SELF-ASSEMBLED MONOLAYERS ON III-V SEMICONDUCTOR AND SILICON SURFACES

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

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Notre Dame, Indiana
July 2015
Abstract

by

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Continuous advancement in bio-recognition is an important goal that can improve our everyday lives. From detecting contamination, to identifying and managing diseases, to better understanding our environment, biosensors provide the means to quantify the living world. Developing new sensors for the analytical detection of biological analytes involves creating devices that are either better than current testing methods or provide novel analyte detection. The goal of the research presented in this dissertation is to develop new electrical biosensors through the direct chemical functionalization of semiconductor surfaces with self-assembled monolayers (SAMs). The monolayers serve as a linker that attracts a target analyte, connecting biology with technology.

I first studied the functionalization of gallium nitride, a promising biocompatible material, with carboxylic acid and silane self-assembled monolayers. Although functionalization was successful, I discovered that the native oxide, to which the monolayers are covalently bound, is soluble in aqueous solutions. The solubility of the oxide was explored for both powdered Ga_2O_3 and solid GaN with its native Ga_2O_3 layer.
The powder was found to be soluble in aqueous solutions at around 1-3 ppm. For 1 cm² solid GaN wafers soaked in 5 ml of liquid, the Ga concentration was found to be 0.264 ± 0.05 ppb/mm² for 18 MΩ H₂O and 0.100 ± 0.015 ppb/mm² for pH = 7 buffer.

The second portion of my research focused on the modification of aminopropyltrithoxysilane (APTES) monolayers on silicon and III-V nitride multilayered semiconductors for high electron mobility transistors (HEMT’s). The APTES monolayers were modified via reductive amination with 3 different aldehydes: 5-bromo-2-hydroxy-3-methoxybenzaldehyde, for APTES binding confirmation, 4-formylbenzo-15-crown-5, to create a cation binding monolayer, and dipicolylaldehyde, to create dipicolyamine (DPA) ligands that coordinate Zn²⁺ and create an anion binding monolayer. Although proving ion capture was unsuccessful, the DPA ligands do coordinate zinc. This creates a positively charged surface that I used for attracting negatively charged DNA origami.
To my hero, Amanda Arisio
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I would first like to thank my advisor, Dr. Marya Lieberman. Without her wisdom, guidance, patience, and kindness this work would never have been completed. I learned more from her than any other teacher I have known. I thank Dr. Huili Grace Xing, for providing the nitride samples so critical to my research. I also thank her for taking the time to teach me about semiconductor physics. I would also like to thank my committee members, Dr. Masaru Ken Kuno, and Dr. Prashant Kamat.

I thank the University of Notre Dame, and the Department of Chemistry and Biochemistry for the privilege and opportunity to be a graduate student. I would also like to thank Mrs. Debra Bennett for her constant support of me and for being a champion of the chemistry/biochemistry grad students.

To the past and present members of the Lieberman group, I could not have asked for better labmates. I would like to recognize Koshala Sarveswaran, Kyoung Nan Kim, Valerie Goss, and Brighid Corcoran; thank you for being my friends and colleagues.

I thank my undergraduate research advisor, Dr. Stanislaus S. Wong at SUNY Stony Brook, for opening my eyes to Nanotechnology, teaching me to do research, and giving me the undeniably wonderful opportunity to work at Brookhaven National Lab.

Lastly, I thank my family, my rock. My husband, Dana, my mother, Leisa, my brother, Michael, my sister, Amanda, and my cousins, Rhea and Aaron. I love you all so much. Thank you for always believing in me.
CHAPTER 1:
INTRODUCTION

1.1 Overview

Inorganic materials that serve as molecular biosensors are those that use optical, electrical, or magnetic properties to detect a biological analyte. Some of the challenges of the technological advancement of these biosensors involve developing devices that are smaller, less expensive, have increased specificity for target analytes, have better limits of detection for target analytes, or have the potential to be manufactured on an industrial scale to meet the demands of intended usage. The goal of the research presented in this dissertation is to develop new electrical biosensors through the direct chemical functionalization of semiconductor surfaces with self-assembled monolayers (SAMs).

Sensors that work by electrical detection have the advantage of being easier to integrate into electronic circuits to create functional device systems. Carbon nanotubes, for example, have unique electrical properties that make them good candidates for molecular electronics because networks of carbon nanotubes can act as field effect transistors. and based on these properties, numerous studies have been done on the use of single-walled carbon nanotubes to make biosensors. Using SWNTs for biosensors takes advantage of the fact that carbon nanotubes can be functionalized in a variety of ways. It is through this functionalization that the nanotubes can be linked to various biomolecules, triggering electrical changes. Single-stranded DNA (ssDNA) can link
with SWNTs through non-covalent wrapping,\textsuperscript{11} and this interaction has been exploited to make a biosensor from a carbon nanotube network field effect transistor.\textsuperscript{9} The transistor was used for label free detection of DNA hybridization.

In a typical transistor, two metal contacts serve as a current source (S) and drain (D). The contacts are separated by a semiconducting channel, and current flow between the source and drain is regulated by a “gate” when a voltage (Vg) is applied to the channel. In the case of the carbon nanotube field effect transistor, devices can be fabricated by growing SWNTs onto a silicon wafer, creating a random network of nanotubes (Figure 1.1 A). Conductance (G) as a function of gate voltage (Vg) was monitored for the bare single-walled carbon nanotubes, SWNT with ssDNA, and SWNT after hybridization of the DNA (Figure 1.1 B). Changes in electronic characteristics of the nanotube network field effect transistor were observed upon DNA hybridization.
Figure 1.1 (Adapted from reference 9) A. Scanning electron microscopy image of the random network NTNFET device. B. Conductance ($G$) as a function of gate voltage ($V_g$) for the bare single-walled carbon nanotubes, SWNT with single stranded DNA, and SWNT with hybridized DNA.\(^9\)

The technological advantage of the carbon nanotube field effect transistor is that the device exists on a silicon wafer chip which can easily be incorporated into more complex electronic systems. The drawback is that the carbon nanotubes serve as a “middle man”. There is an added device fabrication step of growing the SWNTs before functionalization. Furthermore, differences in electrical measurements rely on the nanotubes, not the wafer itself, creating added variables. Are there enough nanotubes present on the surface? Are all the tubes grown the same (as mentioned earlier, conformation affects electrical properties)? Is there an even distribution of functionalized tubes across the surface? Practically speaking, it is more convenient to have direct functionalization of a semiconductor surface for biosensing applications.
As stated earlier, the research presented in this dissertation focuses on the development of new electrical biosensors through the direct chemical functionalization of semiconductors with self-assembled monolayers (SAMs). These SAMs function as a molecular glue used to attract and attach biomolecules to the semiconductor surface, providing an interface between hard technology and soft biology. Binding of biological targets causes changes in charge density at the semiconductor surface which can be electrically detected by changes in current flow within the semiconductor.

In the remainder of the first chapter of this dissertation, I will give an introduction to the self-assembled monolayers and semiconductor surfaces used for making biosensors. I will also give explanations of the characterization techniques used throughout this research. In chapter 2, I will discuss the functionalization and characterization of gallium nitride (GaN), starting with an overview of the bare surface and preparation techniques. Functionalization of GaN was carried out using various carboxylic acid and siloxane self-assembled monolayers. Characterization of the monolayers will be given along with detailed studies of monolayer stability. A comparison of these monolayers on other surfaces is also explored. It was found that the SAM’s completely desorb in water and common buffers due to the solubility of the native oxide to which the monolayers are covalently anchored. Many biosensor devices are intended to measure target molecules in an aqueous environment. Therefore, the stability of functionalized GaN surfaces in water is critical for the lifetime of the sensor.

Chapter 3 involves the synthesis and characterization of two ion sensing monolayers on both Si and III-V (nitride) heterostructures. Schiff base formation and reductive amination to aminopropyltriethoxysilane (APTES) were employed to attach
various aldehyde molecules to the semiconductor surfaces. I will describe the attachment of fluorinated and brominated aldehydes to the surfaces, and then describe the attachment of a crown ether for a cation binding sensor, and the attachment of a dipicolylamine ligand for anion and DNA binding sensors. Attachment chemistry of the ion binding SAM's is difficult to prove, particularly by x-ray photoelectron spectroscopy, due to the fact that the monolayer ligands are composed of only carbon, oxygen, and nitrogen. These elements are already present on the semiconductor surface and in the XPS chamber environment. Therefore, the fluorinated and brominated aldehydes were used for confirmation of attachment chemistry since F and Br are unique element additions to the sample. The ion binding monolayers were evaluated for ion and DNA capture capabilities using x-ray photoelectron spectroscopy and atomic force microscopy.

1.2 Self-Assembled Monolayers

“Self-assembly is the autonomous organization of components into patterns or structures without human intervention.” – George M. Whitesides

1.2.1 Background

A self-assembled monolayer is a highly ordered and oriented arrangement of single layer thick molecules that have a chemical or physical attraction to a surface. These arrangements form spontaneously and independently by placing a substrate in a solution or vapor of surface favored molecules. Due to the strong surface interaction, such films are self-limiting to a single molecular monolayer. There are a wide variety of well-known surface-molecule combinations, such as thiols on gold surfaces and silanes and carboxylic acids to oxide surfaces. Although carboxylic acids were briefly
studied for this work, the main self-assembled monolayers used in my research were siloxanes grown on the native oxides of semiconductor surfaces, particularly, silicon, gallium nitride, aluminum gallium nitride, and indium aluminum gallium nitride.

1.2.2 Siloxanes

Oxide surfaces, such as the native oxide on Si, that are exposed to silane molecules in dry conditions will form stable siloxane self-assembled monolayers.\textsuperscript{18} Siloxane functionalization of the semiconductors in my research was carried out with octadecyltrichlorosilane (OTS) and aminopropyltriethoxysilane (APTES). SAM growth for both molecules on Si surfaces has been well studied.\textsuperscript{18-23} The silane end of the monolayer binds to the SiO\textsubscript{2} layer on silicon, with Si-O-Si crosslinks forming between SAM molecules giving added stability. The Lieberman group has also studied the growth mechanism of these siloxane SAMs on Si.\textsuperscript{24,25} Figure 1.2 shows the growth mechanism of OTS proposed by the Lieberman group. OTS consists of a long carbon chain that terminates in a trichlorosilane (SiCl\textsubscript{3}) group. There is potential for OTS to form a multilayer if water is present during deposition. The group found that an ultra-smooth monolayer can be achieved with a dry, non-aqueous solvent deposition.\textsuperscript{24} In dry conditions, what little water is present in solution is attracted to the hydrophilic Si surface. OTS molecules near the surface will first hydrolyze, then covalently attach to the surface through dehydration. Further dehydration forms the Si-O-Si crosslinks.
The APTES molecule consists of a short carbon chain terminated with an amine group on one end and a triethoxy silane \([\text{Si(OC}_2\text{H}_5)_3]\) group on the other end. APTES binds to Si in a similar fashion to OTS, with the formation of stabilizing crosslinks. APTES monolayers however, are particularly useful because of the attachment chemistry potential at the terminal amine end. The presence of the amine group allows the chemistry required to link biosensing molecules to semiconductor surfaces. APTES attachment chemistry with aldehydes via Schiff base formation was used in this research.

1.3 Semiconductors

Throughout this research, III-V (nitride) semiconductors, such as gallium nitride (GaN) and heterostructured aluminum gallium nitride/gallium nitride (AlGaN/GaN) were used. Samples were supplied by Dr. Huili Grace Xing (Dept. of Electrical Engineering, University of Notre Dame). The nitrides are epitaxially grown on sapphire substrates. Commercially purchased silicon wafers were also used in this research. Si wafers are less expensive and more readily available than the nitrides, and were used a substitute for observing monolayer formation.
1.3.1 GaN

Gallium nitride is an optically transparent wide band-gap semiconductor. It has a direct band gap of about 3.4 eV. The wide bandgap allows for short wavelength visible light emission, making GaN an ideal material for light emitting diodes (LEDs), particularly blue LEDs. Due to its electrical properties, GaN is a widely used material for field effect transistors. GaN is also stable at high temperatures and under harsh chemical environments, allowing for a greater range of possible device applications. The native oxide that forms on the surface of GaN in ambient conditions allows for surface functionalization with a variety of self-assembled monolayers (SAM’s) such as phosphates, carboxylic acids, and silanes. These SAM’s are used to create sensing devices by providing a chemical link between the semiconductor and specific analytes.

