Optimization of Dry and Wet GaN Etching to Form High Aspect Ratio Nanowires

Matthew Hartensveld
mth4891@rit.edu

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Optimization of Dry and Wet GaN Etching to Form High Aspect Ratio Nanowires

Matthew Hartensveld

B.S. Microelectronic Engineering, Rochester Institute of Technology, Rochester, NY, 2018

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Material Science in the School of Chemistry and Materials Science, College of Science, Rochester Institute of Technology

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Signature of the Author _________________________________

Accepted by _________________________________________

Director, M.S. Degree Program Date
The M.S. Degree Thesis of Matthew Hartensveld has been examined and approved by the thesis committee as satisfactory for the thesis required for the M.S. degree in Material Science.

Dr. Jing Zhang, Thesis Advisor

Dr. Rob Pearson

Dr. Karl Hirschman

Dr. Sean Rommel

Date
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Dedication

Dedicated to my parents Brian and Lisa Hartensveld who had no idea what I was doing, but always supported me anyways.
Abstract

Nanowire devices are emerging as the replacement technology to planar devices, such as Light Emitting Diodes (LEDs) and Field Effect Transistors (FETs), due to better performance and higher device densities. Here, top-down GaN nanowire fabrication is studied through the use of dry and wet etching techniques. Specifically, dry etching is studied focusing on the effects of etching power, pressure, and the use of chloroform during the process. Wet etching of GaN nanowires takes the initial structures formed by the dry etch to create the desired high aspect ratio, tunable-diameter nanowires. Effects of etching time, temperature, concentration, and ability to remove etch damage are thoroughly studied. Insights of these results are utilized to form high aspect ratio vertical wires with diameters smaller than 100 nm for high-performance GaN devices.
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Chapter 1. Introduction

Displays are increasingly found everywhere: phones, watches, glasses, cars, refrigerators, etc. In the information society of today the list of places displays are used is ever increasing. The currently available technology for these displays consists primarily of Liquid Crystal Displays (LCDs) or Organic Light Emitting Diodes (OLEDs). The issues with these displays are the inherent inefficiencies of the systems, currently only 5-7% efficient\(^1\), while state of the art Gallium Nitride (GaN) LEDs are around 70% efficient\(^2\). GaN is a wide bandgap semiconductor which can emit light across the visible spectrum with the incorporation of Indium. However, GaN LEDs suffer reduced efficiencies as they are scaled down in size. In order to make use of GaN LEDs in displays, LEDs must be made to overcome the drawbacks of reduced size. Instead of the traditional planar LEDs, GaN nanowire LEDs perform exceedingly well at the nanoscale which is ideal for display applications. Two separate approaches exist for the formation of GaN nanowire LEDs: bottom-up growth through Metal Organic Chemical Vapor Deposition (MOCVD)\(^3\), or top-down through a dry etching process. The bottom-up growth method of nanowire LEDs leads to random placement of wires and high costs. The top-down approach allows for exact placement of the structures, though introduces damage to the structure during the etch\(^4\). Dry etching GaN is also difficult, often showing a slow etch rate and producing tapered structures which are non-ideal for nanowires. In order to overcome these issues, the dry etch process is studied alongside a wet etch to create GaN nanowire structures.
1.1 Overview of Wet Etching

The first etching processes used in the semiconductor industry were simple wet chemical etches. Wafers were immersed into liquid chemistry that would selectively attack and remove films exposed to the solution. The chemicals in the liquid react with the film forming water soluble byproducts or gasses\textsuperscript{5}. In certain processes this is accomplished though the chemistry oxidizing the exposed surface layer which is then dissolved into the liquid\textsuperscript{5}. One major advantage of a wet etch process is the high selectivity which occurs in the etch, which is defined as a ratio of etch rates between the film to be etched and the masking material. In most cases the wet etch proceed isotropically, meaning etching the same amount vertically as horizontally. The horizontal etching creates an undercut, as shown in Figure 1, which limits the size of the dimensions to greater than 2\textmu m\textsuperscript{5}. An exception to this occurs in alkaline chemistry such as KOH which etches certain crystal planes, such as the <100> plane in silicon creating a ‘V’ shaped groove\textsuperscript{5}, shown in Figure 1.

