Spring 5-15-2019

Multifunctional Properties of GaN NWs Applied to Nanometrology, Nanophotonics, and Scanning Probe Microscopy/Lithography

Mahmoud Behzadirad

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MULTIFUNCTIONAL PROPERTIES OF GaN NWs APPLIED TO
NANOMETROLOGY, NANOPHOTONICS, AND SCANNING
PROBE MICROSCOPY/LITHOGRAPHY

by

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B. S., Physics, Semnan University, 2006
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2015

DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Doctor of Philosophy
Optical Science & Engineering

The University of New Mexico
Albuquerque, New Mexico

May, 2019
Dedication

To my parents, and my fiancée for their endless love and supports.
Acknowledgments

I heartily acknowledge my adviser Dr. Tito Busani for his endless guidance and support during my research endeavors at CHTM, UNM. He is someone you will instantly love and never forget once you meet him. He has not only been my adviser, also my best friend through past five years. By giving me the opportunity to join his group to explore nanotechnology engineering, Tito helped me to develop my knowledge, skills, and taught me a professional way to face and troubleshoot problems.

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MULTIFUNCTIONAL PROPERTIES OF GaN NWs APPLIED TO NANOMETROLOGY, NANOPHOTONICS, AND SCANNING PROBE MICROSCOPY/LITHOGRAPHY

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ABSTRACT

GaN nanowires are promising for optical and optoelectronic applications because of their waveguiding properties and large optical bandgap. Recent researches have shown superior mechanical properties of GaN nanowires which promises their use in new research areas e.g. nanometrology. In this work, we develop a scalable two-step top-down approach using interferometric lithography as well a bottom-up growth of NWs using MOCVD, to manufacture highly-ordered arrays of nanowires with atomic surface roughness and desired aspect-ratios to be used in nanophotonics and atomic precision metrology and lithography. Using this method, uniform nanowire arrays were achieved over large-areas (~1 mm²) with aspect-ratio as large as 50, radius as small as 17 nm. The mechanisms involved in the wet-etch process are thoroughly investigated and FDTD modeling is employed to study modal
properties of the fabricated GaN NWs. It is shown that HE$_{11}$ is the dominant transverse mode in the nanowires with sub-100 nm radius. Single-mode lasing with high Q-factors of ~1139-2443 were obtained in nanowire array lasers, corresponding to a linewidth of 0.32-0.15 nm. We also demonstrate the preliminary result of including nanoporous Al$_x$Ga$_{1-x}$N DBRs in the GaN nanowire structures grown on Si, not only to enhance modal reflectivity, but also to alleviate accumulating tensile stress due to the lattice and thermal expansion constants mismatch between overgrown GaN and Si.

Top-down fabricated GaN NWs and sharp bottom-up grown GaN NWs were used to fabricate AFM and STM tips for nanometrology. The advantages of these tips are to assist nanometrology in scanning high-aspect-ratio structures, provide cost-effective and durable tips for scanning probe lithography for the creation of sub-10 nm features, and enabling tip-based nanometrology with Raman spectroscopy. GaN NWs as a new material for AFM tips, enhanced image resolution in scanning high-aspect-ratio structures with straight sidewalls. Using sharp GaN NWs as STM tips, we could demonstrate atomic resolution imaging and sub-10 nm lithography with a high stability over large-area scanning tests. Employing sharp GaN NWs in active AFM cantilevers demonstrated improvement in the image resolution compared to the standard Si-tips and accomplished ~10 nm linewidth structures under applied bias in field emission lithography.
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Chapter 1

Introduction

1.1. Nanofabrication

1.1.1 History of nanotechnology

The idea of nanofabrication for building machines out of individual atoms was proposed by Nobel laureate Richard Feynman in 1959. He predicted the resulting machines would be artificial molecules which might themselves be larger than nanometer, but they are built based on atomic level manipulation. But not only was this kind of manipulation impossible at the time, but few people had any idea why it would be useful to do it! [1]

Later in the 1980s, this new field of study got a name “nanotechnology” by physicist K. Eric Drexler, who pointed out that nanotechnology had been predicted much earlier and now we emerged it to our technology. Drexler revived Feynman’s vision and helped introduce the general public to the basic concepts of nanotechnology.

Today, nanotechnology not only is of great interests for research and development, also has been employed in many of current devices and tools e.g. Cell phones, Light emitting
diodes (LEDs), Lasers, Energy storages, and almost all of electronic devices in form of nanoscale building blocks e.g. nanowires (NWs) [2-9], nanodisks [10], nanobelts [11], nanotubes [12], nanocolumns [13], and their efficiency is improving at an increasing speed.

### 1.1.2 Lithography Techniques

Lithography is a method of printing and patterning fin structures in nanotechnology and is the main part of every nanofabrication process. According to the feature size, shape of the structures, and scale of fabrication different methods may be employed;

**Photolithography:** In photolithography or optical lithography a UV light source is used to transfer structure patterns from a photomask to a light sensitive chemical (photoresist). The minimum feature size can be printed in this method is limited to optical wavelength and numerical aperture of the lenses and optical elements (usually 500 nm-1 µm). Shorter-wavelength sources, such as extreme ultraviolet and X-ray, are being developed to allow lithographic printing techniques to reach dimensions from 10 to 100 nm [14]. This technique is now widely used in wafer-scale micro and nanofabrication industries.

**Electron Beam (E-beam) Lithography:** In this maskless technique, the pattern is written by sweeping a finely focused electron beam across the surface that is covered by an electron-sensitive film [14]. This technique provides patterns down to about sub-10 nm, but is a serial process that is not scalable and can be used for low throughput fabrication.

**Nanoimprint lithography:** patterns are created by mechanical deformation of imprint resist, typically a monomer or polymer formulation that is cured by heat or UV light during imprinting [15]. This technique provides high throughput fabrication, but resolution is still not as good as other methods.
Interferometric Lithography (IL): In this technique, a UV laser source is used to make an interferometry pattern on sample. In the IL setup, beam is split into two coherent beams by means of a beam splitter. Superposition of beams creates an interference pattern which can be used to pattern UV-sensitive films. Nanostructures in this method are limited to lines (1D pattern), holes and pillars (2D pattern), and the minimum achievable feature size is limited to \( \sim \frac{\lambda}{2n} \) (where \( \lambda \) is the optical wave length of the laser beam, and \( n \) in the refractive index of the medium) [16].

1.2. Nanometrology and nanolithography

Metrology is the science of measurement and inspection as defined by the International Bureau of Weights and Measures (BIPM). The measurement of length or size, force, mass, electrical and other properties is included in metrology. Nanometrology is a sub-major of the metrology that addresses science of measurement in nanoscale (<10^{-9} nm) level. Since a great part of researches in academies and industries are devoted to help nanotechnology and nanomanufacturing for today and future applications, nanometrology takes a crucial role to assist nanotechnology to produce devices with very high degree of accuracy.

The challenges in this field are the creation new or improved methods to enhance reliability and accuracy of measurements in available techniques to meet all the needs for next generation of nanoscale manufacturing and technology. Controlling size and shape of the structures in nanofabrication is challenging and the importance of a precise metrology technique is revealed when we know a small deviation from actual dimension or shape may results in a totally undesirable operation. Today, various techniques have been developed and employed in nanometrology which can provide different degree of accuracy. Some of
these techniques are, scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical metrology, and atomic force microscopy (AFM). Table 1.1 compares advantages and limits of different nanometrology instruments.

1.2.1. Atomic Force Microscopy

As indicated above, AFM is very high-resolution type of scanning probe microscopy (SPM) to measure and inspect structures in nanoscale dimension. AFM gathers data by

**Table 1.1 Comparison (Pros and cons) of various nanometrology instruments.**

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Advantages</th>
<th>Limits</th>
<th>Instrument feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>✓ Capable of doing high resolution imaging in nanoscale.</td>
<td>• Needs vacuum</td>
<td>![SEM Image]</td>
</tr>
<tr>
<td></td>
<td>✓ Fast imaging of large area.</td>
<td>• Sensitive to conductivity of the sample</td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Scalable.</td>
<td>• Expensive</td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Implementing manipulation.</td>
<td>• Destructive</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>✓ Provides atomic resolution.</td>
<td>• Needs vacuum</td>
<td>![TEM Image]</td>
</tr>
<tr>
<td></td>
<td>✓ Enable of performing crystallography study in atomic scale.</td>
<td>• Super expensive</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Non-scalable</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Needs sample preparation.</td>
<td></td>
</tr>
<tr>
<td>Optical metrology</td>
<td>✓ Scalable</td>
<td>• Limited to optical wavelength.</td>
<td>![Optical Metrology Image]</td>
</tr>
<tr>
<td></td>
<td>✓ Very accurate atomic resolution.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Not sensitive to conductivity of the sample.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Reasonable inspection cost.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>✓ Image nano and atomic scale structures.</td>
<td>• Low speed scanning.</td>
<td>![AFM Image]</td>
</tr>
<tr>
<td></td>
<td>✓ Works in ambient.</td>
<td>• Possibility of including artifacts to the image due to the tip interaction with sample.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Cost-effective.</td>
<td>• Hard to image nanostructure with straight walls.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Not sensitive to conductivity of samples.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Non-destructive in tapping mode.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>✓ Enable of doing characterization and manipulation.</td>
<td></td>
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</table>
touching the sample with a mechanical probe. Figure 1.1 illustrates a schematic of AFM machine and shows how data is collected. As seen, the inspection sample is mounted on a piezoelectric holder. A laser source is used to illuminate back side of the cantilever and reflected light is collected by a photodiode (photodetector). Any deflection of the cantilever due to the interaction between tip and sample surface can be monitored and detected by this photodiode. Collected information is converted to an image by feedback electronics which are connected to the AFM machine. AFM can be used in three different modes; i) contact mode, ii) noncontact mode, and iii) tapping mode. In contact mode tip is touching the sample and measurements are typically morphology study. Unlike the contact mode, in noncontact mode tip oscillates close to the sample with amplitude <10 nm. When the oscillation amplitude increases (>10 nm), the operation mode is called tapping. Since in contact mode tips is touching sample, this mode is recognized as destructive inspection, while tapping mode is totally non-destructive.

Since invention of atomic force Microscopy (AFM) [17,18], it has been recognized by semiconductor industry and material science in general to be a powerful device to obtain information of material surface in the nanoscale orders. It is used for measuring not only inorganic materials such as metals and semiconductors but also organic materials and

![Figure 1.1. Schematic of data collection by an AFM machine.](image-url)
biomaterials [19-22]. Also by applying the technology of AFM to microscopy, new functions, such as mechanical property study [23-25], electrical property measurement [25,26], magnetic force microscope (MFM) [27], scanning near-field optical microscope (SNOM) [28,29], and Raman Enhanced Microscopy (REAFM) [30] are put to practical use. Silicon, silicon-nitride, and carbon nanotubes are the most common materials used for AFM tips. We discuss pros and cons of each in the following section.

1.2.1.1. Current AFM tip materials

Silicon

As the most abundant and technologically developed material on the earth and the cost-effective fabrication process, silicon has often been used as the tip material in atomic force microscopy. Silicon probes are easy for batch fabrication and as a result very interesting for industries. According to the thickness, width, and length of the cantilevers, these tips are suitable for fast and slow scanning of the nanostructures and enable to provide atomic scale resolution if the tips apex is sharp enough. As seen in Figure 1. 2, silicon tips have pyramidal (conical) geometry and can be coated by metals or dielectric material for specific applications and measurements.

Figure 1. 2. SEM image of different geometry of silicon AFM tips.
For precise scanning of very deep 3D nanostructures with sharp edges in sub-100 nm dimensions, AFM requires stiff tips with straight side walls and minimal roughness to yield reliable information about the inspection structure in the output image. In this matter, we can consider two major problems associated with applying silicon tips; 1) geometry and conical shape of the tips, 2) poor mechanical property and short lifetime of the tips [31].

The manufacturing techniques for Si-based tips are developed based on the crystallographic etching of the Si wafers results in pyramidal shape due to the formation of (111) planes on the sidewall of the tips. The resulted conical shape can be transferred to the output AFM images as shown in the schematic and SEM image in figure 1.3. This problem is even more severe when inspection sample contains high-aspect-ratio structures with straight walls and sharp edges.

Mechanical properties of the tip materials are important because of two main reason; i) any deformation or defects on the tip may result in observing artifacts in output AFM image (Figure 1.4), and ii) short lifetime of the tips may increase inspection cost for any process. Sohn et al [32] has shown Si nanowires have a Young’s Modulus about <100 Gpa. This
low mechanical property is showing up during measurement in form of either breaking/losing the tip or tip deformation and artifacts in the image.

Amorphous/polycrystalline metal-coated tips also suffer from the same problem and are typically higher cost due to the metal coating.

**Silicon-nitride**

Silicon nitride tips are suitable for measurement in fluids and contact modes. The shape of these tips is identical to silicon tips (due to the fabrication process) and so the same issues might be expected here as well. Figure 1.5 demonstrates the geometry of the silicon nitride tips. Since these tips have soft cantilever (made of Pyrex wafer) due to the fabrication method, they have low natural frequency and are not a good choice for fast scanning measurement.
Carbon nanotube (CNT)

Carbon nanotubes (CNT) have superior mechanical properties (3-10 times higher Young’s Modulus [33]) to silicon-based probes and can be grown in different aspect ratios which make them a robust material with excellent geometry for metrology of high-aspect ratio nanostructures. Despite of these advantages, impossibility of patch fabrication and the cost of fabrication process are still a big challenge for their application. In Figure 1.6 (a) and (b) an example of CNT tips and different aspect ratio CNTs are shown.

