Investigation of Surface Properties for Ga- and N-polar GaN using Scanning Probe Microscopy Techniques

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Investigation of Surface Properties for Ga- and N-polar GaN using Scanning Probe Microscopy Techniques

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Nanotechnology and Nanoscience
at Virginia Commonwealth University.

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Abstract

INVESTIGATION OF SURFACE PROPERTIES FOR Ga- AND N-POLAR GaN USING SCANNING PROBE MICROSCOPY TECHNIQUES

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor in Philosophy at Virginia Commonwealth University

Virginia Commonwealth University, 2013

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Because the surface plays an important role in the electrical and optical properties of GaN devices, an improved understanding of surface effects should help optimize device performance. In this work, atomic force microscopy (AFM) and related techniques have been used to characterize three unique sets of n-type GaN samples. The sample sets comprised freestanding bulk GaN with Ga-polar and N-polar surfaces, epitaxial GaN films with laterally patterned Ga- and N-polar regions on a common surface, and truncated, hexagonal GaN microstructures containing Ga-polar mesas and semipolar facets. Morphology studies revealed that bulk Ga-polar surfaces treated with a chemical-mechanical polish (CMP) were the flattest of the entire set, with rms values of only 0.4 nm. Conducting AFM (CAFM) indicated unexpected insulating behavior for N-polar GaN bulk samples, but showed expected forward and reverse-bias conduction for periodically-patterned GaN samples. Using scanning Kelvin probe microscopy, these same patterned samples demonstrated surface potential differences between the two polarities of up to 0.5 eV, where N-polar showed the expected higher surface potential. An HCl cleaning procedure
used to remove the surface oxide decreased this difference between the two regions by 0.2 eV. It is possible to locally inject surface charge and measure the resulting change in surface potential using CAFM in conjunction with SKPM. After injecting electrons using a 10-V applied voltage between sample and tip, the patterned-polarity samples reveal that the N-polar regions become significantly more negatively charged as compared to Ga-polar regions, with up to a 2-V difference between charged and uncharged N-polar regions. This result suggests that the N-polar regions have a thicker surface oxide that effectively stores charge. Removal of this oxide layer using HCl results in significantly decreased surface charging behavior. A phenomenological model was then developed to fit the discharging behavior of N-polar GaN with good agreement to experimental data. Surface photovoltage (SPV) measurements obtained using SKPM further support the presence of a thicker surface oxide for N-polar GaN based on steady-state and restoration SPV behaviors. Scanning probe microscopy techniques have therefore been used to effectively discriminate between the surface morphological and electrical behaviors of Ga- vs. N-polar GaN.
Chapter 1: Introduction and Experimental Overview

1.1 Motivation

While silicon- and gallium arsenide-based devices dominate much of the applied semiconductor landscape, GaN-based material systems have found several niche uses in optoelectronic applications, including visible-to-UV LED lighting applications and blue/UV laser diodes.\(^1\) More recently, electronic applications of GaN for high electron mobility transistor (HEMT) devices are showing promise.\(^2,3\) GaN is also a promising candidate for utilization in non-linear optical material for second harmonic generation.\(^4\) Although the GaN system has many desirable traits, there are numerous long-standing and yet unresolved issues that have limited the implementation of GaN in semiconductor devices. Among these concerns, the internal spontaneous polarization of GaN and the associated internal electric fields result in deleterious effects for optoelectronic devices including a significantly high degree of the quantum confined Stark effect in GaN-based quantum well lasers.\(^5,6\) These polarization effects are largely due to the wurtzite structure of the GaN crystal structure (see Figure 1.1). Another concern is with GaN lattice-matched substrates for epitaxial GaN growth, where present options are costly and typically contain high densities of structural or extended defects. Such defects (namely screw, edge, and mixed dislocation sites) lead to unwanted electrical behaviors and have limited the efficiency and lifetimes of GaN-based devices. The surface effects for GaN are of particular interest, as a depletion region formed at the polar GaN surface typically leads to undesirable electrical and optical behaviors. On the other hand, the sensitivity of the charged surface to adsorbates may be exploited for sensing applications.

Generally, surface effects are categorically defined as internal and external, where internal effects originate from crystallographic considerations including defects and imperfections, spontaneous polarization, dangling bonds at the surface, and surface reconstruction / morphological effects. External effects are much less predictable as they typically originate from chemical interactions at the GaN interface and influence surface electrical behaviors. While it is known that a ~1 nm native oxide forms at the surface of Ga-polar GaN,\(^7\) the extent and properties of additional oxide formation, especially for N-polar GaN, is not well-known, yet
directly influences electrical behaviors at the surface. In the case of Ga-polar GaN, an amorphous, monoclinic $\beta$-Ga$_2$O$_3$ is widely considered to be the predominant surface oxide which forms upon exposure to air.$^8$ As negative charge (of either internal or external origin) accumulates on the GaN surface, upward band bending in $n$-type GaN is also known to inhibit the recombination of photogenerated charge carriers, leading to decreased exciton emission, as work within this group has shown previously through photoluminescence and studies.$^9$ We have also seen that atmospheric oxygen may eventually become chemisorbed to the GaN surface, thus establishing a semi-insulating surface oxide. In studies performed elsewhere, a linear relationship was observed between the increase of apparent oxide layer thickness and corresponding increase of the calculated band bending as measured by complimentary secondary electron microscopy and photoemission spectroscopy methods.$^{10}$

This dissertation represents a continuation of our group’s work on localized surface properties of the GaN system. To study such localized effects, we have extensively used atomic force microscopy (AFM) and related surface probe microscopy (SPM) techniques in order to complement other characterization techniques used within the group (Kelvin Probe, photoluminescence, Hall effect measurements, etc.) Specifically, traditional AFM, conductive AFM (CAFM), and Scanning Kelvin probe microscopy (SKPM) techniques have been used for investigation into morphological effects, local conductivity, and local surface potentials. However, we have also investigated localized surface charging behaviors by combining CAFM and SKPM into one experimental technique, and have developed a preliminary, rate-based model to model the discharge characteristics after locally injecting negative charge in dark conditions. We have also studied local surface photovoltage (SPV) effects by exposing the surface to UV light while monitoring the surface potential signal over time with SKPM. During these studies, we have reported upon surface polarity and surface treatment effects for a set of free-standing GaN films$^{11}$ and, more recently, investigation into laterally-patterned Ga- and N-polar GaN surfaces.$^{12}$ We have expanded upon the existing research in regard to surface oxide growth behavior,$^{13}$ and have gained some additional insight into local electrical and morphological effects for polar and semi-polar GaN surfaces. While not reported in these studies, AFM methods
were also used to assist with surface characterization for other projects which were being conducted by colleagues at VCU (e.g., Refs 14, 15).

The following chapters in this report are presented in the sequence by which samples were typically characterized during the course of study. After an introductory chapter about the GaN systems and experimental techniques used for these studies, the second chapter presents topography and morphology studies, while the third chapter focuses on local conductivity behaviors using CAFM. The fourth chapter details findings obtained by Scanning Kelvin Probe Microscopy (SKPM) data which investigated local surface potential behavior, and the fifth chapter investigates surface charge injection and depletion by using a combination of CAFM and SKPM methods. Finally, SPV behaviors were investigated at the sub-micron level, and are discussed in the sixth chapter.

1.2 Experimental Techniques

Data presented in this dissertation was obtained by a commercial AFM (Bruker Icon) operating in air ambient unless noted otherwise. Simplified schematics outlining the various AFM techniques are presented in Figure 1.2. For topographic data, tapping-mode AFM (Figure 1.2 (a)) was performed using standard tips (Mikromasch NSC 15 Al-BS; $k_{tip} = ~35$ N/m, $f_{tip} = .325$ kHz.). For conducting AFM (CAFM) measurements (Figure 1.2 (b)), two current-sensing application modules were employed while scanning in contact-mode operation- a “Tunneling” AFM (TUNA) module, whose current detection range is ± 120 pA, and a standard CAFM module possesses a detection range of ± 1 μA. While performing CAFM, the convention of applying voltage to the sample is used throughout, and is representative of the standard current-voltage (I-V) lexicon; for example, with an $n$-type sample, negative current ($I_{sample} < 0$ A) flows as a negative bias ($V_{sample} < 0$ V) is applied, and is said to be in the forward bias regime. Conversely, reverse bias conditions exist on $n$-type samples when $V_{sample} > 0$ V. For CAFM measurements, as well as for SKPM and SPV measurements, metallized AFM tips (Mikromasch NSC-15 Ti-Pt or Budget Sensors Tap 300E-G) were used, and the samples were connected electronically to a conductive sample disc using indium solder in all cases.
Contrast imaging of local surface potential variations were obtained through SKPM (Figure 1.2 (c, d)), whose data represent precise contact potential differences (CPD) between an AFM tip and the sample surface while raster scanning.\textsuperscript{16,17} Although SKPM data are precise in terms of contrast resolution, reproducible data are difficult to obtain while operating in ambient conditions, as measurement of absolute CPD values between the surface and AFM tip are subject to environmental effects. For instance, with an Au reference surface, which is expected to have a very consistent CPD value in relation to a metal-coated AFM tip, variations in the measured valence band minimum via SKPM methods were around 0.15 eV (n-type GaN) 0.18 (p-type GaN). These variations illustrate that that even with an ideal sample, significant changes in the CPD between tip and sample occur in ambient SKPM operation and introduce significant error into associated metrics such as the magnitude of band bending and valence band minimum for a given sample.\textsuperscript{18} Therefore, caution must be exercised during analysis of these SKPM data.

For SKPM operation, surface potential mapping is accomplished via a two-pass scan technique, where standard tapping-mode AFM is employed to measure first the topography of a scan line (Figure 1.2 (c)). Secondly, feedback electronics are employed to measure the surface contact potential via a lock-in amplifier operating at a preset height above the sample (Figure 1.2 (d)). Further details about SKPM theory will be discussed in Chapter 4. It should be noted here that the convention used throughout is one by which a positive test charge is used to describe the increase or decrease of the surface potential during SKPM mapping. While it is common practice to describe an increase of the surface potential corresponding to a higher number of negative charge, SKPM imaging is not interpreted as such. Therefore, it is reiterated that a higher surface potential describes a more positively-charged surface, and a lower surface potential describes a more negative-charged surface.

The “charge writing” technique detailed in Chapter 5 represents a combination of CAFM and SKPM methods. In this technique, an initial bias is applied to the sample while either raster scanning or single point-probing with the tip in a pre-defined area or single pre-defined spot, respectively.\textsuperscript{19} For \textit{n}-type GaN surfaces such as those reported here, charge may either be “injected” by applying a positive bias to the sample such that electrons flow from the AFM tip to the sample surface, or may be “depleted” by reversing the bias polarity such that electrons flow
from the sample surface to the AFM tip. As we have seen in previous studies, the charging behavior is asymmetric in that injection of electrons onto \textit{n}-type GaN causes a more dynamic effect than depleting electrons from the surface does. Likewise, studies conducted on \textit{p}-type surfaces showed that depleting electrons caused a larger effect than injecting charge.\textsuperscript{20}

Following the charge transfer which produces charged surface states, subsequent SKPM scans of the surrounding area are then employed to image the charged region. The resulting surface potential differences may be observed and within \textasciitilde2 min. of initially charging the surface. While spatial surface charging characteristics were of particular interest, a phenomenological rate-model describing the discharging behavior of the surfaces to the first approximation was also constructed, and will be presented discussed at length at the outset of Chapter 5.

For surface photovoltage (SPV) data collected using SKPM techniques, temporal scans are used to monitor immediate changes in local surface potential by exposing the surface to above-bandgap UV illumination (100 W low-pass Hg lamp). In contrast to local charge injection techniques which (for \textit{n}-type) temporarily increase the magnitude of band bending by placing additional negative charge onto the surface, SPV data represents a photo-induced decrease of the magnitude of band bending. For \textit{n}-type GaN where an intrinsic, excess negative surface charge causes upward band bending, exposure to UV illumination generates electron-hole pairs within the depletion region. While electrons are readily swept into the bulk due to the strong electric field within the depletion region, holes accumulate at the surface, thereby decreasing band bending by up to 0.5 eV.\textsuperscript{21,22} By monitoring changes in the surface potential signal over time as UV illumination is applied and ceased, band bending characteristics may be further investigated.

\subsection*{1.3 GaN Samples}

There are three major types of GaN samples which were studied in this work: 1) bulk polar GaN (Kyma), 2) patterned polar GaN (NRL), and 3) patterned semipolar GaN (SUNY). All three GaN sample types are schematically shown in Figure 1.3 and will be described in further detail below.

\textit{Bulk GaN (Kyma)}
To investigate the effects of polarity and treatment type on c-plane (Ga-polar, (0001)) and c'-plane (N-polar, (0001)) GaN thin-films, undoped, bulk GaN samples were grown by halide vapor phase epitaxy (HVPE) at Kyma Technologies, Inc. After epitaxial GaN growth, GaN epilayers were removed from their sapphire substrates using a laser lift-off (LLO) process, and were subsequently polished down to a thickness of ~400–450 µm. A schematic of the LLO procedure is shown in Figure 1.4. The surfaces were then finished with either a mechanical polish (MP) or chemical mechanical polish (CMP). The MP-treated surfaces were prepared with a series of diamond slurries, where the diamond particles used in the final polishing had a ~1 µm diameter. For samples treated with the CMP, surfaces were prepared first with a MP, and were subsequently polished with a proprietary HCl-based chemical etchant to further improve surface planarization. From Hall-effect measurements, the measured concentrations of free electrons in the bulk samples were estimated to be $n_e = 5\times10^{15} - 7\times10^{15}$ cm$^{-3}$ at room temperature. A summary of the bulk samples and their surface treatments is shown in Table 1. To remove any surface oxide after initial characterization of the surfaces, a cleaning procedure with HCl for 5 min at 295K followed by a de-ionized water rinse was performed on the samples, as it is known that HCl effectively removes such adventitious surface oxides.24,25

**Patterned, polar GaN (NRL)**

To date, there are few reports which have measured the surface potential contrast between Ga- and N-polar surfaces experimentally, as will be discussed at the outset of Chapter 4. Although polarity switching has been known to occur during GaN growth upon exposure to Mg, only recently has an AlN layer been used to systematically nucleate an inversion domain during epitaxial GaN growth.26,27,28 In previous studies which sought to quantify surface potential differences between Ga- and N-polar surfaces, a reference surface (e.g., an exposed area of sapphire substrate) was employed as a calibration for the observed surface potential signal.29 Laterally patterned GaN samples grown at the Naval Research Lab (NRL) are excellent candidates to investigate real-time, quantifiable differences in surface potential between Ga- and N-polar surfaces, as both of these surface polarity types were grown on the same surface of a GaN epilayer.27,28
To produce the patterned, alternating surface polarity, polar GaN surfaces (also known as lateral polarity junctions) were grown epitaxially on top of N-polar GaN templates. The templates were prepared by either HVPE (CMP, N-polar Kyma GaN) or by metalorganic chemical vapor deposition (MOCVD) techniques. The “#612-H” sample denotes a ~2 µm-tick patterned epilayer grown on the HVPE template (Kyma, CMP-treated N-polar GaN), while the epilayer grown on the MOCVD template (N-polar GaN grown on sapphire) is labeled as “#100430-M” and is of similar thickness.

A patented selective epitaxy process was used to prepare the alternating polarity surfaces on the two separate substrate types. Here, a thin inversion layer comprising AlN was selectively grown inside a silicon nitride mask containing a stripe pattern with 16 mm-wide apertures several millimeters long. After removing the patterning mask, Ga- and N-polar GaN were simultaneously grown over the inversion layer and bare N polar substrate using a Thomas Swan showerhead MOCVD chamber. In addition to the stripe-patterned samples, an epilayer grown on a similar MOCVD-grown N-polar GaN template to the #100430-M sample contains a large (5 × 5 µm²) contiguous Ga-polar region, and is labeled as the “#1208-M” sample.