![Figure 1. General Wet Etch (Left) vs. KOH Etch (Right)](image)

1.2 Overview of Dry Etching

Dry etching has replaced virtually all wet etch processes in state of the art device fabrication to form nanoscale devices\textsuperscript{5}. This form of etching involves exposing the wafer to a plasma where ionized gases will chemically etch and physically bombard the wafer\textsuperscript{5}. Dry etching can produce very vertical, anisotropic, structures which is needed for
nanoscale devices. Though the downside to dry etching is the lack of selectivity which is roughly inversely proportional to the anisotropy, ranging from no selectivity to less than ten$^5$. Anisotropy is the ratio of vertical to lateral etch rates, with high anisotropy required in nanowire formation. Dry etching systems tend to be single wafer processes in order to control the uniformity of the etch. Reactive Ion Etching (RIE) or Inductively Coupled Plasmas (ICP) are the two common forms of dry etching which are used to create features. An RIE system is shown in Figure 2, here the plasma is locally generated with a bias between the two plates in order to facilitate ion bombardment. Typically, these systems operate in the range of tens to hundreds of millitorr in pressure in order to support a plasma. The main difference with an ICP and RIE is in an ICP system the plasma is remotely generated away from the wafer, disconnecting ion generation and applied bias.

Figure 2. RIE system schematic
In a dry etch system there are trade-offs that must be balanced in order to control the key factors such as anisotropy and selectivity. In Figure 3 these factors are summarized showing the balancing effects. In most cases vertical structures are fabricated where the system correspondingly operates at low pressure, and high energy. As the figure shows, the negative outcomes for an anisotropic etch are a lack of selectivity along with increased etch damage as the process physically bombards the surface.

![Figure 3. Dry Etch Overview](image)

To summarize and compare the main pros and cons of both etching approaches, Figure 4 is displayed for simplicity.
1.3 Research Goals and Document Organization

The goal of the research presented here is to develop a better understanding of the wet and dry etch mechanisms for the formation of GaN nanowires, and to establish repeatable processes for vertical device fabrication. High aspect ratio wires with the ability to tune the diameters below 100nm is desired for future device applications.

This document is organized into separate chapters with the first outlining the background information on the subject. The second chapter goes into detail on the background material. The third chapter explains the methods and methodologies put into place for this work, showing how the experiments were conducted and how the results were analyzed. The fourth chapter exhibits the results of the various conducted trials and analyzes the outcomes. The fifth and final chapter summarizes the research work and the conclusions.
Chapter 2. Theory

2.1 Process of Dry Etching

GaN has a wurtzite (hexagonal) crystal structure that is different compared with the cubic diamond lattice used by Silicon and other semiconductors. GaN is commonly grown by MOCVD or Molecular Beam Epitaxy (MBE) on a host substrate such as silicon carbide (SiC) or sapphire (Al₂O₃) due to unavailability of bulk substrates. GaN is a very difficult material to dry etch due to the strong atomic bond strength. The etch rate in a fluorinated environment, such as with SF₆ or CF₄ used to etch Silicon, is extremely low or negligible. Instead the more aggressive Cl₂ based gases are used in an RIE or an ICP system in order to etch GaN with an appreciable etch rate of a dozens to a few hundred nm/min. Etching of GaN typically makes use of a Silicon Dioxide (SiO₂) or a nickel hard mask due to the slow etch rate of the materials in a chlorinated environment. GaN will have selectivity that is greater than 2 times that of Silicon dioxide or greater than 5 times that of nickel. In the dry etch process the typical gas combinations are either Cl₂/Ar, BCl₃/Cl₂/Ar, or Cl₂/N₂/O₂. Each of these combinations has an advantage such as a fast etch rate with Cl₂/Ar, increased anisotropy with the inclusion of BCl₃, or the ability to achieve smoother sidewalls with the inclusion of N₂. The downside to dry etching is the damage that ion bombardment causes during the etch. Defects are induced on the surface layers of GaN during the dry etch which negatively impact LED light emission and performance. Defects cause midgap states in the band structure which allows for recombination of carriers, releasing phonons (heat) instead of light. With nanowire structures the surface area is a greater fraction of the total area making it particularly susceptible to dry etch damage. Etching studies are
needed to understand the various factors involved in both forming the dry etched nanowires and the damage that is incurred.