![Figure 1.6](image)

**Figure 1.6.** (a) CNT AFM tips, (b) different aspect ratio CNT.

1.2.2. **Scanning tunneling microscopy (STM)**

Scanning tunneling microscope (STM) [34,35] is an instrument that provides images of solid surfaces with atomic resolution. The operation of the STM is based on the tunneling current, which flows when a very sharp tip approaches a conducting surface at a distance of approximately one nanometer. The tip is mounted on a piezoelectric tube, which moves the tip vertically (perpendicularly to the sample surface) and horizontally (parallel to the sample surface) by applying a voltage at its electrodes. Thereby, the electronics of the STM
system control the tip position in such a way that the tunneling current or the distance between the tip and the surface is kept constant, while at the same time scanning a small area of the sample surface. This movement is recorded by the computer, which can generate an image of the surface topography. Under ideal circumstances, the individual atoms of a surface can be resolved and displayed. Figure 1.7 illustrates a schematic of STM instrument and the method of imaging of the surfaces using this machine.

1.2.2.1. Current STM tip materials

STM tips are made of robust metals e.g. Pt, W, Ir and not only generate atomic resolution, also can be used for surface modification and atomic-scale lithography through a mechanical, thermal, chemical, and electrical or a combination of these interactions (such as thermochemical, electrochemical, etc.) [36].

Although the available tip materials are providing very high atomic scale resolution in probe microscopy and nanoscale resolution in lithography, however metallic tips experience modification under applied bias due to the very high atomic mobility, they also show significant changes under continued writing. In addition to these problems, the
expensive cost of employed metals, increases the cost of imaging and lithography through STM.

1.2.3. Scanning probe lithography (SPL)

Scanning probe lithography (SPL) is a versatile maskless lithography technique to pattern material in nanoscale using scanning probes (AFM, and STM). This lithography method is capable of writing patterns at high resolution below 10 nm. SPL is considered as a lithography technique in academics and research environment to generate patterns with small feature size where photolithography cannot be applied due to the diffraction limits. Since the first patterning generated by SPL, this technique has shown its ability to pattern 3D nanostructures [37], smallest field effective transistors [38], and patterning protein with 10 nm feature size [39].

Different SPL methods to write nanoscale features can be classified in terms of the driving mechanisms used in the patterning process, namely thermal, electrical (bias

![Figure 1.8](image-url)

**Figure 1.8.** (a) Classification of SPL methods according to patterns nanoscale features. (b) Electrochemical reaction on oxidation SPL. Reprinted by permission from Ref. [36].
induced SPL), mechanical and diffusive [36]. Figure 1. 8(a) depicts classification of SPL methods according to the tip–surface interaction used for patterning.

**Thermal SPL (t-SPL)**

In thermal scanning probe lithography (t-SPL), using a heated scanning probe, materials are efficiently removed from a surface without the application of significant mechanical forces. Indeed, in t-SPL heat is used to modify a material mechanically. In another type of t-SPL, localized heat is used to locally change the chemistry of a material, known as thermochemical SPL (tc-SPL) [36]. The patterning depth t-SPL and tc-SPL can be controlled to create high-resolution 3D structures. [37] Both AFM and STM tips are capable of doing this kind of nanolithography.

**Bias induced SPL (b-SPL)**

In scanning probe microscopy, the small size of the AFM tip’s apex facilitates the generation of extremely high electrical fields and a focused electron current (remarkably high electric fields ~10 V nm\(^{-1}\) (10 GV m\(^{-1}\)) can be achieved by applying moderate voltages (~10 V) [36]). Using this high electric field generated between tip’s apex and sample, chemical properties of the material is modified, and nanoscale patterns can be written on desired areas. In case of conductive samples, a current can be flowed between tip and sample to create patterns by locally changing the chemical properties of the material. This type of SPL requires highly conductive tips and can be performed using both AFM and STM instruments.
Mechanical SPL

Mechanical SPL (nanomachining) uses the mechanical force exerted by the tip to induce the selective removal of material from a surface [36]. This method has successfully applied to modify polymers as well as hard material [40, 41].

Oxidation SPL (o-SPL)

In this method of patterning, scanning probes are in contact with a solid substrate (semiconductors) without need to any extra coating layers (e.g. polymers). Oxidation SPL is based on the spatial confinement of an anodic oxidation reaction between the tip and the sample surface. The oxidation process is mediated by the formation of a nanoscale water bridge [42]. The role of the water meniscus is to act as a nanoscale electrochemical cell that provides the oxyanions by which the reaction takes place (Figure 1. 8(b)). The the tip acts as the cathode (negative) and the sample surface is the anode (positive) in the cell configuration. Both contact and non-contact mode can be employed for oxidation SPL [36].

1.2.4. GaN nanowires as a new material for Next generation nanometrology

To address those challenges in the current nanoscale metrology, new materials need to be investigated and developed for cost-effective, and more durable tips with ability of providing extremely accurate data from the nanostructures to assist metrology in nanotechnology in its path.

Moreover, today technology is mobbed by integrated devices which makes tools multifunctional and versatile for many applications. So, proposing new material as tip for AFM can open new fields for tip metrology such as Photonics and Optical lithography, and
improve previously developed applications e.g. Morphology study, Mechanical property study, Electrical property measurement, Magnetic force microscope (MFM), Scanning near-field optical microscope (SNOM), and Raman Enhanced Microscopy (REAFM). Overall, the goal of such research is to provide accurate feedbacks from tip metrology during fabrication process in which the results assist in-line optical metrology in nanotechnology industry. III-N materials, and especially GaN, have recently received attention from the scientific community for their excellent optical [43], electrical [44-46], and mechanical properties [23, 24, 47, 48]. We recently showed that GaN NWs have very excellent mechanical properties (Young’s Modulus \( \sim 376\pm32 \) Gpa) compared to Si NW [23,24] as shown in Figure 1. 9. Having these superior mechanical properties makes GaN nanowires (NWs) a promising candidate for next generation nanoscale tip-based metrology. At the same time, their optical properties may also be leveraged for advanced AFM applications e.g., nanoscale optical lithography and near-field scanning optical metrology (NSOM). Moreover, the electrical properties of GaN tips can be easily modified by varying the doping, which eliminates the need for metal coatings. Recently, Weber et al reported using Ti/Al and tungsten coated GaN NW probes for near-field scanning
microwave microscopy in AFM [49, 50]. However, no data was shown to illustrate image resolution capabilities for scanning high-aspect-ratio structures or to compare the durability of these tips with conventional probes. Moreover, optical properties of the used NWs were not studied for any possible optical applications in the future. And more importantly, the method has been used to fabricate these probes are not suitable for batch fabrication and is not interesting from commercialization point of view. Therefore, a method must be considered for growing GaN NWs directly on the Si substrate to make them compatible for batch fabrication.

In the present report, our purpose is to show GaN NWs are a great candidate for nanoscale metrology applications where we are dealing with sub-100 nm high aspect ratio structures with sharp edges and straight walls. In this matter, our emphasis is first: making high aspect ratio NW arrays with high optical and mechanical qualities, second: fabricating some prototype GaN AFM tips to measure nanostructures, and third: then our attempt is to grow single GaN NW directly on the Si substrate which can be considered as a method for mass production of such tips for the future nanometrology.
References


Chapter 2

GaN Nanowire fabrication

Direct bandgap III-nitride semiconductors are of great interest for nanophotonic, optoelectronic, and electronic applications [1-17], due to their tunable bandgap (0.7-3.4 eV) [16] and intrinsic waveguiding properties. These interesting properties prompted research in fabricating highly efficient nanostructures, e.g. nanowires (NWs) [1-8], nanodisks [9], nanobelts [10], nanotubes [11], and nanocolumns [12], for photonic and electronic devices. Gallium nitride (GaN) as a binary III-N wide bandgap semiconductor and among III-nitride nanostructures, GaN NWs have demonstrated advanced performance in light emitting diodes (LEDs) [3,4], lasers [6-9,13], nanoscale metrology [18], and research is ongoing to integrate these nanoscale building blocks into photonic devices. As discussed in the preceding chapter, GaN has recently received many attentions not only for
its specific optical properties, also for having excellent mechanical properties in which they have been employed in piezoelectric and MEMS devices [19-22]. GaN exists in two crystal structures; Wurtzite and Zincblend, depending on the growth conditions. Since the majority of the GaN are grown on sapphire substrate, the wurtzite structure is the dominant structure in research and technology works. A schematic of GaN Wurtzite crystal structure and a planar GaN grown on sapphire substrate are shown in Figure 2.1 (a) and (b). Some of the physical properties of wurtzile GaN is listed in table 2.1.

Table 2.1. Basic physical properties of Wurtzite GaN crystal at 300° K.

<table>
<thead>
<tr>
<th>Lattice constants</th>
<th>Melting point</th>
<th>Bandgap</th>
<th>Thermal conductivity</th>
<th>Refractive index</th>
<th>Dielectric constant</th>
<th>Effective electron and hole mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a=3.186 \text{ Å} ), ( c=5.186 \text{ Å} )</td>
<td>( &gt;2500°C )</td>
<td>3.4 eV</td>
<td>1.3 ( W/(\text{cm·K}) )</td>
<td>( \sim 2.4 )</td>
<td>8.9</td>
<td>( m_e=0.2 , m_0 ) ( m_h=0.8 , m_0 )</td>
</tr>
</tbody>
</table>

By controlling the growth condition, different facets can bound the nanowire structure as shown in figure 2.1 (c). In general, these crystal facets are sorted in three groups: i) polar, ii) nonpolar, and iii) semipolar planes. In the polar planes, the crystal plane is terminated by an array of nitrogen or Gallium atoms, so called as N- or Ga-pole, and as a result there would be a built in internal electric field between the bottom and top facets in this orientation. These facets are shown as [0001] planes in Figure 2.1 (c). These facets are

Figure 2.1. (a) Schematic of the GaN Wurtzile crystal structure. (b) A planar GaN grown on sapphire substrate. (c) Different crystal facets of a GaN nanowire.
also called c-plane. In contrast with polar planes, nonpolar planes, appeared as vertical sidewalls in nanowire structure, are terminated with combinations of N and Ga atoms results in total zero surface net electric charge. These planes are also recognized as m-planes and a-planes and their crystal orientations are shown as [1\overline{1}00] and [\overline{2}110] planes in the figure 2.1 (c), respectively. The semipolar plane, tapered surfaces in Figure 2.1 (c), extend diagonally across the hexagonal unit cell and form an angle with the c-plane other than 90°. Semipolar orientations exhibit reduced polarization effects from that of c-plane GaN because the polarization vector is inclined with respect to the growth direction. These planes are shown as [\overline{1}011] planes in figure 2.1 (c).

### 2.1. Nanowire fabrication techniques

In general, two approaches have been considered for GaN NWs fabrication; i) bottom-up epitaxial growth, and ii) top-down subtractive etching. In the bottom-up approach, NWs are grown on a patterned planar GaN on sapphire/Si/SiC substrate using a molecular beam epitaxy (MBE) [23,24], metal-organic chemical vapor deposition (MOCVD) [25], laser assisted catalytic [26], vapor-liquid-solid (VLS) [27], or chemical vapor deposition (CVD) [28]. Despite superior structure quality and the device performance, this approach requires high control of growth parameters during epitaxial growth, making it not a cost-effective procedure. Moreover, controlling uniformity and growing high-aspect-ratio NWs with sub-100 nm diameter is challenging and has proven extremely hard to achieve through all these techniques. Between these methods, VLS and CVD are also suffering from lack of the control of directional growing of the NWs, results in growing NWs that are oriented toward all directions.
In contrast, top-down approach [30-34] is recognized as an alternative technique to alleviate significant challenges associated with epitaxial growth since it provides more control on uniformity, aspect-ratio, and diameter of the nanostructures and offers a cost-effective way to fabricate nanoscale photonic devices. In this technique, either dry-etch or a combination of dry and wet-etch processes are used to control dimensions and morphology of the NWs after patterning a planar GaN in lithography process. However, there remain significant challenges in NW fabrication e.g. sidewall roughness due to the dry-etch step and obtaining high-aspect ratio NWs with uniform sub-50 nm diameters. Although, some progress in top-down fabricated GaN NWs and nanotube light emitters have been reported, to date, the device performance compared to the bottom-up grown structures remains lacking, [6, 29, 35] mostly due to the damage induced during the dry-etch process on the NW sidewalls. There is also no data on the effect of doping on the fabrication process, structure quality, and optical performance of the NWs. So far, the top-down method has been limited to e-beam lithography which makes the process expensive and not scalable for industrial application. So, optimizing fabrication process in top-down technique to control aspect-ratio and quality of the NWs, and making this technique a scalable method for industries seems necessary for higher efficient emitters including lasers and LEDs.

In the present chapter, first a bottom-up approach to grow GaN nanowires and thinning nanowire to achieve smaller diameter (preferably <50nm) for tip-based metrology will be presented. Then, an optimized scalable two-step top-down technique using interferometric lithography (IL) will be presented to fabricate high-aspect ratio GaN NW arrays which can
be an ideal method not only for academic scholars, but also for industrial partners to fabricate uniform III-N nanowire arrays for nanophotonics and optoelectronic devices.

2.2. Bottom-up approach

2.2.1. Epitaxial MOCVD growth

To fabricate the bottom-up NWs, First, a planar c-plane n-GaN (Si doped, ~2μm thickness) was epitaxially grown on a sapphire substrate. Then the GaN film was covered with a thin layer of Si₃N₄ using chemical vapor deposition method. The thickness of the nitride film is about 20 nm. A layer of antireflection coating (ARC) (i-Con-7) was spin coated on Si₃N₄ to avoid reflection from the substrate during exposing in lithography. Then, a thin layer of photoresist (NR7-500) was coated on the ARC layer to pattern Si₃N₄ layer in interferometric lithography (IL). This step can also be done through an e-beam lithography process. The detail discerption of IL patterning will be discussed in the next section where top-down approach is presented. After patterning the resist, an HF solution was used to selectively remove Si₃N₄ and open window to GaN layer under the nitride layer. The whole process is schematically shown in Figure 2. 2. Afterward, photoresist was washed away, and sample was cleaned using following procedure:

Piranha → Acetone → IPA → DI water rinse

Where piranha solution (H₂SO₄:H₂O₂, 4:1) is used to clean organic contamination (also known for hydroxylating surfaces and making them hydrophilic), and acetone and IPA are also applied to clean any residual contamination on the wafer. After removing all contaminations, sample was moved to MOCVD for epitaxial growing of NWs. Crystalline
material can’t grow on amorphous surfaces: and therefore; patterned open windows on GaN substrate are the only regions GaN is growing and forming NWs. Trimethylgallium (TMG), NH₃ were the gas sources used in growth procedure and when doping was needed, SiH₄ was introduced in the chamber to negatively dope NWs. Semipolar planes were observed as extra sidewalls on the top of the NWs as seen in figure 2. 2 and SEM image in Figure 2. 3 (a). By controlling the growth parameters, it is possible to change the dimension of semipolar plane, however, eliminating these planes on the NW structures are challenging during growth procedure. For application in nanoscale tip-based metrology (particularly for AFM tip), it is always preferred a nanowire with straight m-plane sidewalls and a flat c-plane top surface since any irregular shape like slopes and roughness on the tip can be transferred to the final topographic image in scanning high-aspect ratio structures. Thus, to
achieve a NW with perfectly straight sidewalls suitable for AFM applications, the semipolar planes on the sides should be removed somehow after growing.