Structural properties of the patterned polar samples were obtained elsewhere. The total dislocation density (TDD), which includes screw and edge-type dislocations, was measured using electron channeling contrast imaging (ECCI) mounted in a scanning electron microscope (SEM). With the ECCI technique, the TDD values were measured as 2.0×10⁹ cm² for Ga-polar and 1.2×10⁹ cm² for N-polar for the #100430-M sample. For the #612-H sample, N-polar region dislocation densities were calculated as 1×10⁷ cm². The authors suggest that the remarkably low TDD value for the N-polar stripes on the #612-H sample is comparable with those of high quality HVPE material, and is observed for these epilayers since 1) N-polar epilayer growth (homoepitaxial) results in negligible amounts of additional defects at the template/epilayer interface, and 2) that defects which extend into the epilayer are almost exclusively due to pre-existing defects of the underlying HVPE template. The measured TDD on the #612-H Ga-polar region is two orders of magnitude higher (2.0×10⁹ cm²) than the adjacent N-polar regions; these higher values are attributed to additional defects introduced by the heteroepitaxially-grown (lattice mismatched) AlN inversion layer.
After initial characterization of these samples by AFM techniques, the #612-H and #100430-M samples were cleaned in an HCl-based solution as to remove any surface oxide. This process differed from the HCl cleaning process performed on the bulk, polar samples in that submersion of the samples for 10 minutes 0.04 M HCl solution (versus a 0.1 M solution used for polar, bulk samples) was used out of concern of etching the #100430-M template (N-polar GaN on sapphire).

*Patterned semipolar GaN (SUNY)*

Along with polar GaN thin-film surfaces, GaN microstructures offered additional, semi-polar GaN facets which were limited in access in regard to acceptable SPM probe geometries. A sample (labeled as “#1937-S”) containing several GaN microstructure shapes was grown by the WBG Optronix group at SUNY-Albany as part of their group’s ongoing studies focused on growth, kinetics, and control of non-equilibrium GaN structures.30 In this particular study, the growth of 1 μm-tall, hexagonally-shaped GaN microstructures was accomplished by MOCVD growth of GaN on sapphire substrates which were patterned by photolithography methods for the subsequent selected area growth (SAG). Here, a 100 nm mask of SiO₂ was used as the mask material for the SAG technique, where the geometry and orientation of the growth apertures dictated the final microstructure shapes (hexagonal pyramid, arrowhead-type, columnar, etc…). Structures presented in this report are specifically truncated, hexagonal pyramids which include a c-plane (0001) “mesa” and non-trivial {1101} facets, as was predicted by analysis of associated kinetic Wulff plots of GaN.31 For clarity, Wulff plots may predict the growth rate of various facets, and by extension, the final shape of a GaN microstructure, given an initial size and orientation. As well as containing six individual {1101} facets which are of interest for surface studies, a better understanding of these types of structures will be important for development of, for example, GaN quantum dots / LEDs and nanostructures.32
Figure 1.1: (a) Common wurtzite planes and (b) GaN atomic arrangement showing Ga atoms in red and N atoms in blue along with corresponding planes.

Figure 1.2: Schematics showing modes of AFM operation: (a) Tapping-mode, (b) CAFM, and two-step SKPM technique where (c) topography is first recorded and then (d) surface potential is measured with feedback electronics plus topographic height information.
Figure 1.3: Schematic diagrams of three GaN sample types used in this work: a) polar bulk GaN (Kyma), b) patterned polar GaN (NRL), and c) patterned semipolar GaN (SUNY).
Figure 1.4: Schematic of laser lift-off (LLO) procedure to prepare N-polar GaN from HVPE growth (taken from Ref. [23]).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Growth method</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1305, Ga-polar</td>
<td>HVPE+CMP</td>
</tr>
<tr>
<td>#1305, N polar</td>
<td>HVPE+CMP</td>
</tr>
<tr>
<td>#1412-3, Ga-polar</td>
<td>HVPE+CMP</td>
</tr>
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<td>MOCVD</td>
</tr>
<tr>
<td>#1937</td>
<td>MOVPE+SA G</td>
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Table 1: Overview of GaN surfaces used in this study.
Chapter 2 : Topography and Morphology

2.1 Motivation and Background

While GaN growth techniques have improved over the past few decades, GaN surfaces are still limited in their performance by a high density of structural defects which terminate at the surface and negatively affect device performance by acting as centers for non-radiative recombination or as current leakage sites. To improve upon the performance of epitaxial growths and associated GaN materials, high-quality substrates are continuously being sought. HVPE growth of GaN on sapphire substrates followed by a laser lift-off (LLO) of the film is one of a handful of growth methods currently being used to produce bulk, monolithic GaN crystals. However, N-polar surfaces exposed by the LLO process are not ideal as they are typically plagued by near-surface structural damage and chemical impurities arising from polishing / planarization processes which are employed to circumvent near-surface (~50 nm into the bulk) structural damage caused by the LLO procedure. However, these polishing techniques are still not completely effective at producing “atomically-flat” N-polar surfaces. For example, investigation into LLO-exposed N-polar layers prepared by MOCVD and using a KOH-based CMP treatment revealed that a 2-5 nm-thick amorphous oxygen-containing material was present at the GaN/air interface. By using cross-sectional transmission electron microscopy (TEM), it was observed that structural and chemical modifications do occur to N-polar surfaces as a result of the LLO process, although these effects are thought to be confined to the first ~50 nm into the bulk. A representative image of such an LLO + polished N-polar surface is shown in Figure 2.1. For the bulk, N-polar surfaces studied here, the CMP or MP polishing procedure was safely extended beyond 50 nm such that effects from the LLO procedure are presumably negligible for these samples.

N-polar GaN growth techniques have been the subject of much discussion, namely due to the increased chemical reactivity of this orientation, which would imply an improved performance in regard to sensing devices versus their Ga-polar counterparts. Aside from the HVPE + LLO method of obtaining N-polar GaN surfaces, high-quality N-polar GaN growth on
sapphire has been realized by employing, for example, a mis-oriented sapphire substrate (where defect densities are effectively reduced by growth on a 4° offcut of the sapphire substrate) or by exposing the substrate to high nitrogen precursor fluxes. Molecular beam epitaxy (MBE) has also produced smooth N-polar GaN surfaces, but with two caveats: 1) HVPE-grown, LLO N-polar GaN was used as a substrate for the N-polar growth, and 2) that high-quality crystal growth was obtained at substantially higher temperatures than are typically used for similar deposition procedures. For samples presented in this report, the MOCVD-grown N-polar GaN surfaces are qualitatively similar to ones observed by Weyher et al. using MOCVD growth on an underlying HVPE substrate. The similarity of N-polar surfaces morphology presented here and those presented in the literature are remarkable, as it illustrates that N-polar GaN samples grown by MOCVD possess similar surface features, where hexagonal (and truncated hexagonal) pyramids populate the surface. An example image of one such N-polar surface reported in the literature is presented in Figure 2.2. While theoretical and experimental studies have shown that the N-polar surfaces are more chemically active than Ga-polar ones, the knowledge base in regard to acid etching behaviors on N-polar GaN is quite lacking. Wet etching characteristics of Ga- and N-polar GaN have been investigated in some capacity, although again, Ga-polar GaN is overwhelmingly the focus of such studies. Indeed, strong bases (KOH) and acids (H₃PO₄) have since been observed to selectively etch N-polar GaN, but leave Ga-polar GaN largely unaffected.

Our studies evidenced distinct surface morphologies between N-polar surfaces prepared by the LLO + polishing technique (bulk, polar GaN) and MOCVD-grown N-polar surfaces (patterned, polar GaN). We have observed that on patterned, polar GaN, grain texture and step morphology differs significantly between Ga- and N-polar orientations, such that the surface polarity for these samples may be identified through AFM characterization alone. Additionally, we have observed preferential etching of N-polar GaN by treating the patterned, polar GaN surface with an HCl solution, whereas adjacent Ga-polar areas remain largely unaffected by the acid treatment.
2.2 Findings from AFM Topography Studies

**Bulk GaN (Kyma)**

*Figure 2.3* shows representative surface topographies for the as-received GaN samples, with N-polar surfaces in the left-hand column and Ga-polar surfaces in the right-hand column. The N-polar surfaces have a larger root mean square (rms) roughness and a higher density of surface scratches as compared to the Ga-polar surfaces. Further, the CMP treatment appears to be more effective at planarizing the surface, resulting in the CMP-treated Ga-polar surfaces (*Figure 2.3* (b, d)) having the lowest rms values (<1 nm) as compared to the MP-treated N-polar surfaces (*Figure 2.3* (c)), which were observed to have the highest rms values (>8 nm). The morphology of the Ga-polar surfaces is quite distinct for the two surface treatments, with characteristic hexagonal pits (~400 nm in diameter) on the CMP-treated surfaces, and step bunches on the MP-treated ones (~700 nm wide, several micrometers long).

We also examined the effects of an HCl cleaning on the as-received surfaces (*Figure 2.4*). Only the MP-treated Ga-polar surface demonstrated any significant change in topography after cleaning. The step bunches appear to be etched and result in a high density of protrusions (~50 nm in diameter, ~5 nm in height) on the surface. While these observations were mostly elucidated, it remains unclear as to why the MP-treated Ga polar surface exhibits such changes when cleaned with HCl while the other surface types show minimal change after similar cleaning. As observed in subsequent HCl-based surface cleaning process conducted on the patterned, polar GaN samples (see below), N-polar regions were preferentially etched as opposed to Ga-polar regions, which demonstrate little to no response to HCl cleaning.

*Patterned polar GaN (NRL)*

The patterned, polar GaN samples offer a rich morphological environment by which several characteristic surface behaviors are seen between surface orientation (Ga- vs N- polar) and between type of template (HVPE vs. MOCVD) used for the epilayer growth. The morphologies of these samples have also been previously characterized by scanning electron microscopy
(SEM) and demonstrate distinct differences between the two types of templates, as was observed in these studies. Ga-polar regions, which were smoother overall versus N-polar regions, also show distinct terracing behavior. These surface features likely form as a result of the underlying surface morphology. While N-polar MOCVD growth is observed to be rough through optical microscopy (surface features in the micron regime), the HVPE template (Kyma, CMP-treated N-polar GaN) used for the #612-H sample growth represents a surface whose roughness is in the tens of nanometer regime (see Figure 2.3 (a, c)). Similar homoepitaxial growth of N-polar GaN on HVPE-grown substrates shows comparable morphological characteristics. SEM studies performed on those surfaces indicate hexagonal features 10-50 μm in diameter which were observed at a density of $10^5$ cm$^{-2}$. Representative images of N-polar surfaces grown by Weyher et al. are presented in Figure 2.2, and bear striking similarity to N-polar surfaces studied here as the surface is similarly populated by hexagonal hillock formations. For samples used in this study, a slightly lower density of such features ($5\times10^4$ cm$^{-2}$) was measured on the large contiguous N-polar region present on the #1208-M sample.

Optical microscope images presented in Figure 2.5 (a-f) show representative areas for each surface and illustrate key morphological differences evident at the microscopic level. AFM images of the epilayer on the #1208-M sample presented in Figure 2.5 (e, f) are indicative of the most apparent distinction between the Ga- and N-polar surface morphology. Here, terracing behavior considerations alone were sufficient to correctly identify the surface orientation: Ga-polar surface features tend to follow circular terracing formations, whereas N-polar regions are dominated by hexagonal terracing formations. While the Ga-polar region Figure 2.5 (e) does contain some structures which do suggest a hexagonal base, it is assumed that this is due to underlying hexagonal pyramids on the MOCVD-grown N-polar substrate; subsequent Ga-polar epilayers grown on top must conform to the template, but eventually are able to form the preferential, disc-like formations.

For the smoother N-polar template used for the #612-H sample, epilayer growth shows much more consistent stripe growth than on the #100430-M sample. Here, smooth Ga-polar stripes are separated by apparently trenched N-polar regions which during growth, conform to the faster Ga-polar growth at the IBD between the stripes. A topographic image and
cross-section data for a representative area of the #612-H sample are presented in Figure 2.6 (a) and Figure 2.6 (b) respectively. Here, Ga-polar regions are approximately 300 nm higher than the trough of the N-polar regions, ascertaining that Ga-polar growth is faster and is contained vertically within the stripe pattern, as opposed to any evidence of undesired lateral overgrowth (which was not observed anywhere during the course of study).

Confined growth within the patterned stripe was also evident on the comparatively rougher MOCVD template, even as the substrate was much more morphologically rich. On the #100430-M sample, it was observed that the epilayer growth resulted in stripes with fractured, complex surface morphology, as illustrated in Figure 2.7 (a) and Figure 2.7 (b). Again, it is evident that N-polar growth regions conform to the presumably higher Ga-polar growth rates during simultaneous epilayer growth and result in an apparent trenching of the N-polar stripes, although the template is not categorically “flat” as was the case for the #612-H sample.38 Within N-polar regions on the #100430-M sample, characteristic step edges containing hexagonal, terraced steps are formed. For the contiguous Ga-polar box on the #1208-M sample, vertical features along the IDB are generally too large for AFM investigation (> 7 μm). A representative AFM image at the interface between the Ga- and N-polar regions grown on the #1208-M surface is shown in Figure 2.8 (a). As indicated by the corresponding cross-section (Figure 2.8 (b)), the IBD demonstrates a vertical change of over 1 μm between the higher, flat Ga-polar region and the beveled, conformal N-polar region.

To compare surface roughness, rms values were obtained for several 10 × 10μm² regions on each surface type. Ga polar regions for the #612-H sample are significantly smoother (rms = 2 nm) than those on the #100430-M sample (rms = 15 nm). N polar growths on the #612-H (Figure 2.6) and on the #100430-M (Figure 2.7) samples both have calculated rms values of around 50 ± 20 nm.

After HCl cleaning, Ga-polar regions showed no observable change in morphology, while small hillock formations (~50-100 nm wide, ~5-15 nm tall) populate the N-polar surfaces, suggestive of a preferential etching at the N polar surface as illustrated in high-resolution 3-D perspective images in Figure 2.9 taken on the #612-H sample. These images illustrate the roughening effect on N-polar regions due to HCl cleaning in contrast to the veritably unchanged
morphology of the Ga-polar regions in agreement with HCl cleaning characteristics for polar GaN (e.g., Ref. 39) Here, HCl cleaning led to decreased Ga-polar rms values (changes of less than ~10%), while N-polar regions indicated a ~50% increase in surface roughness (~75 nm vs ~50 nm) versus the as-received condition. As shown in Figure 2.9 (b), the protrusions populate the entire N-polar surface; these features were too small to accurately characterize their morphology or structure via AFM. Similar nanostructures resulting from acidic cleaning processes on patterned, polar GaN samples have been observed after phosphoric acid (H₃PO₄) treatment and were proposed to be dodecahedral pyramids as suggested by SEM image analysis on the H₃PO₄-cleaned, N-polar surface. However, GaN is generally considered to be immune to etching by HCl, yet we have seen clear evidence that for N-polar GaN, some degree of etching occurs.

Interestingly, the bulk, polar GaN samples did not demonstrate the same degree of etching behavior; it is unclear as to whether the bulk, polar N-polar HVPE surface is in fact far less susceptible to etching, or if a consistent etching rate was present such that changes in morphology were not as discernible as changes which were observed on the patterned polar surfaces. A 3-D perspective of the interface boundary presented in Figure 2.9 shows a magnified view at the interface boundary for the as-received versus HCl-cleaned surface for the epilayer grown on the HVPE substrate. As is evident in the two images, preferential roughening (i.e., etching) of the N-polar regions occurs, whereas Ga-polar regions do not. Interestingly, rms roughness values did not significantly change on either Ga- or N-polar surfaces after the surface treatment. This may be due to the large sample area (10×10 μm²) used for calculation combined with competing factors which affect the calculated rms roughness.