Gallium nitride wafers used in this research were grown on sapphire substrates by metal organic chemical vapor deposition (MOCVD). The GaN has a hexagonal wurtzite structure with lattice constants: $a = 3.189 \text{ Å}$ and $c = 5.185 \text{ Å}$. Figure 1.3 shows a typical atomic force microscope image of the surface of GaN. GaN will be discussed in further detail in chapter 2 of this dissertation.
1.3.2 High Electron Mobility Transistors

The heterostructures used in this research are AlGaN/GaN and InAlN/GaN, with AlGaN/GaN being the main structure used. Samples were grown by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) on sapphire substrates. Both AlGaN and GaN have a hexagonal wurtzite structure. The lattice parameters of AlGaN (given as AlN) are $a = 3.112 \, \text{Å}$, and $c = 4.982 \, \text{Å}$, while the lattice parameters of GaN are $a = 3.189 \, \text{Å}$ and $c = 5.185 \, \text{Å}$. Strain within the crystal structure

Figure 1.3 Atomic force microscope image of unfunctionalized Gallium Nitride
arises from the lattice mismatch between the AlGaN and GaN.\textsuperscript{36} The bandgaps for AlGaN and GaN are 4.2 eV (6.2 eV for AlN\textsuperscript{37}) and 3.4 eV\textsuperscript{26}, respectively.

High electron mobility transistors (HEMTs) are heterostructured semiconductor devices with source and drain metal contacts. The structures consist of two materials with differing bandgaps that form a 2-dimensional electron gas (2DEG) at the heterojunction, or interface, between the two semiconductors. The 2DEG is essentially a triangular quantum well, where electrons are spatially confined in 1 dimension, but can move more freely in the other 2 dimensions. The 2DEG of AlGaN/GaN is induced by both spontaneous polarization as well as piezoelectric polarization due to strain.\textsuperscript{35,38,39} The total polarization of one of the III-V layers is the sum of the spontaneous and piezoelectric polarizations, and a gradient of polarization due to the multilayered HEMT material causes a sheet charge density. For the AlGaN/GaN HEMT, the sheet charge is positive. Free electrons compensate a positive sheet charge. The difference in spontaneous polarization between the AlGaN and GaN layers confines electrons at the interface, and piezoelectric polarization increases the total polarization difference between the layers, increasing the sheet charge.\textsuperscript{35} Thus variations in composition and strain can alter the electron concentration or size of the 2DEG. Charge distribution/polarization is also altered by changes in charge density at the device surface, which in turn will affect the size of the 2DEG. Figure 1.4 shows the band diagram for AlGaN/GaN. When the size of the 2DEG changes, the resistivity of the device changes. Therefore, HEMTs can be used for a multitude of sensor applications by utilizing the sensitivity of the 2DEG to surface charges and measuring changes in device electronic characteristics.
1.4 Surface Characterization Techniques

1.4.1 Atomic Force Microscopy

Atomic force microscopy, or AFM, is a non-optical scanning probe microscopy technique used primarily to obtain information on surface topography, and can be used to image surface features with sub-nanometer resolution. The invention of AFM came from the modification of scanning tunneling microscopy (STM). STM relies on the tunneling of electrons between a conductive surface and tip. AFM however, does not
require a conductive sample surface. The technique utilizes the repulsive and attractive forces between a sharp tip (typical end radius ~10 nm) and sample surface when the two are brought in close proximity to one another. Although there are many forces that contribute to tip/sample interactions, the forces that dominate the interactions include van der Waals forces, Pauli repulsion, and capillary forces due to a “water layer” from humidity surrounding the tip and the surface. The distance between the tip and the surface dictates which type of force is involved. When closest to the surface (less than a few nm), repulsive forces dominate, while further away, weak van der Waals attractive forces dominate.

Figure 1.5 illustrates the basic setup of an AFM. The tip is situated at the end of a cantilever, which bends in response to changes in force between the tip and the surface. The cantilever behaves like a spring, and force between the tip and surface follows Hooke’s Law. The back of the cantilever has a reflective coating on it. This coating is used to bounce a laser beam off the cantilever onto a position sensitive photodetector (PSPD). The PSPD includes multiple photodiodes (2 or 4) that convert the light of the laser beam into a voltage. As the tip moves over variations in surface height, the cantilever deflects due to changes in force. The deflection changes the position of the laser reflection on the PSPD, changing the output voltage. In order to maintain a constant force between the tip and the surface, a computer controlled feedback mechanism is used to move the sample, which is mounted on a piezoelectric tube scanner. After receiving the change in voltage from the PSPD, the computer sends a voltage out to the piezoelectric scanner causing it to expand or contract in the x,y,z directions to move the sample. A topographic image is obtained by measuring z (height) at an (x,y) data point.
The AFM images in this dissertation were taken with a Veeco Dimension (Di) atomic force microscope. Images were typically 512 samples per line, between 1 μm x 1 μm up to 10 μm x 10 μm, and scanned at speeds between 0.5 Hz and 1.5 Hz. Image processing was carried out using Veeco Di Nanoscope software (versions 3 and 7). Images were further processed using Image J freeware. All images were taken in tapping mode AFM in air. Dynamic AFM modes, such as tapping mode, involve vibrating the cantilever near its resonance frequency. In tapping mode, the large amplitude of vibration allows the tip to come into close contact or “tap” the surface. The tip does not actually touch the surface due to the repulsive forces involved at such close distances. Being as the oscillation amplitude is so large, the tip experiences both attractive and
repulsive forces during its up and down swing. As the tip moves over variations in surface height, changes in force result in changes in the amplitude of oscillation. The feedback loop maintains an amplitude setpoint by moving the piezoelectric scanner. For this research, Vista Probes silicon tips/cantilevers were used. These cantilevers have a resonant frequency of ~ 300 KHz and a spring constant, k, of ~ 40 N/m.

Being as AFM is a non-optical, probe technique, it is not subject to lens quality and optical/visible light limitations. However, there are image artifacts (incorrect/artificial measurements) that can arise. Some such artifacts are due to tip complications (dull, dirty, and/or split tip), tracking/feedback errors in the trace and retrace of the raster scan, optical interference due to laser reflection off the sample reaching the photodetector, and external vibration interference.

1.4.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy, or XPS, is a quantitative elemental surface analysis technique. In addition to obtaining information about the composition of a surface, XPS can be used to obtain information on stoichiometry, chemical states, and surface contamination. The technique involves irradiating a surface with monoenergetic kα x-rays under ultra-high vacuum (UHV). The adsorption of the x-rays results in the ejection of electrons with orbital specific kinetic energies. The electrons are collected, filtered, and “counted” by a detector which converts kinetic energy to binding energy by the equation $KE = h\nu - BE - \phi_s$, where $KE$ is the measured kinetic energy, $h\nu$ is the energy of the x-ray, $BE$ is binding energy, and $\phi_s$ is the spectrometer work function.\textsuperscript{43} The layout of spectra obtained shows electron counts per second (CPS) vs. binding energy. The instrument is sensitive for electrons only from the top 5-10 nm of a surface
due to the short mean free path the electrons can take before having an inelastic collision. The detection limits of XPS are as low as 0.1%. Figure 1.6 shows a diagram of a Kratos XSAM800 XPS analysis chamber.

The Kratos XSAM 800 XPS system was used to for all XPS data given in this document. The x-rays used were mostly from a Mg kα source (1253 eV), however, an Al kα source (1468 eV) was also used. The vacuum level used for data acquisition was primarily in the low x10^-7 Torr to high x10^-9 Torr range. The x-ray beam spot size was roughly a 1 mm x 3 mm ellipse. Data acquisition was obtained using Kratos Vision 2 software. Data analysis was carried out using CasaXPS analysis software (version 2.3.15 and 2.3.16).
1.4.3 Water Contact Angle

In the contact angle technique, a droplet of water is placed on a surface, and the angle, \( \theta \), formed at the solid/liquid/air interface is measured. Contact angle measurements give information on if a surface is hydrophobic or hydrophilic. The angle can also be affected by surface roughness and contamination. Knowing the water contact angle of a surface also gives information on surface energy, adhesiveness, and wettability. Figure 1.7 represents hydrophobic and hydrophilic contact angles.

![Figure 1.7 Representation of hydrophilic and hydrophobic water contact angles.](image)

When the contact angle is less than 90°, the surface is considered hydrophilic. It has high wettability, adhesiveness, and surface free energy. Conversely, when a surface is hydrophobic, water beads up, and \( \theta \) is greater than 90°. Such surfaces have low surface free energy, poor adhesiveness, and low wettability. The contact angle
measurement technique does suffer from human eyesight error, which is typically $\pm 5^\circ$ from person to person.

Water contact angle was used in this research as an additional method for confirmation of surface functionalization. Prior to functionalization, the clean semiconductor surfaces are very hydrophilic, with contact angles less than $10^\circ$. Functionalization results in an increase in contact angle, the degree of increase depends on the SAM used. For this work, a Kruss G10 contact angle goniometer and ultra-pure (18 MΩ resistivity) water were used. The angle, $\theta$, was measured with an “advancing” drop, meaning the measurement was taken while the size of the droplet was increased. Typically, a 1 cm$^2$ sample was used, and 3-4 angles were measured at varying locations on the surface. The average and standard deviation were reported.

1.4.4 Ellipsometry

Ellipsometry is a powerful technique that gives information on the dielectric constant and refractive index of thin films, as well as film thickness, with sub-nm limits of detection. It is especially useful when a sample has multiple layers to be considered. For example, a SAM functionalized Si chip consists of the Si underlayer, a SiO$_2$ overlayer, and the SAM as a second overlayer. Ellipsometry can be used to determine the thickness of the oxide and the SAM.

Figure 1.8 shows the general configuration of an ellipsometer. A laser light source is passed through a polarizer and compensator prior to hitting a sample. The light source is reflected from the sample at angle equal to the angle of incidence, $\varphi$ and goes through an analyzer before reaching a detector. The detector measures changes in polarization of the incident light beam as well as the angle of incidence, $\varphi$. The
instrument can then calculate the refractive index and thickness of an overlayer based on knowing the optical constants, N and K, of the overlayer, as well as the angle of incidence and optical constants for the underlayer in air.

Figure 1.8 Polarizer–Compensator–Sample–Analyzer (PCSA) configuration of an ellipsometer.\textsuperscript{45}

All monolayer thickness measurements presented in this dissertation were obtained on a Gaertner Scientific automated ellipsometer. Ellipsometry is a reflective technique. All III-V nitride semiconductors used in this dissertation have wide band gaps, and are therefore transparent. These samples transmit too much of the laser light to make measurements.