2.2.2. Wet-etch to remove semipolar planes

To remove semipolar planes on sides and reduce the diameter of the grown NWs, they were soaked in AZ 400K (1:4) (H2O:KOH:KBr, 85:2:13) at 65°C. The KOH-based solution is known to be an effective chemical to selectively etch GaN planes, such that the semipolar planes are removed with a fast etch rate while the c-plane remains unaffected by the solution [35-38]. As a result, NWs with smooth sidewalls are formed at the end of the process. Figure 2. 3 (c) depicts NWs after removing semipolar planes in KOH solution. To achieve these NWs, they were etched for 1 hour in the solution.

In addition to [1011] semipolar planes, other planes are also appeared ([1012]) on the grown NWs’ sidewalls (see Figure 2. 4 (a)). Since the wet-etch is a crystal orientation-dependent process, different crystal planes have varying etch rates in the KOH solution, and so some planes are etched faster than others. Schematic in figure 2. 4 (b) shows the etch procedure for different crystal planes in the KOH solution. Usually, Semipolar planes has very fast etch rate compared to m-plane. However, we observed that [1012] planes
have very slow etch-rate which hindered us to achieve NWs with diameter less than 200 nm. According to our experiment, in the KOH-based solution, the relative etch rates of the GaN planes can be explained as:

\[ [0001] < [10\bar{1}2] \ll [00\bar{1}] < [\bar{1}011] \]

If [10\bar{1}2] planes exist on the side of NWs, by increasing the etch time in the solution, the NWs disappeared before becoming thin, because the m-plane etch rate is faster than the etch rate of [10\bar{1}2] planes. This fact can be seen in Figure 2. 5. NWs grown in this method had initial diameter of 400-700 nm and after etching in KOH solution, their diameter reduced to 200-300 nm. NWs grown using this method are limited to relatively large diameters since growing high-aspect-ratio NW with small diameter (<100 nm) is a challenging due to lateral overgrowth. Overall, we found that this method to produce NWs

![Figure 2. 4](image)

Figure 2. 4. (a) appearance of additional semipolar planes in NWs’ structure. (b) Wet-etch mechanism of GaN NW planes in the KOH-based solution.

![Figure 2. 5](image)

Figure 2. 5. Etching bottom-up grown NWs in AZ400 (1:4) solution after (a) 2 hours, (b) 4 hours, (c) 5 hours etching.
with small diameter is not reliable since uniformity, controlling the NWs’ diameters during wet-etch, and avoiding semipolar planes growth in epitaxial growth procedure were challenging.

To address these issues in bottom-up approach, we changed our direction to fabricate our NWs through a top-down approach. In the following section we will discuss about two methods in top-down approach we employed to fabricate high-aspect ratio nanowires with small diameter suitable for application in nanoscale tip-based metrology as well as optical microscopy and lithography.

2.3. Top-down approach

2.3.1. Gold nanoparticle masks

The fabrication process for the top-down GaN NWs using Au nanoparticles is presented in figure 2. 6. Spherical Au particles with Ionic Carboxyl Polymer capping and diameter between 50 to 100 nm were purchased from NANOPARTZ. First, a planar c-plane n-GaN (Si doping concentration about $\sim 10^{17}$ cm$^{-3}$, $\sim 2\mu$m thickness) layer was epitaxially grown on sapphire. Au nanoparticles with $\sim 100$nm diameter were spin coated on the c-plane planar GaN template. The speed of the spin coat determined the density of the NWs at the

![Figure 2. 6. Fabrication process in top-down approach using Au nanoparticles. Reprinted by permission from Ref. [18].](image-url)
end of the process. Then, the planar GaN template was etched in an inductively coupled plasma (ICP) etcher. The Cl\textsubscript{2}-based etching parameters are listed in table 2. 2. Figure 2. 7 shows SEM images of the NWs achieved immediately after the ICP dry etch. NWs fabricated in this way contain a cone shape base, which tapers to straight walls (∼1\textmu m) near the middle and upper sections of the wire. According to the structure of the NWs, the head has a suitable geometry for scanning high aspect ratio structures. The head diameter of the NWs varies from ∼50 to 100nm depending upon the variation in Au nanoparticle diameter used for the dry etch and the degree of dry etch damage from the process. The diameter of the base cone is typically in the range of ∼200–500nm. NWs obtained using this approach contain damage on sidewalls due to the dry etch process.

| Table 2.2. Dry etch parameters in ICP for samples with Au nanoparticle masks. |
|-----------------|-----------------|
| **RF**          | 50 W            |
| **ICP power**   | 500 W           |
| **Cl\textsubscript{2}** | 20 sccm         |
| **Ar**          | 5 sccm          |
| **Pressure**    | 5 mTorr         |
| **Time**        | 10 min          |

Figure 2. 7. SEM images of cone-shape NWs achieved through a one-step top-down approach using Au nanoparticles. (a) Shows distribution of NWs over substrate and low control on selective area fabrication of the NWs. (b) and (c) demonstrate zoom-in SEM images of NWs with different diameters and rough sidewall due to the dry etch.
The reason of forming cone-shape NWs in this approach is the etching the edge of the AU particles mask which gradually happens during the plasma etching. By reducing the etch time that would be possible to eliminate the cone base in the NWs’ structure, however, to make NW tips for scanning high-aspect ratio nanostructures we need to fabricate long NWs and so the etching time is a limiting factor in that case.

As seen in Figure 2.8 (a) NWs achieved through this method have very rough sidewalls on the head part of the structure, due to the damages from the dry etch process. We tried to follow the dry-etch with a KOH-based wet-etch (AZ 400) process at room temperature to smoothen sidewalls of these NWs. Figure 2.8 (b) schematically demonstrate this procedure in the solution. We observed that due to the severe damages induced during the dry-etch process, and also nonuniformity of the NWs diameters, that would be really challenging to

![Figure 2.8](image)

**Figure 2.8.** (a) NWs with rough sidewalls. (b) Schematic of wet-etch process for cone-shape NWs. NWs after etching in KOH-based solution (AZ 400 for (c) 30 min, (d) and (e) 90 min. Inset shows that most of NWs are etched away.
control NWs’ diameters and aspect ratios in the solution. As seen in Figure 2. 8 (c)-(e), after a short time of etching, majority of the NWs are etched away while a few with smaller diameter and straight walls are achieved. The diameters of the achieved NWs are totally different which is due to the dissimilar dry-etch damages on the sidewall.

2.3.2. Two-step top-down approach using Interferometric lithography

Previous techniques could not provide a reliable method to fabricating uniform high-aspect ratio NWs with small diameter and optimized geometry for nanoscale metrology. So, a technique needs to be developed to enable scalable fabrication of high quality GaN NWs in which nanotechnology industries and scholars can rely on this technique for batch fabrication of NW-based nanophotonics, optoelectronics, and metrology devices.

In this regards, three Si-doped GaN films with different doping concentrations of unintentionally doped (UID) (with about $\sim 10^{16}$ cm$^{-3}$ impurity), $\sim 10^{17}$, and $\sim 10^{18}$ cm$^{-3}$, were grown on sapphire substrates by MOCVD. A conventional method of continuous mode MOCVD and typical group III (TMGa) and group V (NH$_3$) precursors had been used to grow n-GaN template on a 2 inch, single-side-polished c-plane sapphire substrate. The GaN template growth carried out at the pressure of 500 Torr, and the growth temperature of 1090°C, with a group V to group III ratio (V/III ratio) of 3200. The rotation speed was held at 1500 rpm during the growth and Silane (SiH$_4$) has been used as a silicon dopant source. The GaN layers thickness variation was 2- to 2.5 µm, which represents the maximum achievable height for NWs in the present experiment. A schematic of the two-
Figure 2.9. (a) Schematic of the fabrication process for high-aspect-ratio GaN NWs: (1) n-GaN grown on a sapphire template, (2) spin-coating photoresist on GaN, (3) 2D-IL process to pattern a photoresist with 500 nm pitch size, (4) metallization and lift-off to prepare the Ni masks, (5) Cl2-based dry-etch, and (6) potassium-based (KOH, KBr) wet-etch solution to smooth NWs sidewall and control NWs’ radii. SEM images of (b) patterned photoresist after IL, (c) Ni mask after lift-off, and (d) created NWs after a Cl2-based dry-etch process. Reprinted by permission from Ref. [34].

step top-down fabrication process and scanning electron microscopy (SEM) images of different steps during fabrication are shown in Figure 2.8 (a)-(d). First, GaN films were cleaned using same protocol mention in section 2.2.1 (Piranha solution (H2SO4:H2O2, 4:1) followed by acetone, and IPA soaking). Then, they were washed in DI water and dried by Nitrogen spray gun followed by baking at 150°C on a hotplate. Cleaned GaN films were spin coated with ARC and photoresist. As shown in the Figure 2.8 (a), the GaN films are patterned by a 2D IL process (experimental setup is shown Appendix A). Table 2.3 lists coating and exposure parameters in interferometric lithography step. After patterning photoresist, Reactive-ion etching (RIE) oxygen-plasma was used to remove the ARC layer.
Table 2.3. Coating and exposure parameters in interferometric lithography.

<table>
<thead>
<tr>
<th>Step</th>
<th>Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>i-Con-7</td>
</tr>
<tr>
<td>2</td>
<td>Bake</td>
</tr>
<tr>
<td>3</td>
<td>NR-7 Resist</td>
</tr>
<tr>
<td>4</td>
<td>Bake</td>
</tr>
<tr>
<td>5</td>
<td>IL</td>
</tr>
<tr>
<td>6</td>
<td>Post-bake</td>
</tr>
<tr>
<td>7</td>
<td>Developing</td>
</tr>
</tbody>
</table>

in the areas where holes were defined in 2D IL. Afterward, a thin Ni layer (~100 nm) was deposited on the samples to make metal masks atop the GaN. The photoresist was removed by lift off and the samples were exposed again to an oxygen plasma to remove the remaining ARC layer. After metallization and lift-off, Ni masks are produced to selectively protect the GaN layer during the Cl2-based dry-etch process (Figure 2.8 (a) part (4)). A Cl2-based dry etch was performed to etch down GaN to create tapered GaN NWs. The dry-etch parameters are listed in table 2.4. After formation of tapered GaN NW arrays (Figure 2.8 (d)), the Ni mask was etched away in a Ni-etchant solution and an unstirred potassium-based wet-etch solution (H2O:KOH:KBr, 85:2:13) at room temperature was used to selectively etch their sidewalls to achieve NW arrays with different aspect-ratio and smooth sidewalls. The pitch size for all samples was adjusted to be 500 nm during the lithography. This pitch size was elected just to ensure that there is enough space between NWs to avoid coupling effect during optical measurement of NWs. Also, a larger pitch size may increase the initial diameter of the NWs due to the formation of larger holes on the photoresist.
Table 2. Dry etch parameters in ICP for prepared samples in IL.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF</td>
<td>50 W</td>
</tr>
<tr>
<td>ICP power</td>
<td>350 W</td>
</tr>
<tr>
<td>Cl₂</td>
<td>20 sccm</td>
</tr>
<tr>
<td>Ar</td>
<td>5 sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>5 mTorr</td>
</tr>
<tr>
<td>Time</td>
<td>4-8 min</td>
</tr>
</tbody>
</table>

during IL; therefore, the wet-etch time must be extended accordingly to achieve a smaller diameter. Pitch size during IL, dry and wet-etch times, concentration of the solution, and temperature of the solution in wet-etch process are the key parameters that contribute to the final aspect-ratio and quality of the NWs.

Different aspect-ratio (6 - 50) NWs were achieved using this method. Figure 2.10 illustrates SEM images of different aspect-ratio fabricated NW arrays and additional images

Figure 2.10. SEM image of NWs with different aspect-ratio (A. R.); (a) r=60 nm, A. R.=14, (b) r=55 nm, A. R.=17.5, (c) r=42 nm, A. R.=20, (d) r=30 nm, A. R.=28, (e) r=20 nm, A. R.=44, and (f) r=17 nm, A. R.=50. Scale bars are 1 µm. Reprinted by permission from Ref. [34].
with different aspect-ratios are shown in appendix B. As seen, orderly arrays of NWs with different radii and aspect-ratios can be obtained with a high degree of uniformity [variation in radius/length of the area (1 mm²) = 1.5×10⁻⁶] through this scalable method. Figure 2.11 shows SEM and transmission electron microscopy (TEM) images of the NWs sidewall at the end of the wet-etch process. TEM image shows that NWs in this procedure have very smooth sidewalls with roughness on the order of atomic scale (Å). These results are interesting since the roughness of the NWs reported through a similar technique in previous works were higher [39,40]. The top-view SEM image in the inset of Figure 2.11 (a) depicts the hexagonal shape of the NWs which results from their single crystal wurtzite structure.
and the facet selective wet-etch [34]. TEM image in Figure 2. 12 illustrates a and c lattice constants of wurtzite GaN crystal in NWs’ facets.

2.3.3. Selective area fabrication of GaN NW arrays

To selectively grow these highly uniform NWs over substrate for any optoelectronic and nanophotonic device application, one photolithography step must be implemented after metallization and lift off in Figure 2. 9 to define desired areas where NWs will be fabricated on. Figure 2. 13 schematically demonstrates the fabrication process for selective area growth of top-down GaN NWs.