Patterned semipolar GaN (SUNY)

Figure 2.10 (a) depicts a large-scale AFM image of the #1937-S sample comprising various microstructures resulting from SAG mask patterning, while Figure 2.10 (b) is a magnified image of a representative hexagonal structure, the type of which was investigated during these studies. These intentionally grown hexagonal pyramid features are ~1.0-1.2 μm tall, with sidewalls corresponding to ~60° off the horizontal, suggesting that the facets are semi-polar {1101} with c-plane mesas. However, higher-resolution images show that the sidewalls contain 5-20 nm tall
steps and ~50 nm terraces, representing non-contiguous facets which are ultimately sought for these types of growths. This observation indicates that the semi-polar growth of the sidewalls is a combination of c-plane terraces and semi-polar facets which form beveled steps between the terraces. A report by the group which prepared the samples contains 

\textit{ab initio} calculations in regard to the ideal growth conditions.\textsuperscript{30} Ideally, these non-equilibrium facets may should complete, smooth semipolar sidewalls versus the step-terrace behavior seen in AFM studies. It should also be noted that the growth rates of individual facets vary depending on growth conditions, where “ideal” conditions were used to prepare the GaN facets investigated here.\textsuperscript{30} Conclusively, hexagonal structures were successfully grown, yet the complete semi-polar faceting on the sidewalls was not realized.

\subsection*{2.3 Concluding Remarks}

One particular inquiry which was further elucidated was in regard to the preferential etching behaviors of N-polar surfaces. Here, we find apparently conflicting results: for the bulk HVPE samples, only MP-treated, Ga-polar surfaces displayed any morphological response to HCl etching, whereas on the laterally patterned epilayer samples, N-polar surfaces indicated very clear and discernable preferential etching. The small protrusions which populated each HCl-treated surface (MP, Ga-polar and patterned N-polar) were similar in size (~50 nm in diameter) and height (5-10 nm tall). We may argue that small GaN material may have been rearranged on the surface during the MP polishing process, much like ball milling processes. Indeed, ball milling of GaN in oxygen atmospheres has produced Ga$_2$O$_3$ nanoparticles of 20-50 nm,\textsuperscript{40} similar to the size of the particles observed in \textbf{Figure 2.4} and \textbf{Figure 2.9}.

The patterned, polar GaN samples indicated that there is a clear preferential etching for N-polar regions, which agrees with the general consensus of experimental and theoretical reports in the literature. Unfortunately, the MP surfaces that were used (#1412-2, #1412-3) were etched with a reactive ion etch (RIE) before additional measurements were taken, such that additional, similarly MP-polished surfaces were not available. In practice, MP polishing techniques would not be employed, as they were shown to be of an overall inferior quality to CMP-treated surfaces.
In summary, we have used AFM to compare several types of GaN surfaces, namely Ga- and N-polar and surfaces with different surface treatments (MP- or CMP-polished, as-received or HCl-cleaned). N-polar surfaces prepared by LLO and subsequent polishing (MP- or CMP-treated) had significantly higher rms roughness values compared to epitaxially-grown Ga-polar surfaces with similar surface treatments. Structural damage near the N-polar surface caused by the MP / CMP treatment is attributed to this observed surface roughening. MOCVD-grown epitaxial layers of patterned Ga-polar and N-polar regions as well demonstrate that Ga-polar surfaces are smoother by about one order of magnitude, and evidence the faster growth rates of Ga-polar GaN. Finally, HCl treatments on the sample set give mixed results, with MP-treated Ga-polar GaN being exclusively affected within the bulk, polar, HVPE-grown sample set. Here, the lower-quality MP-treated surface may allow for increased near-surface reactivity; additionally, N-polar surfaces may have been homogenously etched, but not observable through AFM imaging in the post-treated condition. For the laterally-patterned GaN surfaces, however, similar HCl treatment applied to these samples shows a clear preferential etching of N-polar regions, while Ga-polar regions are unaffected.
Figure 2.1: Cross-sectional TEM image of the N-polar GaN surface after laser lift-off procedure. Image taken from Ref. [34].

Figure 2.2: (a) Optical micrograph of MOVCD-grown N-polar GaN depicting hexagonal pyramid formation on the surface (scale not given) and (b) SEM image of hillock formations including “pointed-top” (H_p), “flat-topped” (H_f) and “disrupted” (H_d) hillock formations. Images taken from Ref. 33.
Figure 2.3: AFM topography of (a) N-polar and (b) Ga-polar surfaces with CMP treatment (#1305). (c) N-polar surface with MP treatment and (d) Ga-polar surface with CMP treatment (#1412-3). (e) N-polar surface with CMP treatment and (f) Ga-polar surface with MP treatment (#1412-4). Images (a), (c), and (e) use color scales of 20 nm; images (b), (d) while (f) use color scales of 5 nm.
Figure 2.4: AFM topography of (a, b) as-received Ga-polar, MP-treated surface (#1412-4) and (c, d) the same surface after HCl cleaning showing a high density of protrusions (color scale for all images = 10 nm).
Figure 2.5: Optical (CCD) images of Patterned GaN samples, showing (a) patterned GaN stripes grown on an N-polar, HVPE-grown GaN template (#612-H) and (b) magnified view. (c) Corner of growth region for similar patterning for GaN stripes grown on N-polar MOCVD substrate (#100430-M) and (d) magnified view, and (e) the corner of a 5×5 mm² Ga-polar region grown on an N-polar MOCVD substrate (#1208-M) and (f) magnified view.
Figure 2.6: (a) Topography (75×75 µm², color scale = 1 µm) and (b) cross-section for polar GaN growth on HVPE substrate (#612-H).

Figure 2.7: (a) Topography (75×75 µm², color scale = 1 µm) and (b) cross-section for polar GaN growth on MOCVD substrate (#100430-M).
**Figure 2.8:** (a) Topography (30×30 µm², color scale = 2 µm) and (b) cross-section for polar GaN growth on an MOCVD substrate (#1208-M).

**Figure 2.9:** (a) 3-D perspective image at interface domain between Ga- and N-polar regions for the as-received surface and (b) HCl-cleaned surface on laterally patterned GaN (#612-H). Color scale is approx. 200 nm.
Figure 2.10: (a) Topography (50×50 µm², color scale = 1.5 µm) of GaN microstructures grown on sapphire (#1937-S) by selective area growth and (b) cross-section. (b) Magnified perspective view (7×7 µm², color scale = 2 µm) of a typical hexagonal pyramid structure along with (d) cross-section.
Chapter 3: Local Conductivity

3.1 Motivation and Background

Localized conductivity at the GaN surface is of increasing importance, especially in regard to detrimental reverse bias leakage sites. For high-power applications, these leakage sites lead to the failure of devices. CAFM has been used to investigate current leakage sites in GaN grown by molecular beam epitaxy (MBE), and has correlated these sites to local topological features such as screw, edge, and mixed-type threading dislocations.\(^{41}\) CAFM studies of GaN performed within our group found that ~10\% of defective hillock formations are active leakage paths for applied voltages up to +12 V. Here, MBE-grown epilayers on MOCVD-grown GaN templates demonstrated reverse bias leakage site at ~50\% of these hillock dislocations at higher applied voltages (\(V_S \sim +25\) V), and indicated that at these higher bias regimes, pure screw-type dislocations may not be solely responsible for reverse current leakage.\(^{42}\) Another study examined current leakage in a-plane GaN grown by epitaxial layer overgrowth (ELO), where it was definitely shown that the leakage was significantly higher in the “window” vs. “wing” regions.\(^{43}\) In this study, CAFM is used to contrast and compare the local surface conductivity behavior between Ga- and N-polar regions. With increasing interest in N-polar material for device applications such as flip-chip LEDs, the characterization of local conductivity is of interest.

Laterally-patterned, polar GaN samples studied elsewhere have demonstrated higher conductivity for N- versus Ga-polar regions.\(^{44}\) Using secondary ion mass spectrometry (SIMS), preferential oxygen incorporation in the N- vs. Ga-polar material was shown to preferentially increase the free carrier density. Since oxygen acts as a shallow donor in \(n\)-type GaN, the authors speculate that this is the likely cause for the higher observed conductivity in the N-polar regions.\(^{44}\) Similarly-grown samples are studied in this investigation (\(i.e.,\) patterned, MOCVD-grown epilayers on “epi-ready” templates), and presumably contain comparable impurity levels. Thus, we may expect significant differences in the Ga- and N-polar conductivities, where it has been observed that N-polar GaN incorporates ~400 times more oxygen (donor species) than adjacently-grown Ga-polar GaN. Additional studies on laterally-patterned polar GaN have demonstrated that current conduction is not hindered by the presence of interface domain
boundaries (IDB). This result is relevant to our patterned polar GaN samples which have such IDBs between the Ga- and N-polar regions, as we thus expect to see markedly higher forward- and reverse-bias conduction at the IDBs for the patterned, polar sample set.

3.2 Findings from CAFM Studies

*Bulk GaN (Kyma)*

N-polar surfaces from the bulk GaN were found to be largely insulating at both bias voltages, where maximum current signals on the order of 1 nA were detected only at large forward bias voltages ($V_s = -10$ V). Figure 3.1 illustrates that conducting areas on the #1305 N-polar surface (dark regions in Fig. 3.1b) are exclusively located away from scratch or ridge features formed during polishing. For Ga-polar bulk GaN surfaces, the expected diode-like behavior was observed uniformly on the surface. Reverse-bias current leakage sites were not resolved for either surface orientation, although such sites have been seen for MBE- and ELO-grown GaN surfaces. Local current-voltage (I-V) spectra presented in Figure 3.2 reveal that the Ga-polar surface has a lower turn-on voltage than the N-polar surface ($V_s = -3$ V vs. -8 V, respectively). These findings on this sample are in contrast to predicted behaviors obtained via density functional calculations, which suggest a lower surface barrier for N-polar GaN. Additionally, several other experimental reports have verified a higher conductivity for N-polar GaN surfaces. The surface treatment (CMP or MP) had little effect with regard to CAFM behavior for N-polar GaN; however, the CMP-treated Ga-polar surface shows a substantially lower turn-on voltage (-1.5 V cleaned versus 3 V as-received) and increased conduction after HCl cleaning, presumably due to the removal of a surface oxide. Again, for this sample set the observed higher conductivity on the Ga-polar surfaces is unexpected, although damage induced by the LLO treatment and subsequent polishing (MP or CMP) may play a significant and detrimental role in the surface conductivity of N-polar GaN, while epitaxial Ga-polar surfaces on the freestanding bulk samples are comparably more conductive.

*Patterned polar GaN (NRL)*
A clear distinction in local conductivity was observed between Ga- and N-polar areas on the patterned polar GaN surfaces grown on both template types (HVPE and MOCVD). In contrast to the bulk N-polar GaN discussed in the previous section, N-polar areas on the patterned samples demonstrate a more ideal diode-like behavior. In forward bias (Figure 3.3 (b), sample #612-H), N-polar regions are more conductive than Ga-polar ones for the same sample bias of -4 V. In reverse bias (Figure 3.3(c)), a small but detectable current of ~25 pA (at +4 V) was measured exclusively within Ga-polar areas. However, current leakage of 2 to 3 nA occurs at step edges within N-polar regions, where it may be that these steps are semipolar facets, or due to significant tip-sample interaction leading to higher observed current signals. The increased conduction behavior of semipolar regions is in fact consistent with studies that suggest a more electrically active behavior for crystallographic orientations inclined away from the c-plane, and are in reasonable agreement with studies that suggest an enhancement of field emission for GaN nanowires comprising non-polar facets. At reverse bias regimes of over a +5V bias, N-polar areas show increased CAFM signals on the order of ~100 pA. In contrast to N-polar bulk surfaces prepared by LLO + polishing, the Schottky barrier height (SBH) of these N-polar samples appears to be lower than those of the Ga-polar regions, consistent with predictions by Zyweitz et al. A higher crystalline quality near the surface on these N-polar regions versus the LLO-prepared ones may also account for the observed higher conductivity. As the samples were not subjected to polishing, it is a reasonable to assume that these N-polar surfaces are of a higher quality than the bulk, LLO + polished ones, and are more representative of the N-polar GaN behavior.

It has been previously reported that when performing CAFM under high voltages that electrochemical reactions can occur in the tip-sample regions due to environmental oxygen, presumably leading to the formation of an insulating oxide. These findings were limited to Ga-polar surfaces, but are in agreement with our results (as presented for the #612-H sample) in Figure 3.4 (b). After scanning once in reverse bias (+4 V), a larger scan at the same bias voltage was obtained, and a clear decrease in the current signal was observed in the Ga-polar region which had been previously scanned. These data support the claim that an oxide was grown in the Ga-polar region, thereby decreasing the local surface conductivity. The conducting behavior in
the N-polar region remains unaffected, indicating that an oxide layer already exists in this area. For reference, the local electric field at the AFM tip/sample interface is on the order of 1 to 10 MeV/cm², such that dielectric breakdown of the interfacial oxide is possible, as suggested for β-Ga₂O₃ oxide species which are reported to have a breakdown field of 3.6 MeV/cm².⁴⁹ The conduction behavior of the N-polar regions was substantially affected by the HCl cleaning procedure which removes the surface oxide. As presented for sample #612-H in Figure 3.5, forward-bias current values dramatically increased to beyond current detection ranges (±10 nA) at a -4 V bias for the N-polar regions (Figure 3.5 (b)), and also demonstrated substantial reverse-bias leakage (Figure 3.5 (c)). The conduction behavior in the Ga-polar regions showed little effect after HCl cleaning, and is consistent with the removal of a surface oxide preferentially found in the N-polar regions.

*Patterned semipolar GaN (SUNY)*

In the case of the patterned semipolar GaN samples, the very tall (1 μm) microstructures limit the accessibility of SPM characterization; the high approach angle (60° off of the horizontal) also leads to limited confidence with regard to CAFM signals at or near the semipolar facets. For contact-mode AFM used in CAFM, these structures caused frequent tracking errors and therefore did not produce reliable data. As the growth techniques for non-equilibrium structures is refined, one may envision that size reduction of the microstructures will allow for more favorable sample geometries in terms of SPM characterization.

### 3.3 Concluding Remarks

CAFM data between the bulk, polar GaN and the patterned polar GaN samples gave conflicting results. While N-polar surfaces in the bulk GaN sample set suggest high degrees of insulating behavior, N-polar stripes in the patterned polar GaN sample set showed remarkably higher conduction. In addition, CAFM studies on Ga-polar surfaces revealed opposing behaviors, where for Ga-polar surfaces of the bulk GaN sample set were uniformly conducting. However, for the heteroepitaxially-grown Ga-polar stripes on the patterned polar GaN sample set, lower conductivity versus adjacent N-polar stripes was observed. We explain these observations by
again noting that the bulk, N-polar surface quality is inferior to that of the patterned N-polar surfaces.

HCl cleaning of the surfaces in all cases correlated to improved conductivity behaviors for both sample sets, as evidenced by I-V spectra for Ga-polar surfaces (bulk, polar sample set) and by CAFM images for N-polar stripes on patterned, polar GaN. In both cases, higher CAFM signals were observed with similar biases applied after HCl cleaning. This suggests that an insulating surface oxide layer was likely removed by the HCl. As will be discussed in subsequent chapters, the surface oxide is preferentially grown on N-polar surfaces, thus explaining the insulating behavior for low-reverse bias regimes, while the presumably less prominent oxide formed on the Ga-polar surface shows increasing insulating behaviors as CAFM scans are performed sequentially. This effect is likely due to an electrochemical oxidation of the surface while scanning in CAFM mode, which catalyzes growth of the insulating oxide through a high electric field between the AFM tip and the GaN surface.