Ellipsometric measurements were only taken on Si semiconductor samples. Thickness measurements were repeated approximately 8 times for all samples, over
various locations on the chip. The ellipsometer measurements optical parameters, $N$ and $K$, were taken from a standard table provided in the instrument’s user manual. The angle of incidence and the analyzer angle were set at 70º. For the silicon substrate, $N = 3.87$ and $K = 0.018$. For the native oxide on Si, $N = 1.55$ and $K = 0$. Monolayer thickness estimates were made by using the theoretical thickness of the SAM molecule, and assuming no tilt angle of the molecule (SAM is oriented perpendicular to the surface).
CHAPTER 2:
GROWTH AND CHARACTERIZATION OF CARBOXYLIC ACID AND SILOXANE MONOLAYERS ON GALLIUM NITRIDE

2.1 Introduction

Gallium nitride has shown much promise as a material for biosensor applications. It is used in high electron mobility transistors (HEMT’s) in which the conductive channel is a two-dimensional electron gas (2-DEG) that lies between the interface of two semiconductors of differing band-gaps.\textsuperscript{39,46} The conductivity of the 2-DEG is strongly affected by nearby electrical charges. Therefore, if the surface of the HEMT structure is exposed to a solution containing ions, they can act as a gate for the conductive channel.\textsuperscript{47} Hernandez showed that clean GaN in UHV conditions reacts with electron donors such as aniline and thiols.\textsuperscript{48,49} Although these reactions are not germane to sensing done under ambient conditions, they suggest that molecular sensing could be mediated by self-assembled monolayer (SAM) formation. Indeed, a SAM of thiolated DNA can assemble on a protective and conductive film, such as gold, to create GaN-based HEMT sensors with good chemical sensitivity and selectivity.\textsuperscript{50}

The native oxide that forms on the surface of GaN in ambient conditions allows for direct surface functionalization. A variety of self-assembled monolayers (SAMs) based on siloxane precursors reacting with this surface oxide have been used to create sensing devices by providing a chemical link between the semiconductor and specific...
Many of these HEMT devices are intended to measure target molecules in an aqueous environment. Therefore, the stability of functionalized GaN surfaces in water is critical for the lifetime of the sensor.

In chapter 2, the functionalization of GaN will be discussed. GaN, with a thin passivating layer of Ga$_2$O$_3$, was functionalized with self-assembled monolayers of carboxylic acid and siloxane molecules. Prior to functionalization, the bare GaN surface was characterized both before and after various surface preparation treatments. The carboxylic acids used were stearic acid, perfluorotetradecanoic acid and 6-aminohexadecanoic acid. The siloxane molecules used were octadecytrichlorosilane (OTS) and aminopropyltriethoxysilane (APTES). Water contact angles, atomic force microscopy, and x-ray photoelectron spectroscopy were used for characterization of the bare and functionalized surfaces. (XPS was only performed on bare GaN and the siloxane SAMs.) These techniques were also used to test monolayer stability by characterizing the GaN surface after various immersion times in aqueous environments. Monolayer stability was tested by soaking fully functionalized GaN samples in common buffer solutions and water, which are typical biological media. Additionally, stability tests were performed on the native oxide of GaN in order to explain monolayer behavior in aqueous environments. Finally, comparisons of monolayer formation on other common semiconductor surfaces are also given in this chapter.

2.2 Characterization and Preparation of the Bare GaN Surface

All gallium nitride samples used for this research were obtained from Dr. Huili Grace Xing of the Electrical Engineering Department (University of Notre Dame). The
samples used ranged in size from approximately 5 mm x 5 mm to 10 mm x 10 mm chips. These samples were diced from GaN wafers that were grown in house by metal organic chemical vapor deposition (MOCVD). The hexagonal structured GaN is grown 2 μm thick on top of a sapphire substrate. The samples were made approximately 2 years before they were acquired for this research.

2.2.1 Contact Angle and AFM Imaging

The GaN samples underwent rigorous cleaning procedures prior to functionalization. Proper pretreatment of the GaN surface is important to remove surface contaminants. Samples were used for self-assembled monolayer growth within 1-2 hours (or less) of the cleaning treatment to reduce recontamination of the surface. Initial treatment of the GaN surface involved rigorous rinsing with acetone, followed by isopropanol (or 200 proof ethanol), then ultra-pure, 18 MΩ resistivity water. The samples were dried with nitrogen gas. The average water contact angle obtained after this treatment procedure was 34°±1°. After using the GaN samples for SAM growth, it was determined that a stronger cleaning procedure was needed. For new samples, after rinsing the surface with acetone, alcohol, and ultra-pure water, the samples were soaked in 2 M NH₄OH for 5 minutes. If the sample was used, it was sonicated in 2 M NH₄OH for 15 - 20 minutes (Figure 2.1). All base soaks were followed by a rinse with 18 MΩ H₂O. The base cleaning procedure typically resulted in a contact angle of 38°±1°, which was not an improvement from solvent cleaning alone.
Figure 2.1 AFM image of the surface of gallium nitride after the growth and removal of one stearic acid monolayer, followed by a 15 minute sonication in NH₄OH. The root mean square roughness (2 μm x 2 μm image) is 0.253 nm.

AFM imaging of the solvent + base cleaned surface showed the presence of surface contaminants (particles seen along the surface). Additionally, water spots were often seen in AFM images, indicating that contaminants were mobile, but did not “rinse off”. Instead they dried in rings on the surface. It is also possible that these rings were caused by contaminated 18 MΩ water.

In order to significantly reduce surface contamination on the GaN, an acid soak was used, following typical Si wafer cleaning procedures. Silicon semiconductor wafers are commonly prepared by a series of strong acid soaks involving hydrogen peroxide and sulfuric acid. After solvent washes with and acetone and alcohol (and an ultra-pure water rinse), the GaN samples were soaked for 20 minutes in a “piranha” acid solution. Piranha
acid is a 1:3 mixture of 30% H\textsubscript{2}O\textsubscript{2} to H\textsubscript{2}SO\textsubscript{4} (concentrated). During the acid etch, bubbling and light foaming was observed at the surface of the GaN. This foaming subsided within 10-15 minutes of being in the acid. After 20 minutes, the samples were rinsed with ultra-pure water and dried with flowing nitrogen gas.

The water contact angle for the acid cleaned GaN surface was very hydrophilic, measuring less than 10°. The drop in contact angle is caused by the acid effectively etching away surface contaminants. This was confirmed with AFM. AFM imaging (Figure 2.2) of the piranha etched bare GaN surface shows little to no surface contamination, indicated by the absence of particles on the surface. The samples exhibit classic GaN surface features. Dislocations in the GaN lattice appear as black pits or holes in the surface. Also visible on the surface are step features which appear as diagonal lines across the image. The root mean square (RMS) roughness for a 1 μm\textsuperscript{2} image of piranha etched GaN is approximately 0.160-0.210 nm. Variations in this value predominantly depend upon the number of lattice dislocations captured in an image.
Figure 2.2 AFM image of a bare GaN surface after cleaning with piranha acid. RMS roughness (1 μm x 1 μm) = 0.211 nm. RMS roughness (10 μm x 10 μm) = 0.788 nm.
2.2.2 XPS

X-ray photoelectron spectroscopy (XPS) data was obtained for the bare gallium nitride surface after cleaning. Samples were prepared with a piranha etch, as described in section 2.2.1, to minimize surface contamination. The x-rays used were from a Mg kα source (1253 eV), and the data obtained was calibrated to the C 1s peak at a literature value of 284.5 eV.\(^{43}\) Calibration of the XPS data is critical because the GaN surface exhibits significant positive charging under x-ray impingement, as electrons are ejected. The charging is due to the fact that the GaN is grown on an insulating sapphire (aluminum oxide) substrate. The exact offset of charging varies from sample to sample, but was generally found to be between approximately 5-10 eV. Data analysis and calibration was performed using CasaXPS software. Figure 2.3 shows a comprehensive survey scan of the clean GaN surface with all peaks labeled. Individual region scans and a quantification report can be found in Appendix B.1.
Figure 2.3 X-ray photoelectron spectroscopy (Mg source) comprehensive survey scan of piranha etched GaN.
The strongest C 1s peak was found at 292.906 eV, therefore, a calibration offset of 8.406 eV (the difference between the raw peak value and the literature value for C 1s) was subtracted from all data peaks. Table 2.1 lists peak positions after calibration vs. literature values.

**TABLE 2.1**

**CALIBRATED X-RAY PHOTOELECTRON SPECTROSCOPY PEAK POSITIONS FOR PIRANHA ETCHED GALLIUM NITRIDE**

<table>
<thead>
<tr>
<th>Region/Peak</th>
<th>Literature Position (eV)</th>
<th>Actual Position (eV) after Calibration</th>
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<tr>
<td>Ga 2p 3/2</td>
<td>1116.7</td>
<td>1117.39</td>
</tr>
<tr>
<td>Ga 2p 1/2</td>
<td>1143.54</td>
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<tr>
<td>Ga 3p 1/2</td>
<td>107</td>
<td>108.99</td>
</tr>
</tbody>
</table>

Gallium presents a significant set of Auger peaks that directly overlap the C1s region, making it difficult to determine the correct peak position of adventitious carbon in the piranha cleaned GaN sample. Gallium has a strong Auger L₃M₂3M₄5 at 281 eV with a cluster of less intense peaks around it, at slightly higher and lower energies. Figure 2.4 shows the gallium Auger peak patterns that are near the C1s region. This image was adapted from the Ga literature spectrum (Mg source) given in Moulder et. al.’s Handbook of X-ray Photoelectron Spectroscopy.
The C 1s peak for the piranha etched GaN sample (Figure 2.5) was resolved into 3 peaks, a, b, and c, with the most intense peak (b) taken as the peak used for calibration. After calibration, the location of the 3 peaks are as follows: a.) 282.43 eV, b.) 284.5 eV, and c.) 286.22 eV. There is an additional peak around 275 eV that was not assigned to C 1s, as gallium does have an additional Auger peak near this location.

Figure 2.4 Gallium XPS Auger peaks near the C1s region. Adapted from the Handbook of X-ray Photoelectron Spectroscopy.
Figure 2.5 XPS C 1s region scan of piranha etched GaN resolved into 3 peaks (fit residual included).
During XPS data acquisition, it was noted that the GaN wafer emitted a striking green color under the x-ray beam. Figure 2.6 shows a picture of a GaN wafer chip (~1 cm²) fluorescing green. The image was taken through a leaded glass viewport while the x-rays were on and all other lights in the room off.

![GaN wafer chip fluorescing green](image)

Figure 2.6 GaN wafer chip fluorescing green (picture taken through a leaded glass viewport) under impinging Mg source x-rays.

Not all x-ray excited photoelectrons escape from the sample. Some of these excited electrons will relax and their released energy induces luminescence. This emission characteristic of gallium nitride might prove useful for optical applications of the material. GaN emits near UV and increased defects in GaN (i.e. lattice vacancies and dislocations) generally cause emission near yellow. In fact, when a GaN sample has a high number of defects, it looks yellow under ambient room light instead of having the typical transparent and clear appearance.
2.3 Functionalization of GaN with Carboxylic Acid Monolayers

2.3.1 Stearic Acid

Prior to the use of piranha acid as a cleaning method for GaN, stearic acid (Figure 2.7) SAMs were grown on NH₄OH cleaned GaN wafer chips from a 1 mM solution in ethanol. The base cleaning resulted in an initial contact angle of 37.00 ± 1.41°.

![Structure of Stearic Acid](image)

Figure 2.7 Structure of Stearic Acid.

Given the long hydrophobic carbon chain of the molecule, the presence of a monolayer causes an increase in water contact angle. A timed study was performed on monolayer formation by removing a GaN sample from the solution at various time points. Once removed, the sample was rinsed with ethanol and dried with N₂ gas. Water contact angles were measured on the sample, and it was then placed back into the solution to continue SAM growth. Initial growth of the monolayer was quite rapid, with a contact angle of 107.00 ± 0.82° obtained after 1 minute of soaking in solution. Figure 2.8 shows a graph of contact angle vs. time, illustrating the growth of the stearic acid monolayer. The error bars show the average standard deviation for all time points, at ± 1.09°.
After 1 minute, the contact angle did not significantly change, with the average contact angle from 1 minute to 2 hours being $107.43 \pm 0.67^\circ$. AFM imaging was done on a GaN sample soaked in 1 mM stearic acid in ethanol for approximately 1 hour. The average contact angle for this sample was $106.75 \pm 0.96^\circ$.

Figure 2.9 shows a 1.7 µm x 1.7 µm image of the GaN surface after the 1 hour treatment. The RMS roughness of this image is 0.233 nm. For comparison, the RMS roughness of an NH$_4$OH cleaned sample (2 µm x 2 µm) is 0.253 nm (see Figure 2.1) and a piranha etched GaN sample (1 µm x 1 µm) is 0.211 nm (see Figure 2.2). Monolayer coverage of the GaN surface appears to be patchy, with small island clusters visible. However, the high contact angle suggests a continuous monolayer, and the islands may actually
bilayers on top of compact monolayer. Image J software was used to determine the percent coverage of the stearic acid islands which was found to be 25.14 ± 0.03%. If the islands are monolayered, the low coverage suggests that a longer deposition time is needed for dense monolayer formation.