![Fabrication process of selective area GaN NWs through a top-down approach.](image)

**Figure 2. 13.** Fabrication process of selective area GaN NWs through a top-down approach.
To fabricate selective area NW arrays, we design a photolithography mask with 100 µm × 100 µm squares which labeled by numbers enables tracking NW arrays during and after process for investigation. Table 2. 5 lists photolithography parameters we have followed to define selective area on the sample after metallization/lift off. Figure 2. 14 demonstrates NW arrays fabricated through selective area top-down techniques on a sapphire substrate. As seen in Figure 2. 14 (c), NWs with sub-50 nm diameter were also obtained in this method.

Figure 2. 14. (a) Low magnification SEM image of selective area GaN NW arrays on sapphire substrate. (b) Zoom-in SEM image of a NW array fabricated selectively on the sapphire substrate. (c) Sub-50 nm diameter GaN NW arrays achieved after wet-etch process in selective area fabrication.

<table>
<thead>
<tr>
<th>Step</th>
<th>Recipe</th>
<th>Step</th>
<th>Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning</td>
<td>Acetone-IPA-DI water-Bake at 150 °C</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Bake</td>
<td>90 s at 90 °C</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Develop</td>
<td>AZ 400 (1:4) for 90 s</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2. 5. Photolithography recipe for fabricating selective area GaN NW arrays.
As we already pointed in chapter 1, the research plan in this project is to make this NW as tip for nanoscale tip-based metrology, therefore, we must fabricate this NWs on the Si substrate where this substrate will work as a cantilever in atomic force or optical microscopy and lithography.

The same method has been used to make selective area NW arrays on Si substrate. First a Si [111] was cleaned using the protocol mentioned in section 2. 2. 1, followed by soaking in 49% Hydrofluoric acid (HF) solution. Combination of these steps remove both organic and inorganic contamination on the substrate. In addition to cleaning samples, HF solution is removing native oxide layer on the surface and so prepared surface for growth crystalline material by removing dielectric layers. It is known that Si [111] has closer lattice constant (0.3823 nm) to III-N material (especially AlN with lattice constant of 3.112 and hexagonal shape surface structure) compared to other orientation and so, it has been selected for growing III-N for electronic and optical devices [41-45]. In case of GaN on Si, AlN is usually used as buffer layer to compensate lattice mismatch and thermal expansion difference between GaN and Si. The detail of the growth procedure of GaN on Si including gaps and challenges will be discussed later when we talk about single GaN NW growing on a Si cantilever.

**Figure 2.15.** GaN NWs arrays on Si substrate after (a) 30, (b) 60, and (c) 90 minutes etching in KOH-based solution.
Here, one of the challenges we encounter in fabricating NW arrays on Si, is the higher reactivity of AlN in KOH-based solution compared to GaN. Due to this reactivity, we might lose NW from bottom before smoothing and narrowing them in the solution. Equation 2.1 (a)-(d) compare reactivity of AlN and GaN in a KOH solution:

Figure 2.15 demonstrates NW arrays on Si substrate after different times etching in KOH-based solution. As seen in Figure 2.15 (b), an undercut etching is observed on the bottom of NWs due to fast etching of AlN in the solution. After 90 min etching, almost all the NWs are fallen as seen in Figure 2.15 (c). To overcome this issue, the AlN layer needs to be protected in the solution during the wet-etch process. To protect this layer, we decide to stop dry-etch process before entirely etching GaN film, so that a thin GaN layer is left on the top of the AlN layer to protect it during the wet-etch process. Figure 2.16, shows

\[
\begin{align*}
2\text{AlN} + 3\text{H}_2\text{O} & \xrightarrow{\text{KOH}} \text{Al}_2\text{O}_3 + 2\text{NH}_3 & \Delta G_r &= -350.1 \text{ kJ/mol} \quad (2.1\text{a}) \\
\text{AlN} + 3\text{H}_2\text{O} & \xrightarrow{\text{KOH}} \text{Al(OH)}_3 + \text{NH}_3 & \Delta G_r &= -334.2 \text{ kJ/mol} \quad (2.1\text{b}) \\
2\text{GaN} + 3\text{H}_2\text{O} & \xrightarrow{\text{KOH}} \text{Ga}_2\text{O}_3 + 2\text{NH}_3 & \Delta G_r &= 1399.9 \text{ kJ/mol} \quad (2.1\text{c}) \\
\text{GaN} + 3\text{H}_2\text{O} & \xrightarrow{\text{KOH}} \text{Ga(OH)}_3 + \text{NH}_3 & \Delta G_r &= 723.5 \text{ kJ/mol} \quad (2.1\text{d})
\end{align*}
\]
SEM images of selective area GaN NW arrays fabricated on Si substrate by protecting AlN layer during wet-etch process.

In the present chapter, we discussed and demonstrated different methods to fabricated high-aspect ratio GaN NWs through either bottom-up or top-down approach. Our developed scalable two-step top-down approach enabled us to fabricated NWs with small diameter (<50 nm) and high-aspect ratio (>50) with a perfect control on the sidewall roughness and uniformity of the NW arrays on both sapphire and Si substrate. In the next chapter, we will study the effect of doping concentration on the wet-etch procedure and optical properties of the fabricated NW arrays.
References


[34] Behzadirad, Mahmoud, Mohsen Nami, Neal Wostbrock, Mohammad Reza Zamani Kouhpanji, Daniel F. Feezell, Steven RJ Brueck, and Tito Busani. "Scalable Top-


Chapter 3

Characterization of GaN NW arrays

So far, we discussed different methods to fabricate high-aspect ratio GaN NW arrays on sapphire and Si substrates. The top-down approach looks promising as it provided a reliable method for uniform and scalable fabrication of high-aspect ratio NWs. However, to have a better control on fabrication process, a precise analysis of wet-etch parameters is needed. There will be plenty of applications for these NWs in nanophotonics, MEMS, and optoelectronics [1-5] each of which requires different doping concentrations, dimensions, and optical cavity properties. In this chapter, first, we study the wet-etch mechanism in detail by considering the doping concentration, and then, we focus on optical properties of the fabricated GaN NW and their potential application for optical microscopy.
3.1. Wet-etch mechanism and doping concentration effect

Cl2-based ICP dry-etch process is known for chemical and ion-induced etching of GaN. Due to the mechanical damage of ion-induced etching process, NW sidewalls are very rough and tapered [6] as schematically shown in Figure 3.1(a). This mechanical damage, inherited from the dry-etch procedure, creates some open bonds on the localized atoms close to the crystal surface. Since these localized atoms are unstably bonded to the crystal, they can make a new dangling bond with OH- molecules in a potassium-based solution and leave the crystal structure. The products of the GaN etch-reaction in the potassium-based solution are [7]:

\[ 2\text{GaN} + 3\text{H}_2\text{O} \xrightarrow{\text{KOH, KBr}} \text{Ga}_2\text{O}_3 + 2\text{NH}_3 \quad \Delta G_{298} = 1399.9 \text{ KJ/mol} \quad (3.1 \text{a}) \]

\[ \text{GaN} + 3\text{H}_2\text{O} \xrightarrow{\text{KOH, KBr}} \text{Ga(OH)}_3 + \text{NH}_3 \quad \Delta G_{298} = 723.5 \text{ KJ/mol} \quad (3.1 \text{b}) \]

Figure 3.1. (a) Schematic of NWs top and sidewalls after dry-etch. (b) First, and (c) second step of the wet-etch process in the solution. Reprinted by permission from Ref. [7].
Figure 3. 1(b) and (c) are schematics showing the different steps of the wet-etch procedure of GaN in the solution. The wet-etch process can be divided in two steps; i) OH-molecules in the potassium-based solution react with atoms with open bonds on the NW sidewalls and as a result Ga and N atoms dissolve into the solution forming the reaction products (figure 2(b)). Since the surface atoms on the NWs sidewalls have open bonds (very high density of dangling bonds), we can expect a fast etch rate for this step which continues till the sidewalls reach the non-polar m-planes \{1 \bar{1} 00\}, as illustrated in Figure 3. 1(b). Once the m-planes are reached, the etch rate slows down due to the lower dangling bonds density compared to the initial rough walls. On c-plane \{0001\} surface, there would be a strong repulsive force between nitrogen atoms and OH- after removing Ga layer by the solution in addition to very low dangling bonds density [8], and as a result there is insignificant etching on this plane during the wet-etch process. ii) After m-plane formation, the wet-etch process is continued until the desired radii of the NWs are obtained (Figure 3. 1(c)). At this point by increasing wet-etch time smaller radii can be achieved and so aspect-ratio of the NWs can be controlled. In this step, it would be possible to measure etch rates for the m-planes as we increase the time in the wet-etch process.

To study the doping effect on the etch rate and quality of the NWs, three Si-doped GaN films with different doping concentrations of unintentionally doped (UID) (with about \(\sim 10^{16}\) cm\(^{-3}\) impurity), \(\sim 10^{17}\), and \(\sim 10^{18}\) cm\(^{-3}\), were grown on sapphire substrates by MOCVD, and were inspected at various etching times using a SEM. Figure 3. 2(a)-(c) presents the etch procedure of the GaN NWs with different doping concentrations as a function of etching time. Here, due to the tapered shape of the NWs after dry-etch, we
consider separate top and bottom diameters as shown in the plots. The time when the bottom and top diameters reach the same value indicates formation of the m-planes on the sidewalls. This time is circled on each plot in the Figure 3.2. After this time, the etch rate of the m-planes for different doping concentrations can be obtained [7]. Figure 3.2(d) schematically depicts NW shape change in the wet-etch process. Table 3.1 lists the formation time and etch rate of the m-planes for different doping concentrations. It is evident that by increasing the doping concentration, the etch rate also increases. By increasing the doping concentration of the GaN crystal, more Ga atoms in the crystal structure are replaced by Si atoms. Having one free electron available for bonding and very
Table 3.1. Comparison of etch time and formation of the m-plane during wet-etch procedure.

<table>
<thead>
<tr>
<th>Doping concentration (cm(^{-3}))</th>
<th>m-plane formation time (~h)</th>
<th>m-plane etch rate (~nm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UID</td>
<td>24</td>
<td>2.5</td>
</tr>
<tr>
<td>~10(^{17})</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>~10(^{18})</td>
<td>1</td>
<td>70</td>
</tr>
</tbody>
</table>

low Gibbs free energy of the reaction in the potassium-based solution make the doped Si atoms extremely reactive in the solution compared to Ga and N atoms. The following reactions are expected during wet-etch process of Si-doped GaN in addition to the reactions (1) and (2) [7]:

\[
SiN + H_2O + 2KOH \rightarrow K_2SiO_3 + NH_3 + 1/2H_2 \quad \Delta G_{298} = -801.294 KJ/mol \quad (3.2 \text{ a})
\]

\[
SiN + 4H_2O \xrightarrow{\text{KOH, KBr}} Si(OH)_4 + NH_3 + 1/2H_2 \quad \Delta G_{298} = -717.7 KJ/mol \quad (3.2 \text{ b})
\]

Extraction of Si atoms from the crystal leaves many open bonds in the crystal and as a result Ga and N atoms can react with the solution and leave the structure much faster. Due to the very high reactivity of dopant atoms, some damage was also observed on the c-plane during wet-etching of higher doped GaN NWs (~10\(^{18}\) cm\(^{-3}\)) which was not seen in lower doped samples.

3.2. Optical characterization

3.2.1. Simulation

Single GaN NWs have been shown to operate as an optical Fabry-Perot waveguide when geometry (radius, length, and sidewall roughness) and reflectivity from both ends of
the cavity meet the resonance condition [9-11]. However, in most reported works, laser emission was observed in NWs that were extracted from their initial substrate and placed horizontally on to a host substrate. In a horizontal cavity, the optical wave is guided along the cavity length (parallel to the substrate) and reflected from two ends of the cavity with the same boundary condition (GaN-air interfaces) (Figure 3. 3(a)). Due to a relatively large refractive index mismatch between GaN and air, a stimulate-emitted optical wave can conveniently resonate in the cavity if the mode confinement in the cavity (which is a function of radius of the NW) is adequate. In this configuration, the emission is expected from both ends of the NW. By changing the boundary condition of bottom end to GaN-sapphire in the vertical cavity condition (Figure 3. 3(b)), the reflectivity from the bottom decreases and Q-factor consequently drops. Therefore, lasing can happen only if cavity loss is minimized by controlling roughness of the sidewalls and crystal defects to compensate for increase in the mirror loss in a gain medium. As another way to improve the reflectivity in a NW cavity, DBRs can be included in the NW structures which will be discussed later in the next chapter.

**Table 3.2. Input parameters used in FDTD modeling.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index of GaN (n)</td>
<td>2.5</td>
</tr>
<tr>
<td>Emission wavelength (λ)</td>
<td>365 nm</td>
</tr>
<tr>
<td>Diameter</td>
<td>100-200 nm</td>
</tr>
<tr>
<td>Geometry</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Bottom substrate</td>
<td>Sapphire &amp; Si</td>
</tr>
</tbody>
</table>
The nanowire cavity with diameter <200 nm can support fundamental modes; transverse electric (TE\textsubscript{0m}), transverse magnetic (TM\textsubscript{0m}), and hybrid (HE\textsubscript{nm}) modes. TE\textsubscript{0m} and TM\textsubscript{0m} have only three field components and no dependence on azimuthal angle (ϕ), while HE\textsubscript{nm} modes have all six field components with cos (nϕ) and sin (nϕ) dependence [10]. The index m denotes the radial dependence of the field, and n denotes angular symmetry (see appendix C). For the larger structures where dimension of the structure is greater than the optical wavelength, the reflectivity from top and bottom facets are given by the Fresnel formula since the wave-packet can be approximated by a plane wave. However, this formula cannot be applied for the nanowires because their diameter is typically smaller than the lasing wavelength (subwavelength regime). In this case, the diffraction and scattering at the edges must be taken into account which makes it rather a difficult problem.

