon substrate. A schematic diagram of the completed device is shown in Figure 8.2.
8.2 Schematic diagram of a possible mbe-cvd homojunction LED.

A second device possibility would be to use n-type Silicon and grow a Nitride nanowire consisting of initial n-type material followed by p-type material within the same nanowire growth. Following growth, the sample could be coated with a dielectric much like the use of BCB as discussed before. The dielectric material could then be etched back leaving just the tips of the wires to offer top contacts as before.

The advantages of this device design are that first, it offers the use of the inexpensive Silicon substrate. Second, the active region, or p-n junction, is a homojunction between the p- and n-type Nitride inside the nanowires. This allows for fabrication without exposing the active region to atmosphere as was done in the previous example.
The last suggestion for future optical devices is a take on the patterned nanowire growth discussed earlier in Chapters 3 and 4. Here, instead of using a Titanium mask as done by Kikuchi \(^{29,30}\) and replicated here in this work, the use of an insulating material grown on GaN is recommended as shown in Figure 8.4. This change of masking material would eliminate any metal atoms near the active region which could be detrimental to the optical properties of the device.

Once this substitution of masking materials is made, the growth of short InGaN nanowires is recommended in the patterned areas. Then without breaking vacuum, conditions should be changed to grow a p-type GaN thin film covering the insulating material along with the patterned InGaN nanowires.

A device of this type offers a few important features. First, the insulating material will force the carriers to funnel through the InGaN nanowires allowing for high carrier densities in the active region of the device. Second, the growth can be done in one
setting. There is no need to remove the device between growths of different sections. Third, as mentioned earlier in this chapter, coating the nanowires with the top thin film could help to passivate any surface states that are on the edges of the InGaN wires.

As just discussed, another degree of freedom that could be used in optical devices using the nanowires is to take advantage of the ability to control the spacing of patterned nanowires. If the wires were grown with their spacing equal to \( n\lambda \) \([n:0.5, 1, 1.5\ldots]\) where \( \lambda \) is the wavelength of the light generated, then they would act as a photonic crystal. This has yet to be demonstrated in Nitride nanowire technology but has been shown in thin films\(^5\). Wavelengths which match the spacing will have their intensity enhanced, and all other wavelengths’ intensities will be diminished. This will allow for a smaller full width half maximum (FWHM) of the emitted light. This translates to a narrower window of color emitted from the device.

Worth mentioning again, further enhancement of the quality of the nanowires optical properties would be to include GaN/InGaN quantum well structures as was done...
with the AlGaN/GaN wires. Wetzel et al. have shown thin films of GaN/InGaN quantum wells yielding 40% efficiencies. The quantum well structure helps gather the electrons and holes by capturing them in the lower bandgap material and thus increasing the probability that they will combine for desired emission.

Once realized, by applying a few fabrication techniques including adding reflective edges, the LEDs could be formed into lasers. Since InGaN and AlGaN nanowires have been realized, not only green lasers but also UV lasers are a possible use for the nanowires. A semiconductor laser that emits in the ultraviolet spectrum could revolutionize several technological applications. UV LEDs have uses spanning from material cutting and welding to purification of water.

8.2 Electronic device applications

Due to their high length to diameter ratio, the nanowires can be thought of as a one directional transport structure. The carrier confinement in their radial direction is defined by their radius alone. Taking advantage of this, if quantum barriers were added into the nanowires, quantum confinement structures could be formed. While the radial dimensions are not small enough for quantum confinement, it does offer confinement none the less. These structures could be used for electron ‘islands’ as seen in single electron transistors. Additionally, with the incorporation of thin barriers, the nanowires could be used in tunneling devices. A schematic diagram of a nanowire along with its corresponding band diagram is shown in Figure 8.5.
8.5 Band diagram along with nanowire schematic showing how the wires offer confinement in their radial along with grown barriers will offer quantum confinement.

8.3 Further Growth Studies

Future experiments that the author sees as worthwhile concerning the growth of the nanowires are the following. While the EDX spectra of InGaN wires that have been taken in this study reveal Indium clustering which in turn gives a variation in the bandgap of the material in the wire, this is not usually a desired trait. The ability to control the Indium to Gallium ratio throughout the growth would be a great advantage in tailoring device characteristics. Therefore, further MBE growths targeted at that goal are
warranted. One possible method to reduce the Indium concentration gradients is to introduce growth interrupts in which the cells are closed periodically during growth. This may allow the materials on the substrate to better associate into the lattice. Once this occurs, it may lower the dramatic Indium gradients that were seen in the InGaN nanowires grown here.

Further comments on future wire studies also include work done on patterned substrates. A device engineer may see the need to obtain nanowires of certain diameters. This could possibly be accomplished by varying the diameter of the FIB holes as Kishino et al. have shown \(^{30}\). Also, the patterns need not be circular holes. Rings could be patterned, and if grown under the right conditions, cylindrical materials could be realized as in Figure 8.6.