![Image Statistics](image)

**Image Statistics**

<table>
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</thead>
<tbody>
<tr>
<td>Img. RMS (Rq)</td>
<td>0.233 nm</td>
</tr>
</tbody>
</table>

Figure 2.9 AFM image (1.7 μm x 1.7 μm) of a GaN surface after a 1 hour soak in 1 mM stearic acid in ethanol.

2.3.2 Perfluorotetradecanoic Acid and 6-Aminohexadecanoic Acid

Two additional carboxylic acid monolayers were studied for their growth on GaN, perfluorotetradecanoic acid (FC14, Figure 2.10, a) and 6-aminohexadecanoic acid (Figure
The fluorinated carboxylic acid treatment was performed by soaking an NH$_4$OH cleaned GaN sample in a 1 mM solution of FC14 in a 9:1 hexane to ethanol mixture. Given the rapid increase in contact angle seen with stearic acid, a time study was performed on the GaN in FC14 solution paying particular attention to change in contact angle within the first minute of deposition.

A typical contact angle measurement for each time point consisted of taking 3 to 4 measurements on varying locations of the sample. For the FC14 growth, it was found that there was a wide variation in contact angle for each location measured, with standard deviations on the time points ranging anywhere from 6.5° to almost 12°. Figure 2.11 shows a graph of the 1 minute time study of GaN in FC14 solution. After 1 minute in solution, the water contact angle of the GaN sample was 100.75 ± 6.55°. The sample was allowed to stay in solution for 1 hour, resulting in a surprising drop in contact angle to 73.25 ± 11.95°, indicating possible loss in coverage of the SAM, or formation of a bilayer structure with the upper layer’s carboxylic head group facing out. 

Figure 2.10 Structures of a.) perfluorotetradecanoic acid and b.) 6-aminohexadecanoic acid.
The amino-carboxylic acid treatment involved soaking base cleaned GaN in a 1 mM solution in water. This deposition resulted in unsuccessful attachment of the carboxylic acid. The initial contact angle of the base cleaned sample was approximately 37 °. After 1 hour in solution, the contact angle was 38.75 ± 10.81°, and after 2.5 hours the angle was 42.75 ± 7.27°. The large standard deviations mean the measurements overlap with that of the bare, base cleaned substrate.

2.3.3 Stability of Carboxylic Acid Monolayers on GaN

The stability of stearic acid and perfluorotetradecanoic acid functionalized GaN was tested in 18 MΩ H₂O. It was found that for both carboxylic acids, the contact angle

Figure 2.11 One minute time study of GaN in a 1 mM solution of perfluorotetradecanoic acid in 9:1 hexane to ethanol.
dropped back down close to that of bare GaN after soaking in water. For the fluorinated carboxylic acid sample, an overnight soak in water resulted in a contact angle of 53.00 ± 3.46°. A timed water desorption study was performed on a GaN sample that formed by soaking the substrate for 1 hour in a 1 mM stearic acid solution. The graph in Figure 2.12 shows the gradual drop in contact angle for the stearic acid functionalized GaN sample as it soaks in water for 3 hours. The error bars show the average standard deviation for all time points, at ± 4.61°. The initial contact angle (1 hr deposition) was 105.75 ± 0.96°. After 1 hour in water, the contact angle dropped to 69.75 ± 2.75°, and after 3 hours, the contact angle was 36.5 ± 2.64°.

![Desorption of Stearic Acid in 18 MΩ Water](image)

Figure 2.12 Timed water desorption of stearic acid on GaN.
AFM imaging (Figure 2.13) of a water soaked stearic acid GaN sample showed residual islands of stearic acid remaining on the surface. However, due to a tip artifact, no cross sectional measurements were made on the image.

![Image Statistics]

<table>
<thead>
<tr>
<th>Image Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Img. Z range</td>
</tr>
<tr>
<td>Img. Rms (Rq)</td>
</tr>
</tbody>
</table>

Figure 2.13 AFM image of residual stearic acid on GaN after soaking in water.

2.4 Functionalization of GaN with Siloxane Monolayers

2.4.1 Octadecyltrichlorosilane

Octadecyltrichlorosilane SAMs were grown from 5 mM OTS in a 1:4 mixture of CHCl₃: Isopar G for approximately 5 days. Special care was taken to dry all solvents.
since it was previously determined that dry conditions promote the formation of an ultra-smooth monolayer on SiO$_2$.$^{24}$ A timed study was performed on monolayer formation by removing a GaN sample from the OTS solution at various time points. Once removed, the sample was rinsed with CHCl$_3$ and dried with N$_2$ gas. Water contact angles were measured on the sample and atomic force microscope imaging was performed. The sample was then placed back into the OTS solution to continue SAM growth. AFM imaging of the surface shows that growth occurs by island formation, with small patches of OTS molecules evenly distributed across the Ga$_2$O$_3$ surface at early time points. The islands continue to grow, forming complete monolayer coverage within approximately 3.5 days. Figure 2.14 shows AFM images taken at various time points throughout the growth of the SAM.
Figure 2.14 AFM images at varying times (t) of the growth of an OTS monolayer on GaN. All images are 1 μm². (a) t = 1 hour, Contact angle 87.6° ± 8.3°, Surface coverage = 4.8 % ± 0.9 %, RMS = 0.152 nm (b) t = 22 hours, Contact angle 102.3° ± 2.8°, Surface coverage = 12.5 % ± 2.1 %, RMS = 0.240 nm (c) t = 45 hours, Contact angle 107.8° ± 1.5°, Surface coverage = 97.2 % ± 1.3 %, RMS = 0.164 nm (d) t = 88 hours, Contact angle 117.5° ± 2.6°, Surface coverage = 99.9 % ± 0.01 %, RMS = 0.121 nm.
Within an hour, small features were observed, uniform in height and evenly dispersed across the surface (Figure 2.14 a) at 4.8 % ± 0.9 % coverage. At this point, the RMS roughness is still similar to that of bare GaN, 0.152 nm. (Note only one lattice dislocation is visible.) Within 22 hours, OTS patches, 0.7 – 0.9 nm in height, cover a larger amount of the GaN surface at 12.5 % ± 2.1 % coverage (Figure 2.14 b, Figure 2.15), and the increase in particles caused an increase in RMS roughness to 0.240 nm. The island height is less than half of the theoretical thickness of OTS (~2.6 nm).

Figure 2.15 AFM cross-section of OTS growth time point, t= 22 hours. The vertical heights of 3 captured particles, a, b, and c are 0.722 nm, 0.936 nm, and 0.749 nm respectively.
After 45 hours (Figure 2.14 c) and 88 hours (Figure 2.14 d) of soaking in solution, the OTS molecules have coalesced into a smooth layer across the surface, causing a decrease in RMS roughness (0.164 and 0.121 nm, respectively). Surface coverage values for the longer time points are 97.2 % ± 1.3 % for 45 hours and 99.9 % ± 0.01 % for 88 hours. The monolayer is compact enough that looking from the top down, it resembles the bare GaN surface. In addition to the AFM imaging results, water contact angles confirm the growth of an OTS monolayer as the surface hydrophobicity increases from ~10˚ for the bare clean surface to a maximum angle of 117˚ obtained for a full SAM.

2.4.2 Aminopropyltriethoxysilane

APTES self-assembled monolayers were found to grow much quicker than OTS. These SAMs were grown by soaking a clean GaN chip in a 1-2% v/v solution of APTES in 18 MΩ H₂O. The APTES solution was immediately prepared before deposition, and deposition was not carried out beyond 1 hour. This is necessary to prevent excess hydrolysis of the APTES, which causes the formation of APTES multilayers in solution.

As with the OTS deposition, growth of APTES monolayers was monitored over time by AFM imaging and contact angle measurements. The growth mechanism of an APTES SAM on GaN appears to be similar to that of OTS, with initial island formation. Within 15 minutes of soaking in the APTES solution, the majority of the GaN surface was densely covered with APTES islands at 64.8 % ± 1.2 % coverage (Figure 2.16 a). The RMS roughness increased to 0.255 nm while the contact angle increased to 50˚ ± 1.5˚. By 30 mins (Figure 2.16 b), more of the APTES molecules have populated the surface with a coverage of 82.5 % ± 0.9 %. At this time point, the contact angle
increased to 69° ± 3.2°, and there was a decrease in RMS roughness to 0.168 nm. The RMS value reflects a 0.375 um x 0.375 um area in the center of the image to exclude the tall (> 3 nm) features seen in Figure 2.16 b from the calculation. Including these features, which are more than triple the height of an APTES monolayer, results in an RMS of 0.280 nm.

Figure 2.16 AFM images at varying times (t) of the growth of an APTES monolayer on GaN. Both images are 1 μm². (a) t = 15 min, Contact angle low 50 degrees, RMS = 0.255 nm, Coverage = 64.8 % ± 1.2 % (b) t = 30 min, Contact angle upper 60 degrees, RMS = 0.168 nm (center, 0.375 um x 0.375 um area), Coverage = 82.5 % ± 0.9 %.

2.4.3 Stability of Siloxane Monolayers on GaN

Fully functionalized GaN samples were soaked in various solvents, water, and common buffers. Contact angle measurements show that OTS SAMs (Figure 2.17) were stable in acetonitrile for longer than 3 days, but they were unstable in all aqueous
The SAMs in 18 MΩ H₂O and pH = 9 buffer began to desorb after 24 hours, and the samples showed a steady decline in contact angle over the following 2 days. OTS on GaN was highly unstable in pH = 7 buffer, and was completely removed within 2 days. However, duplications of this experiment have shown complete monolayer loss can occur within a few hours of soaking in buffer.

Figure 2.17 Contact angle monitoring of OTS monolayer stability over time in various solvents.
AFM imaging provides visual confirmation of the loss of the monolayer. Figure 2.18 a shows an OTS monolayer that was soaked in pH = 7 buffer for approximately 30 minutes. This image shows the break-up of the monolayer from the smooth compact surface seen earlier to a rough surface with small OTS island patches. The RMS roughness has increased to 0.285 nm, and the contact angle has decreased to ~70°. Surface coverage has decreased to 42.1 % ± 1.9 %. Figure 2.18 b shows the remains of an OTS monolayer after soaking in pH = 7 buffer for 2.25 hours. The contact angle is ~68°, surface coverage is at 11.3 % ± 1.7 %, and the RMS roughness has dropped to 0.175 nm. Though the sample resembles bare, unfunctionalized GaN at this point, random, residual patches of OTS remain on the surface. Repeat solubility tests have shown that the time necessary for loss of the OTS SAM in pH = 7 buffer can vary from 1 hour to 24 hours. Even after long soaking times, small amounts of the GaN surface remain covered by small islands, giving a bulk contact angle of 40-50°, which is believed to be residual OTS. Cleaning with piranha acid recovers a smooth bare surface with a hydrophilic contact angle of less than 10°.
Figure 2.18 AFM images of the loss of an OTS monolayer after soaking in pH = 7 buffer for various lengths of time (t). (a) t = 30 mins, Contact angle = 70°, RMS = 0.285 nm, Coverage = 42.1 % ± 1.9 % (b) t = 2.25 hr, Contact angle = 68°, RMS = 0.175 nm, Coverage = 11.3 % ± 1.7 %.
The stability of APTES monolayers on GaN was similar to that of OTS monolayers. Figure 2.19 a shows an AFM image of an APTES on GaN sample after 7 hours of soaking in ultra-pure water. The image shows a break-up of the monolayer with small islands covering the surface. The contact angle decreased to 41°, the RMS roughness increased to 0.207 nm, and the coverage slightly decreased to 69.7 % ± 1.4 %. After 2 days of soaking in water, the APTES monolayer has been completely removed (Figure 2.19 b). The contact angle dropped to ~20° and the RMS roughness was similar to that of bare GaN, at 0.169 nm. The % coverage of APTES remaining was negligible. As with OTS, APTES was very unstable in pH = 7 buffer, which completely removed the monolayer within a few hours to 1 day.
Figure 2.19 AFM images of the loss of an APTES monolayer after soaking in 18 MΩ H₂O for various lengths of time (t). (a) t = 2 hr, Contact angle = 41°, RMS = 0.207 nm, Coverage = 69.7 % ± 1.4 % (b) t = 2 days, Contact angle = 20°, RMS = 0.169 nm, Coverage = n/a.
2.4.4 X-ray Photoelectron Spectroscopy of Siloxane Self-Assembled Monolayers on GaN