In summary, CAFM was used to investigate the conductivity behaviors of several GaN surface types. It was confirmed that N-polar areas are more conductive than Ga-polar ones, although detrimental polishing techniques and preferential oxide growth at this surface strongly affect local conductivity behaviors. In addition, CAFM scanning was shown to influence the conductivity behavior, as an electrochemical oxidation occurs during CAFM scanning and subsequently decreases the observed current signal. Therefore, attention must be paid while investigating GaN surfaces via CAFM, as GaN surfaces are subject to surface oxide growth, and that conductivity measurements for GaN surfaces should be taken on freshly-cleaned surfaces as to minimize the influence of the surface oxide.
Figure 3.1: (a) AFM topography of N-polar, CMP-treated surface (#1305, color scale = 15 nm) and (b) simultaneous C-AFM current image in forward bias ($V_S = -10$ V, color scale = 30 pA).

Figure 3.2: CAFM I-V spectra of Ga- (red) and N-polar (blue) surfaces of the CMP-treated bulk polar sample (#1305).
Figure 3.3: (a) Topography at interface boundary (30×15 µm², color scale = 300 nm) of polar GaN growth on HVPE substrate (#612-H). Corresponding C-AFM images under (b) -4 V forward bias (color scale = 650 pA) and under (c) +4 V reverse bias (color scale = 50 pA).
Figure 3.4: (a) Topography at interface boundary (40×40 µm², color scale = 300 nm) of polar GaN growth on MOCVD substrate (#100430-M). (b) Corresponding CAFM image (40×40 µm², scale = 40 pA) taken immediately after previous CAFM scanning within a smaller area (dotted box) at same bias voltage (+4 V) for both scans.
Figure 3.5: (a) Topography (25×15 μm², color scale =1 μm) of HCl-cleaned GaN surface (#612-H, color scale = 900 nm) and CAFM images (b) under -4 V forward bias (color scale = 25 nA) and (c) under +4 V reverse bias (color scale = 10 nA).
4.1 Motivation and Background

The scanning Kelvin Probe microscopy technique was developed as a non-destructive technique in order to measure the surface contact potential on the sub-micron scale. In 1991, Nonnenmacher et al. reported the successful simultaneous mapping of the topography and surface potential of several metals (Au, Pt, Pd) using an AFM setup. This first study resolved the local surface potential difference between two materials on a common surface, e.g., a difference of 0.065 eV between Pd and Au films. In a similar manner, SKPM studies in this work provide valuable information regarding the surface potential differences between the Ga- and N-polar orientations on patterned GaN, with values up 0.5 eV observed. Semipolar facets on GaN microstructures were also investigated and showed discernible surface potential differences of 0.15 eV between c-plane mesas and sidewalls. SKPM studies on bulk surfaces provided little useful information, where local potential variations on these samples were typically within SKPM noise levels (0.02 eV).

As suggested by its name, SKPM is closely related to the Kelvin probe technique, which uses an electrical circuit to measure the surface potential vs. a local force-sensing method for SKPM. Another difference between the techniques is the significantly larger probe size for Kelvin probe (~1 cm$^2$) as compared to the nanometer-scale contact area of the SKPM probe (~400 nm$^2$). Current state-of-the-art SKPM spatial resolution has demonstrated surface potential variations for individual pentacene ($C_{22}H_{14}$) molecules. In this work, a CO molecule was attached to the apex of the AFM tip, thus enabling the functionalized tip to probe the surface with atomic resolution. Additionally, these images were obtained in cryogenic conditions (5 K) in ultrahigh vacuum as to minimize thermal fluctuations and environmental effects. In these studies, SKPM experiments are carried out in air ambient at room temperature, thereby limiting spatial resolution to approximately ~400 nm$^2$.

In SKPM, the measured surface potential can be quite sensitive to environmental effects such as water adsorption. We have observed variations of ~0.2 eV on a gold foil reference periodically measured over the course of several days, in agreement with variations of ~0.15 eV.
seen elsewhere. For the GaN surface, storage in ambient can lead to changes in the surface potential due to surface oxide growth. To remove this oxide, we have used HCl treatments and have investigated subsequent changes in the surface potential. Also, we have seen that the N- vs. Ga-polar regions preferentially grow a thicker surface oxide. It should be noted that the difference in surface contact potential between the two polarities indicates the difference in band bending for these two orientations, where the electron affinities $\chi_{\text{GaN}}$ are presumed to be quite comparable. In practice, band bending values are more accurately obtained using a Kelvin probe apparatus in a controlled environment, which was not possible in the SKPM setup. Regardless, valuable information with respect to variation in the local surface potential was readily obtained by SKPM with $\sim 0.025$ eV nominal resolution.

Surface potential studies on polar GaN surfaces have shown a range of values for the band bending between Ga- and N-polar surfaces, ranging from 0.05 to 3.4 eV. Key results from a variety of studies is presented in Table 2. These values utilize other techniques to measure surface potential or band bending such as scanning electron microscopy and photoelectron spectroscopy. In all of these studies but one, the N-polar surface was reported to have a more positive surface potential versus the Ga-polar. In addition to the reported differences between Ga- and N-polar GaN surface potential values, one study using SKPM on MBE-grown GaN nanostructures containing semi-polar sidewalls showed slight surface potential increases of around 0.04 eV compared to the surrounding Ga-polar substrate. Similar experimental studies regarding comparison between polar and semi-polar GaN surfaces are lacking. In this chapter, such studies are conducted in order to better understand local surface potential behaviors for different GaN surface orientations including Ga-polar, N-polar, and $\{1\bar{1}01\}$ semipolar surfaces.

### 4.2 SKPM Theory

SKPM is a microscopy technique that enables direct measurement of the local surface potential by measuring the electrostatic force between the probe with an applied voltage and the surface. Ultimately, a DC voltage is applied to the probe in order to zero the contact potential difference (CPD) between the probe and sample surface (see Figure 1.2). Here, the contact potential difference is defined as
where $\phi_{tip}$ and $\phi_{GaN}$ are the work functions of the tip and the GaN sample respectively, and $e$ is the electronic charge. By convention, $\phi_{GaN}$ is defined as the difference between the vacuum energy level and the Fermi level of the semiconductor. The SKPM technique determines $V_{CPD}$ (reported in $eV$ for simplicity) by applying a combination of DC and AC voltages to the tip to nullify the electrostatic force between the tip and sample through a negative feedback loop scheme. Here, a time-dependent voltage is applied to the tip and is of the form

$$V_{tip} = V_{DC} + V_{AC} \sin(\omega t).$$

(4.2)

In the $z$-direction normal to the sample surface, the electrostatic force $F_E(z)$ between the tip and sample is expressed in the first approximation by a capacitor plate system, such that

$$F_E(z) = -\frac{1}{2} V^2 \frac{dC_z}{dz},$$

(4.3)

where $\frac{dC_z}{dz}$ is the gradient of capacitance in the $z$-direction and $V$ is the total difference between the CPD and the voltage applied to the tip, i.e.,

$$V = V_{tip} - V_{CPD} + V_{AC} \sin(\omega t).$$

(4.4)

By convention the DC bias is applied to the tip, thus prescribing the difference between $V_{CPD}$ and $V_{tip}$. By substitution of Eq. (4.4) into Eq. (4.5), the resulting electrostatic force between the tip and sample is

$$F_E(z, t) = -\frac{1}{2} \left( V_{DC} - V_{CPD} + V_{AC} \sin(\omega t) \right)^2 \frac{dC_z}{dz}. $$

(4.6)

Carrying out the differentiation and using the half-angle identity for the $\sin^2(\omega t)$ term, the re-written electrostatic force,

$$F_E = -\left( \frac{V_{DC}^2}{2} - V_{DC} V_{CPD} + (V_{DC} - V_{CPD}) V_{AC} \sin(\omega t) + \frac{V_{AC}^2}{4} (1 - \cos(2\omega t)) \right) \frac{dC_z}{dz}, $$

(4.7)

may be expressed in terms of one DC and two distinct AC ($\omega, 2\omega$) components which can be analyzed separately:

$$F_{DC} = -\left( \frac{V_{DC}^2}{2} - V_{DC} V_{CPD} + \frac{V_{CPD}^2}{2} \right) \frac{dC_z}{dz} = -\frac{1}{2} \left( V_{DC} - V_{CPD} \right)^2 \frac{dC_z}{dz}, $$

(4.8)
\[
F_\omega = -(V_{DC} - V_{CPD}) V_{AC} \sin(\omega t) \frac{dC_i}{dz}, \quad (4.9)
\]

and
\[
F_{2\omega} = - \frac{1}{4} V_{AC} (1 - \cos(2\omega t)) \frac{dC_i}{dz}. \quad (4.10)
\]

As is apparent in Eq.(4.8), the force component at the resonant frequency of the tip \(f_{tip}\) corresponding to the angular frequency \(\omega = 2\pi f_{tip}\) is exactly zero when the applied DC bias is equal to the CPD between the tip and sample. Thus, through a lock-in feedback loop applying an appropriate DC bias to the tip, the \(F_\omega\) component is “zeroed” such that the output signal of the is minimized and the applied voltage to satisfy this condition is, by default, equal and opposite to \(V_{CPD}\).

To maximize throughput, a two-pass technique is utilized by the SKPM for each line in the image, where the topological profile of the scan line is recorded in the first pass. The profile is re-traced in the second pass as to maintain a constant distance (here, \(d = 80\) nm) from the surface while \(V_{CPD}\) is determined at each sample point. It should be noted that while the DC force component results in mechanical deflection of the AFM tip and is otherwise inconsequential to investigate, the \(F_{2\omega}\) component may be coupled to the lock-in amplifier to determine differential capacitance across sample surfaces - the so-called scanning capacitance microscopy (SCM) technique.

### 4.3 Findings from SKPM Studies

**Patterned polar GaN (NRL)**

Local surface potential studies on the patterned polar GaN samples showed clear but uncorrelated surface potential differences between the Ga- and N-polar regions grown on the two differing substrate types (HVPE and MOCVD). For the HVPE substrate, SKPM images obtained near the edge of the epitaxial growth region on the #612-H sample (Figure 4.1) illustrates Ga-polar regions which were consistently lower in surface potential (more negative surface charge) than N-polar ones by \(\sim 0.5\) eV (Figure 4.1 (c)), with changes in the surface potential at the IDB evidently taking place across microns. While spatial resolution of the SKPM was initially believed to be responsible for the gradual change of the surface potential signal across
the IDB, studies conducted elsewhere have suggested that the change in the local surface potential at GaN inversion domain boundaries should indeed occur over such distances, although the surface structure/morphological changes are highly abrupt (sub-Ångstrom/atomic scale).\(^{54}\)

Interestingly, the Ga-polar material demonstrated only slight contrast variation within individual stripes, while there were discernible variations within N-polar stripes. Specifically, surface potential variations within the scanned N-polar regions were \(-0.15\) eV, compared to \(-0.05\) eV within Ga-polar regions. These observations suggest a more complex local surface potential environment within the N-polar material than within the Ga-polar stripes. Judging from the topography associated with these surfaces, a more complete Ga-polar epilayer growth results in lower surface potential variation within individual stripes, whereas the complex and dynamic topographic environment present in N-polar regions are assumed to result in larger contrast variations in the local surface potential within the N-polar stripes. One such example of variation within the N-polar regions is present toward the bottom-right of Figure 4.1 (c).

In contrast to the consistency of surface potential behavior for the #612-H sample grown on the HVPE template, growth on the MOCVD template (sample #100430-M) results in inconsistent and unexpected behavior. As seen in Figure 4.2 (c), \(-0.2\) eV inconsistencies exist between sequential Ga-polar stripes and in the corresponding cross-section in Figure 4.2 (d). Here, surface potential values for Ga-polar regions were regularly observed to be higher than N-polar regions by between 0.1 - 0.25 eV, representing an unexpected behavior, as Ga-polar surfaces are expected to show lower surface potential values (more negatively-charged surface). This unexpected behavior was present on most areas of the sample. We propose that topographic effects during growth may significantly diminish the surface potential contrast between Ga- and N-polar regions grown on the MOCVD substrates, yet this is speculative. It remains unclear as to the source of this behavior, as the contiguous Ga-polar region formed on a similar template demonstrated the expected surface potential behavior in that Ga-polar surface potential values were 0.2-0.25 eV lower than the surrounding N-polar material, as presented in Figure 4.3.

A large defect structure (~75 µm diameter at base) on the surface of the sample using the MOCVD substrate shows a clear distinction for surface potential contrast and doubly for step growth behavior between the Ga- and N-polar regions (Figure 4.4 (a)). A 3-D rendering
illustrating topographic features superimposed with the color scale from the SKPM signal is presented in Figure 4.4 (c). The overlaying of the SKPM image, or “skin,” on top of the topography 3-D perspective view provides a clear correlation of surface polarity to topographic features, such that for an unknown GaN surface, one may analyze topographic and surface potential behaviors to quickly determine the surface polarity. For this particular structure, it is noted that the SKPM contrast is in the “correct” direction whereby N-polar areas show higher surface potentials. Again, for the growth on the MOCVD template, it was regularly observed that N-polar areas displayed lower surface potentials; this image illustrates that some areas of this sample do show expected behavior, and that further study beyond scanning probe methods must be employed to understand this discrepancy.

To further clarify the surface potential differences between Ga- and N-polar regions, SKPM was performed at the end, or “terminus,” of one Ga-polar stripes grown on the HVPE template, and is presented in Figure 4.5. This large hillock feature is of particular interest as it illustrates two key observations in regard to lateral growth and consequential surface potential behaviors. First, we have seen that at the center of the hillock, and as evidenced by the corresponding SKPM image (Figure 4.5 (b)), the faster Ga-polar growth during deposition results in faceting of the conformal, N-polar areas. Secondly, on highly inclined terraces formed on N-polar facets, correlative increases of ~0.15 eV were observed, evidencing that these facet orientations result in relatively higher surface potential values thus inferring lower band bending. This terminus feature, although an unwanted artifact of epilayer growth, sheds some additional light on growth behaviors of lateral polarity junctions between Ga- and N-polar GaN. For illustrative purposes, a 3-D rendering of the surface topography with the surface potential data superimposed on top of the topography is presented in Figure 4.5 (c).

In addition to Ga-polar material within N-polar regions, we have also observed the converse situation wherein a small N-polar inversion domain was observed slightly beyond the inversion domain boundary, as is shown in Figure 4.6. Here, the small inversion domain region (~250 nm diameter) exhibits an apparent localized field emission versus the surrounding Ga-polar environment. A local surface potential increase of ~0.15 eV compared to the surrounding N-polar field was observed at this feature. Such localized field effects stemming from these types
of features are of interest, as their behaviors may be exploited (formation of 2-D quantum dots) or unwanted (detrimental surface charging/leakage). Although further analysis of field effects from nanometer-scale inversion domains is beyond the scope of these studies, the presence and extent of field localization due to isolated and nanometer-scale inversion domains has been observed, although of little consequence to the focus of this study.