2.2 Process of Wet Etching

In order to overcome the dry etch damage, a wet etch approach has been purposed to remove the surface layers of the GaN which contain defects from the dry etch. Wet etching involves immersing samples in chemistry which attack, oxide, or modify the target material. Wet etching is known to be isotropic, traditionally producing a large undercut in films to be etched giving a 1:1 etch rate vertically to horizontally. For nanoscale features this form of etching is not normally feasible, however alkaline chemistry often has a unique property when wet etching crystals. Alkaline solutions, such as Potassium Hydroxide (KOH), have been known to etch silicon selectively along the <100> plane creating a ‘V’ shaped groove which defies the traditional wet-etch nature. GaN has a different crystal structure, wurtzite (hexagonal), compared with the diamond lattice of silicon, this is shown in Figure 5 with pertinent crystal planes highlighted. The outlined shape of Figure 5 shows the unit cell for GaN which is the fundamental building block on which the crystal structure is based.
Most GaN growth is along the c-plane where the <0001> plane is on the surface of the material with the crystal unit cell paralleling how nanowires are typically oriented. Similar to how KOH selectively etches the <100> plane of silicon, for GaN the <1101> and <1120> planes are selectively etched. The KOH rapidly etches the <1101> plane, while slowly etching the <1120> plane, leaving the <0001> plane unetched. This process is shown in Figure 6 where the initial RIE etch will roughly approximate the <1101> plane (figure 6a) and the KOH will rapidly remove the dry etch damage along with any tapered shape (figure 6b). This reveals the <1120> plane (figure 6c) creating wires that are perfectly vertically oriented. Continued etching of the diameter of the wires can be controllably accomplished through the slow <1120> plane etching to achieve a desired diameter (figure 6d). When wet etching an LED structure the p-type region has a slower etch rate creating a slight ‘torch’ type of shape that can be seen (figure 6d). The wet etching process removes the drawbacks of a top-down approach to nanowire formation, though it is a new process and research needs to be done in order to better characterize the etch.
2.3 Process of Patterning Submicron Features

In order to miniaturize LED structures, submicron patterning is necessary. Traditional lithography in which photoresist is exposed by UV light and developed may be performed, however smaller wavelengths are needed to produce smaller features. As wavelength decreases the processing complexity increases along with the cost. Instead, nanospheres can be used as the masking material during the etch to create submicron features. These spheres can be made of many different materials, though in this case SiO$_2$ spheres are used due to the good selectivity during a chlorine dry etch$^{19}$. The spheres can be purchased commercially in various diameters and are often diluted in deionized water. The patterning process is simple and accomplished through spin coating the spheres on to a hydrophilic material$^{19}$. During spin coating the spheres form a close packed 2-D array on the surface as shown in Figure 7$^{19}$. The hexagonal arrangement
is created due to the orientation having the highest density. If desired the spheres can also be dry etched in order to provide spacing between neighbors. An SEM of coated and shrunken spheres are shown in Figure 7.

Figure 7. SiO$_2$ Shrunken Nanospheres
Chapter 3. Experimental Methods

In order to study dry and wet etching of nanowires, various tools and techniques need to be utilized. These include nanosphere lithography, Scanning Electron Microscopy (SEM), and Photo-Luminescence (PL).

3.1 Experimental Setup

The material used in these studies includes 6.2 µm of unintentionally doped GaN grown in the <0001> direction on Al₂O₃. The background doping due to defect incorporation of these samples is n-type, low to mid 10¹⁶ cm⁻³. Additional samples included the structure of an LED without the p-type layer on top. This was also grown in the <0001> direction on Al₂O₃ with 2.5 µm unintentionally doped GaN, followed by 2 µm of n-type GaN at 7*10¹⁸ cm⁻³, followed by 6 pairs of Multiple Quantum Wells (MQW) consisting of 30Å In₀.₁₃Ga₀.₈₇N wells with 125 Å GaN Barriers, topped off by 125 Å of GaN. The structure of this is shown in Figure 8.