8.6 Schematic showing possibility of growing nano-cylinders using FIB patterning of rings instead of holes.

Cylindrical material such as this could be used for nano-scaled transport of liquids or gases. Further uses include optical & acoustic devices such as resonators and waveguides.
The experimental results shown in this dissertation include the growth and characterization of Nitride nanowires by Molecular Beam Epitaxy. The nanowires were characterized structurally, optically, and electrically. Further, the nanowires were used in the fabrication of p-n junctions in attempts to produce LEDs emitting in the green region. The results of this work offer a plethora of insight in the field of nanowire technology much of which is state of the art in the nanowire field.

Gallium Nitride, InGaN, and AlGaN/GaN multi quantum wells have successfully been grown by MBE using four main growth techniques. Growth using an AlN buffer layer resulted in nanowire growth yielding a growth rate of ~75 nm/hr. Growths using Gallium droplets resulted in a higher density of nanowires and a faster growth rate of roughly 250 nm/hr. It was found that the density of the nanowires grown using this technique could be increased or decreased by changing the metal flux and time of deposition in regards to the initial Gallium droplets. Further, data shows that the droplets do not need to be deposited to successfully result in nanowire nucleation, which agrees with results seen by others.

Patterned growth of GaN nanowires following the works of others using Titanium growth masks was also successful. While this achievement is not new to the field, it does offer important data to future growers at Notre Dame. By using the data obtained in the growth of the patterned GaN nanowires, future work composed of growth of patterned
InGaN wires along with growth of nanowires on patterned insulating material has been brought a step closer to realization.

AlGaN/GaN heterostructures have been successfully grown. There have been reports of nanowire growth composed of multi quantum wells of these materials before, but this work shows the first ever reports of the quantum confined stark effect shown in MBE grown Nitride nanowires. Additionally, successful band flattening by optical carrier generation has been shown for the first time in nanowire technology.

The major achievements of this work are a thorough exploration of optimal growth conditions for InGaN nanowires on Silicon substrates, the extensive characterization of the structural and optical quality of these InGaN wires, and studies into their potential integration into a device. The results from this work reveal that growth temperatures need to be near 650°C in order to obtain vertical InGaN nanowires. A temperature below this will result in a flattening or horizontal spreading of the growth, while a temperature above 750°C will result in evaporation of the Indium from the substrate resulting in the growth of GaN nanowires.

The optical characterization of the MBE InGaN wires is the first ever reported in the nanowire field. The internal quantum efficiency of the InGaN nanowires is found to be near 8%. Further, the structural characterization of the InGaN nanowires also reveals that the Indium composition along the growth direction of the InGaN nanowires is non-uniform. This non-uniformity correlates with reports showing Indium segregation in thin films.
The most important scientific data obtained from the experiments herein would be the results obtained from the fabrication and testing of Silicon/nanowire p-n heterostructure devices. The successful demonstration of injecting holes from Silicon substrates into MBE grown Nitride nanowires is the first ever reported. This achievement proves that it is possible to include inexpensive and easily p-type doped Silicon in Nitride nanowire devices.

Further results which have been shown for the first time in nanowire technology were the successful MBE growth of GaN and InGaN nanowires on an ALD layer of Al$_2$O$_3$. Growth of nanowires has elsewhere been reported to occur on SiN layers which grow on Silicon growth substrates. However, this is the first documentation of Nitride nanowire growth on a controlled and deliberately deposited oxide film. The growth on the oxide has led to the first demonstration of incorporating a controlled oxide between the n-type Nitride wires and p-type Silicon.

Examination of the data obtained in this research leads to the following conclusions. AlGaN/GaN heterostructures grown in nanowires demonstrate the quantum confined Stark effect. It is possible to flatten the band bending caused by the internal polarization in the wires by optical carrier generation.

It is also shown that bulk InGaN nanowires are subject to Indium segregation, yielding material which is optically active at different wavelengths. While this creates material that can be used in a broad spectrum emitter, it is not a desired result for constructing devices yielding thin emission peaks. The internal efficiency extracted from the InGaN nanowires is shown to be 8%. This value is substantially lower than that of
materials which incorporate quantum wells. At this time, this data indicates that the bulk InGaN nanowires cannot compete with current thin film quantum well devices emitting in the green region. However, due to their high structural quality, the nanowires may prove useful if their efficiency can be increased.

Suggestions for enhancing the efficiencies of the InGaN nanowires are the use of quantum wells along with surface passivation. Surface passivation of the material can be accomplished by coating the nanowires with a thin film of GaN material. This may also prove useful in obtaining a flat surface for electrical contacts in devices.

It has been shown in this work that it is possible to inject holes from Silicon into the InGaN nanowires, and is possible to grow GaN and InGaN nanowires on controlled oxide layers. The oxide layer can successfully be incorporated between the Silicon and nanowires in device fabrication. While the Nitride/Silicon p-n heterostructures do produce rectifying currents, the experiments reveal no light emission from the devices. Suggestions to improve upon these device designs are to use a thinner contact metal for the devices.


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