After initial characterization, the samples were cleaned with HCl, and in the case of the epilayer grown on the HVPE template, the resultant changes in surface potential in the post-HCl condition were apparent. Upon removal of the presumed surface oxide, the difference in surface potential signal between Ga- and N-polar was decreased from ~0.5 eV for the as-received condition to ~0.3 eV for the freshly-cleaned condition, as is shown in Figure 4.7. The change in surface potential contrast between the Ga- and N-polar surfaces after the cleaning procedure is believed to be predominantly due to the removal of a preferential oxide on the N-polar surface, which is to be expected as N-polar surfaces are more reactive than Ga-polar ones. It has also been reasoned that oxide growth on surfaces leads to a decreased band bending, which in the case of N-polar surface, causes larger differences in the surface potential contrast in the as-received (oxide-laden) condition. The larger expected band bending at the Ga-polar surface is arguably less prone to oxide growth due to an increased repulsion from negatively-charged species impinging the surface in ambient. As this is the case, the decrease of band bending as a thicker oxide is formed on the N-polar may have exacerbated the observed surface potential contrast across the IDB. However, upon removal of the oxide, the as-grown N-polar band bending is presumably restored, and thus a lesser degree of surface potential contrast is observed. With this in mind, we conclude that the presence of a well-established oxide on the N-polar regions leads to a corresponding increase of the surface potential (i.e., less negative surface charge) of ~0.2 eV. Upon removal of the oxide, e.g., via HCl cleaning, the N-polar surface is restored to its initial, as-grown condition.

Investigation of the epilayer grown on the MOCVD surface is in agreement with this conclusion, where differences between Ga-and N-polar stripes were less than 0.1 eV after HCl cleaning. Interestingly, the N-polar stripes on this sample still show lower surface potential values than adjacent Ga-polar stripes, which is still unexpected. Nevertheless, if the Ga-polar
GaN is appreciably less prone to oxide formation and thus is chosen as a “reference”, freshly-cleaned N-polar stripes are expected to exhibit a ~0.2 eV increase in surface potential as the oxide forms, and is in agreement with observations for the epilayer grown on the HVPE template.

Although the effects of the surface oxide are apparent for the N-polar regions, Ga-polar regions show little change in qualitative surface potential behavior. The growth and effects of surface oxides on Ga-polar GaN has been documented in previous studies,\textsuperscript{13,20} and to a lesser extent on N-polar GaN\textsuperscript{11} within the group. It stands to reason that the surface electrical environment on the Ga-polar stripes may also be affected by the growth of a surface oxide, as we have seen experimentally in several studies. However, these effects were much less apparent on this sample set, as the HCl cleaning procedure did not affect either the surface morphology or the overall surface potential behavior of the Ga-polar stripes to the extent that was observed for N-polar stripes.

**Patterned semipolar GaN (SUNY)**

Surface potential data were obtained on several comparable microstructures, where there were slight surface potential increases (~0.17 V) along the sidewalls, as shown in Figure 4.8. It should be noted that these data are subject to convolution of the potential signal with topological features, such that data on these structures are limited in scope and interpretation. Careful attention was taken to minimize tip convolution effects, e.g., by rotating the raster scan direction by 90° to verify surface potential contrast behaviors as the scan direction is changed. Although the dark-state SKPM data acquired on these samples was of little importance, changes in the surface potential upon surface exposure to UV light resulted in contrasting behaviors between the mesa and sidewalls, as will be discussed in Chapter 6.

**4.4 Concluding Remarks**

While the semipolar GaN samples provided limited but informative data, patterned polar GaN samples provided a wealth of information with regard to surface potential contrast between different surface orientations of GaN, namely Ga- and N-polar ones. For the higher-quality epilayer (#612-H), large potential differences (0.5 eV) were observed, where Ga-polar regions
showed a lower surface potential, as is expected. However, the epilayer grown on the MOCVD template (#100430-M) N-polar regions possess a lower surface potential, which is certainly unexpected, and is presumably due to the inferior quality of the Ga-polar stripe growth. This suggests a lower effectiveness of the AlN inversion layer for this sample, since SKPM data for similar growth on an MOCVD template (#1208-M) reveals the expected behavior whereby a lower surface potential of ~0.25 eV was seen for the Ga-polar area. Further, we observed that while the inversion domain boundary between Ga- and N-polar was highly abrupt and presumably beyond SKPM resolution ($r_{tip} \sim 20$ nm, IDB $\sim 100$ nm), the effective surface potential changes appear to occur over the range of 1-2 $\mu$m. For future device applications which may attempt to exploit the surface potential switching behavior of laterally-patterned GaN (e.g., lateral polarity junctions, sensors) individual channel widths (or geometric diameters for quantum dots, etc…) may be limited to ~2 $\mu$m for full effectiveness as suggested by these SKPM data.

The presence of a thicker oxide on N-polar regions was also experimentally observed, as removal of the oxide with HCl cleaning resulted in decreased contrast for the surface potential difference between Ga- and N-polar stripes. This is consistent with the theory that preferential oxide formation at the N-polar surface leads to decreased band bending, which, in this case, corresponds to a smaller potential contrast of 0.3 eV. It is here concluded that a well-established surface oxide on the N-polar GaN surface can lead to an increased surface potential (more positive charge) of ~0.2 eV. Also, prolonged UV exposure may lead to a larger contrast as the preferential N-polar surface oxide is more fully formed. The effect of the preferential oxide on the N-polar GaN surfaces will be discussed in further detail in the following two chapters.
<table>
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<tr>
<th>Reference</th>
<th>GaN type</th>
<th>Method</th>
<th>Ga-polar (eV)</th>
<th>N-polar (eV)</th>
<th>ΔV (eV)</th>
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<td>0.2</td>
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<td>EFM (SKPM)</td>
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**Table 2:** Summary of observed band bending differences between Ga- and N-polar GaN
Figure 4.1: (a) Topography (75×75 µm², color scale = 1 µm) with (b) corresponding cross–section for #612-H sample. (c) Corresponding SKPM image (75×75 µm², color scale = 1 eV) with (d) associated cross–section.
Figure 4.2: (a) Topography (75×75 µm², color scale = 1.5 µm) and (b) cross-section for #100430-M sample along with (c) corresponding SKPM image (color scale = 1 eV) and (d) associated cross-section.
**Figure 4.3:** (a) Topography (30×30 µm², color scale = 2 µm) and (b) cross-section for the #1208-M sample along with (c) corresponding surface potential (color scale = 0.5 eV) and (d) associated cross–section.
Figure 4.4: (a) Topography (50×50µm², color scale = 4 µm) and (b) corresponding surface potential image (color scale = 1 eV) of a large defect and faceting behavior for Ga- and N-polar stripes on the #100430-M sample. (c) Perspective view of the topography with surface potential overlay and (d) corresponding surface potential cross-section.
**Figure 4.5**: (a) Topography (50×50 µm², color scale = 3 µm) and (b) corresponding surface potential image (color scale = 1 eV) of the terminus of a Ga-polar growth stripe and conformal N-polar pyramidal structure on #612-H sample. (c) Perspective view of the topography with surface potential overlay and (d) corresponding surface potential cross-section.
Figure 4.6: (a) Topography (5×3 μm², color scale = 300 nm) and (b) SKPM image (color scale = 1 eV) with (c) cross-section on #612-H sample showing field localized enhancement about a small inversion domain (circled) at the interface domain boundary.

Figure 4.7: (a) Topography (30×15 μm², color scale = 2 μm) and (b) cross-section for HCl-cleaned #612-H sample with (c) corresponding SKPM image (color scale = 1 eV) and (d) cross-section.
**Figure 4.8:** (a) Topography (2×2 µm², color scale = 1.5 µm) and (b) corresponding SKPM image (color scale = 0.5 eV) of mesa (Ga-polar) and {1101} facet of hexagonal GaN pyramid (#1937-S). (c) Perspective view of the topography with surface potential overlay and (d) corresponding surface potential cross-section plot.
Chapter 5: Charge Injection

5.1 Motivation and Background

While investigating local reverse leakage sites on GaN, members of our group realized that performing CAFM results in the introduction of charged surface states within CAFM-scanned regions.19 For these injected charges, the band bending at the surface was increased by ~0.5 eV for bias voltages of <8 V, while for larger bias voltages over 10 V, a saturation of these charged states results in an induced band bending of up to 3 eV as measured by subsequent SKPM imaging. A band structure diagram shown in Figure 5.1 depicts such a change in the band bending near the surface of n-type GaN being altered by local injection of negative charge (green dotted lines). These tip-induced charges were able to persist for hours on the surface in dark conditions, suggesting that the surface states (shown by a position $E_S$ in Figure 5.1) are relatively stable; however, exposure of the charged regions to UV illumination caused a rapid neutralization of the charge (i.e., discharge) as measured by temporal SKPM scanning of the charged area. In addition, subsequent studies showed that the presence of below-bandgap light (He-Ne laser) enabled a faster restoration rate of the surface charge than in dark conditions, indicating that these surface states lie exclusively within the bandgap and may become activated via below-bandgap illumination.61

In addition to the assumption that the density of surface states is exacerbated by the presence of thicker surface oxides at the GaN surface, we assume that a high electric potential on the order of $\sim 10^9$ V/m produced by the localized electric field between the AFM tip and surface may catalyze an electrochemical oxidation of the surface during localized charging experiments in the CAFM scanning mode.62 The generally accepted theory for surface oxidation using an AFM tip is that a residual water layer (present in ambient) acts as a source for OH$^-$ and O$^2-$ ions, and that these molecular ions act as oxidants in the anodic processes (whereby a DC bias is established between two “electrodes”) during CAFM scanning.63 In the case of GaN surfaces, these ionic species are presumed to be responsible for the formation of Ga$_x$O$_y$ complexes at the surface, yet the surface electrochemistry which occurs for the AFM tip / GaN surface is still largely unresolved and such study lies beyond the scope of this work.
Semi-controllable oxidation of GaN using an AFM tip, a 1.2 V tip bias, and a UV lamp in high humidity has been observed elsewhere. Here, the oxidation process at the AFM tip/GaN interface is claimed to be due primarily as the result of a photo-assisted oxidation mechanism since minimal oxidation was observed at significantly larger bias voltages ($V_S = +10$ V vs $+1.2$ V) without UV light present. To reiterate, their studies indicated that oxidation generally takes place when UV is present. However, even in dark conditions and low humidity throughout these studies (< 30% relative humidity), we have seen comparable results without the use of UV assistance. It should be clear that the techniques, and more importantly, environmental conditions, were significantly different between these two groups’ studies.

Interestingly, the “surface charging” procedure utilized here has been independently developed elsewhere for experimental testing with regard to insulating versus semiconducting diamond surfaces. For those studies, nanocrystalline diamond (NCD) particles deposited on Au thin films show slight but persistent charge trapping (0.15 eV) using a very similar CAFM–SKPM procedure. It should be noted that these changes were observed at substantially higher bias regimes ($|V_S| = 30$ eV) than ones used here ($|V_S| \leq 10$ eV). In another similar report, charging experiments were conducted on amorphous SiO$_2$ surfaces, and showed smaller changes in the surface potential for the charged regions (0.08 eV for SiO$_2$, 0.15 eV for NCD).

Charge injection techniques have been used in this group to investigate the surface potential behavior resulting from charging, and to gather information about discharging characteristics for such applied surface charges. One past study within the group contained a construct for modeling the discharge over time for the injected charge, which for times $t < 10^4$ s, accurately matched discharge behavior. However, any correlation between band bending restoration from locally charging the surface and by above-bandgap light (i.e., surface photovoltage) has not yet been established, and is thus presented in this work.

5.2 Model for Restoration of Locally-Induced Surface Charge

We first define the change in band bending caused by external charging (via the AFM tip) $\gamma$ and its evolution in time $t$ after charging is stopped at $t=0$ s as

$$\gamma(t) = \Phi(t) - \Phi_0$$

(5.1)
where $\Phi(t)$ is the change in band bending with respect to time, and $\Phi_0$ is the band bending value in dark, i.e., equilibrium conditions (see Figure 5.1). To construct a formula for $\gamma(t)$, we utilize an electron transport rate equation-based model similar to one which has been utilized for surface photovoltage measurements.\textsuperscript{21} We begin by expressing the change in the density of surface charges $n_s$. With respect to time, $\frac{dn_s}{dt}$, is the value of the difference in the rate of transfer of electronic charge between surface-to-bulk ($R_{SB}$) and bulk-to-surface ($R_{BS}$) states such that the effective rate may be written as

$$\frac{dn_s}{dt} = R_{BS} - R_{SB}.$$ \hspace{1cm} (5.2)

Following a similar model which has been used for describing the restoration of band bending after UV illumination,\textsuperscript{21} we write the rates

$$R_{SB} = s_n N_C e^{\frac{(E_C - E_F)}{kT}},$$ \hspace{1cm} (5.3)
$$R_{BS} = s_n N_C e^{\frac{\Phi(t) + (E_C - E_F)}{kT}},$$

where $s_n$ is the surface recombination velocity which is a product of the electron capture cross-section and the density of the surface states. $N_C$ is the effective density of states in the conduction band, $E_C$ is the conduction band energy, $E_F$ is the Fermi level energy (in equilibrium conditions), $k$ is the Boltzmann’s constant, and $T$ is the temperature in Kelvin. In this first-approximation model, we assume that a single surface state located at a fixed distance ($E_C - E_S$) from the top of the conduction band is sufficient to describe the restoration behavior for $\gamma(t)$. Additionally, we neglect $R_{BS}$, as the barrier for bulk-to-surface electrons is exacerbated for the increased band bending due to charge injection. For example, if $\Phi_0 = 0.8$ eV, $E_C - E_F = 0.1$ eV, and $E_C - E_S = 0.9$ eV, an equilibrium is reached whereby $R_{BS} = R_{SB}$ (since $\Phi_0 + E_C - E_F = E_C - E_S$). However, the introduction of a small but significant additional amount of band bending due to charging ($\gamma = 0.2$ eV) results in a significant reduction of the $R_{BS}$ flow, such that the ratio of bulk-to-surface transport compared to surface-to bulk transport is less than one-tenth of one percent:

$$\frac{R_{BS}}{R_{SB}} = s_n N_C e^{\frac{\gamma + \Phi_0 + (E_C - E_F)}{kT}} = e^{\frac{\gamma + \Phi_0 + (E_C - E_F)}{kT}} = e^{\frac{1.1eV}{0.0254eV}} = e^{\frac{0.9eV}{0.0254eV}} = 3.8 \times 10^{-4}.$$ \hspace{1cm} (5.4)
It should also be noted that the rate of electron emission from the surface state $E_s$ is at a fixed value from the top of the conduction band, such that the rate of emission ($R_{SB}$) is independent of both the initial band bending value and the magnitude of the additional band bending $\gamma$ caused by locally charging the surface. However, bulk-to-surface bound electron transfer ($R_{BS}$) is increasingly diminished at band bending increased. In this case, electrons must overcome a much larger potential barrier to reach the surface after charging. Therefore, by illustrating that the bulk-to-surface rate is negligible for even small increases of band bending, we proceed with the approximation that

$$\frac{dn_s}{dt} = -R_{SB}. \quad (5.5)$$

The change in surface charge density may also be described in terms of the potential barrier height $\Phi$ such that

$$W = \frac{n_s}{N_D} = \sqrt{\frac{2\Phi \varepsilon \varepsilon_0}{q^2 N_D}}, \quad (5.6)$$

where $W$ is the depletion region width caused by band bending, $\varepsilon$ is the dielectric constant for GaN ($\varepsilon = 9.8$), $\varepsilon_0$ is the vacuum permittivity, $q$ is the electron charge, and $N_D$ is the number of uncompensated donors in the conduction band. Taking the derivative with respect to time we obtain

$$\frac{dn_s}{dt} = \frac{d}{dt} \sqrt{\frac{2(\Phi_0 + \gamma) \varepsilon \varepsilon_0}{q^2 N_D}} = \frac{n_s(0)}{2\Phi_0 \sqrt{1 + \frac{\gamma}{\Phi_0}}} \frac{d\gamma}{d\gamma}. \quad (5.7)$$

Setting the surface state density rate equations (5.5) and (5.7) equal to each other, we have

$$-R_{SB} = \frac{n_s(0)}{2\Phi_0 \sqrt{1 + \frac{\gamma}{\Phi_0}}} \frac{d\gamma}{d\gamma}. \quad (5.8)$$