Figure 8. MQW LED Structure (a) with MQW band diagram (b)
For the nanowire hard mask SiO\(_2\) nanospheres 750 nm in diameter, from Bangs Laboratories Inc. Part Number #SS03001, were deposited in a spin coating process at 900 rpm. In order for the silica spheres to adhere to the substrate, the samples were first oxidized in an O\(_2\) plasma at 100 W, 100 Standard Cubic Centimeters per Minute (sccm) flow of oxygen, at 120 mTorr, for 1 minute. This was done in a Lam-490 etcher as the electrode biases are flipped compared to an RIE, minimizing ion damage. This converts the GaN surface from hydrophobic to a hydrophilic through the formation of a thin oxide layer. Next, 10 % by weight silica spheres in deionized water are micropippeted unto the surface to cover the sample. The samples are next spin coated at 900rpm for a total of 80seconds to form a 2-D closed packed array. The spheres are then shrunk slightly by use of the same Lam-490 tool with SF\(_6\) at 90 sccm, O\(_2\) at 30 sccm, pressure at 250 mTorr, and power at 270 W. The radial etch rate is 119 nm/min for the spheres in this etch. The spheres on the samples were shrunk 80 nm in order to minimize neighboring wires bridging during the later dry etch.

The nanowire dry etch of the samples are performed in a Lam-4600 RIE using various combinations of BCl\(_3\), Cl\(_2\), Ar, CHCl\(_3\) (chloroform), power, time, and pressure. After the etch an HF dip of 10:1 BOE was performed for 5 minutes to remove the spheres.

The wet etch used AZ400K developer which contains a high concentration of KOH. This developer was diluted with deionized water in various amounts as specified. Samples were fully submersed in the liquid contained in a glass beaker. Solutions were heated on a hotplate as specified, with the liquid temperature recorded with a thermometer. During heated etches the
beaker top was covered with aluminum foil to minimize evaporation. All temperatures stated are with respect to the temperature of the liquid and not the set temperature of the hotplate.

### 3.2 Analysis Setup

In order to judge the results of the experiments two primary analysis methods were used, SEM and Photoluminescence. These analysis techniques are the best choice for studying the outcomes as the physical wire attributes (diameter, height, texture) are easily obtained through SEM while the topology effect on the light emission is gathered through PL. Any defects will be observed through PL as defects reduce the amount of re-emitted light.

The SEM used was Dr. Brian Landi’s Hitachi S-4000 with the imaging done at a lower accelerating voltage of 5 kV. This lower voltage minimized charging effects of the GaN, along with giving the needed surface roughness detail without losing much signal to noise ratio. Higher accelerating voltage was found to miss the surface details as the electrons penetrated further into the wires obscuring the surface.

The PL system was a Horiba system which illuminates the sample with a He-Cd laser at a wavelength of 325 nm and a power of 33 mW. The laser light excites the sample generating electron-hole pairs which then recombine to re-emit light which is then collected by a silicon photodetector. Wavelength intensity from 325 nm to 900 nm are recorded and plots generated. A schematic of the Horiba PL system is shown in Figure 9 where mirrors reflect the laser light to the sample.
Figure 9. Photoluminescence System Layout
Chapter 4. Results and Discussion

Presented here are the results of various etch trials used to establish a repeatable nanowire fabrication process. Dry etching and wet etching are optimized separately in order to establish nanowires with high aspect ratio (large heights and small diameters).

4.1.1 Process of Record for Dry Etching GaN

The current process of record (POR) GaN etching recipe in the Lam 4600 leads to a nanowire with a low aspect ratio of ~2, reaching heights of only 930 nm with widths of 475 nm. The etch recipe is shown in Figure 10 next to an SEM of the etch profile. An etch rate of only 20 nm/min is recorded, leading to long etch times. Additionally, a large taped base at the bottom of the wires forms.

![Figure 10. POR GaN Etch (a) with corresponding recipe (b)](image)

The etch proceeds nearly vertically operating as a physical process more than a chemical one. Shown in Figure 11 is a POR etched sample at a view of around 80° with the silica
nanospheres on top. Due to the vertical nature of the etch the initial silica sphere shape will become flat as the etch proceeds. The etch must stop before half the sphere is etched or damage will occur to the wire. Initial stages of nanowire damage from over etch can be seen to occur in Figure 10 towards the top of the wire, as it shows a rough sidewall vs. the bottom of the wire showing a smooth crystallographic dependence.