In subwavelength regime, the optical modes are partially extended out of the cavity, as schematically shown in Figure 3. 3(c). This mode expansion causes the wave to experience different indices of refraction in and out of the cavity during propagation and so an effective refractive index is defined for different modes. To understand what transverse modes can
exist in the GaN NW cavity and their corresponding effective refractive index and reflectivities, a finite-difference time-domain (FDTD) simulation method was employed using Lumerical software to model NW cavity. Table 3. 2 lists all parameters used in our simulation. In Table 3. 3, we study modal property of hexagonal GaN NW cavity by presenting transverse field distribution in the NW as function of diameter for first three fundamental modes [7].

Table 3. 3. Comparison of three fundamental modes field distribution in a hexagonal GaN NW cavity. Reprinted by permission from Ref. [7].

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>$HE_{11}^x$</th>
<th>$HE_{11}^y$</th>
<th>TM$_{01}$</th>
<th>TE$_{01}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td>N. C.$^1$</td>
<td>N. C.</td>
</tr>
<tr>
<td>105</td>
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<td><img src="image4" alt="Image" /></td>
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<td>N. C.</td>
</tr>
<tr>
<td>110</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td>N. C.</td>
<td>N. C.</td>
</tr>
<tr>
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<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>N. C.</td>
<td>N. C.</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------</td>
<td>-------------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>120</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>N. C.</td>
<td>N. C.</td>
</tr>
<tr>
<td>125</td>
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<td><img src="image6.png" alt="Image" /></td>
<td>N. C.</td>
<td>N. C.</td>
</tr>
<tr>
<td>130</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>N. C.</td>
<td>N. C.</td>
</tr>
<tr>
<td>135</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td>N. C.</td>
</tr>
<tr>
<td>140</td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td>N. C.</td>
</tr>
<tr>
<td></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>----</td>
<td>----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>145</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>150</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>155</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
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<td><img src="image19.png" alt="Image" /></td>
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<tr>
<td>165</td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 3. 4 demonstrates the geometry of the cavity we used in our modeling in Lumerical software and Figure 3. 5(a) presents the simulation results of calculated effective refractive index for the first three fundamental modes (HE$_{11}$, TM$_{01}$, and TE$_{01}$) in a GaN NW cavity as a function of radius. These results are obtained by using mode solver module in Lumerical. As seen, at small radii (radius <$\lambda_0$/3), the fundamental hybrid mode (HE$_{11x}$, HE$_{11y}$) is the only mode that can exist in the cavity. By increasing the radius, TM$_{01}$ and TE$_{01}$ modes also appear to exist, however, it has been shown due to their lower effective index and Q-factor [7, 11-14], HE$_{11}$ is the dominant mode for NWs with radius less than

Figure 3. 4. Geometry used in FDTD modeling of GaN NW cavity. (b) Zoom-in image to show function and boundary condition used in the model.
100 nm. The detail of mode competition in III-nitride NW cavities with subwavelength dimensions are already discussed in previous works [11-15], which confirms our modeling data. Therefore, since we are dealing with NWs with radii less than 100 nm, it is appropriate to assume that HE$_{11}$ is the only bound mode in the NWs cavity. Figure 3.5 (b)-(d) depicts FDTD simulation results of reflectivity into the same mode for HE$_{11}$ from GaN-air, GaN-sapphire, and GaN-Si interfaces. To model reflectivity, we first solved function in mode solver module, and then we selected and propagate HE$_{11}$ mode in the NW as seen in Figure 3.4(b). To get the reflectivity into the same mode, we picked net_reflection between

![Figure 3.5](image_url)

**Figure 3.5.** (a) Effective refractive index of the first three fundamental modes for different NW diameters. Inset is a schematic of mode expansion out of cavity. Reflectivity of HE$_{11}$ mode from (b) GaN-Sapphire, (c) GaN-air, and (d) GaN-Si substrates. Reprinted by permission from Ref. [7].
outputs. For more accuracy, we located monitors in the back of the source to avoid interreference effect due to the superposition of propagated and reflected waves. In case of GaN-Si interface, to be close to the real structure, we designed a thin AlN layer (50 nm) between GaN NW and Si substrate in the model. The refractive index of this layer was assumed 2.2 in our modeling. It was observed when the diameter of the NW is about \( \frac{3}{2} \left( \frac{\lambda}{2n_{\text{eff}}} \right) \) (~d=140-150 nm), indicating mode confinement of ~90% for \( \lambda = 366 \text{ nm} \), a plateau is formed on the reflectivity plots. This is much clear in Figure 3. 5 (c) where reflectivity from the GaN-air interface is suppressed to ~20%.

As seen, increasing the radius of the NWs has a small effect on the mode reflectivity from GaN-sapphire interface. This is because of a small mismatch between effective index of the HE_{11} mode and refractive index of the sapphire \( (n_{\text{sapphire}}=1.75 \text{ at } \lambda=366 \text{ nm}) \). This indicates that lasing condition in standing NWs would be harder to achieve compared to the dispersed NWs on a host substrate. In contrast, the reflectivity from GaN-Si interface shows a better condition for lasing since it goes up to 32% for a NW with 200 nm in diameter. Accordingly, the Si substrate provides a better cavity condition for extracting emission out of NW and this is a promising result for us in which our final goal in this research is to make emitter GaN NW tips on Si cantilevers.

According to Figure 3. 5(a), single transverse-mode regime is obtained for NWs with diameters less than 130 nm, since TE_{01} and TM_{01} modes do not exist in this range of diameter. So, to achieve single mode GaN NW laser we need to make NWs with diameter no larger than 130 nm. In small diameter cavities, as we already discussed, we have confinement issue. Therefore, it looks 130 nm is an optimized diameter as not only it
represents single-mode regime, also it supports highest amount of confinement and reflectivity in this regime according to Table 3.3 and Figure 3.5(a)-(b).

### 3.2.2 Experiment

To experimentally characterize our high-aspect ratio NWs, we fabricated NW arrays out of three different doped samples (UID, $10^{17}$ cm$^{-3}$, $10^{18}$ cm$^{-3}$) on sapphire substrate. To ensure we are in the single-transverse mode regime and to achieve the optimized

**Figure 3.6.** (a) SEM image of NW arrays with 130 nm and 2 μm in diameter and length, respectively. Photoluminescence measurement of (a) UID, (b) $10^{17}$ cm$^{-3}$, and (c) $10^{18}$ cm$^{-3}$ doped GaN NW arrays with diameter of 130 nm on sapphire substrate. Inset schematic in part (b) is a cross section view of NW during mode round trip in the cavity. Reprinted by permission from Ref. [7].
confinement and reflection, we adjusted NWs diameter to be 130 nm, as shown in Figure 3. 6 (a). The longitudinal mode spacing in the Fabry-Perot cavity is given by \( \Delta \lambda = \frac{\lambda^2}{2L(n_{\text{eff}} - \frac{dn_{\text{eff}}}{d\lambda})} \) where \( L \) is the length of the NW, \( n_{\text{eff}} \) is effective refractive index at wavelength \( \lambda \), and \( dn_{\text{eff}}/d\lambda \) accounts for the dispersion of the medium. The longitudinal mode spacing for the NWs with the given dimensions is ~20 nm. According to the length of the NWs, uniformity in NWs’ radii, gain band width of the GaN crystal, and longitudinal mode spacing of the cavity, we expect to observe single longitudinal mode lasing from NW arrays as well. Figure 3. 6(b)-(d) illustrate experimental photoluminescence (PL) data for GaN NW array lasers with different doping concentrations. In the PL setup, fabricated NW arrays on sapphire were optically pumped at 266 nm (20 kHz repetition and < 0.6 ns pulse duration) and their emission spectra were collected by a photodetector (see Appendix D). Lasing emission was observed close to the bandgap energy in all cases. A small deviation in the lasing spectra of the NWs from the bandgap energy is attributed to the slight variation in radii of the NWs in the pumped area, since the emission spectrum is a strong function of NW diameter. A slight blueshift was observed in emission spectrum after increasing pump intensity due to the temperature induced refractive index variation [16-18]. Table 3. 4 lists lasing emission

<table>
<thead>
<tr>
<th>Doping concentration (cm(^{-3}))</th>
<th>Threshold (MW/cm(^2))</th>
<th>Emission wavelength (nm)</th>
<th>FWHM (nm)</th>
<th>Q-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>UID</td>
<td>~4.55</td>
<td>366.4</td>
<td>~0.15</td>
<td>~2443</td>
</tr>
<tr>
<td>~10(^{17})</td>
<td>~3.89</td>
<td>364.4</td>
<td>~0.32</td>
<td>~1139</td>
</tr>
<tr>
<td>~10(^{18})</td>
<td>~3.31</td>
<td>366.2</td>
<td>~0.2</td>
<td>~1831</td>
</tr>
</tbody>
</table>
parameters from the spectra in the figure 3. 6(b)-(d). As seen NW arrays can lase with a very low power density threshold ranging from 3.31 to 4.55 MW/cm² with a very large Q-factor of 1139-2443 correspond to a full width at half maximum (FWHM) of 0.15-0.32 nm. By increasing doping concentration, the threshold decreases due to the rise in carrier concentration in the gain medium. The narrow broadening of the spectra (<0.32 nm) demonstrates very high uniformity in NWs’ diameter. The lasing peaks observed close to the band gap of the NWs with slight deviation from 366 nm. The lasing peak is highly sensitive to the geometry and diameter of the NWs. To show its sensitivity, in Table 3. 5 we provide modeling results of the possible wavelength emission in two different NWs with only 1 nm difference in diameter. As seen, a small change in diameter, can greatly affect emission wavelength due to the effective refractive index variation. The small deviation in the emission wavelength seen in figure 3. 6(b)-(d) is therefore attributed to a possible small variation in diameter (less than 1 nm according to the modeling) between three different samples. This again validates our fabrication method to make uniform high-aspect ratio GaN NW arrays.

In summary, these experimental and modeling results endorse our fabrication process as a perfect method to achieve high quality GaN NW emitters over a large area with minimum cavity loss that helps to observe single-mode lasing even with low reflection of the HE₁₁ mode from the GaN-sapphire interface as the poorest interface for vertical cavity

<table>
<thead>
<tr>
<th>NW Diameter (nm)</th>
<th>( n_{\text{eff}} )</th>
<th>Emission wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>1.655</td>
<td>365.2</td>
</tr>
<tr>
<td>131</td>
<td>1.662</td>
<td>362.3</td>
</tr>
</tbody>
</table>

Table 3. 5. Simulation result of emission wavelength change due to 1 nm variation in NW diameter.
GaN NW emitter. Since our method is developed to be compatible with all substrates, replacing sapphire with Si substrate will facilitate achieving lasing from GaN NWs.
References


Chapter 4

GaN NW tips for Scanning Probe Microscopy (SPM) and Lithography (SPL)

In the preceding chapters, we demonstrated and developed a fabrication method to fabricate high aspect ratio GaN NWs. We also characterized NWs in which if they optical qualities meet criteria for nanoscale optical application. Likewise, in the first chapter, we talked about current challenges in using conventional tips in nanometrology e.g. durability, shape and geometry, artifacts, costs, and possibility for batch fabrication. In this chapter, we review on probe fabrication using GaN NW for scanning probe microscopy (SPM), and scanning probe lithography (SPL). In the first part, we focus on application of GaN tips in atomic force microscopy (AFM) imaging to show their advantages in providing higher resolution images and more durable tips compared to the conventional tips, and in the second part, we will use epitaxially grown sharp GaN NWs for field emission SPL and atomic resolution imaging.
4.1. GaN NW AFM probes for morphology study

4.1.1. Probe Fabrication

The fabricated top-down (including the method of using Au nanoparticles and IL technique to pattern large area), and bottom-up NWs, as discussed in chapter 2, were used to make AFM probes. Focus Ion Beam (FIB) was used to transfer fabricated NWs on Si cantilever. A commercial Si tip (AC240-TM) was flattened by ion beam (Fig. 4. 1(a)) and a hole was made on the flat area (Fig. 4. 1(b)). This hole is the place where NW is positioned. By means of an omniprobe needle, a GaN NW is detached from its substrate (Fig. 4, 1(c)) and transferred to seat on the hole in flattened Si cantilever (Fig. 4. 1(d)). Then, omniprobe was detached from NW and Pt-source was used to weld the NW on Si cantilever as seen in Fig. 4. 2(a)-(d) for bottom-up and top-down fabricated NWs. At the end of the process, a top view SEM image was taken to insure NW is bonded perpendicular to the cantilever substrate, as presented in the insets of Figure 4. 2(a)-(c).

To investigate the influence of welding angle in respect to the cantilever surface, and to find the best angle for welding NW on the cantilevers at which more accurate data can be obtained in tapping mode without need to do any correction angle, it was attempted to

![Figure 4.1](image)

**Figure 4.1.** (a) Flattening Si cantilever using ion beam. (b) Drilling flattened area by ion beam to make hole. (c) Detaching NW from sapphire substrate after dry or wet etch process by omniprobe needle. (d) Transferring NW to the processed cantilever [1]. Reprinted by permission from Ref. [1].

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position GaN NW at different angles onto Si cantilever. Figure 4. 1(a) shows SEM image of an incline-welded tip which its angle is very similar to the commercial Si tip (35 degrees from its front). Figure 4. 2(d) demonstrates an inclined tip made of a bottom-up fabricated NW. The fabricated tips in Figure 4. 2(a)-(d) have radius of ~137 nm, 40 nm, 42 nm, and 170 nm, respectively.

A single crystalline, p-type, Si (110) wafer is used as an inspection sample to test our fabricated high-aspect ratio GaN tips. The Si wafer was patterned by interferometric lithography and was masked with chromium in metal evaporator. Then Si wafer was etched in KOH (30%) solution at 70°C for 20 second to make trenches with ~90° angle and straight sidewalls (~1µm width and ~380 nm height). Figure 4. 3 presents SEM images for different steps in fabricating Si trenches.