X-ray photoelectron spectroscopy monitoring of the GaN surface was performed to provide confirmation of SAM growth and subsequent removal. Overlays of Ga 2p region specific scans of the clean, unfunctionalized GaN surface (Figure 2.20 a) and the surface fully functionalized with siloxane SAMs (Figure 2.20 b) show an attenuation of signal from Ga atoms. Signal strength from Ga increases after buffer removal of the monolayers (Figure 2.20 c). The % concentration ratio of carbon 1s to gallium 2p (C:Ga) is 2 ± 0.44 to 1 for piranha etched GaN. This ratio increases to 2.5 ± 0.55 to 1 for a full APTES SAM and 6.5 ± 1.55 to 1 for a full OTS SAM. The carbon to gallium ratio decreases significantly for the surface after buffer removal of OTS, at 0.34 ± 0.1 to 1.
2.5 Discussion

2.5.1 Growth and Instability of Monolayers on GaN

The growth mechanisms for OTS monolayers vs. APTES monolayers are similar to one another in that they require hydrolysis, however, they differ greatly in the length of time that growth takes to occur. Previously, our group has detailed the slow growth of ultra-smooth OTS monolayers on Si\textsuperscript{24}. In this study, AFM and water contact angles show a similar slow growth for OTS on GaN. The 3.5 day growth time is due to the fact that
the SAMs are grown from very dry solution conditions. There is very little water present to hydrolyze the OTS molecules. Because piranha etching of GaN leaves a very hydrophilic surface, what little water that there is in solution will be found at the GaN surface. The time it takes for the monolayer to grow thus becomes a diffusion issue as OTS molecules must be near the surface for hydrolysis to occur. APTES monolayers are grown from a solution of APTES in ultra-pure water. Hydrolysis begins as soon as the APTES is placed in solution, and SAM formation is much more rapid. The early hydrolysis step requires fresh APTES solutions to be used, to prevent multilayer formation as APTES molecules can excessively crosslink.

The full coverage contact angle obtained with APTES is not as high as that seen for OTS because the APTES chain is terminated with an amine group and not a simple hydrophobic carbon chain. Additionally, the full coverage contact angle varied according to the length of time the sample was out of solution. This observation may be due to changes in the amount of protonated amines (NH$_2$ vs. NH$_3^+$).

Data obtained from XPS corroborate with AFM imaging and contact angle measurements for the growth and loss of the SAMs. The percent concentration ratio of C 1s to Ga 2p obtained for the bare surface is $2 \pm 0.44$ to 1. This ratio appears high when comparing the raw signal from Ga 2p to C 1s in a survey scan of the piranha etched GaN surface (Figure 8a). However, the relative sensitivity factors (RSF) for Ga 2p and C 1s are drastically different, at 4.284 and 0.318 respectively (values specific for Kratos XPS instruments). Monolayer growth is confirmed by an increase in the C:Ga ratios for full OTS and APTES SAMs when compared to the bare surface. This increase in carbon is due to the presence of the carbon chains of the siloxanes. The Ga 2p signal is also
attenuated after the growth of a monolayer. The penetration depth of the x-rays is approximately 5-10 nm. With a monolayer at the surface, there are fewer x-rays that penetrate through the added thickness of the SAM to reach the gallium underneath. The affect is slightly more prominent for an OTS monolayer than for APTES because the OTS chain is longer with 18 carbons compared to only three for APTES. Gallium signal attenuation is also caused by an increased escape depth for Ga electrons, again, due to the added height of a monolayer. After soaking a full SAM in aqueous solution, the Ga signal increases in intensity and the C:Ga ratio decreases, indicating monolayer loss. The C:Ga ratio for the GaN surface after buffer removal of OTS is 0.34±0.1 to 1, which is less than that obtained for the piranha etched GaN. This decrease shows loss of not only the monolayer, but also surface contaminants not removed by the piranha cleaning process.

Siloxanes are not the only molecules to exhibit SAM loss in aqueous environments. Stearic acid, an 18-carbon chain carboxylic acid, was also used to functionalize GaN, and the stability of the monolayer grown was tested in water. A monolayer was successfully grown by soaking a GaN sample in a 1 mM stearic acid in ethanol solution. Water contact angles were used to monitor growth of the monolayer, with a final contact angle of 107° obtained for a full SAM. However, after soaking a functionalized chip in water for approximately 3 hours, the contact angle dropped to around 30-40 degrees, indicating monolayer loss.

2.5.2 Solubility of Gallium Oxide and the Native Oxide on GaN

Given that the attachment of different types of molecules each result in monolayer loss, siloxanes and carboxylic acids alike, and since the covalent siloxane bond to the surface is very strong, I hypothesized that dissolution of the amphoteric gallium oxide
layer is the cause of monolayer loss in aqueous environments.\textsuperscript{18,34} If the oxide is dissolving in water below the SAM, the monolayer would not only be lost, but there would be trace amounts of gallium in solution. To test this theory, I measured the solubility of both powdered $\text{Ga}_2\text{O}_3$ and solid $\text{Ga}_2\text{O}_3$ on GaN in ultra-pure water and pH = 7 buffer ($\text{K}_2\text{PO}_4$/\text{NaOH}). For the powdered samples, 50 mg of $\text{Ga}_2\text{O}_3$ was placed in 50 ml of 18 MΩ $\text{H}_2\text{O}$ or 50 ml of buffer. The samples were stirred over a 2 day period and centrifuged at 10,000 rpm for 30 min, followed by syringe filtration. The filtrate was analyzed for Ga with inductively coupled plasma optical emission spectrometry (ICP-OES). The powder was found to be soluble in both water and buffer at around 1-10 ppm. The broad range in solubility is most likely due to undissolved oxide crystals that are small enough to pass through the 0.45 μm polypropylene syringe filter.

Because this experiment could be subject to artifacts based on particles rather than dissolution of the oxide surface, I repeated it using monolithic GaN samples with their native oxide, $\text{Ga}_2\text{O}_3$. ICP-MS was chosen for the analysis on the basis of its higher sensitivity over ICP-OES. The detection limit of the ICP-MS was calculated using 3 times the standard deviation for the average Ga concentration of a 4% HNO$_3$ acidified blank (ultra-pure water or pH = 7 buffer) and was found to be approximately 4 pg/g (0.004 ppb), which is below the limit of detection for the ICP-OES.

The solid GaN leachate samples were prepared by soaking a piranha etched 10 mm x 10 mm GaN chip in 5 mL of ultra-pure water or pH = 7 buffer for 24 hours, after which the solution was analyzed for Ga by ICP-MS. All samples, including blanks, were acidified to contain 4% HNO$_3$ and the samples were calibrated by 3 point standard addition after blank subtraction. Machine drift was monitored using $^{75}\text{As}$ as an internal
standard (~30 ppb). Potential interferences were monitored by tracking the measured $^{69}\text{Ga}/^{71}\text{Ga}$ ratio (1.507 in nature) and using medium resolution mass discrimination. The Ga concentration for the solid samples was found to be $0.264 \pm 0.05$ ppb/mm$^2$ for 18 MΩ H$_2$O and $0.100 \pm 0.015$ ppb/mm$^2$ for pH = 7 buffer. The ppb/mm$^2$ unit reflects the concentration obtained by soaking a 100 mm$^2$ GaN wafer chip in 5 ml of liquid.

The estimated concentration (Figure 2.21) for the loss of one atomic layer of gallium from Ga$_2$O$_3$ (assumes β-monoclinic structure)$^{59}$ from a 100 mm$^2$ chip in 5 ml of water is 0.25 ppb/mm$^2$. The data suggests that an equivalent of one layer of oxide has been lost. GaN is stable to bulk etching in aqueous solutions,$^{60}$ but its surface oxide is not.

![Calculation of Ga concentration in solution for the loss of one atomic layer of oxide from the surface of a 10 x 10 mm solid GaN semiconductor chip. The calculation assumes a β monoclinic structure for Ga$_2$O$_3$.](image)

Figure 2.21 Calculation of Ga concentration in solution for the loss of one atomic layer of oxide from the surface of a 10 x 10 mm solid GaN semiconductor chip. The calculation assumes a β monoclinic structure for Ga$_2$O$_3$.}$^{59}$
The inconsistent length of time for the loss of an OTS monolayer is mostly due to the hydrophobic chains of OTS protecting the native oxide from water. A better OTS monolayer is more water resistant than one that has a lot of imperfections in the packing density of the OTS molecules. These imperfections can be thought of as pin holes in the monolayer. The more holes there are, the faster water can reach the underlying oxide and dissolve it.

During my research, I also observed that OTS on GaN samples underwent a decrease in contact angle when under ambient laboratory light, which saturated at 90°. n-Type GaN that is derivatized with long-chain siloxanes has been shown to undergo photocatalytic cleavage of the SAM molecules under UV illumination. Under 254 nm light, the contact angle of a dry SAM/GaN sample decreased from 110° to under 25° in about half an hour, and this time was decreased to a mere 1 minute when the sample was illuminated under water. It is possible that C-C bond cleavage events could create disorder or pinholes in the SAM, which would enable water to reach the oxide layer more easily, but cleavage of C-C bonds in the SAM would not account for the presence of the equivalent of a monolayer of dissolved gallium after loss of the SAM. Since my own GaN samples were not purposefully illuminated with UV, the drop in contact angle for the OTS in ambient lab light is due to the innate instability of the gallium oxide on which these siloxane SAMs are anchored, rather than C-C bond cleavage from stray UV.

The use of III-V semiconductors that contain surface Al, and thus a native aluminum oxide layer, can provide a solution to the monolayer instability problem, as Al₂O₃ is very robust in aqueous environments. Good examples of Al terminated nitrides
for HEMT structures are AlN or AlGaN, and many sensor examples of these HEMT’s are in use. Additionally, very thin GaN caps that are grown on top of these Al-nitride structures can have reinforced gallium oxide stability as Al may intercalate itself into the surface oxide. Studies of APTES on AlGaN/GaN HEMT’s structures with a 2 nm GaN cap show promising results of longer stability times in aqueous solutions, and will discussed in Chapter 3.

2.5.3 Comparison of OTS Monolayers on other Surfaces

For direct comparison to the GaN surface, octadecyltrichlorosilane SAMs were grown on Si, GaAs, and Sapphire (Aluminum Oxide) surfaces. OTS on GaN had been previously well studied by the Lieberman research group, however, the study was repeated alongside GaN functionalization to ensure the deposition was correctly being performed. Four Si wafer chips were cleaned with a piranha etch and standard RCA 1 & RCA 2 cleaning baths, resulting in an average contact angle of less than 15°. The samples were brought into a dry box and each placed in 5 mL of 5 mM OTS solution in dry 1.5:1:10 CHCl₃:CCl₄:Isopar G for 6 days. The average contact angle after OTS deposition was 123.43 ± 2.90°. The Si samples have remained functionalized for several years, and are continually used for contact angle goniometer training purposes as an example of a hydrophobic surface.

A GaAs sample with its native oxide was cleaned for 10 mins in 2 M NH₄OH resulting in a contact angle of 28.00 ±4.36°. The sample was placed in an 8 mM 5 mM OTS solution in dry 1.5:1:10 CHCl₃:CCl₄:Isopar G for 5 days (deposition performed in a dry box). The contact angle after OTS deposition was 102.00 ± 2.94°. Figure 2.22
shows an AFM image (1 μm x 1μm) of the GaAs surface after deposition. The image shows the presence of a multilayer, as opposed to a smooth monolayer.