![Figure 11. POR Etch view at ~80°](image)

If the samples continue to be etched further, the wires start to lose shape. This is shown in Figure 12 with a sample that has undergone a 40% over etch compared with the POR. Here the spheres are completely etched away and the insides of the wires are starting to hollow out. The sidewalls also show much more roughness compared with the POR, leaving just a small area at the base smooth due to shielding from the wire top.
4.1.2 Effect of Varying Chloroform

The POR recipe was modified in order to study the effect of chloroform on the etch. Chloroform is used to form a carbon polymer, which on contact with the substrate, conformally coats the material for the purpose of etch resistance\textsuperscript{20}. Due to the vertical nature of the etch from the generated ions and electrode biasing, the bombardment breaks up this polymer on the base of the wires, while the sidewalls of the wires stay passivated. The polymer also helps reduce etch damage as any stray ions will damage the polymer instead of the wire itself. The POR has a chloroform flow of 8 sccm and this flow was varied in these tests. The power was also raised and pressure lowered in order to highlight the role of the polymer. First the 8 sccm amount was maintained under these conditions, shown in Figure 13 on the left. The pillar, (a), is shown to have a slightly higher etch rate of 33 nm/min compared with the POR of 20 nm/min due to the changes in pressure and power.

For the second sample, (b), a flowrate of 2 sccm of chloroform is chosen and is shown in the center of Figure 12. The wires here are 1500 nm tall and show the smooth crystallographic
dependence just as shown by the first sample. The reduction in chloroform allows for more vertical etching while still protecting the sidewalls of the wires, producing taller structures. The recorded etch rate was 60nm/min which is roughly double the previous run at 33 nm/min.

The third sample, (c), was run with no chloroform under the same conditions and is shown on the right of Figure 13. Here the wire is even taller at 2300nm, though has been over etched as can be seen by the damage at the top. The wire is perfectly round showing no crystallographic dependence that the other samples show. As there is no polymer build up the sides of the wire are etch producing an undercut near the base. A high etch rate of 91 nm/min is produced from this test.

The damage which occurred without flowing any chloroform is undesirable for LED applications, though the good selectivity and high etch rate is desired. Crystal damage is signified by the loss in observed crystallographic planes, along with PL data. The small changes in flow of chloroform have a dramatic effect on the etch rate and profile of the nanowires.

Figure 13. Chloroform etch tests: 8 sccm (a), 2 sccm (b), 0 sccm (c)
4.1.3 Effects of Pressure

Pressure plays an important role in the formation of the wire structure, particularly the tapered base. The tapered base is the cone type shape at the bottom of the nanowires. The base of the nanowire can be seen in the previous SEM figures as a shallow slope up to the wire itself. A 90° view of the tapered base is shown in Figure 14 with a larger diameter wire.

![Nanowire base at 90° view](image)

This base forms due to an effect known as etch shadowing\textsuperscript{21, 22}. Due to high pressure during the etch there are more gas molecules in the chamber. The increased number of gas molecules inflate the chance for collisions to occur which will scatter ions from the vertical direction. This results in ions which impact the sample at an angle, shown in Figure 15. Most of the ions travel vertically though as the pressure increases the fraction that scatter goes up. The scattered ions are blocked by the sphere and the wire, etching only the upper portion of the wire casting a shadow to the other side. Since this effect occurs radially around the wire this shadowing effect circles the base, creating the tapered base as seen in the micrographs.
Low pressure during the etch will reduce the shadowing, while higher pressure will make it more evident. A secondary control is the power, where higher power will direct the ions to the surface. Pressure impacts this process by inversely changing the free path for the ions. Higher pressure creates a lower mean free path, while lower pressure creates a higher mean free path where the ions are less likely to collide and scatter. Figure 16 presents samples which have been exposed to different pressures. Here pressure is varied from 50 mTorr to 200 mTorr as mean free path is reduced and more ions collide correspondingly creating a larger tapered base.