Separating variables, we set up an integral relation where

$$\int_{\gamma_0}^{\gamma} 2\Phi_0 R_{SB} \frac{1}{n_s(0)} d\gamma = \int_{\gamma_0}^{\gamma} \frac{1}{\sqrt{1 + \frac{\gamma}{\Phi_0}}} d\gamma. \quad (5.9)$$
as $\gamma$ goes from an initial maximum $\gamma_0$ at $t=t_0$ to some value $\gamma$ at arbitrary $t=t_1$. Integration over these bounds gives

$$-\frac{2\Phi_0 R_{SB}}{n_s(0)} (t_1 - t_0) = 2\Phi_0 \sqrt{1 + \frac{\gamma}{\Phi_0}} \left[ \sqrt{1 + \frac{\gamma_0}{\Phi_0}} - \sqrt{1 + \frac{\gamma}{\Phi_0}} \right]$$

(5.10)

or

$$\frac{R_{SB}}{n_s(0)} (t_1 - t_0) = \left[ \sqrt{1 + \frac{\gamma_0}{\Phi_0}} - \sqrt{1 + \frac{\gamma}{\Phi_0}} \right].$$

(5.10)

With $\kappa \equiv \frac{R_{SB}}{n_s(0)}$ and $(t_1 - t_0) \equiv t$,

$$\kappa \cdot t = \sqrt{1 + \frac{\gamma_0}{\Phi_0}} - \sqrt{1 + \frac{\gamma}{\Phi_0}}.$$

(5.11)

Re-expressing in terms of $\gamma$ yields a quadratic form in time which is well-defined for $\gamma > 0$:

$$\gamma = \kappa^2 \Phi_0 \cdot t^2 - 2\kappa \Phi_0 \sqrt{1 + \frac{\gamma_0}{\Phi_0}} \cdot t + \gamma_0.$$

(5.12)

By tabulating several values for $(E_C - E_S)$, we may examine the corresponding variation in $\kappa$:

<table>
<thead>
<tr>
<th>$E_C - E_S$ (eV)</th>
<th>$\kappa$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.95</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.9</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.85</td>
<td>$7.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.8</td>
<td>$5.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$7.1 \times 10^{2}$</td>
</tr>
<tr>
<td>0.3</td>
<td>$1.9 \times 10^{6}$</td>
</tr>
</tbody>
</table>

Here, we note that decreasing the value of $(E_C - E_S)$ by 20% (from 1 to 0.8 eV) corresponds to a variation in $\kappa$ by three orders of magnitude, demonstrating the sensitivity of the $\kappa$ factor (present in both prefactors for the first and second order terms in Eq. (5.12)) to changing values of $E_C - E_S$. For these tabulations, we have used nominal values for GaN of $\Phi_0 = 0.8$ eV, $s_n = 1 \times 10^5$ cm$^{-2}$ s$^{-1}$, $N_C = 2.5 \times 10^{18}$ cm$^{-3}$, $n_s(0) = 1 \times 10^{12}$ cm$^{-2}$, and $kT = 0.0254$ eV. Plots of $\gamma$ vs. $t$
for several values of \((E_C-E_S)\) are shown in Figure 5.2 along with experimental data for discharge on the patterned N-polar surface (#612-H) for comparison.

By evaluating the real roots of \(\gamma\) we express the condition at which \(\gamma = 0\) which corresponds to the complete discharge of the applied surface charge by solving for the roots of (5.12), which we label as \(t_{\text{restore}}\) and is thus

\[
t_{\text{restore}} = \frac{-\left(-2\kappa \Phi_s \sqrt{1 + \frac{\gamma_s}{\Phi_s}}\right) \pm \sqrt{\left(-2\kappa \Phi_s \sqrt{1 + \frac{\gamma_s}{\Phi_s}}\right)^2 - 4 \cdot \kappa^2 \Phi_s \cdot \gamma_s}}{2 \cdot \kappa^2 \Phi_s} = \frac{\sqrt{1 + \frac{\gamma_0}{\Phi_0}}}{\kappa}
\]  

(5.13)

or

\[
t_{\text{restore}} = \frac{n_s(0) \cdot \sqrt{1 + \frac{\gamma_0}{\Phi_0}}}{R_{SB}} = \frac{n_s(0) \cdot \sqrt{1 + \frac{\gamma_0}{\Phi_0}}}{s_n N_c e \frac{(E_C-E_S)}{kT}}
\]  

(5.14)

by using the appropriate sign (-) for the subtraction of the discriminant from the vertex in (5.13).

It is noted that this estimate yields a systematic underestimation of the full discharge time since bulk-to-surface transitions which have been omitted will affect the restoration, especially as \(R_{BS}\) becomes comparable to \(R_{SB}\) at times tending toward \(t_{\text{restore}}\). Again, even for small values of \(\gamma\), the rate transport is predominantly \(R_{SB}\) flow (see Eq. 5.4). By using nominal experimental values, we may tabulate \(t_{\text{restore}}\) for several \(E_C-E_S\) values:

<table>
<thead>
<tr>
<th>(E_C-E_S) (eV)</th>
<th>(t_{\text{restore}}) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(8.5 \times 10^5)</td>
</tr>
<tr>
<td>0.95</td>
<td>(1.2 \times 10^5)</td>
</tr>
<tr>
<td>0.9</td>
<td>(1.7 \times 10^4)</td>
</tr>
<tr>
<td>0.85</td>
<td>(2.3 \times 10^3)</td>
</tr>
<tr>
<td>0.8</td>
<td>(3.2 \times 10^2)</td>
</tr>
<tr>
<td>0.5</td>
<td>(2.4 \times 10^{-3})</td>
</tr>
<tr>
<td>0.3</td>
<td>(9.1 \times 10^{-7})</td>
</tr>
</tbody>
</table>

Using these values, we find an experimental form for the restoration, where
\begin{align}
  t_{\text{restore}} &= \frac{n_s(0) \cdot \sqrt{1 + \frac{\gamma_0}{\Phi_0}}}{s_n N_C e^{\frac{(E_C-E_S)}{kT}}} \approx 6.7 \times 10^{-12} \cdot e^{39.4 (E_C-E_S)}. \quad (5.15)
\end{align}

Similarly, by measuring the time at which \(\gamma = 0\) and using appropriate values for \(\gamma_0, \Phi_0, s_n, N_C, n_s(0)\), and \(kT\), one may resolve the value of \((E_C-E_S)\) for room temperature operation as
\begin{align}
  (E_C - E_S) &= kT \ln \left( \frac{s_n \cdot N_C}{n_s(0) \cdot \sqrt{1 + \frac{\gamma_0}{\Phi_0}}} \cdot t_{\text{restore}} \right) \approx 0.0254 \cdot \ln \left( 1.5 \times 10^{11} \cdot t_{\text{restore}} \right) \quad (5.16)
\end{align}

Caution should be exercised when employing these models to fit experimental data, as many of the parameters used in modeling are sample dependent (namely \(\Phi_0, \gamma_0, \) and \(n_s(0)\)). Additionally, the application of this model is limited to relatively deep \(E_S\) values; for AFM experiments which may only begin SKPM observation \(\sim 2\) min after initially charging the surface \((t = 0)\), such that surface states for \(E_C - E_S < \sim 0.75\) eV will not be observed in subsequent SKPM scanning (see \textbf{Figure 5.2}).

\section*{5.3 Findings for Charge Injection Studies}

\textit{Patterned polar GaN (NRL)}

Local surface charging experiments on the patterned, polar GaN samples reveal a clear distinction between Ga- and N-polar charging and discharging behaviors. Here, surface charge applied to the as-received N-polar regions is both larger in magnitude and persists for several hours, while Ga-polar charging was much less apparent and rapidly dissipated. Most of the applied surface charge on the as-received Ga-polar regions (> 90\%) dissipates within minutes, and thus was not readily obtainable by SKPM. However, the clear asymmetry of surface charging behavior between the polar orientations can be seen in \textbf{Figure 5.3} (b) and (e) for both samples (#612-H and #100430-M), where the application of surface charge (inside dashed box) is well-defined on the N-polar regions, but either readily discharges or is not effectively trapped on Ga-polar regions due to a less-established oxide on Ga-polar.
The change in surface potential within the N-polar regions from locally-applied charging is much larger, where a \(~1.6\) V difference is observed between charged and uncharged areas, as is indicated in the cross-section presented in Figure 5.3 (c). Although not immediately apparent, the Ga-polar stripe Figure 5.3 (a) shows a \(~0.6\) eV increase in the surface potential as raster scanning progresses from top-to-bottom over the course of the scan (\(~35\) min). Upon completion of the SKPM image, the difference in surface potential values between the charged Ga-polar stripe and an uncharged Ga-polar region differ by less than 0.1 eV (Figure 5.3 (a)), and reiterates the more diffuse charging and faster discharging characteristics for the Ga-polar orientation.

Charge writing procedures performed on these patterned, polar samples evidence stark differences between charging behaviors of Ga- and N-polar GaN surfaces. The epilayer present on the higher-quality HVPE substrate (#612-H) shows a higher degree of change in the surface potential after locally charging the surface; this observation is most apparent by comparing the N-polar areas on each surface, where local changes of over \(1.5\) V were seen for the higher-quality #612-H sample. In comparison, for N-polar areas on the #100430-M sample, changes in the surface potential were about smaller in magnitude (\(0.75\) eV), although identical experimental parameters were used in both cases. After charging both surfaces at \(+5\) V reverse bias CAFM scanning, subsequent SKPM of the areas show a decreased surface potential signal at the left-hand side of the Ga-polar region as raster scanning began (image has been rotated \(90^\circ\) counter-clockwise for clarity, such that the left-hand side of the image represents areas scanned first). This behavior reinforces the idea that surface charge is more mobile on or within Ga-polar stripes as compared to the N-polar stripe. As evidenced in Figure 5.3, both samples reveal that negative surface charge is confined laterally on the N-polar surface, where it is assumed that a thicker surface oxide on the N-polar orientation acts as an effective charge-trapping layer. Positive surface charging (\(i.e.,\) charge depletion) persists on both surfaces, as shown in Figure 5.4, although for surface states formed in forward bias (positively-charged), it is assumed that the surface states are formed entirely within the surface oxide layer, whose formation may be catalyzed during CAFM scanning thorough presumed electrochemical oxidation.

Along with differences in surface charge magnitude and persistence over time, an asymmetry with respect to changes to the topography exists between the Ga- and N-polar charge
writing processes. Specifically, during local charge writing, the N-polar surface appears to be more reactive with the environment, leaving an ensemble of small (diameter < ~5nm) surface protrusions in the CAFM-scanned regions and an enhancement of these types of features as the edge of the scanning region (Figure 5.5). Because the AFM tip spends a longer amount of time at the edges of the scan, it is expected that the lateral edges of a scanned area should show an increased amount of evidence from these types of oxidative processes. Additionally, as mentioned previously, research conducted elsewhere has investigated the oxidation of GaN during CAFM scanning, although those studies were limited to Ga-polar surfaces.62,64

Following HCl cleaning, local charging experiments were conducted on the cleaned surfaces. SKPM scans taken after charge injection on the freshly cleaned surface (< 1 hr) show little to no persistence of surface charge on either polar region. Like the as-received Ga-polar regions, the cleaned N-polar regions show intra-stripe increases over the course of the scan. Only after a 3+ hour UV aging treatment is any persistent surface charge on N-polar regions observed through the technique. As presented in Figure 5.6, the amount of surface charge trapped by the surface after HCl cleaning and UV aging (Figure 5.6 (c) and (d)) is much less than the as-received surface (Figure 5.6 (a) and (b)). Surface potential changes of only 0.3 eV are seen (Fig. 2(d)) on N-polar regions in this condition, whereas the presumably thicker oxide on the as-received (more fully aged) surface registers changes of ~1.6 eV after charging the surface.

Preliminary data collected on the patterned polar samples were used for evaluating the phenomenological model. Because the Ga-polar stripes discharge within only a few minutes after initial charging, fits were applied to the N-polar surfaces which show persistent charging behaviors. Here, using nominal values for N-polar GaN ($\Phi_0 = 0.8$ eV, $\gamma_0 = 1.07$, $s_n = 1 \times 10^5$ cm$^2$ s$^{-1}$, $N_C = 2.5 \times 10^{18}$ cm$^{-3}$, $n_s(0) = 1 \times 10^{12}$ cm$^{-2}$, and $kT = 0.0254$ eV), we find that a reasonable fit is observed when using $(E_C-E_S) = 0.805$ eV, as illustrated in Figure 5.7. Unfortunately, we did not anticipate the need for extended temporal scans for the discharging behavior before HCl cleaning was applied and the phenomenological model was constructed. Because of the extremely limited data for discharge characteristics on the as-received sample, an impetus for future studies of discharge characteristics is clearly present within the group.
Patterned semi-polar GaN (SUNY)

Surface charging studies performed on the #1937-S microstructures (Figure 5.8) shows the surface potential behavior after a charge injection was performed on the top of a hexagonal feature by placing (or “parking”) the AFM tip in the center of the feature and then applying a +10 V bias for a 10 s. interval. By comparing surface potential images from before (Figure 5.8 (b)) and after charging, the resultant SKPM image (Figure 5.8 (c)), taken between 2-10 minutes after the initial charge was injected, shows the lateral spread of the surface charge into the surrounding features. It remains unclear as to the nature by which charges are effectively diffused (i.e., on the surface or vertically through the structure). The geometry of these samples may affect SKPM resolution, especially on the semipolar facets where tip-sample interactions are expected to be present since the surface is tilted ~60° away from the ideal horizontal orientation. However, the non-localized charging behavior for the Ga-polar mesas is in agreement with behaviors on the Ga-polar stripes on the patterned, polar GaN set discussed previously. While Figure 5.8 (c) appears to show preferential charging of the facet at the top of the image, this artifact is believed to be caused by tip/sample interaction and should be considered as a tip artifact.

Attempts to charge individual facets did not produce consistent data; for these attempts, charge diffusion onto the surrounding substrate and onto the mesa was noted. Again, it remains unclear if there is in fact localization of charge or if tip convolution effects were the source of the diffusive properties, as the large topographic nature of the microstructures complicates SKPM interpretation.

5.4 Concluding Remarks

Surface charging experiments reveal stark differences between Ga-polar and N-polar GaN, where patterned, polar GaN surfaces served as an especially appropriate sample set to investigate these charging /discharging behaviors. For these studies, air-exposed N-polar surfaces show a larger degree of localized, persistent charging on the order of 1.5 eV. In addition, the discharge behavior for N-polar stripes was significantly slower than adjacent Ga-polar stripes. It is believed
that the presence of a thicker oxide at the N-polar surface enables the effective trapping of locally-applied surface charges. To test whether or not the oxide plays a significant role in the charging behaviors, an HCl cleaning procedure was performed on the samples. After removal of the oxide, the magnitude of persistent negative charge on the N-polar stripes immediately after cleaning was much less than for the as-received surfaces. However, as was noted in SKPM studies, the re-growth of the oxide preferentially on the N-polar surface using prolonged UV exposure resulted in a (slight) increase in effective charge trapping as verified by SKPM. Additionally, a higher degree of induced oxidation during charging was observed for N-polar stripes, suggestive of the higher reactivity for N-polar GaN. Future studies on these types of surfaces should be aimed at chemical identification of both the thermal oxide and the electrochemically-grown one.

By construction of a first-approximation phenomenological model, we have been able to model the discharging behavior with reasonable agreement, and by doing so, have approximated the position of a single “effective” surface state with respect to the conduction experimentally. Realistically, a distribution of mid-gap states is likely a more accurate description of where surface charges are trapped; however, by approximating the net effect of these states into one effective surface state, we have estimated the position of $E_S$ relative to $E_C$ with reasonable agreement.