![AFM image of OTS on GaAs, 5 day dry deposition, RMS = 1.342 nm.](image)

Figure 2.22 AFM image of OTS on GaAs, 5 day dry deposition, RMS = 1.342 nm.

The GaN samples used in the study were grown on a sapphire (aluminum oxide) substrate, and so for further comparison, OTS was deposited onto the sapphire, simply by flipping a GaN chip over to study the substrate underside. The sapphire was cleaned using a piranha etch resulting in a widely varying contact angle of 31.50 ± 10.61. A dry OTS deposition was performed as previously done on GaN, resulting in a contact angle of 116.25 ± 0.96°. The sapphire sample was then soaked in pH = 7 buffer for 22 hrs,
resulting in a drop in contact angle to $96.25 \pm 11.87^\circ$. The hydrophobic contact angle after soaking indicates that OTS is still present on the sapphire surface. The remaining OTS also means that the aluminum oxide layer is still present, unlike gallium oxide, which has been found to dissolve.

2.5.3.1 Aluminum Deposition on GaN

Aluminum oxide, Al$_2$O$_3$, is a very stable and robust surface for self-assembled monolayers to grow on.$^{16,33}$ In an attempt to reinforce the GaN surface for monolayer stability, a thin layer of Al was deposited on the surface by physical vapor deposition using a thermal evaporator. The evaporator works by passing a current through a resistive filament which heats up, melting and evaporating a deposition metal of choice which is attached to the filament. The process is carried out in a sealed chamber under vacuum. The evaporated metal condenses on samples placed inside the chamber. To Al growth on GaN, 2 piranha etched GaN samples were placed in the evaporator chamber, with Al wire as the metal source, and a tungsten wire basket filament. The aluminum was deposited at a rate of 0.2 Å/sec using a current of 10A for 4.5 mins, with an additional cool down time of 5.5 mins. When the current was shut off, the thickness of the Al film was read at 1.1 nm, and after the cool down time, it was 2.8 nm. Aluminum oxide grows instantaneously when aluminum is exposed to air. Immediately upon exposing the deposition chamber to air, the thickness reading jumped to 6.6 nm.

Figure 2.23 shows a 1 µm x 1 µm AFM image of the aluminum film deposited on GaN. The RMS roughness of this image is 1.424 nm. The image shows the aluminum is blanketing the step features and lattice dislocations typically visible on GaN.
The Al film on GaN tinted the samples a silver gray color. The average contact angle for the Al films on GaN was 74.63 ± 1.49°. One sample was used for OTS deposition. The sample was brought into a dry box and placed a 5 mM OTS solution in dry 1.5:1:10 CHCl₃:CCl₄:Isopar G for 5 days. Upon removing the sample from the OTS, and rinsing it with chloroform, it was noticed that a portion of the Al film was gone and the gray tint was no longer visible over various spots of the surface. The average contact angle of the remaining tinted areas was 116.33 ± 2.52°, indicating successful monolayer growth on the film. However, the loss of portions of the film only strengthen the claim that the native oxide on GaN is lost in solution, removing any overlayer in the process. To further test this, the sample was placed overnight in pH = 7 buffer (potassium
phosphate monobasic sodium hydroxide). Upon removal from the aqueous buffer, the gray tint was no longer visible on the sample, indicating loss of the Al film.

2.6 Conclusions

The surface of gallium nitride can be functionalized with siloxane self-assembled monolayers. An increase in water contact angle shows an increase in the hydrophobicity of the GaN surface. This is attributed to the hydrocarbon chains of OTS, and to a lesser extent, the amine terminated carbon chains of APTES. AFM imaging shows the evolution of the monolayers over time. XPS shows attenuation of the Ga signal due to SAM growth. The self-assembled monolayers are not stable in aqueous solvents. After soaking in aqueous solutions, there is a loss of water contact angle hydrophobicity, a loss of monolayer islands by AFM, and an increase in XPS Ga signal.

Instability of the monolayers in aqueous solution is due to the solubility of the native oxide on GaN. This is proven by the presence of Ga in solution seen with ICP-OES and ICP-MS. Further studies need to be performed to determine the mechanism of oxide dissociation. GaN biosensing applications predominantly involve biological mediums that are aqueous environments. The instability of the gallium oxide surface in such environments will limit sensor lifetime and usage. Though OTS is stable in acetonitrile, a non-aqueous solvent, this is not very useful for biosensors. GaN does have other technological applications\textsuperscript{63-65} in which non-aqueous SAM functionalization may be used\textsuperscript{66-69}.
2.7 Experimental Section

2.7.1 Sample Preparation

All glassware and tweezers were rinsed with acetone (Fisher), then boiled in ethanol (absolute, Aaper) for 30 minutes and given a final rinse with ultra pure (18 MΩ, milli-Q) H₂O. Gallium nitride samples were provided by Dr. Huili Grace Xing, Department of Electrical Engineering, University of Notre Dame. The samples were approximately 10 mm x 10 mm chips, consisting of 2 μm thick MOCVD (metal organic chemical vapor deposition) grown n-type GaN on a sapphire substrate. The chips were rinsed with acetone, then ethanol, followed by a final rinse with 18 MΩ H₂O. The chips were then etched for 20 minutes with a piranha acid solution of 1:3, 30% H₂O₂ (Fisher): H₂SO₄ (concentrated, Fisher), rinsed with 18 MΩ water, and dried with flowing nitrogen gas.

2.7.2 Monolayer Deposition

To avoid excess surface contamination, samples were immediately used after cleaning. All solutions were made in 20 ml glass scintillation vials (Kimble) which were cleaned by the procedure mentioned above and dried in an oven. Each chip was placed in its own vial to avoid sample contamination. Carboxylic acid monolayers were grown by soaking a chip in 5-10 ml of 1 mM stearic acid (J. T. Baker) in absolute ethanol for a maximum time of 2 hours. The functionalized samples were rinsed with ethanol and dried with nitrogen.

3-Aminopropyltriethoxysilane (Gelest Inc.) monolayers were grown by soaking a chip in 5-10 ml of 2% APTES in 18 MΩ water for a maximum time of 1 hour. Because
APTES tends to hydrolyze over time due to moisture from lab ambient, a fresh supply of
APTES (less than 6 months old) was used for making solutions in water. After growth,
the samples were rinsed with 18 MΩ water and dried with nitrogen.

Octadecyltrichlorosilane (90%, Aldrich) monolayers were grown from dry
solution conditions in a dry box (nitrogen environment). Aluminum oxide (50-200 μm,
activated, Acros Organics) was dried overnight in an oven to remove any absorbed water,
and then used in a column to dry the OTS solvents. The AAO was first “wet” with
CHCl₃ (99.8%, Aldrich). A 1:4 mixture of CHCl₃: Isopar G (Exxon Mobil) was then
dried by passing through the column and collected into a flask with molecular sieves (8-
12 mesh beads, Aldrich). The solvents were placed under vacuum and transferred along
with sample vials and GaN chips into a dry box. GaN samples were soaked in 5-10 ml of
a 5 mM OTS solution which was made by adding OTS to the 1:4 solvent mixture. OTS
monolayers were allowed to grow over a period of 5 days. The functionalized GaN chips
were rinsed with CHCl₃, then with 18 MΩ water, and dried with nitrogen.

Piranha etching after stability testing allowed GaN samples to be used for
regrowth of another siloxane monolayer without any complications. However, multiple
growth, removal, and acid cleanings of a single GaN sample does eventually damage the
GaN surface.

2.7.3 Stability and Solubility
Monolayer stability tests were carried out by soaking a functionalized GaN
sample in 5 ml of solvent (aqueous and non-aqueous) for 4 days. Stability was tested in
ultra pure water, pH = 7 buffer (K₃PO₄/NaOH, Fisher), pH = 9 buffer
(B(OH)₃/KCl/NaOH, Fisher), and acetonitrile (dry, Fisher). Powdered gallium(III) oxide
stability tests were performed by placing 100 g of Ga₂O₃ (powder, Aldrich) in 50 ml of ultra-pure water or pH = 7 buffer. The mixtures were stirred on a stir plate for 2 days and allowed to settle by gravity. The saturated solutions were decanted and filtered by passing through a syringe filter (0.45 μm, polypropylene, VWR). The solution was then centrifuged at 10,000 RPM for 30 minutes, decanted, and given a final syringe filtration. The solution was analyzed using ICP-OES. Solid gallium oxide stability tests were carried out by placing a clean GaN chip in 5 ml of ultra pure water or pH = 7 buffer for 2 days. The chip was removed and the solution was analyzed using ICP-MS.

2.7.4 Instrumentation

Contact angle measurements were taken using a Krüss G10 goniometer. All measurements were taken using ultra-pure water and an advancing drop. Reported values are an average of 4 locations on a single chip. Atomic force microscopy was performed using a Nanoscope IIIa Multimode Instrument (Digital Instruments) in tapping mode. Silicon cantilevers were used (spring constant = 40 N/m, resonant frequency = 300 KHz, Vista Probes). Image analysis was performed using the Nanoscope III software. X-ray photoelectron spectroscopy was performed using a Kratos XSAM800 instrument with either an Al-Kα or Mg-Kα source, and a 0° take off angle. Samples were mounted via carbon tape to the instrument’s metal sample slugs. Data acquisition was carried out at high x10⁻⁸ Torr. Data analysis was performed using Kratos Vision II software and CasaXPS. All peaks were calibrated against the C 1s (284.5 eV) peak. Relative standard deviations were applied to all % concentrations and % conc. ratios. RSD's were obtained from the averages and standard deviations of % N, % O, % C, and % Si for multiple APTES on Si depositions.
Inductively coupled plasma-optical emission spectroscopy was performed with a Perkin Elmer Optima 3300 XL instrument. Gallium emission wavelengths scanned for were 417 nm and 294 nm. A Ga parent standard in 4% HNO₃ was used to make all calibration standards. Standards used were between 0.1 and 4.0 ppm. Ultra-pure water and pH = 7 buffer samples were acidified to contain 4% HNO₃. Water samples were tested with a blank of 4% HNO₃ in ultra-pure water, and buffer samples were tested with a blank of 4% HNO₃ in pH = 7 buffer. Inductively coupled plasma-mass spectroscopy was performed with a Thermo Finnigan Element 2 High Resolution ICP-MS. As with ICP-OES experiments, all samples were acidified to contain 4% HNO₃. All samples were tested with a blank of 4% HNO₃ in ultra-pure water.
CHAPTER 3: GROWTH AND CHARACTERIZATION OF ION SENSING MONOLAYERS ON SILICON AND III-V (NITRIDE) HETEROSTRUCTURES

3.1 Introduction

There is much interest in the use of wide band gap semiconductors, such as AlN, AlGaN, and GaN, in high electron mobility transistors (HEMT’s) for biosensor applications. The sensing component of such devices utilizes the response of the HEMT’s two-dimensional electron gas (2DEG) to changes in surface potential after binding of target biomolecules. The ability to rapidly detect biologically prevalent ions at low concentrations has numerous applications, such as quantifying ion concentrations in blood for patients with potassium and sodium deficiencies. Currently, ion selective electrodes (ISE’s) are commonly used for the recognition of bio-ions. Reversible binding of ions to carrier molecules is critical to the function of an ISE. These carriers transport ions across a membrane to an internal electrolyte solution. However, there are some drawbacks to the use of ISE’s, such as interference from competing ions, leakage of electroactive components into test solutions, difficult construction procedures, and damage of the electrode membrane by the sample. Functionalized HEMT structures can provide an ideal alternative to ISE’s with simple construction of the gate region through chemical modification and direct measurements of test samples without the need for membrane transport.
The native oxide on Al containing heterostructures structures, such as AlGaN/GaN and InAlN/GaN, consists in part of Al$_2$O$_3$, which unlike Ga$_2$O$_3$, is stable in aqueous solutions. Therefore, monolayers bound to this oxide will be stable under the liquid conditions that are involved in the testing of biological/ion samples. A stable APTES monolayer on Al$_2$O$_3$ will be very useful for anchoring ion selective molecules to the semiconductor surface. The terminal amine group can be employed for reductive amination with aldehydes and ketones or DCC couplings with carboxylic acids.