Figure 4. 2. AFM probes after Pt deposition. Vertically welded (a) bottom-up, (b) top-down using Au nanoparticles, (c) top-down through IL technique, GaN NWs on a Si cantilever. Insets show SEM top-view of welded NWs, indicating vertical positioning of the tips. (d) Bottom-up GaN NW welded inclinedly on a Si cantilever [1]. Reprinted by permission from Ref. [1].

Figure 4. 3. (a) Patterned photore sist on Si (110) after IL. (b) Cr-mask on Si. (c) Appearance of trenches on Si after etching in KOH-30% solution.
4.1.2. Results and discussions

The inspection sample was scanned using tapping mode in both trace and retrace. Scanning in trace and retrace helps determine if the tip is welded perfectly normal to the cantilever surface as inspected in SEM images (insets of Figure 4. 2(a)-(c)). For all measurements, the scan direction is parallel to the cantilever axis and perpendicular to the grating lines, as illustrated in Figure 4. 4(a). To analyze the AFM images, we compare them with the scanned structures (SEM images) by taking into consideration four parameters; left and right-angle offsets, width, and length of the trench as defined in Figure 4. 4(b). Width and angle offsets in all cases are measured at the half maximum of the height, where artifacts due to the edges are minimized. Figure 4. 4 compares the results of scanning a single trench using a commercial Si, top-down, bottom-up, and inclined welded GaN probes. 2D analytical results of scanning the structure in trace mode are illustrated in Figure 4. 4(d), (g), (j), and (m). In case of using GaN NW tips, a width-correction was carried out by subtracting the NWs diameter from the obtained width in AFM measurement, while, other parameters like height and offset angles do not need any correction since the side wall of the NW is perfectly straight (single crystal) and NW is normally bonded to the cantilever surface. The same width-correction cannot be applied for Si tip in Figure 4. 4 (d) and (e) due to its conical geometry. The red lines in the line analysis (for NW GaN tips) in the Figure 4. 4 are the AFM data right after scanning Si trench and the black lines are the width-corrected data. As seen in Figure 4. 4(d), a tail on right side of the image appears when the commercial Si tip is used, which results from the combined effect of the angle of the tip and the geometry of the side wall of the trench (the apex of the tip is tetrahedral and symmetric, with a tip angle of 35 degrees from its front side, and half angle of 18 degrees
Figure 4.4. (a) Schematic of the inspection sample and scan direction, (b) definition of parameters. (c), (d), (f), (g), (i), (j), (l), and (m) present SEM images of the used tips and compare the trace-line analysis of scanning trench for commercial Si, cone-shape top-down GaN NW, bottom-up GaN NW tips, and inclined welded tip. (e), (h), (k) and (n) show the same line analysis in retrace for Si, Cone-shape top-down, bottom-up, and inclined tips, respectively. Numbers are width, height, left and right-angle offsets of the trench measured after scanning. (Blue arrows show the scanning direction in trace and retrace, and insets are SEM image of the scanned trench) [1]. Reprinted by permission from Ref. [1].
from the side of a cantilever free end). This can negatively affect measurement of the width, angles, and height of the structure. The measured left angle offset in the commercial Si tip shows a small deviation from 90° but the right angle is off by ~47°. Likewise, the width of the trench is measured to be ~1.29 µm, which deviates by 290 nm from the actual width of 1 µm.

In contrast, both top-down and bottom-up GaN tips demonstrate much better performance in imaging the trench as they give more accurate data based on the measured parameters. The same comparison for retrace gives identical results as illustrated in Figure 4. 4(e), (h), (k) and (n) (trace and retrace analysis overlap well). However, the inclined tip presents very similar behavior to commercial Si-tips as shown in Figure 4. 4(n) and (m). This analysis reveals when the NW is welded vertical to the substrate such as the tips shown in Figure 4. 4(f) and (i), more accurate data can be extracted from the image while images of inclined tips need angle correction as it is needed for Si-tips, too.

Table. 4. 1 lists all the aforementioned parameters for the commercial Si and GaN tips. The edges of the trench in the AFM images obtained by the GaN tips are not perfectly sharp like the actual structure (inset images in plots) as seen in the plots, which we attribute it to the roughness of the NW sidewalls, especially in the cone-shape top-down fabricated NW, as the similar defects are observed in the SEM image due to the damage from dry-

Table 4. 1. Comparison of structural parameters obtained by applying different AFM tips in trace and retrace for scanning the vertical trench on a Si substrate [1].

<table>
<thead>
<tr>
<th>Structure &amp; Tips</th>
<th>Trace</th>
<th></th>
<th></th>
<th>Retrace</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left angle</td>
<td>Right angle</td>
<td>Width (µm)</td>
<td>Height (nm)</td>
<td>Left angle</td>
<td>right angle</td>
</tr>
<tr>
<td>Si Trench</td>
<td>~0</td>
<td>~0</td>
<td>1 380</td>
<td></td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>Commercial Si tip</td>
<td>11</td>
<td>47</td>
<td>1.29 395</td>
<td></td>
<td>6.5</td>
<td>48</td>
</tr>
<tr>
<td>Bottom-up GaN tip</td>
<td>4</td>
<td>1</td>
<td>1 370</td>
<td></td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Top-down GaN tip</td>
<td>4</td>
<td>14</td>
<td>1.02 390</td>
<td></td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Inclined GaN tip</td>
<td>16</td>
<td>39</td>
<td>1.05 395</td>
<td></td>
<td>17</td>
<td>38</td>
</tr>
</tbody>
</table>
etch process (Figure 4.4 (f)). The scanning was repeated several times, over 20 scans on a large-scale area (10 µm by 10 µm), and the tips were inspected for any damage due to the interaction between the tip and surface. Interestingly, GaN tips maintained their initial quality after more than 20 scans (Figure 4.5) while Si tips were observed to be broken after a few scans (between 1 to 5), which suggests that GaN tips are more resistant to mechanical damage. However, in some cases, we observed detaching of the NW from the welded connection to the substrate. This issue will be resolved by growing NWs directly on the cantilever along with a two-step etching process to make small diameter NWs.

In addition to all the advantages mentioned above, GaN tips showed scan direction-independence due to their symmetric geometry. The scan direction always matters if Si-based tips are applied since they have different side angles that causes scanning results be a function of scan direction and a complex correction procedure must consequently be considered after each scan test.
4.2. **Field emission scanning probe microscopy and lithography**

Since the first usage of Atomic force microscopy in nanopatterning, it has been used in many device fabrications by research group [2-8]. We proposed sharp GaN nanowire for atomic resolution SPM/SPL [7, 8], since this single crystal robust material can provide cost-effective nanopatterning by enhancing tip lifetime and making it possible for batch fabrication of SPM probes. The electrical conductivity of the tip and sharpness of the tip apex are the main characteristics for SPM and SPL tips. The conductivity of the tip material influences the tunneling current between tip and sample, and the apex diameter determines resolution of the nanopatterning. Sharp GaN NWs reflect both characteristics as they have very sharp apex and tunable conductivity by controlling doping concentration during growth procedure.
A bottom-up method was used to grow sharp GaN NW for fabricating AFM tips. The sharp GaN NW arrays were epitaxially grown on sapphire substrate in metal organic chemical vapor deposition. The fabrication process is schematically shown in Figure 4. 6(a). The NWs grown in this method has facet diameter of 0.5-0.7 µm, length up to 4 µm (as seen in scanning electron microscopy (SEM) image presented in Figure 4. 6(b)), and resistivity $\sim 10^{-2} \, \Omega \cdot \text{cm}$ corresponds to the doping concentration of $10^{18} \, \text{cm}^{-3}$. Transmission electron microscopy (TEM) image also showed that these GaN NWs have apex less than 1 nm (Fig 4. 6(c)) which are considered as perfect sharp tips for field emission imaging and lithography.

### 4.2.1. Active GaN AFM probes for field emission nanolithography and imaging

Active AFM cantilevers (Figure 4. 7(a)) contains piezoresistive read-out and thermomechanical actuator that enable reproducible atomic-resolution imaging and nanoscale lithography. These integrated properties are suitable for excitation of the cantilever at its resonance frequency and a static displacement without interference to the mechanical AFM-setup [9]. Si and diamond tip on active cantilevers have been using for field emission imaging and lithography [10-12]. To demonstrate capability of GaN material for field emission lithography, the sharp GaN nanowires were integrated into the standard active-cantilevers using the same method in Figure 4. 1, to make self-sensing and self-actuating probes (Figure 4. 7(b)) [13, 14]. Figure 4. 7(d) demonstrates the scanning results of imaging a Si substrate using fabricated tips and compares it with the results obtained by a standard Si tip (Figure 4. 7(e)). As seen, using GaN tip, higher resolution image could be
achieved with higher durability compared to the standard Si tips [1]. Figure 4. 7(c) demonstrate tunneling current between tip and sample surface as a function of their distance. As seen, when tip-substrate distance is below 20 nm, a constant 2 PA current is tunneled between tip and sample.

Field emission lithography was performed in vacuum using the same GaN tip and the results are presented in Figure 4. 8(a)-(c). To write patterns in field emission lithography following steps were followed: 1) Cr layer (5nm) and 30nm Au layer was coated on a 1cm×1cm n-doped Si substrate to prevent surface modifications due to the field emission current, 2) calixarene resist with ~12 nm thickness was spin coated, 3) an AFM pre-imaging was taken to find the area, 4) electric field was biased between tip and sample to write pattern (10 pA current with 1μm/s writing speed giving 100 nC/cm does), 5) a post-AFM imaging was taken using same tip to image written pattern. The AFM images in Figure 4. 8 illustrate written patterns after these steps. The process can be followed by etching and
resist stripping to transfer the pattern to the substrate. Figure 4. 8(a)-(c) are representing the field emission lithography under different biased using GaN NW tips. As seen lines with ~11 nm width could obtain using GaN probes which is in the same range of the

Figure 4. 8. AFM image of the field emission lithography using GaN NW under (a) 80 V, (b) 90 V, and (c) 100 V. 100 nC/cm dose was used for all samples. (d) The AFM image of field emission lithography using Si tip under different lithography doses.
nanopatterns achieved using Si tips (Figure 4. 8(d)). Figure 4. 8(d) presents field emission lithography on same substrate using a Si tips under different lithography dose. Comparing the AFM images in Figure 4. 8, the resolution as same as Si tip can be achieved by applying GaN NW tip. However, for GaN tip, higher bias voltage was applied to achieve a stable lithography condition. A larger bias voltage results in a larger tip-to-sample distance, which can result in a larger line width [13, 14]. So, the 10 nm linewidth that is much larger than the tip apex is attributed to the approximately high applied voltage. By implementing more conductive tips, the applied voltage can be reduced to obtain smaller feature sizes below 10 nm.

4.2.2. GaN STM probes for atomic-resolution imaging and nanoscale patterning

We used the same GaN NW arrays as shown in Figure 4. 6(b) to fabricate STM tips. The process to fabricate this probe are shown in Figure 4. 9(a)-(d). As already discussed in Figure 4. 1, focused ion beam was used to transfer NW on a flattened W STM tip. A silicon (100) was hydrogen terminated and used for STM imaging/lithography. An area as large as 48×48 nm was scanned with the speed of 234.4 nm/s in imaging and lithography. Figure 4. 10(a)-(d) demonstrate the field emission imaging and lithography results of using GaN
tip in STM and as seen in Figure 4.10(a) atomic resolution imaging obtained in scanning Si substrate. The same tip was used to write lines and boxes on the Si surface by removing Hydrogen from the surface. Vertical line and boxes were written on the Si substrate using this method as presented in Figures 4.10(b)-(d). 10,000 boxes were written as shown in Figure 4.10(c) and (d) and a perfect stability was observed on both atomic-scale imaging and nanoscale

![Figure 4.10](image)

**Figure 4.10.** (a) STM imaging a silicon substrate. STM Lithography; (a) Writing line, (c) and (d) low and high magnification of double writing of boxes, respectively. Figure (e)-(h) same measurement implemented by a standard W-tip. Images are achieved using equipment at Zyvex Lab.

![Figure 4.11](image)

**Figure 4.11.** TEM images to compare sharpness of (a) standard W-tip, and (b) GaN tip.
lithography. The same measurement was implemented using W-tip. Figure 4. 10(e)-(h) represent the imaging and writing on a Si substrate using W-tip. As seen, except observation of shadow in the lithography in Figure 4. 10(b) and (d), the GaN STM tips can provide higher resolution in imaging samples and almost as same resolution in lithography as a standard W-tip and so promising for application in nanoscale and atomic resolution field emission lithography and imaging. The higher resolution in imaging is attributed to the sharpness of the GaN NW. Figure 4. 11 compares the W- and GaN tip sharpness on the apex. As it is expected, since the apex on GaN tips is formed by convergence of the semi-polar crystal planes in epitaxial growth, its apex has smaller radius (r=0.5-0.6 nm) compared to the standard W-tip (1-1.2 nm).