Certainly additional data is left to be desired in order to further test and refine this discharge model. For these studies, it was not forethought that discharge behaviors would be investigated as thoroughly as was needed for verification of the discharge model. Therefore, data presented in this study was quite limited. In addition, due to the deleterious effect of the HCl cleaning procedure and inability to fully restore the charging behaviors with prolonged UV exposure, future studies on more appropriate surfaces will be required to better test this phenomenological discharge model. Ideally, future studies will be conducted to observe the discharge until $\gamma = 0$, such that the value of $E_C-E_S$ may be readily obtained (see Eq. 5.13) given an appropriate value of $\Phi_0$, $\gamma_0$, and $\kappa$. Furthermore, the “switching” time between locally injecting charge via CAFM and subsequent measurement of charge via SKPM should be decreased. It is certainly plausible that a computer program may be written in order to facilitate the CAFM $\rightarrow$ SKPM switch to be on the
order of seconds vs. minutes as was the case during these studies. By decreasing the time needed for this switch, shallower surface states may be resolved and incorporated into future, more refined discharging models. Additionally, as Ga-polar and HCL-cleaned surfaces showed minimal evidence of charging using the present experimental setup, faster switching times may enable observation of these faster discharging processes.

In summary, charge writing was used to illustrate the presence of a preferential oxide for air-exposed N-polar surfaces as compared to air-exposed Ga-polar ones. Furthermore, HCl cleaning on these surfaces verified that an insulating oxide layer is likely responsible for the surface charge trapping, as the charging characteristics were greatly diminished in the post-HCl condition. By constructing a first-approximation phenomenological model, we have used a single surface state to describe the discharging behaviors with reasonable agreement to the available data (#612-H sample). Future directions of this type of study should aim to refine the discharging model in order to account for several surface states responsible for electron emission from surface states to bulk ones compared to a single state which was used in these studies, where \((E_C-E_S)= 0.805 \text{ eV}\) for the oxide-laden N-polar GaN surface. The notion of injection and subsequent observation of discharging characteristics is certainly desirable to better understand surface electronic properties. At present, the experimental procedure and associated phenomenological modeling may be considered as proof-of-concepts which both require improvements before being used as commonplace characterization tools. However, we have successfully demonstrated that such characterization may be possible to probe mid-gap surface state positions experimentally.
Figure 5.1: (a) Band diagram depicting dark-state band bending (red lines) and increase of band bending due to injected surface charge (green, dotted lines). A single surface state located at \((E_C-E_S)\) is calculated by fitting the change in band bending over time, \(\gamma(t)\), to experimental data.
Figure 5.2: Theoretical restoration curves plotted for various values of \((E_C-E_S)\). For illustrative purposes, data from an N-polar stripe (#612-H) is shown alongside curves, illustrating that \(E_C-E_S\) is approximately 0.8 eV.
Figure 5.3: (a) Topography (50×50 µm², color scale = 2 µm) with (b) corresponding surface potential (color scale = 2.5 eV) and (c) cross-section for #612-H sample after charge injection of +5V (box) using AFM tip. (d) Topography (75×75 µm², color scale = 2 µm) with (e) corresponding surface potential (color scale = 2.5 eV) and (f) cross-section for #100430-M sample after charge injection of +5 V (box) using AFM tip.
Figure 5.4: (a) SKPM image (30×30 µm², color scale = 2 eV) of interface domain boundary immediately after ±10 V surface charging (dotted boxes) was applied across the interface (#100430-M) along with (b) cross sections for Ga- and N-polar regions. (c) SKPM image (30×30 µm², color scale = 2 eV) of interface domain boundary 12 h. after surface charging along with (b) cross sections for Ga- and N-polar regions.
Figure 5.5: (a) Topography (10×10 µm², color scale = 1 µm) and (b) amplitude error data (10×10 µm², color scale = 15 meV) after charge injection at -10 V (reverse bias, white box) with AFM probe #100430-M sample. (c) Topography of Ga-polar surface at edge of charge injection area (5×5 µm², color scale = 4 nm) with (d) averaged cross-section across growth (black box).
Figure 5.6: (a) Surface potential image (50×50 µm², color scale = 3 eV) of as-received #612-H surface after charge injection of +5V (box) using AFM tip and (b) cross-section. (c) SKPM image (50×50 µm², color scale = 3 eV) of HCl-cleaned +3 h UV treatment for the #612-H surface after charge injection of +5 V (box) using AFM tip along with (d) cross-section.
Figure 5.7: Experimental discharging data for N-polar stripe (#612-H) along with phenomenological fit, using $\Phi_0 = 0.8 \text{ eV}$, $\gamma_0 = 1.07 \text{ eV}$, $s_n = 1 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$, $N_C = 2.5 \times 10^{18} \text{ cm}^{-3}$, $n_s(0) = 1 \times 10^{12} \text{ cm}^{-2}$, and $kT = 0.0254 \text{ eV}$. $E_C - E_S$ was calculated as $(E_C - E_S) = 0.805 \text{ eV}$. 
Figure 5.8: (a) Topography (10×10 µm², color scale = 2 µm) of SUNY microstructure (#1937-S) along with (b) SKPM of the structure taken in dark conditions (color scale = 1 eV), along with (c) SKPM of the same area after a point-probe injection of -10 V over a 10 s time interval (color scale = 1 eV) and (d) corresponding cross-sections showing the magnitude of injected charge.
Chapter 6: Surface Photovoltage

6.1 Motivation and Background

It has been well established that the surface of air-exposed, \( n \)-type Ga-polar GaN shows an upward band bending of approximately 1 eV due to the presence of negative charge at the surface.\(^{29,68,69} \) While this band bending effect has been well-characterized, little is well-understood. Defects within the GaN crystal and adsorbed negative charge may be predominantly responsible for the observed negative surface charge (and, by extension, the associated band banding), although the exact source(s) of negative surface at the GaN surface have not been established. The value of band bending \( \Phi_0 \), which is representative of an equilibrium condition of electron transport between surface and bulk states, produces a corresponding depletion width \( W \), of which a \( W \sim \sqrt{\Phi_0} \) dependence exists. Band bending may be reduced by exposure to above-bandgap UV illumination due to the accumulation of photo-generated holes at the surface, thus producing a non-equilibrium condition at the surface. This photo-induced change in surface band bending, known as surface photovoltage (SPV), is commonly measured by the Kelvin probe technique, although SKPM methods may be employed to probe the local SPV behavior for samples in air ambient conditions. A simplified diagram showing decreases in band bending due to light is shown in \textbf{Figure 6.1}.

The SPV response of a given sample may be well-characterized by three separate response metrics. The first is the initial, transient response (the so-called “fast” component), where the photovoltage rise is proportional to the incident illumination power density, and is generally too fast for SKPM observation; therefore the first data point acquired after illumination begins (for these studies, \( t_1 \geq 0.67 \text{ s} \)) is interpreted as an approximate measure of the initial SPV response. The secondary, “steady-state” response refers to the changes in SPV value while under illumination; for instance, as holes form at the surface under illumination, negatively-charged adsorbates may influence the SPV value. Although the quantitative response of photo-induced species on the GaN surface is not well-understood, many of these processes are expected to be self-limiting, whereby the surface reaches a saturated, steady-state SPV value. In air ambient,
photo-induced adsorption occurs as surface-bound holes may interact with negative species impinging the surface, thus causing a reduction in the SPV signal. These species may become physisorbed and potentially chemisorbed to the surface after some time, and thus will influence the surface chemical environment and resultant SPV response characteristics. For example, past studies on Ga-polar surfaces studied by Kelvin probe indicate a ~0.1 eV reduction of SPV signal over the course of 1 h illumination. For studies conducted here, however, a much less intense illumination than the Kelvin probe illumination source (0.04 vs 0.4 W/cm²) is employed, such that more dynamic photo-induced processes are expected to occur in the Kelvin probe setup.70

The steady-state SPV for n-type, Ga-polar GaN has been studied extensively, and shows SPV values in the 0.3-0.9 eV range upon switching on UV light. However, the SPV behavior is strongly influenced by surface condition and experimental technique.9 Much attention has been paid within the group to study the effects of photo-induced adsorption and desorption behaviors of surface species under UV illumination.9,13 We have reported that samples with many hours of ambient UV exposure do not show this slow decrease during SPV measurements, consistent with the UV-induced growth of a thicker surface oxide. These are in agreement with similar studies; for example, a report investigating N-polar GaN adsorption/desorption kinetics suggests that band bending is reduced by the presence of surface contamination.55

Admittedly, the Kelvin probe setup used within our group has provided a much higher level of versatility (pressure, temperature, and ambient control) and more reproducible behavior than the SKPM technique. In the SKPM setup, the control of the ambient condition is limited, and atmospheric conditions affect reproducibility of scans as temperature, pressure, and humidity levels are constantly in flux. Additionally, research within the group has shown that surface charges may overcome near-surface barriers with energy absorbed from below-bandgap light, notably the residual red light from the laser used in the AFM setup.61 These factors may influence the quality of SPV data obtained via SKPM, adding to the limited reliability of SKPM methods to accurately measure true SPV behaviors.

After the UV illumination is ceased, the surface restoration behavior is monitored over time. This restoration behavior is of particular interest; a phenomenological model has been developed within the group, and may be applied to SPV data taken via SKPM. Many of the theoretical
considerations in regard to the rate-based thermionic model have been discussed in Chapter 5, and are thusly omitted here for brevity; details of the model may be found in Ref. [21]. For the SPV restoration model, we prescribe the function $y(t)$ (cf. $\gamma(t)$ in Chapter 5), which decreases toward zero as the surface restores to the dark-state, equilibrium condition. As determined by the thermionic, rate-based model, the band ending $y$ at a time $t$ after illumination ceases is of the form

$$y(t) = y_0 - \eta kT \ln \left( 1 + \frac{t}{\tau} \right)$$  \hspace{1cm} (6.1)$$

where $y_0$ is the surface photovoltage produced at the surface, $\eta$ is a fit parameter (ideal value = 1), $k$ is the Boltzmann constant, $T$ is the ambient temperature, and $\tau$ is a characteristic time delay constant of the sample. The delay constant varies from surface to surface, and typical values for $n$-type GaN tend to vary between 0.0001 to 10 s, where a derivation of this parameter, as well as omitted details about the model can also be found in Ref. [21].

In addition to investigating the SPV response for sample the sample set, one point of order was to determine if locally charging the sample before exposure to UV light would significantly affect the SPV response of the surface when exposed to UV. A Si-doped, $n$-type, Ga-polar GaN sample was grown on an $\text{Al}_2\text{O}_3$ (sapphire) substrate. A 1 $\mu$m growth of GaN was accomplished on the substrate, followed by a 370 nm-thick AlGaN buffer layer. Finally, a 200 nm-thick GaN layer doped with Si was deposited on the buffer layer. This Si-doped sample was chosen as a proof-of-concept sample as it is expected that the band bending at this particular surface is larger than an undoped GaN sample. This increased degree of band bending would expectedly show a more dynamic response to induced changes at the surface, either by local charging or through exposure to UV illumination. As illustrated in Figure 6.2 (a), the saturation SPV of the sample, i.e., the flattening of the conduction band under illumination, reached a common value between the two experiments (where the surface was initially charged or not), indicating that regardless of the baseline CPD value, a unique and characteristic CPD value is achieved upon UV illumination. However, in order to calculate the true SPV value, a dark-state, equilibrium CPD must be established; and this is not the case for previously-charged regions as seen in Figure 6.2. Furthermore, Figure 6.2 (b) illustrates that the restoration behavior is consistent with negligible
differences in the restoration curves (shown in Figure 6.2 (b)) for the charged and uncharged surfaces. By using SKPM and a consistent, dark-state baseline CPD signal (equilibrium condition), SPV behaviors were characterized for the three sample sets, as will be discussed below.

6.2 Findings from SPV Studies

Bulk GaN samples (Kyma)

Extensive SPV data on these polar surfaces has been collected primarily by Kelvin probe techniques, again due to the reliability and reproducibility of establishing a baseline CPD signal on this setup and because of its environmental control. SPV data on these samples (Figure 6.3) were used as a comparative measure for SPV behaviors observed on the Kelvin probe apparatus while operating in air ambient. Complementary SKPM-based SPV measurements show higher SPV values for Ga-polar for both CMP and MP polishing types than Kelvin probe measurements of comparable light intensities, where both Ga-polar surfaces show ~0.35 eV changes immediately upon exposure. For N-polar surfaces, however, the CMP-treated bulk N-polar surface shows slightly lower SPV values than the MP-treated bulk N-polar surface (~0.17 eV for CMP-treated, ~0.2 eV for MP-treated). For both polarities, the MP treatment causes increased photodesorption under UV, as evidenced by the decrease in SPV signal under illumination for both Ga- and N-polar surfaces treated with MP (Figure 6.3 (b)). These findings are covered in detail in Ref. [11] and are in agreement with behaviors observed by collaborators using an SPV similar to our AFM setup.60 For those studies, the authors report an increased degree of chemisorption on the N-polar surface, although their experimental setup differs in that the illumination power density of the UV illumination source is much higher than the UV source used in our setup. Additionally, we express some skepticism about the manner in which this data was collected in regard to the “dark-state” baseline just before illumination. Disregarding these concerns, both studies showed that Ga-polar surfaces possess larger SPV values than the LLO-prepared N-polar surfaces in air ambient. Additionally, N-polar GaN surfaces were shown to be more susceptible to photo-induced processes, as SPV values are more dynamic (i.e., show larger changes in SPV values) than Ga-polar ones.
For these surfaces, Kelvin probe techniques were predominantly employed to model the SPV restoration behavior. Using this apparatus, it was found that surfaces treated with the MP process showed much faster restoration behaviors, as illustrated in Figure 6.4. Here, temperature-dependent studies on the four surface types (Ga-polar, CMP; Ga-polar, MP; N-polar, CMP; N-polar, MP). It was found that on both Ga- and N-polar surfaces that the MP treatment leads to faster restoration behavior. We interpreted this behavior by suggesting that faster restoration for the MP surfaces is at least partly due to the highly defective surface which enables hopping-electron conduction, thereby enabling the faster restoration.\textsuperscript{11} The quality of electrical contacts was also a concern, especially for Kelvin probe measurements which rely on electronic means of determining CPD values, while SKPM uses an electrostatic force mechanism and is thus less affected by the quality of the electrical contact. Regardless, the transfer of electrons between defect states would have a high probability if the defect density in the depletion region and bulk is appreciably high, as was predicted from PL measurements for the MP-treated surfaces. A comparably fast transfer of electrons via defect states would be independent of the near-surface barrier height and thus will have a strong dependence on temperature. This could explain why the SPV restoration rate increased with increasing temperature, but not in direct proportion to $kT$, as was predicted by the thermionic model. The results from temperature-dependent SPV restoration measurements and the observed reduction of measured photoluminescence intensity from MP-treated GaN surfaces suggest that the surface treatment plays a significant role in the electrical and optical properties of bulk GaN.\textsuperscript{11}

*Patterned polar GaN (NRL)*

Surface photovoltage measurements taken simultaneously on Ga- and N-polar orientations grown on the HVPE template (sample #612-H) are presented in Figure 6.5 and evidenced further distinction between surface polarity and, to a lesser extent, between the two types of growth template (HVPE vs MOCVD). SPV data collected on the as-received Ga-polar regions lower SPV values than their adjacent N polar regions on all three samples (~0.3 eV for Ga polar, ~0.45 eV for N polar). While Ga-polar regions show negligible amounts of photo-induced processes as indicated by the consistent SPV signal under UV (Figure 6.5), N polar surfaces all show some degree of photo-induced desorption of negative charge as indicated by
the rise of the associated SPV under illumination. Sequential UV illumination times of 1 and 3 minutes were applied to #612-H sample to test steady-state SPV behaviors, and these data are presented in Figure 6.6. Here, we note that N-polar SPV, while subject to a higher degree of photo-induced processes, clearly shows a higher SPV signal than adjacent Ga-polar regions by approximately 0.15 eV.