In this chapter, the functionalization of Si and III-V nitride heterostructures (AlGaN/GaN and InAlN/GaN) with ion sensing monolayers will be discussed (Figure 3.1). Functionalization of each of these surfaces consisted of the growth of an APTES monolayer followed by the attachment of cation or anion selective molecules via Schiff base formation and reductive amination.
Figure 3.1 Progression of the growth of ion sensing HEMT structures.

Prior to functionalization, the bare heterostructure surfaces were characterized both before and after various surface preparation treatments. Atomic force microscopy, x-ray photoelectron spectroscopy, and ellipsometry were used for characterization of the bare and functionalized surfaces. Ion selectivity of the monolayers was tested by exposing the surfaces to various ionic solutions and scanning for ion binding with XPS. Finally, the binding of DNA origami, which has a negatively charged phosphate backbone, was tested on the anion binding monolayer surfaces and imaged with AFM.

There are many commercially available aldehyde modified ion binding molecules which can be used for the purpose of attachment to APTES. For example, there are
several crown ethers that have been synthesized with a benzaldehyde group attached. The selectivity of crown ethers for cation binding has been well documented. Modified crowns, such as formylbenzo-15-crown-5 (Figure 3.2 a) and formylbenzo-18-crown-6 (Figure 3.2 b), were bound to an APTES monolayer thus making a cation sensor. Due to the crown’s cavity diameter vs. ionic radius, 15-crown-5’s are selective for sodium ions while 18-crown-6’s are selective for potassium ions. Attachment of these molecules to the gate region of an InAlN/GaN or AlGaN/GaN heterostructure surface creates a K+ and/or Na+ selective sensor.

![Figure 3.2 Benzaldehyde modified crown ethers.](image)

To create an anion sensor, Zn$^{2+}$ coordinated dipicolylamine (DPA, Figure 3.3, right) ligands were used.

![Figure 3.3 Structure of picolylaldehyde (left) and DPA (right).](image)
Fluorescent molecules bound by two DPA ligands, each coordinated to a Zn$^{2+}$, have been successfully used to bind phosphate containing molecules ($R$-$PO_4^{2-}$), with a significant increase in fluorescence upon anion binding. The open coordination site on the zinc allows for binding to the anion. Bradley Smith’s group has used reductive amination of picolylaldehyde (Figure 3.3, left) with the amino terminus of N-Boc-ornithine to create DPA ligands attached to polypeptides for the detection of anionic phosphatidylserine. I hypothesized that this chemistry could be used to attach DPA to the amine group of APTES, in order to form an anionic sensor.

Similar to the cation binding monolayers, the anion binding SAMs were grown by reductive amination to an APTES monolayer. The APTES monolayers were treated with picolylaldehyde and NaBH$_3$CN to attach 2 picolyl groups to the APTES amine, forming DPA ligands (Figure 3.4). The monolayers were then treated with Zn(NO$_3$)$_2$ to coordinate Zn$^{2+}$ to DPA. FeCl$_2$ was also used to explore the DPA ligand’s ability to coordinate other divalent metal cations.

![Figure 3.4 Reaction scheme of picolylaldehyde and APTES.](image-url)
3.1.1 Using Silicon for Chemistry Confirmation

Because silicon is less expensive than the heterostructures, and more readily available, APTES formation and subsequent ion binding molecule attachment was first carried out on Si(100) chips which have a native SiO$_2$ surface. The Lieberman research group has already used APTES to anchor biomolecules, or specifically, DNA origami, to the surface of silicon.$^{25}$ The growth of APTES on Si is very similar to what I observed for growth on GaN, which was discussed in Chapter 2. Using the group’s previously developed method, APTES monolayers were grown on piranha/RCA clean SiO$_2$ from aqueous solutions. Similar to what was observed for the GaN surface, a full APTES monolayer gives a contact angle in the mid to upper 60°’s. Figure 3.5 shows a typical Si surface before (a) and after after (b) APTES functionalization.

![Figure 3.5](image)

*Figure 3.5 (a) Bare Si(100) surface after piranha etching, water contact angle <10°. (b) Si (100) after 20 min soak in 1% APTES, water contact angle ~65°.*
3.2 Characterization of the Bare HEMT Surfaces

3.2.1 AlGaN/GaN

AlGaN/GaN samples grown by metal organic chemical vapor deposition (MOCVD) were obtained from Dr. Huili Grace Xing (Electrical Engineering, University of Notre Dame). The layered composition of the samples is as follows: 3 nm GaN cap / 19 nm Al$_{0.28}$Ga$_{0.72}$N / 2 μm GaN buffer / Sapphire substrate.

The samples were treated similarly to GaN with a solvent rinse of acetone and isopropanol, followed by 18 MΩ H$_2$O. After the solvent rinse, samples were piranha etched for 20 mins, water rinsed and N$_2$ dried. The contact angle of the bare surface prior to any cleaning was in the upper 60°’s. A single piranha etching dropped the contact angle to mid 20°’s to upper 30°’s. AFM images of the surface (Figure 3.6) look very similar to the GaN surface described in Chapter 2. The RMS roughness was 0.249 nm for a 1 μm x 1 μm scan. As was the case with GaN, the surface of AlGaN/GaN has clearly defined steps and lattice dislocations. However, unlike GaN, where there are only one or two large dislocations for a 1 μm x 1 μm image, the AlGaN has numerous tiny dislocations scattered all over. In fact, there are so many in some areas, you can see step features nicely aligned in one direction, then a string of dislocations, followed by steps aligned in another direction.
Figure 3.6 Bare AlGaN/GaN Surface. RMS = 0.249 nm (RMS for smooth regions without lattice dislocations is about 0.189 nm).
Contact angle after piranha etching = 25° - 32°.
Also similar to the GaN surface, optical interference is present when obtaining larger AFM images. Figure 3.7 shows a 5 μm x 5 μm AFM image of AlGaN/GaN.

![AFM Image](image)

Figure 3.7 Bare AlGaN/GaN, 5 μm x 5 μm scan.

X-ray photoelectron spectroscopy analysis (Mg-Kα source) of the bare AlGaN/GaN surface showed the presence of all expected elements with no contamination other than adventitious carbon. Figure 3.8 shows the comprehensive survey scan of all peaks present between 1200 - 0 eV for a piranha cleaned AlGaN/GaN sample. All major peaks are labeled. Individual region scans and a full quantification report of these peaks can be found in Appendix B.2. Positive electron volt shifts due to charging were corrected for by calibrating all peaks against the central C 1s peak, which was set to 284.5 eV. The ratio of C 1s to Ga 3p was found to be 1.96 ± 0.43 to 1, indicating a large
amount of carbon contamination; however, Ga Auger peaks are present in the C 1s region. The ratio of O 1s to Ga 3p was found to be $0.33 \pm 0.09$ to 1, indicating a small amount of oxide present. The N 1s to Ga 3p ratio is $1.20 \pm 0.34$ to 1 and the ratio of Ga 3p to Al 2p is $2.77 \pm 0.76$ to 1, which was expected due to the GaN cap and low mole fraction of Al in the AlGaN layer.

![Piranha Etched AlGaN/GaN Survey Scan](image)

**Figure 3.8** X-ray photoelectron spectroscopy survey scan of piranha etched AlGaN/GaN.

3.2.2 InAlN/GaN

InAlN/GaN samples grown by MBE were also obtained from Dr. Huili Grace Xing (Electrical Engineering, University of Notre Dame). The layered
composition of the samples is as follows: 10 nm In$_{17}$Al$_{83}$N / 0.5 nm AlN / 2 μm GaN Buffer / Sapphire substrate. The InAlN/GaN material, like GaN and AlGaN/GaN, is transparent. The as-received samples were imaged by AFM prior to any surface cleaning steps. Figure 3.9 and Figure 3.10 show 1 x 1 μm and 5 x 5 μm images of the InAlN surface. Larger images (Figure 3.10 and Figure 3.11) of the surface do result in visible optical interference. This material does not have a GaN cap, and the surface was not expected to look like that of GaN, which was indeed true. Unlike GaN, the material does not have clearly defined step features or lattice dislocations. The surface appears to have a grainy, uneven texture. This is due to the low vaporization temperature of the indium precursor resulting in lower deposition temperatures of the InAlN film. The material nucleates and grows faster on the GaN buffer without wide and even diffusion across the surface. Annealing does not completely eliminate this issue.

![AFM image](image.png)

Figure 3.9 AFM image (1 μm x 1μm) of as-received InAlN/GaN. RMS = 0.236 nm.
Figure 3.10 AFM image (5 µm x 5 µm) of as-received InAlN/GaN. RMS = 0.350 nm.

Figure 3.11 Large AFM image (10 µm x 10 µm) of InAlN.
The InAlN/GaN samples were cleaned in a similar fashion to the treatment of GaN and AlGaN/GaN. This included a solvent rinse with acetone and isopropanol, followed by a rinse with ultra-pure 18 MΩ H₂O. The samples were also cleaned with piranha acid, following the protocol outlined in Chapter 2 for the treatment of GaN. AFM imaging of the InAlN surface revealed that piranha acid caused damage to the sample (Figure 3.12). The acid cleanse resulted in etching away of the InAlN material itself. The grainy surface texture of the sample provided easy access points within the material for the acid to soak in and begin dissolving the surface. The acid damage appears as small breaks or channels in the surface. After a single ~20 min acid cleanse, the channels are approximately 10 nm wide and at least 3 nm deep. It is difficult to get exact depth measurements due to the fact that the AFM tips, which generally have an end radius of 10 nm, are not able to fully descend into the narrow channels.
In the preparation of most semiconductor surfaces, acid etchings of samples are commonly used in addition to solvent rinses in order to remove various contaminants. InAlN/GaN is a relatively new HEMT material, and it is important to understand how to treat the surface. As piranha acid provided too harsh of an etching environment for the material, a soak in moderately concentrated HCl was tested. Unfortunately, the HCl etch also proved too harsh for the surface. A 10 minute soak in 6 M HCl resulted in a similar damage pattern to what was observed with piranha acid. The acid etched narrow channels into the surface. Figure 3.13 shows an AFM image of the surface after acid exposure.

Figure 3.12 InAlN/GaN after piranha etching. The image shows damage to the surface after soaking in the acid.
Figure 3.13 InAlN/GaN after a 10 minute soak in 6 M HCl. The image shows damage to the surface after soaking in the acid. The lower portion of the image was not captured due to an AFM tracking error.

Considering the damage that acid soaks cause to the InAlN surface, it was concluded that the surface would be treated with solvent and ultra-pure water cleanings only. X-ray photoelectron spectroscopy (Mg-Kα source) analysis of the bare InAlN/GaN surface showed the presence of all expected elements with no contamination other than adventitious carbon. The comprehensive survey scan of all peaks present between 1200 - 0 eV for a solvent cleaned InAlN/GaN sample can be seen in Figure 3.14. All major peaks are labeled. Individual region scans and a full quantification report of these peaks can be found in Appendix B.3. Positive electron volt shifts due to charging were corrected for by calibrating all peaks against the C 1s peak, which was set to 284.5 eV.
The ratio of C 1s to Al 2p was found to be 0.94 ± 0.23 to 1, indicating carbon contamination. This was not a surprising result due to the lack of acid etching to remove organic surface contaminants. The ratio of Al 2p to In 3d was found to be 7.34 ± 2.13 to 1, which was expected due to the low mole fraction of indium in the InAlN layer. The O 1s to Al 2p ratio was found to be 0.73 ± 0.21 to 1, indicating a large amount of oxygen present. It is unclear if this oxygen is strictly from the native oxide on the InAlN surface. The O 1s peak is rather broad, with a center peak position at 533.86 eV and a FWHM = 2.76. This suggests the presence of more than one type of oxygen, however, resolving the peak into 2 components resulted in a poor fit with a residual of 3.45 (Figure 3.15).
The residual of a single fit peak was 1.02. No peaks from gallium in the underlying buffer layer could be seen with XPS. This is due to the fact that the 10 nm thick InAlN (with native oxide) is thicker than the escape depth of the photoelectrons.