According to the images in figure 4. 10(b) and (d), a secondary shadow to the right side of the written patterns is observed as shown by the arrows. This shadow effect could be due to the tip modification under applied bias during measurement. The tip was inspected in a TEM and it is observed there are two spires on the apex which could be either due to removing material from the apex or adding contamination on the apex of the tip during
scanning, as seen in Figure 4.12(a). However, to make a conclusion the tip must be cleaned and re-inspected in the TEM. Energy Dispersive X-Ray Spectroscopy (EDS) revealed that the added materials on the top are carbon (Figure 4.12(b)). We checked some of the GaN nanowires on TEM before being used for imaging/lithography and this carbon contamination was observed on this NW too (Figure 4.12(c)). One possible scenario is that under applied bias, these carbons are flowing down and made those spires on the apex after missing some GaN material there. The complete EDS analysis of GaN NW after usage is presented in Figure 4.13. However, it is hard to make a precise conclusion about the source of these spires’ appearance on the tip apex and more experiment must be conducted to investigate what happened to the tip during experiment which will be part of the future work.
References


Chapter 5

Enhancing optical properties of GaN nanowires

In chapter 3, we presented optical properties of fabricated GaN NWs with focus on modal properties and bottom and top reflectivities of HE\textsubscript{11} mode in the cavity. It was properly discussed that due to the mode expansion out of cavity in the subwavelength regime and close refractive index of substrate and NW material, the reflectivity of the HE\textsubscript{11} mode would be small, result in high thresholds in any photonic integrated circuits (PICs) and nanophotonic devices. To address this issue, some research must be implemented to improve mode reflectivity from the bottom of the NW. Two basic solutions would be available in this regard; (i) Replacing substrate with some materials in which higher index contrast can be achieved to obtain higher reflection, and (ii) including Distributed Bragg Reflectors (DBRs) into the NW structures. Since epitaxial growth of semiconductor materials on a substrate is limited to the lattice constant contrast between material and substrate, there are not many options to use as substrate for growing GaN crystal. Al\textsubscript{2}O\textsubscript{3},
Si, and SiC are the three substrates have been mostly used as a template for growing III-N materials and between them Si can provide greater index contrast with GaN. On the other hands, including DBRs into the NW structure can enhance reflectivity of optical modes from the bottom interface regardless of the substrate materials. DBRs have been using in optical and optoelectronic devices such as vertical cavity surface emitting lasers (VCSEL) [1-5] and could enhance optical properties of the device by improving optical reflections. However, these structures have been employed in large structures (micro-scale) and there would be challenges to use these periodic structures in nanoscale structures particularly sub-wavelength nanostructures. There are some reports about using dielectric DBRs in nanowire lasers [6-10], however, these dielectric DBRs can be only added on the top interface which does not help low reflection from the bottom. To add dielectric DBRs on both ends, NWs must be dispersed from the host substrate and so this reduces our control to fabricate devices in desired area. It seems the only solution is to grow DBR layers with the gain material through an epitaxial growth procedure. Therefore, the proper DBR materials must be composed of periodic semiconductor lattice match layers. Here in this chapter, we present preliminary results of our studying on optimization of growing GaN on Si and incorporating nanoporous semiconductor DBRs into NWs structure to improve bottom reflectivity which can make this nanoscale building blocks a practical structure in fabricating PICs.

5.1. Growing high quality GaN on Si substrate

One of the challenges in GaN based devices is transferring technology on Si substrate to scale down the overall market price per device. However, due to the large lattice mismatch between Si and GaN, it was hard to get high quality crystal grown on Si through
epitaxial growth. Transferring high quality GaN crystal to a Si substrate after growing on sapphire was suggested as an approach to solve this problem. In this approach, first, the high quality GaN is grown on sapphire, and then using flip-chip bonding the GaN layer is transferred on a Si substrate [11-13]. However, this method is low yield and still expensive compared to GaN films directly grown on Si. The other method that looks promising is to grow GaN directly on Si <111> substrate. Si <111> has the closest lattice constant to GaN compared to other orientations in Si substrate. To compensate the lattice mismatch between substrate and GaN, a buffer layer is grown on the substrate which is usually AlN. After a certain thickness (40-70 nm), Ga atoms are introduced into the chamber and its flow gradually increase while Al concentration is reduced. This results in having a graded composite layer of AlGaN on the AlN buffer layer before start growing GaN. When Al concentration reaches zero, the GaN film growing begins. Following is the processes we pursue to grow GaN on Si in MOCVD:

A 2” Si <111> wafer was cleaned by Acetone, IPA, DI water, piranha solution, and then right before transferring to the chamber it was soak into 5% HF solution to etch any native oxide layer and inorganic contamination from the substrate. Then the wafer was again cleaned in DI water and dried using Nitrogen gun blowing. Trimethylgallium (TMG), trimethylaluminum (TMA), and ammonia (NH$_3$) were used as sources of elemental Ga, Al, and N, respectively and N$_2$ was used as carrier gas. First, a cleaning of the Si surface under H$_2$ was initiated at the substrate temperature of 1100 $^\circ$C to remove native oxides and potential contaminants and to ensure clean surface prior to the growth initiation. Then, the sample surface was pre-exposed to TMA for 10 second to avoid surface nitridation and resulting polarity inversion. NH$_3$ was then flowed into the chamber to start a thin nucleation
layer of AlN at a growth temperature of 1060 °C and reactor pressure of 70 Torr followed by growth of a high temperature AlN buffer layer at 1080 °C and V/III ratio of 2370. The total thickness of AlN layer was aimed to be around 50 nm. Then, a linearly graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer ($x = 1$ to $x = 0$) was grown to partially alleviate the accumulating tensile stress due to the lattice and thermal expansion coefficient mismatch between overgrown GaN and Si. The total duration of the graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer was set to 20 mins providing a total thickness of close to 500 nm. Finally, ~1 µm-thick GaN layer was grown at the growth temperature of 1060 °C, reactor pressure of 200 Torr, and V/III ratio of 1370. The sample was then brought back to the ambient temperature at a reduced cool down rate of 15 °C/min to minimize the possibility of cracking which usually occurs during cool down process.

To follow our plan to fabricated single GaN nanowire AFM tip directly on Si cantilever (check our future works), the high quality GaN film needs to be grown on a SOI wafer. A double-side 3” polished SOI wafer (purchased from Ultrasil Corporation) with the specification mentioned in table 5. 1 was cleaved in a 2” by 2” square shape substrate

<table>
<thead>
<tr>
<th>Table 5. 1. SOI wafer specification</th>
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<tbody>
<tr>
<td>Device layer orientation</td>
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<td>Device layer thickness</td>
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<td>Device layer doping</td>
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<td>Handle wafer doping</td>
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according to the susceptor of MOCVD chamber. The same method was followed to grow high quality GaN film on a SOI wafer.

Figure 5.1 compares the PL spectrum obtained from GaN films grown on sapphire, Si <111>, and SOI wafer. As seen, GaN films grown on both Si <111> and SOI wafer demonstrate broadening (FWHM: 9.4 and 10.7 nm for GaN grown on sapphire and Si, respectively) in the spectrum and small red-shift in the PL peaks (363, 366, and 367 nm for GaN on sapphire, Si <111>, and SOI wafer, respectively). This broadening and shift in the bandgap are attributed to the crystal strain due to the lattice mismatch between Si and GaN. This strain is a more serious issue in SOI wafer because of surface tension on the device layer transferred on handle layer. According to the PL intensity peaks, it is obvious the GaN film grown on sapphire substrate has better quality and lower defects compared to the GaN grown on Si substrates.
5.2. Nanoporous semiconductor Distributed Bragg Reflectors (DBRs) on Si substrate

5.2.1. Experiment

As already mentioned in this chapter, III-nitride nanowire light-emitting diodes (LEDs) and lasers are considered potential building blocks for future photonic integrated circuits (PICs) and nanophotonic devices as light sources due to their tunable band gap and excellent waveguide properties. Monolithic integration of III-nitride nanowire lasers using heteroepitaxy of III-nitride on Si is a major pathway for integrating efficient light-sources with Si-based electronics for PICs. However, the integration of III-nitride nanowire on Si is still suffering from poor crystalline quality, low optical mode confinement, and poor modal reflectivity from bottom interface in a vertical cavity nanowire laser. Insertion of an AlN buffer layer partially improves the crystal quality of the overgrown films by alleviating the strain and corresponding defect reduction in the overgrown films. To improve the modal reflectivity of the NWs, as already mentioned in the introduction of this chapter, some approaches e.g. transferring the grown nanowires to a secondary substrate, and dielectric DBRs were suggested, however, none of the aforementioned methods are proposing a scalable method for integration of III-nitride nanowire lasers on Si as building blocks for photonic PICs. In this section, we propose a scalable and practical method of fabricating low-threshold nanowire lasers using nano/mesoporous semiconductor DBRs. The nanoporous DBRs are designed and inserted on high-aspect-ratio III-nitride nanowire cavity emitters with sub-wavelength diameter grown on silicon substrates to (i) provide tunable lattice-matched DBRs while simultaneously (ii) alleviating stress in the layers on
Si and consequently reducing defects, and (iii) enhance modal reflectivity in a nanowire cavity.

The MOCVD growth of the structures on Si is initiated by growing a buffer layer followed by a thick layer of alternating Si-doped and unintentionally-doped Al$_x$Ga$_{1-x}$N ($x=1$ to $x=0$). The method of growth is already explained in the preceding section. This method can be also applied to any other III-V alloy on Si substrate. Tuning composition of the ternary layer is based on the refractive indices and critical thickness of the layer. The thickness of each DBR layer (doped and undoped) is calculated by a quarter-wavelength equation ($\frac{\lambda}{4n_{eff}}$), where $\lambda$ and $n_{eff}$ are the wavelength and the effective refractive index of the layer for the guided mode, respectively. A thick GaN layer is then grown on top of the ternary alloy to serve as a gain medium. The composition and thickness of the ternary layer is designed to also reduce the stress in the GaN film and to minimize defect generation and crack formation during cool down process.

A top-down approach can be used to fabricate the nanowires using e-beam lithography or interferometric lithography as discussed in the chapter 2 [14]. The dry-etch process through the top-down approach has to be stopped right at the top of the ternary alloy (which will then be turned into the DBR) to protect it from a subsequent KOH-based wet-etch process during fabrication of the nanowires. Then, the ternary layer will be etched down to the Si substrate by ICP while protecting the same metallic mask. The ternary structure will then turn into the DBR following an electrochemical (EC) nano-porosification etching process in an oxalic acid solution [5]. During EC etching process, the doped ternary layers are selectively etched and become porous while undoped layers are remained pristine.
Figure 5. 2 shows schematics of the fabrication process for making nanoporous DBRs in nanowire emitters.

To analyze and calibrate DBR growth process, we grew 5 pairs of doped/undoped layer of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on a GaN substrate. The XRD analysis revealed the grown layer has composition of $\text{Al}_{0.13}\text{Ga}_{0.87}\text{N}$ as presented in Figure 5. 3(a). A PL measurement was also carried out to see ternary layer’s photoluminescence peak and compares it with GaN layer. Figure 5. 3(b) displays the PL measurement of $\text{Al}_{0.13}\text{Ga}_{0.87}\text{N}$ and as it seen the ternary layer’s peak is 29 nm apart from the GaN layer’s peak.

To analyze electrochemical etching, micro-mesa structures ($100 \mu\text{m} \times 100 \mu\text{m}$ squares) were made from $\text{Al}_{0.13}\text{Ga}_{0.87}\text{N}$. An indium contact was used to enable applying bias to the
samples. A Pt metal was used as cathode in Oxalic acid solution and samples were etched for minutes at 7, 8, and 9 V. Figure 5. 3(c)-(e) show SEM images of samples etched at
different biases. As seen by increasing bias from 7 to 9 V, the pore size increases (from ~20 nm- 60 nm). To have denser porosity, the doping concentration must be increased. Therefore, by adjusting doping concentration and applied bias, one can control density and size of the nanoporous structures. As a plan for future work, we are going to optimize pores size aiming to make nanoporous DBRs in NW emitters.

5.2.2. Modeling

To understand how nanoporous DBRs affect model reflectivity in a NW cavity, we used a FDTD model (Numerical software) to simulate optical reflectivities of fundamental optical modes due to the DBR layers. This will help us to optimize our structure in fabrication process to obtain more efficient photonic device out of the NWs.

In our analysis we consider single hexagonal GaN NW with radius R surrounded by air. For being close to the actual structure, we consider a thin AlN buffer layer on the Si substrate. The thickness of this buffer layer is also determined by quarter-wavelength equation. For refractive indices of layers, we used 2.65, 2.3, 1.7, and 2.12 for GaN, AlGaN, nanoporous AlGaN, and AlN, respectively. The nanowire cavity with diameter <200 nm can support three fundamental modes; HE$_{11}$, TE$_{01}$, and TM$_{01}$, as already discussed in detail in chapter 3 where we studied the modal properties of the vertical cavity GaN NW emitters. Using the same method of modeling, we considered NW with diameter of 200 nm, DBR layers thickness of 73.5 nm, and 48.5 nm corresponding to porous and non-porous AlGaN, respectively, according to quarter-wavelength relation ($\frac{\lambda}{4n_{eff}}$). We used optical mode source by using mode solver in Lumerical. After solving for finding optical modes, HE$_{11}$
was selected as the mode source for propagation. Two Monitors were used behind the source to collect reflection of the optical mode inside and out of the cavity. Subtraction of optical power inside the cavity from the total reflected power, will give the expansion of the optical mode out of the cavity after reflection. To increase accuracy of the model, a fine mesh (2 nm, 2 nm, 1 nm in x, y, and z direction, respectively) was used. Figure 5. 4(a) demonstrates geometry design of a cavity with 200 nm diameter and semiconductor DBRs on a Si substrate. Figure 5. 4(b) depicts the reflectivity of the HE\textsubscript{11} mode from the bottom of the cavity as a function of DBR pairs. As seen, without using DBRs, the cavity has about 40\% reflectivity due to the large index contrast between Sia and AlN (\(\Delta n = 4.34\)). By adding few DBR layers (up to 3), the reflectivity goes down to reach its minimum value at 24\% by using two pairs of DBRs. This drop in the reflectivity plot might be attributed to the wave-broadening and the edge effects on HE\textsubscript{11} mode during cavity round trip, however, more study needs to be conducted to understand the main reason of this suppression. Then, the reflectivity goes up by adding more layers and reaches 76\% at 10 pairs DBRs.
To make more efficient and cost-effective structure in NW devices, DBRs can be embedded into an appropriate metal. The chosen metal must have very low loss for the wavelength of interest and a good index contrast with DBR materials. Surrounding metal avoids wave-broadening and results in higher confinement during wave propagation inside the DBRs. In our mode we used silver as metal to surround DBR structure. It has refractive index of \( n = 0.074 + i \times 1.6 \) at \( \lambda = 366 \) nm. Figure 5.5(a) and (b) demonstrate geometry of the embedded DBRs into metal and reflectivity of the mode HE\(_{11}\) for different DBR pairs. As seen by burying DBRs into Ag, using one pair DBR a reflectivity up to 52% can be achieved. However, no enhancement was observed by increasing number of DBR layers embedded in metal.