As can be seen from the 200 mTorr sample (d) the device has a large tapered base where crystallographic facets can be viewed. Lowering the pressure leads to a higher fraction of ions which are normal to the surface, both reducing the formation of the base along with etching away any crystallographic facets. This effect is similar to the observed damage on the POR recipe where damage occurs at the top of the wires removing the crystal graphic dependence. At 50mTorr the pressure is low enough to remove most of the base as the majority of the ions are normal the surface. Having the ions normal to the surface and not scatter allows for a high
vertical etch rate both by having more ions impact the base as well as imparting more energy into the etch since the scattering is not a major loss mechanism. It is desired to have a taller vertical structure with no base, as the base takes height away from the useable portion of the wire.

![Images of pressure samples at different torr levels](image)

Figure 16. Pressure samples: 50 mTorr (a), 80 mTorr (b), 100 mTorr (c), 200 mTorr (d)

### 4.1.4 Effects of Power

Applied RF Power during the etch controls the intensity of the ion bombardment which shapes the etch profile. The higher applied power leads to a larger etch rate as more ions are generated along with increased electrostatic pull the ions have to the sample. Shown in Figure 17 is a comparison that highlights these effects. In this trial the same recipe is run with different power, 75 W vs. 150 W. The figure on the left had the lower power of 75 W and was run for a longer time of 15 additional minutes to be able to see the structure underneath. The selectivity is lower for the lower power etch as the chlorine based chemistry chemically attacks the sphere
vs. the more physical sputtering at higher power. The wire height is shorter with lower power due to less ion etching along with the base. Although pressure is the dominant factor in forming the tapered base of the wires, power also plays a key role in order to funnel ions in the direction normal to the sample. If the bias is not high enough, just like the effects of pressure, the ions can scatter and will not impact the sample directly normal to the surface, leading to a tapered base.

![Image of wire samples](image)

Figure 17. Effects of Power: 75 W (a), 150 W (b)

To further explore these effects a 30 sccm Chlorine, 20 sccm Argon mix at 65 mTorr was studied at various power levels for a fixed time of 15 minutes. Argon will only physically and not chemically etch the material, making the etch rate very sensitive to the applied power. For different applications it is desirable for the nanowire to have an undercut and this gas combination was seen to produce one. Figure 18 shows the results of these etching trials. As power is increased the wire height is seen to increase, as seen in the previous trial. The undercut depth initially increases then disappears as the power is increased past 175 W. The Argon is
presumably reflected off the base of the wires and hits the sidewalls to form the undercut. After power is increased past a certain point this effect is overridden by the large substrate bias which pulls down a larger number of ions to the sample.

Similar to the previous trial the tapered base is further reduced with the higher power, though it is also less visible due to the lower chamber pressure. Slight etch damage occurs at the tops of the wires for the lower power samples as they are slightly over etched due to the lower selectivity. For the higher power samples of 200 and 225 W the ions effectively smooth out any roughness as the sphere shrinks. This can be seen in the lack of crystallographic facets in the higher power samples. Adjusting the RF applied power allows the tailoring of the profile to obtain the desired structure depending on the application. Generally, for most purposes the higher power is desired to obtain a tall vertical structure.
4.1.5 New Dry Etch Process

From this work a number of nanowire structures can be obtained such as triangular, perfectly vertical, or inverted pyramidal, shown in Figure 19. Each design opens the doors to a number of applications. For LEDs or FETs a taller vertical structure is desired. Increased height allows for more tolerance for manufacturing, while a vertical structure assures there will be no material deposited on the sidewalls during processes such as metal evaporation.
With these various experiments performed, the best case is selected out the experiments. The best dry etch results were found using the recipe outlined in Figure 20. The high power with low pressure supports a fast etch with a vertical profile. This sample has a very high etch rate of 227 nm/min while reaching a max height of 3400 nm with the 700 nm silica spheres before the wire starts to take damage. In this sample the best of each tests are chosen, corresponding to high power, low pressure, and no chloroform. This low pressure regime allows for smooth etching to occur vertically without needing the chloroform due to less ions impacting at off angles.
4.2.1 Developing and Optimizing the KOH wet etch