The restoration signals after UV illumination is also analyzed for the surfaces, and show logarithmic dependence. The phenomenological model (Eq. 1) is applied to all four surface types; these fits are shown in Figure 6.7 for the as-received surfaces. The fitting parameters \( \eta \) and \( \tau \) were chosen as follows: HVPE, Ga-polar: \( (\eta = 1, \tau = 0.0015 \text{ s}) \); MOCVD, Ga-polar: \( (\eta = 1.2, \tau = 0.003 \text{ s}) \); HVPE, N-polar: \( (\eta = 1.125, \tau = 0.75 \text{ s}) \); MOCVD, N-polar: \( (\eta = 1.1, \tau = 35 \text{ s}) \). The larger time decay constants \( \tau \) for the N-polar regions are significantly larger than Ga-polar, and indicate a suppressed transfer of electrons from the bulk to the surface after illumination ceases, which is attributed to the inclusion of an insulating oxide layer preferentially at the N-polar surface.

After HCl cleaning, the N-polar regions showed higher initial and steady-state SPV than Ga-polar regions; here, N-polar SPV values roughly doubled after HCl cleaning. SPV values for Ga-polar regions all fell within the 0.3 - 0.4 eV range before and after HCl treatment, and showed a nearly complete restoration within \( \sim 5 \) min of ceasing UV illumination. Although changes in the Ga-polar SPV characteristics were not as dynamic as changes in the N-polar ones, slightly faster restoration is observed for the HCl-cleaned Ga-polar surfaces on both HVPE (#612-H) and MOCVD (#100430-M) templates, evidencing a lesser degree of charge trapping at the surface, presumably due to the removal of the surface oxide. For these data (Figure 6.8), experimental fits used \( \eta = 2, \tau = 0.001 \text{ s} \) for Ga-polar “clean” condition; \( \eta = 2, \tau = 0.005 \text{ s} \) for Ga-polar “15 hr. UV” condition (#612-H); \( \eta = 1.85, \tau = 1 \text{ s} \) for N-polar “cleaned” condition (#100430-M); and \( \eta = 1.8, \tau = 6 \text{ s} \) for N-polar “15 hr. UV” condition (#612-H).

Patterned semi-polar GaN (SUNY)

Figure 6.9 shows a sequence of illumination times while simultaneously measuring changes in the CPD of the c-plane mesa and edges. As evidenced in these data, the SPV at sidewall “edges” are characterized as having a lower SPV (0.2-0.3 vs. 0.4 eV for mesa), as well as a
higher degree of presumed photo-induced desorption of negative surface species, as suggested by
the increase of surface potential during constant illumination. A sequence of UV exposures
increasing in time was performed while monitoring the SPV signal to compare SPV behavior for
the Ga-polar mesa and the semipolar \{1\underline{1}01\} sidewalls. As is shown in Figure 6.9 (a), the mesa
is characterized as having a larger SPV than the mesa, and restores at a faster rate than the
semipolar edge sidewalls. As is shown in Figure 6.9 (b), the edge \{1\underline{1}01\} surfaces show slightly
longer restoration behaviors, while SPV at the mesa is effectively restored over the first ~45
seconds after illumination is ceased. A similar extent of restoration occurred over the course of
3-4 min for the SPV at the sidewalls, indicating the longer restoration times for the sidewalls.
SPV decay data for mesa and edge (averaged over six separate facets) were modeled with
experimental fits using \(\eta = 2\), \(\tau = 0.125\) s, and \(y_0 = 0.41\) eV for the mesa, and \(\eta = 1.3\), \(\tau = 0.35\) s,
and \(y_0 = 0.29\) eV for the edge. An average SPV signal was used for the edge data, where all six
individual \{1\underline{1}01\} SPV data sets were averaged together, as the variance between separate facets
was insignificant, \textit{i.e.}, all sidewalls appear to have similar SPV and restoration behaviors.

6.3 Concluding Remarks

SPV experiments performed on these samples show several general characteristics in regard
to polar GaN surfaces. For Ga-polar GaN, all three sample sets showed steady-state SPV values
of 0.3-0.4 eV; these values are on the lower bounds of known SPV values for GaN; however, the
incident power density of the UV used in these studies is likely lower than in other lab setups
where larger (up to 0.9 eV) SPV values have been observed.

N-polar SPV studies showed that the surface treatment plays a significant role in the SPV
characteristics. For MP-polished, bulk N-polar GaN, a faster-than-expected restoration is
attributed to a high degree of near-surface defects, thus allowing for an electron hopping
mechanism to contribute to the transfer of electrons from the bulk to the surface. N-polar
restoration behaviors for these surfaces were faster than the Ga-polar sides, which was not the
case for the epitaxially-grown N-polar stripes. For those samples, a preferential oxide formed on
the N-polar stripes is assumed to inhibit the rate at which the surface restores to the dark-state
equilibrium condition. Removal of the oxide from the surface led to increased restoration rates
for the N-polar, while Ga-polar stripes showed little change in SPV response after HCl cleaning. This may be explained by the presence of comparably thicker oxide on N-polar or by the resilience of Ga-polar surfaces to HCl, which shows a significantly less drastic change than N-polar HCl cleaning. It is clear that more complete studies should be undertaken on N-polar surfaces, as the growth technique and surface preparation has been demonstrated to greatly influence the optoelectronic behaviors of these more reactive N-polar surfaces.\(^\text{11}\) In comparison, the electrical and optical properties of Ga-polar GaN have been more well-established, therefore an impetus exists to further understand differences between well-characterized Ga-polar GaN and the much less-understood N-polar GaN. It was also found that Ga-polar mesas on the #1937-S sample show comparable restoration rates to HCl-cleaned Ga-polar surfaces on the patterned, polar sample set where the restoration was observed to be about twice as fast as expected (\(\eta \approx 2\)). Finally, semipolar GaN facets on the #1937-S sample were shown to have a lower SPV (0.3 vs. 0.4 eV for mesa) and slower restoration than the Ga-polar mesa, illustrating that polar surfaces have more dynamic band bending than semipolar (and arguably non-polar) surfaces, as is to be expected.
Figure 6.1: Simple band diagram showing dark-state band bending (red lines) and decrease of band bending due to above-bandgap illumination (green lines).

Figure 6.2: (a) Surface photovoltage signal for Si-doped GaN sample (#1149) for charged (red) and uncharged (blue) regions.
Figure 6.3: (a) Surface photovoltage signal for CMP-treated Kyma surfaces (#1305). (b) Surface photovoltage signal for MP-treated Kyma surfaces (#1412-3, #1412-4). Taken from Ref. [11].
Figure 6.4: SPV restoration in oxygen for MP- and CMP-treated surfaces (#1412-3; #1412-4) after short (3 s) exposure times for (a) Ga-polar and (b) N-polar GaN. Solid lines are calculated using $\eta = 1.1$, $\tau = 0.1$ s, and $\gamma_0 = 0.47$ eV for Ga-polar, and $\eta = 1$, $\tau = 0.01$ s, and $\gamma_0 = 0.46$ eV for N-polar surfaces. SPV restoration in vacuum after short (3 s) UV exposure for N-polar surfaces of (c) CMP-treated GaN (#1412-4) and (d) MP-treated GaN (#1412-3) at 295 and 425 K. Solid lines are calculated with Eq. (3) using $\eta = 1$, $\tau = 0.101$ s, and $\gamma_0 = 0.42$ eV (at 295 K) and 0.38 eV (at 425 K). Taken from Ref. [11].
Figure 6.5: SPV response for Ga- (red) and N-polar (blue) surfaces grown on sample #612-H for the HCl-cleaned state (thick lines) and after 15 h of subsequent UV exposure (thin lines).

Figure 6.6: Sequential UV exposures for 1 min and 3 min on #612-H sample after HCl cleaning and subsequent 15 h UV exposure showing Ga-polar (red) and N-polar (blue) SPV response.
Figure 6.7: SPV restoration for patterned GaN surface types in the as-received condition. Experimental fits used $\eta = 1$, $\tau = 0.0015$ s for Ga-polar on MOCVD (#100430-M); $\eta = 1.2$, $\tau = 0.003$ s for Ga-polar on HVPE (#612-H); $\eta = 1.125$, $\tau = 0.75$ s for N-polar on MOCVD (#100430-M); $\eta = 1.1$, $\tau = 35$ s for N-polar on HVPE (#612-H).

Figure 6.8: Restoration curves and experimental fits plotted logarithmically for (a) Ga-polar and (b) N-polar surfaces grown on the HVPE template (#612-H). Experimental fits used $\eta = 2$, $\tau = 0.001$ s for Ga-polar “clean”; $\eta = 2$, $\tau = 0.005$ s for Ga-polar “15 hr. UV” (#612-H); $\eta = 1.85$, $\tau = 1$ s for N-polar “cleaned” (#100430-M); $\eta = 1.8$, $\tau = 6$ s for N-polar “15 hr. UV” (#612-H).
**Figure 6.9:** (a) Surface photovoltage signal for mesa and edge (sample #1937-S) under illumination times of 10, 30, 100, and 300 s. (b) Decay data for mesa and edge (averaged over six separate facets) including experimental fits using $\eta = 2$, $\tau = 0.125$ s, and $y_0 = 0.41$ eV for the mesa, and $\eta = 1.3$, $\tau = 0.35$ s, and $y_0 = 0.29$ eV for the edge.
Chapter 7: Summary and Conclusions

By using AFM methods, we have investigated several aspects of GaN surfaces, namely of Ga- and N-polar surfaces. Several distinguishing characteristics were observed in different AFM modes. Topography studies have verified that as-grown Ga-polar surfaces are smoother than N-polar samples by at least one order of magnitude for both the bulk, polar samples and for the laterally-patterned polar samples. The N-polar surfaces prepared by HVPE+LLO exhibited structural damage which is presumably caused by the MP/CMP polishing. MOCVD-grown N-polar surfaces display characteristic hillock formations on the surface, which is to be expected for this type of growth. For MOCVD-grown Ga-polar epilayers, smooth terracing behavior in contrast to the hexagonal terracing for N-polar stripes was observed. HVPE-grown N-polar templates appeared to be of higher quality, as the stripe pattern growth was consistent and the interface boundaries were comparably much more defined than the MOCVD-grown N-polar template. Preferential etching of N-polar surfaces was also seen in topography studies after cleaning the laterally-patterned surfaces.

Local conductivity studies on the samples indicated conflicting but explainable behaviors, especially for N-polar surfaces. For LLO-prepared N-polar surfaces, highly insulating behavior was observed on most of the surface, showing forward-bias conduction only on areas exclusively located away from pitting (scratch features) from the polishing. However, for the patterned polar samples, N-polar areas were remarkably more conductive than adjacent Ga-polar regions in forward bias, but displayed more insulating behaviors for the air-exposed surface. After presumably removing a surface oxide layer with HCl, an increase in the conductivity was seen on the N-polar surfaces. Ga-polar stripes showed a highly insulating behavior in both forward and reverse biases, which was unaffected by HCl cleaning. Both forward and reverse bias CAFM scans reveal that the inversion domain boundary is highly conductive for the patterned epilayer, and may be attributed to an increased number of defect sites near the IDB.

Surface potential (SKPM) data exposed large (< 0.5 eV) differences between Ga-polar and N-polar stripes on the patterned, polar sample set. The largest differences were observed for the air-exposed epilayer grown on the HVPE template, where Ga-polar surfaces showed lower surface potential values (i.e., more negatively charged). Interestingly, the epilayer grown on the
MOCVD template exhibited opposing surface potential differences, where N-polar regions showed a lower surface potential by 0.3 eV. It was expected that a preferential oxide formed on the N-polar surface may have led to decreased band bending at the N-polar surface, thus leading to larger calculated surface potential differences between the two polar surfaces. Indeed, smaller surface potential differences (0.3 eV) were measured on the HCl-cleaned surface. These data suggest that the formation of a well-established surface oxide on N-polar GaN decreases the band bending (and thus the observed surface potential) by ~0.2 eV, assuming that Ga-polar surface potential values did not change significantly after the HCl cleaning. This is a fair assumption as Ga-polar GaN is thought to be highly resistant to HCl etching.

N-polar surfaces also demonstrated behaviors indicative of a thicker surface oxide versus Ga-polar ones. By locally charging both Ga- and N-polar stripes simultaneously, we have observed that N-polar stripes facilitate highly localized and persistent charge. In comparison, Ga-polar stripes appeared to have slight, residual charging effects, but were delocalized and were quickly dispersed. This delocalization on Ga-polar surfaces was seen on the GaN microstructures, where charge injection while the AFM tip was “parked” at the center of the mesa was highly diffuse versus localized. To further verify the effect of preferential oxide formation at the N-polar stripes, HCl-cleaned N-polar surfaces did not demonstrate surface charging behavior. However, the localized and persistent charging effects were partly restored by intentionally accelerating the oxide growth by prolonged UV exposure. A phenomenological model similar to one used for describing surface photovoltage restoration behaviors was constructed here to model the surface charge restoration behavior, and is in fair agreement with the observed data.

Finally, the SPV behavior on these surfaces was used to illustrate distinctive response to above-bandgap illumination. SPV values were larger for N-polar surfaces, and as was observed on polar bulk samples, N-polar surfaces also demonstrated a larger degree of photo-induced processes, which is indicative of the higher chemical reactivity for the N-polar surface. The restoration after illumination was remarkably slower for N-polar stripes on the patterned samples, where these surfaces take several days to reach equilibrium after being exposed to UV.
These clear and convincing behaviors displayed by epitaxially-grown polar GaN may be used to quickly determine the polarity for unknown samples, or to resolve inversion domains on GaN surfaces using scanning probe techniques. Based on the data presented here, there are certainly many opportunities for future studies to better establish contrast mechanisms between Ga- and N-polar GaN. Surface-sensitive chemical analysis, namely Auger electron spectroscopy, may be able to establish the relative thickness of the oxide formed on the N-polar versus Ga-polar surface. Many other candidate techniques (Raman spectroscopy, Kelvin probe, photoluminescence, etc…) are not sample-friendly for the patterned, polar GaN samples, as the sampling size is typically larger than the 16 μm-wide channels. It stands to reason future growths of these types of samples would be better served by choosing growth parameters which are more conducive to these types of experimental techniques in order to better characterize the behaviors of the polar GaN surfaces.

The phenomenological model which was constructed to model the restoration of surface charge after locally injecting charge may certainly be subject to future refinement, as we have simplified the model to only account for a single mid-gap surface state. While the model is in good agreement with the observed restoration, the model is quite sensitive to small changes in the position of the surface state \((E_C-E_S)\). A more realistic model should include a distribution of many surface states to account for the disagreement between the model and the limited experimental data within this report. Nevertheless, this phenomenological model is a promising first step for the development of future rate-based models. If constructed correctly, it is envisioned that simply by injecting charge into an unknown surface and by observing the restoration signal, one may calculate the position(s) and density(-ies) of mid-gap states for different surfaces in various conditions (as-grown, air-aged, HCl-cleaned, etc..).

In summary, this work represents a continuation of basic research investigating the GaN surface, specifically differences between Ga- and N-polar GaN surfaces. Because the surface plays an important role in the electrical and optical attributes of GaN devices, a better understanding of these surface effects should hopefully improve GaN-based device performance. Scanning probe microscopy techniques have been used here to effectively discriminate between
Ga- and N-polar surfaces, and have provided useful information regarding surface morphological and electrical behaviors between these polar GaN surfaces.
Chapter 8: References