In summary, our preliminary results show that including semiconductor nanoporous DBRs can enhanced mode reflectivity in NW cavity to provide emitters with lower loss, low threshold power, and tunable emission modes. Burying DBRs in metal assists to achieve higher reflection with fewer DBR layers to simplify structure and facilitate fabrication process.
References


Chapter 6

Conclusion and future works

6.1. Conclusion

In this dissertation, different approaches to fabricated high-aspect ratio GaN NWs for application in nanoscale metrology and nanophotonics were discussed. In chapter one, different methods in nanofabrication and nanometrology were compared by presenting their advantages and disadvantages. It was presented that GaN NWs can be potentially used as a new tip material in scanning probe microscopy to assist tip-based nanometrology to obtain high-resolution image in scanning high-aspect ratio nanostructures, enabling optical microscopy, atomic-resolution imaging, and nanoscale lithography due to their superior mechanical properties, suitable geometry, and excellent optical properties. In chapter two, we demonstrated different methods to fabricate high aspect-ratio NW through top-down and combination of top-down and bottom-up approaches. There we presented an optimized room-temperature two-step top-down approach to fabricate large-area (~1 mm²) high
optical quality GaN NW arrays with a precise control on radius and aspect-ratio. In our method, GaN film is patterned using an interferometric lithography setup and etched in Cl₂-based dry-etch followed by a potassium-based wet-etch solution. Uniform NW arrays with radii of sub-50 nm, sidewall roughness of <1nm, and aspect-ratio up to 50 were achieved through this optimized approach. Selective area GaN NW arrays with the same optical and mechanical properties were also fabricated on sapphire and Si substrates. Fabricating GaN NWs selectively on desire areas makes this two-step method mature for large area fabrication of nanoelectronics and photonics devices.

The etch mechanism of GaN and the influence of Si-doping on etch behavior of the NWs in potassium-based solution were investigated in chapter 3 and it was shown that due to the higher reactivity of the Si atoms in the potassium-based solution, the etch rate increases with doping concentration. We also used our approach to obtain the etch rate of m-plane facets in the wet-etch solution for different doping concentrations. Using FDTD modeling, modal properties of the fabricated NW array lasers were studied and HE₁₁ mode was found to be the dominant transverse mode to propagate in the vertical cavity for the NW arrays with radii less than 100 nm. Although having NW arrays on a sapphire substrate reduces reflectivity of the optical modes, the advantages of our approach mitigated cavity loss in the GaN NWs in which single-mode lasing spectra with FWHM < 0.32 nm and pump intensity threshold of 3.31-4.55 MW/cm² were observed in GaN NW arrays with the radius of ~65 nm. Realizing GaN NWs with excellent optical quality and very smooth sidewalls using our method is promising for the future assembly of more efficient III-nitride nanophotonic devices.
Chapter 4 is dedicated to reporting the fabrication of scanning probe microscopy tips from our GaN NWs for nanoscale metrology and lithography. The fabricated GaN NWs through top-down approach were used to make AFM tips. These NWs were bonded normal and inclined to a Si cantilever using a Focus Ion Beam (FIB). The vertically welded GaN tips demonstrated superior performance in scanning structures with straight sidewalls and 90°-angles, compared to a commercial Si tip, while their results are independent of scan direction, and as a consequence they can provide more accurate surface topography information for analytical studies in nanometrology. Moreover, the GaN tips were observed to have very high durability and experienced negligible mechanical damage after scanning of a large area, which makes them an excellent candidate for next generation AFM probes. The sharp GaN NWs with an apex less than 1 nm fabricated through a bottom-up approach were also used in STM and AFM imaging and lithography processes. The same method is used to bond sharp GaN NWs to a standard tungsten STM and active Si AFM tips. Using GaN NWs as tip in STM, atomic resolution imaging was obtained and sub-10 nm lines and arrays of boxes were written on a Si substrate. The acquired image and lithography feature size have the same quality as standard metallic tips that are commonly used in STM/SPL. Employing sharp GaN AFM tips on an active cantilever provided higher resolution images compared to the standard Si tips and could write small feature sizes (~11 nm) in lithography mode under applied bias. The methods of growing GaN NWs are suitable for batch fabrication of AFM/STM tips and since their conductivity can be tuned by controlling doping concentration during growth procedure, these tips are promising for the next generation of cost-effective SPM tips.
In chapter 5, we presented a method to improve poor modal reflectivity in vertical GaN NWs. We demonstrated preliminary modeling results of including nanoporous semiconductor DBRs on the bottom of the NW grown on a Si substrate which are created by introducing periodicity in doping concentration of the Al$_x$Ga$_{1-x}$N layer under the GaN film. Having this periodic structure under the gain medium not only addresses the poor modal reflectivity of the NWs, it also alleviates stress due to the lattice mismatch in the grown film on the silicon substrate. Preliminary modeling results show that using 10 pairs of DBRs in a NW, with diameter of 200 nm boosts reflectivity from bottom of the NW up to 76%. We also presented a metal embedded DBR structure in which high reflectivity can be achieved by adding few pairs (1-2 pairs) of DBRs to simplify and facilitate fabrication process.

6.2. Future works

6.2.1. Fabrication of GaN NW tips directly on Si cantilever

To continue and complete our research in fabricating GaN NW AFM tips, these NWs are made directly on a Si substrate. Having these tips directly grown on a Si cantilever increases their stability and helps the commercialization of the fabrication process. We have already calibrated fabrication steps and are very close to achieve these tips on a Si cantilever. We also calibrated growing GaN on SOI wafer as presented in chapter 5. Figure 6.1 demonstrates a schematic of the fabrication process that can be followed to fabricate GaN tips on a SOI wafer. As seen, after growing GaN on a SOI wafer, double side lithography needs to be conducted on top and bottom of the wafer to fabricate cantilevers and make GaN tips standing on them.
2.2. Enabling tip metrology to implement optical microscopy

Another promising topic for future work is enabling fabricated GaN AFM tips for optical microscopy e.g. near field scanning optical microscopy (NSOM). The optical and modal properties of GaN NWs are well discussed in chapter 3, where it was demonstrated

Figure 6. 1. Schematics of batch fabrication process for GaN NW AFM tips on SI cantilever.

Figure 6. 2. Schematic of integrating optical microscopy into an GaN AFM tip.
that GaN NWs are promising for application in nanophotonic and optoelectronic devices due to their excellent crystal and waveguiding properties. Fibers have been used to guide and collect optical waves in current optical microscopy. This requires employing external waveguiding system into the tip metrology. However, thinking of having single system to scan, emit, and collect optical information from substrate pave the way to make more efficient metrology/microscopy tool for the future application. As seen in Figure 6.2, a waveguide is built on the back side of the cantilever support for enabling optical pumping. Using an optical pump, the GaN tip is excited to emit at its optical gain. The corresponding fluorescence of the surface is collected by the same GaN tip and send to an optical feedback for analysis.

6.2.3. Electrically pumped GaN NW emitters

For an optoelectronic device, electrical pumping is always required. The high optical quality of the fabricated GaN NWs through our presented method was proved in chapter 2 and 3. However, a more attractive idea is to bring this NWs to emit by an electrical pumping system which is more interesting for industrial applications. In this regard, a p-n or p-i-n...
junction is needed to be built in the NW’s structure. After fabricating GaN NWs in two-step top-down approach, one can regrow quantum wells (QWs) and p-layer to make core-shell high-aspect ratio NW. The fabricated NW emitters (Figure 6.3) are promising for being used in high-efficient nanophotonics, displays, and optical communication.

6.2.4. Fabrication NW lasers with nanoporous semiconductor DBRs

In chapter 5, we discussed the application of semiconductor nanoporous DBRs in nanostructures and presented some preliminary results of enhancement in reflectivity by means of DBRs. This topic still needs more researches and an actual NW cavity with nanoporous DBR layers on the bottom must be fabricated and characterized to confirm our simulation results. One plan is to make metal-nanoporous DBRs as a perfect reflector in NW cavities. The deposited metal on the sidewalls of the DBR, as discussed in chapter 5, can also be annealed after the deposition to obtain even higher reflectivity with fewer number of pairs in the DBR. The annealed metal will penetrate to the pores and make sort of a metal-semiconductor composite which increases the overall modal reflectivity at the bottom interface (Figure 6.4(a)).

Figure 6.4. (a) Metal-nanoporous semiconductor DBRs’ structure. (b) Structure for electrically pumped NW emitters with DBRs on the bottom interface.
Another structure is a pathway to electrically pumped NWs with bottom interface DBRs. An example of this structure is shown in Figure 6.4(b). To achieve this structure, ternary and n-type layers are initially grown on a patterned silicon substrate, and then nanoporous layers are introduced into the DBR structures. Then, a thick dielectric layer is deposited to cover DBR and n-type nanowire sidewalls. A chemical-mechanical polishing can be used to remove dielectric layer from the top following with a quick dip into a diluted HF solution to remove any residual of the dielectric on top of the nanowire (and also to remove any dielectric deposited on the side of the nanowire). Then, the active region and p-type layer are grown on top of the n-type nanowire. A transparent ITO p-contact and a metal deposition for n-contact can be used to electrically bias this nanowire.
Appendix A

Interferometric lithography (IL) experimental setup

A pulse third harmonic Nd:Yag laser (355 nm wavelength) is used as a source to make the interference pattern. A function generator is used to control the pulse energy, pulse repetition, and exposure time during the experiment. As seen in the figure A1, the laser beam was first expanded by means of a lens and then it is reflected toward a corner cube stage by Mirror 1. Part of the reflected beam is directly illuminating the sample, while the other part, after a second reflection from Mirror 2 on the corner cube stage, superposes with the first beam on the stage where sample is mounted. This different optical path is making a phase difference between split beams and as a result an interference pattern forms on the sample position. The pitch size can be adjusted by changing the incident angle of the beams on a corner cube stage. The sample holder can be rotated 90 degrees to produce orthogonal lines (2D patterning) and consequent holes on the photoresist film for our two-step top-down fabrication process.
Figure A1. Schematic of IL experimental setup.

Reference

Appendix B

Different aspect-ratio GaN NW arrays fabricated through two-step top-down technique
**Figure A2.** Different aspect ratio (A. R.) NW arrays fabricated in two-step top-down approach using IL.

**Reference**

Appendix C

Transverse optical modes in subwavelength regime

Transverse optical modes are electromagnetic field patterns of the guided wave in the plane perpendicular to the propagation direction. These patterns depend on boundary condition imposed on the guided wave by the geometry of the waveguide. In general, according to the direction of the electromagnetic filed components, three type of modes can be found in waveguides; Transverse Electric (TE), Transverse Magnetic (TM), and Hybrid modes. In TE mode, there is no electric field in the direction of propagation and electric field is perpendicular to the propagation plane. In TM mode, there is no magnetic field in the direction of propagation and magnetic field is perpendicular to the propagation plane. In contrast, in the Hybrid modes, electromagnetic field has also components in the direction of propagation. The components of the electromagnetic field in cylindrical coordinate system is expressed as:

\[
\begin{align*}
E_r(r, \phi, z, t) &= i e_r(r, z, t) \exp(i \nu \phi) \\
E_\phi(r, \phi, z, t) &= e_\phi(r, z, t) \exp(i \nu \phi) \\
E_z(r, \phi, z, t) &= i e_z(r, z, t) \exp(i \nu \phi) \\
H_r(r, \phi, z, t) &= h_r(r, z, t) \exp(i \nu \phi) \\
H_\phi(r, \phi, z, t) &= i h_\phi(r, z, t) \exp(i \nu \phi) \\
H_z(r, \phi, z, t) &= h_z(r, z, t) \exp(i \nu \phi)
\end{align*}
\]
Where \( \nu \) is the integer azimuthal mode number, \( E_r, E_\phi, E_z \) and \( H_r, H_\phi, H_z \) are the components of electric and magnetic field, respectively. \( e_r, e_\phi, e_z \) and \( h_r, h_\phi, h_z \) are the corresponding reduced field components that are independent from azimuthal angle. If \( \nu = 0 \), the corresponding mode is transverse electric (TE) or transverse magnetic mode (TM). If \( \nu \neq 0 \), the mode is hybrid (HE, EH) and it has azimuthal angle (\( \phi \)) dependency. To distinguish between different modes, they are labeled by two indices (TE\(_n\)m, TM\(_n\)m, HE\(_n\)m) that are integers value obtained from Bessel function. The first subscript (n) denotes angular symmetry and the second subscript denotes the radial dependency of the field. Figure A4 compares the optical transverse modes (\( \lambda = 366 \) nm) solved by mode solver in a cylindrical and hexagonal waveguide with 200 nm diameter.

![Figure A4](image)

**Figure A4.** Comparison of optical transverse modes in a waveguide with cylindrical and hexagonal cross section.

**Reference**

Appendix D

PL measurement setup

The excitation source for the photoluminescence setup is a diode laser with the following properties: 266nm, 20kHz, <0.6ns pulse width. The emission of the diode laser is routed through three optical components (as shown in figure S1) before reaching the sample: 1) an attenuator to vary the pumping intensity reaching the sample, 2) a beam splitter to allow simultaneous measuring of pumping power while exciting the sample, and 3) an aperture to reduce the spot size of the emission to about 1 um. The emission from the sample is collected with a spectrometer, model number SP-2300i.

Figure A4. Schematic of the optical setup for PL spectroscopy.
Since the pumping power is measured through transmission of the beam splitter, a transmission to reflection ratio had to be obtained to calculate the actual power exciting the sample. The environmental power was noted and subtracted from the excitation power calculation. The sample mounts on an XYZ axis stage. Three axes allow for focus of the laser spot and translation of the spot across the sample. A light and viewing camera is used to view the surface of the sample and avoid the sample’s edge and any potential scratches. The light source is turned off before any measurements are made. The area of the laser spot is estimated by measuring a pixel calibrated image from the viewing camera in Fiji. The area of the spot is used to calculate the power intensity of the pump laser.

**Reference**

**Publications and Patents**


[8] Lenk, Claudia, Steve Lenk, Mathias Holz, Elshad Guliyev, Martin Hofmann, Tzvetan Ivanov, Ivo W. Rangelow et al. "Experimental study of field emission from ultrasharp silicon, diamond, GaN, and tungsten tips in close proximity to the


**Patents**