In the last few years KOH, TMAH, and NaOH chemistries have been used in order to crystallographic etch GaN nanowires. Several recent papers have used low concentrations of these solution in order to form nanowires for nanoscale LEDs, or nanowire FETs\textsuperscript{13,17,18}. Dry etched nanowires can have a slight taper or a large diameter which diverge from the ideal small vertical structures. Immersing samples in these chemistries will crystallographically remove any taper and shrink just the wire diameter. Additionally, surface damage caused during the dry etching process can be removed. RIE damage creates recombination sites that can lower the performance of devices. However, there has been no comprehensive study looking at the effects of time, concentration, and temperature on this process in order to optimize it. Work has been done here looking at these effects on both the topology and the corresponding impact on the PL spectrum. AZ400K is used as the source of KOH with dilutions of DI water as specified. For this work the samples with the multiple quantum wells on top of n-type GaN were used along with unintentionally doped GaN samples.

4.2.2 KOH Effects of Time and Temperature

Temperature of 80\textdegree C, 45\textdegree C, and 23\textdegree C were tested with concentrations of 5\% AZ400K. Intervals of 10 minutes were used to study the 80\textdegree C and 45\textdegree C samples, while the 23\textdegree C samples were studied at intervals of 30 minutes due to the slower etch rate. After each sample was immersed for the set period, both SEM and PL images were taken to study the progression.
Shown in Figure 21 are the SEMs of the etch progressions for the various temperatures and times.

![SEM images of etch progressions for 23°C, 45°C, and 80°C](image)

**Figure 21.** Etch progression SEMs with 5% AZ400K

From the SEM images shown, a higher etch rate occurs with samples at higher temperatures. The high temperatures also correspond to a rough surface during the etch process, creating staircase patterns along the wire, as the solution peels away layers. Additionally, the wires follow a pattern of rough to smooth surface as the etch proceeds.

In order to better analyze the wet etch process and see the corresponding effect it would have on LED performance, PL is done. These results are shown in Figure 22 with the PL intensity...
at 450 nm vs time plotted. Accompanying each graph is an additional plot showing the wavelength spectrum for a high and low point during the etch.

Figure 22. PL Results for Different Temps at 5% AZ400K

The PL data shows that the peak intensity oscillates in a downward trend from the starting material. This is due to the active area that generates the light for the nanowire LED shrinking as the wire itself shrinks. This active area is located on the top of the wire structure as highlighted earlier in Figure 10. The oscillations are due to the etch morphology as it proceeds.
from a rough to smooth surface. Rough surfaces are more likely to scatter light which will decrease the PL intensity. The peak position stayed at 450 nm though if the wires are considerably shrunk below 100 nm quantum confinement will shift the peak wavelength to smaller values. From the results the 45° C sample is the best trade off of etch rate and small etch step heights.

4.2.3 KOH Damage Recovery

Damage formed during the dry etch of the nanowires can be detrimental to LED performance and subsequently the PL intensity can be greatly reduced. If the wires experience little to no damage, the samples will see an enhancement in the PL intensity due to better confinement and strain relaxation compared to the planar structure\textsuperscript{13}. Etch damage creates recombination sites where the absorbed light is recombined as phonons (heat) instead of re-emitting light. Low pressure, and high power during an RIE etch generate more ion bombardment that can lead to surface damage. Plots showing the PL results of a high and low damage etches are shown in Figure 23.
Figure 23. Nanowire Etch: Severe damage from RIE etch (a), Minimum damage from RIE etch (b)

For the samples that have been through an RIE process which caused damage and a reduction in PL, a KOH wet etch can remove etch damage and passivate the surface\textsuperscript{13}. The damage is located on the surface of the wires, which allows for a quick dip in the AZ400K solution to remove this damage through etching. To study this an RIE of 150 W, 80 mTorr, 25 sccm of BCl\textsubscript{3}, 20 sccm of Cl\textsubscript{2} and Ar, and 2 sccm of Chloroform is done to induce damage to a sample. The sample is then immersed for 10 or 20 minutes in 5\% AZ400K at room temperature. PL was taken at every step of the process and results are plotted in Figure 24. Compared with the planar structure, the initial RIE which forms the wires shows a large decrease in intensity due to surface damage. After the treatment of 10 minutes in the AZ400K, the sample recovers most of its intensity. Continued treatment time on the sample does not further recover PL intensity as the surface defects have been removed. The intensity after the treatment does not reach the planar


value due to the initial decline and start of oscillatory behavior observed in the PL of all different temperatures samples.

4.2.4 KOH Effects of Concentration

The effects of concentration on the KOH etch were studied in order to determine the optimal concentration value. A fixed time of 30 minutes and fixed temperature of 45° C were used for all samples. Concentrations of 5 %, 20 %, 40 %, 60 %, and 80 % AZ400K, diluted in DI water, were used. SEM images for each sample after the etch is shown in Figure 25. As concentration increases the etch profile goes from a rough ‘staircase’ pattern to that of smooth columns.
Additionally, the tapered base is etched away at concentrations greater than 20%. As the percentage of AZ400K increases, the etch rate of the crystal plane for the tapered base increases as well. This shows additional planes start to etch besides the $<11\bar{2}0>$ and $<1\bar{1}01>$ planes as the fraction of AZ400K rises, figure 23 (b) through (e). With concentration increases, the etch rate also marginally increase along the $<11\bar{2}0>$ plane. The dots visible on the top of wires are small etch defects due to crystal imperfections which are randomly distributed. Etch defects are highlighted by the wet etch process. The etch with 40% AZ400K shows the smoothest sidewall with a removal of the tapered base which increases the height of the nanowire. Removal of the tapered base along with smoother sidewalls are desired for LED or nanowire applications as rough surfaces can scatter light or lead to difficulty in processing, respectively.
4.2.5 Applying the KOH Work

With this study completed nanowire samples can be etched to form desired nanowire structures. The time, temperature, concentration, and dry etch data allows for the nanowire diameter to be pre-determined. Shown in Figure 26 are some of the results of this work. This particular dry etch leads to a slight increase in diameter further down the wire, 300 nm at the top to 500 nm at the base, which would not be desired for nanowire FETs or LEDs. The KOH wet etch is used to shrink the wires to a chosen diameter of ~100 nm. Perfectly vertical wires with diameters ranging from 80 to 110nm are obtained with spacing of 800nm and no loss in height. As the SEM shows, the wires have slight bridging at the base which is caused by the close proximity of wires during the initial etch. This bridging effect is not an issue for the majority of applications such as nanowire transistors as it is of negligible height at the base. As can be seen there is also slight non-uniformity in wire diameter. This is due to local variations in concentration, along with non-uniform initial sphere diameter. The process is repeatable and opens the door to a number of future devices such as nanowire transistors or flexible electronics.

Figure 26. Pre (a) and Post (b) KOH Etch
Chapter 5. Conclusions and Future Work

The etching of high aspect ratio GaN nanowires has been optimized in order to determine the ideal dry and wet etch conditions. The dry etching effects of chloroform flow, pressure, and power have been examined going into more detail than previously published works. Results allow for the optimization of the nanowire fabrication process and provided much more knowledge of etching GaN. These findings allow the dry etch to be tailored to produce a range of shapes from nanopyramids, inverted nanopyramids, and vertical nanowires for a number of new applications. For the production of vertical nanowires, the etch rate has been improved over seven times, while the selectivity has been improved by two times, compared with the POR.

The KOH wet etching has also been advanced, looking at the effects of temperature, time, concentration, and how these factors interact with dry etching. High temperatures are found to have a higher etch rate alongside rougher surface formation. Aspects of the damage recovery of the wet etch were better quantified showing 82 % recovery compared with a planar surface. Effects of concentration observed showing a transition in the etch pattern with less crystal selectivity at higher concentrations, finding 40 % to produce the smoothest surface. These results advance the use of KOH wet etching to create devices that employ a top-down nanowire formation approach without the negative effect of crystal damage. Nanowires combining the dry and wet optimizations allow for high aspect ratio nanowires to be fabricated with custom diameters smaller than 100 nm.

This work has led to a novel GaN nanowire FET device and will continue to pave the way for future projects. Devices such as the one shown schematically in Figure 27 have been realized.
through the GaN wire etching mechanisms presented here. Other studies are also being pursued looking at the effect of wire shape in the fabrication of nanowire LEDs.

Figure 27. Nanowire Transistor schematic
6. References