Figure 3.15 O 1s region scan of solvent cleaned InAlN/GaN, fit with 2 components.

3.3 Growth and Characterization of APTES on HEMT Surfaces

3.3.1 Aminopropyltriethoxysilane on AlGaN/GaN

APTES self-assembled monolayers were grown on the surface of AlGaN/GaN following the same procedure performed for APTES growth on GaN. The SAMs were grown by soaking a piranha cleaned AlGaN/GaN chip in a 1-2% v/v solution of APTES in 18 MΩ H₂O. The APTES solution was immediately prepared before deposition, and
deposition was not carried out beyond 30 mins to prevent excess hydrolysis of the APTES, which causes the formation of APTES multilayers in solution. APTES monolayer growth was monitored by AFM imaging, contact angle measurements, and XPS. The growth mechanism of an APTES SAM on AlGaN occurs via initial island formations which continue to populate and fill out the surface with time. This is similar to the findings of APTES SAMs on GaN and Si surfaces. The full coverage contact angle obtained for APTES is also similar to what has been observed for GaN and Si surfaces, generally in the 60° range. The full coverage contact angle varied according to the length of time the sample was out of solution. Typically, when fresh out of solution, the contact angle was upper 50’s to low 60’s. APTES samples that have been out of solution for a while (~20 mins or more) have higher contact angles, in the mid to upper 60’s. A similar result was seen for APTES on GaN and on Si. It is unclear if this increase is due to surface contamination or the APTES having less protonated amines out of solution.

After 5 minutes of placing a sample in 1% APTES in 18 MΩ H2O, AFM imaging shows the appearance of small APTES islands evenly spaced across the surface. A 1 μm² image (Figure 3.16, left) has an RMS roughness of 0.320 nm. This is an increase from the 0.249 nm (0.189 nm, minimal lattice dislocations) RMS seen for the bare surface. Within 15 minutes of soaking in the APTES solution (Figure 3.16, right) the majority of the AlGaN surface was densely covered with APTES, and islands were no longer visible. The functionalized surface resembles that of the bare AlGaN/GaN. For a 14 minute APTES soak, the RMS roughness of a 1 μm² image decreased to 0.217 nm, while the contact angle increased (in comparison to the bare surface) to upper 60°’s, indicating full
monolayer growth. A deposition from 2% APTES in 18 MΩ water was also imaged (Figure 3.17) after a longer time soak of 30 mins. The contact angle for this deposition was 63.0° ± 10°. For a 1 μm² image, the RMS was 0.232 nm. The surface is similar in appearance to the 14 minute, 1% APTES sample, but there were a few features randomly scattered on the surface that are greater than 5 nm tall. These features may be multilayer formation, or contamination. Figure 3.18 shows 3-D AFM images comparing the surfaces of bare AlGaN, 5 and 14 min, 1% APTES, and 30 min, 2% APTES. 1% APTES for 15 minutes was the best deposition protocol for the formation of a smooth monolayer on AlGaN/GaN.

Figure 3.16 AlGaN with 1% APTES
Figure 3.17 AlGaN/GaN with 2% APTES, 30 minute soak. RMS = 0.232 nm. Contact angle = 63.0° ± 10°.

Figure 3.18 Three dimensional AFM data of the growth of APTES on AlGaN/GaN
X-ray photoelectron spectroscopy (Mg-Kα source) analysis was performed on the AlGaN/GaN surface after a typical 1% APTES in water soak, confirming the growth of APTES on the surface. A comprehensive survey scan (showing all peaks present between 1200 - 0 eV), individual region scans, and a full quantification report of the region component peaks can be found in Appendix B.4. Positive electron volt shifts due to charging were corrected for by calibrating all peaks against the central C 1s peak, which was set to 284.5 eV. Figure 3.19 shows an overlay of the Ga 2p region scans of the AlGaN surface before and after APTES deposition. It is clear from the spectra that the gallium peaks have attenuated due to the presence of an APTES overlayer. Attenuation was also seen for the Ga 3p peaks (Figure 3.20) and the Al 2p peak. Overlaying the Ga 3p regions for the surface before and after APTES growth shows the emergence of a minor Si 2p peak, which overlaps the Ga 3p region (Figure 3.20). The Si 2p peak is located at 102.1 eV, indicating oxygen bound silicon. This is expected with the siloxane bond formation of the APTES molecule to the surface oxide.
Figure 3.19 Overlayed XPS Ga 2p Region Scans of AlGaN/GaN before and after APTES SAM growth showing peak attenuation.

Figure 3.20 Overlayed XPS Ga 3p/Si 2p Region Scans of AlGaN/GaN before and after APTES SAM growth showing gallium peak attenuation and the emergence of a Si-2p peak.
Table 3.1 shows a comparison of the ratios of % concentrations of C 1s, O 1s, N 1s, Al 2p, and Si 2p to the Ga 3p peak both before and after APTES growth. The carbon to gallium ratio more than doubled after the deposition of APTES, due to the presence of the carbon chains of APTES. The ratio of nitrogen to gallium only slightly increased, but it is difficult to distinguish the N 1s peaks of APTES which are dwarfed against the strong N 1s peak of the semiconductor surface. The gallium to aluminum ratio decreased slightly. Surprisingly, the oxygen to gallium ratio nearly tripled. This is most likely due to the addition of oxygen cross links of silicon in the APTES monolayer in combination with the attenuation of the gallium peak, but there may also be some multilayer formation of APTES on the AlGaN surface. However, multilayer formation should also show a greater increase in N 1s and a stronger Si 2p peak, which is not the case. The APTES deposition is performed from a solution in water. It is possible that the water is causing more surface oxide to develop.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s : Ga 3p</th>
<th>O 1s : Ga 3p</th>
<th>N 1s : Ga 3p</th>
<th>Ga 3p : Al 2p</th>
<th>Ga 3p : Si 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piranha AlGaN</td>
<td>1.96 ± 0.43</td>
<td>0.33 ± 0.09</td>
<td>1.20 ± 0.34</td>
<td>2.77 ± 0.76</td>
<td>n/a</td>
</tr>
<tr>
<td>APTES AlGaN</td>
<td>4.90 ± 1.17</td>
<td>0.94 ± 0.26</td>
<td>1.37 ± 0.38</td>
<td>2.26 ± 0.63</td>
<td>9.2 ± 2.57</td>
</tr>
</tbody>
</table>

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The stability of APTES on AlGaN was tested by soaking an APTES functionalized chip in pH = 7 buffer overnight (approximately 20 hours). Figure 3.21 shows an AFM image of the AlGaN surface with a monolayer of APTES after an overnight soak. The image shows the surface is still covered with APTES. The contact angle remained in the low 60°’s with an RMS of 0.423 nm (RMS = 0.269, excluding a large contamination particle). This result shows that the oxide layer on AlGaN has greater stability than that of GaN. This may be due to aluminum diffusion through the GaN cap to the topmost surface during annealing. The aluminum oxidizes, and the aluminum oxide reinforces the gallium oxide.

Figure 3.21 AlGaN with APTES after soaking in buffer for 20 hours. RMS = 0.423 nm (RMS = 0.269, excluding large contamination particle in lower middle region). Contact angle = 61°± 4°.
3.3.2 (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane on AlGaN/GaN

It is difficult to confirm the growth of APTES on AlGaN by XPS because the molecule mostly contains carbons and oxygens, which are always present in the XPS system. Additionally, the N 1s signal from APTES is dwarfed by the N 1s signal from AlGaN, and the Si 2p signal from APTES overlaps with the Ga 3p signal of AlGaN. In order to further study self-assembled monolayer formation on AlGaN and confirm functionalization, a fluorinated triethoxysilane molecule was deposited on the surface of AlGaN/GaN. This molecule has surface binding chemistry analogous to that of APTES, but has a uniquely identifiable fluorinated carbon chain. Fluorine signals are strong in XPS. Being as there is no fluorine in AlGaN/GaN, the presence of a F 1s peak is indicative of successful functionalization. AlGaN/GaN was soaked in a 1% solution of (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (F-TES, Figure 3.22) in toluene for 1.5 hrs. The toluene was not dried prior to making the F-TES solution. After deposition, the sample was rinsed with toluene, and N2 dried.

![Figure 3.22 (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (F-TES)](image)

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For comparison, F-TES was also deposited on a Si wafer (with a native oxide). The samples were analyzed with x-ray photoelectron spectroscopy. Figure 3.23 shows the overlayed survey scans of bare AlGaN/GaN and F-TES on AlGaN/GaN. The survey clearly shows the presence of fluorine after deposition. The comprehensive survey scan of F-TES on Si, individual region scans for AlGaN/GaN and Si, and a full quantification report of the region component peaks for both samples can be found in Appendix B.5.

![AlGaN/GaN Survey Scan](image)

Figure 3.23 XPS Survey Scan of bare AlGaN/GaN and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane on AlGaN/GaN

In both the AlGaN/GaN sample and the Si sample, a strong F 1s peak appeared after F-TES deposition. For AlGaN/GaN, the F 1s peak is positioned at 687.99 eV, and
for Si, the F 1s peak is at 688.11 eV. The presence of the F 1s peak indicates successful addition FTES to the AlGaN/GaN and Si surfaces. Considering this information along with AFM imaging and contact angle measurements, it can be concluded that APTES does functionalize the AlGaN surface.

3.3.3 APTES on InAlN/GaN

APTES functionalization was also tested on the InAlN/GaN surface. An InAlN sample was soaked in a 1% APTES in water solution for 20 minutes and taken for AFM imaging. Prior to APTES deposition, the surface was only cleaned with acetone, isopropanol, and water, since it was previously shown that acid cleaning damages the surface. Figure 3.24 shows the InAlN surface after APTES deposition. The image clearly shows a change in surface morphology after the sample was exposed to the aqueous APTES solution. Similar to what was observed with acid cleaning, small channels have been etched into the surface. This indicates that soaking in the APTES solution damages the InAlN surface.
Figure 3.24 InAlN/GaN after a 20 min soak in 1% APTES in water. The AFM image illustrates a change in surface morphology after soaking in solution. RMS = 0.195 nm.
XPS analysis was also performed on the APTES soaked InAlN. Individual region scans for APTES on InAlN/GaN and a full quantification report of the region component peaks can be found in Appendix B.6. Figure 3.25 shows an overlay of the XPS comprehensive survey scans for the bare InAlN surface and APTES soaked InAlN surface.

![Survey Scan](image)

Figure 3.25 Overlay of InAlN XPS survey scans of bare InAlN/GaN and 20 min, 1% APTES in InAlN/GaN

The survey scans look almost identical to one another, each with similar intensities, before and after APTES exposure. Table 3.2 shows the full XPS quantification report comparing the bare APTES soaked surfaces. No significant change can be seen in the percent concentrations of the surface components before and after APTES exposure, however, 3 peaks can be seen in the Ga 3p/Si 2p region.
Unfortunately, this region was not scanned for in the solvent cleaned sample, but based off the survey scan, they appear to be present. It is doubtful that any of these peaks are due to the presence of APTES.

**TABLE 3.2**

**XPS QUANTIFICATION REPORT FOR BARE INALN/GAN AND 20 MIN, 1 % APTES ON INALN/GAN**

<table>
<thead>
<tr>
<th>Sample Identifier</th>
<th>Name</th>
<th>Position</th>
<th>FWHM</th>
<th>R.S.F.</th>
<th>Area</th>
<th>% Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>O 1s</td>
<td>533.753</td>
<td>2.38641</td>
<td>0.711</td>
<td>19280.78</td>
<td>16.11</td>
</tr>
<tr>
<td></td>
<td>In 3d 5/2</td>
<td>445.631</td>
<td>1.58349</td>
<td>3.777</td>
<td>24655.8</td>
<td>3.878</td>
</tr>
<tr>
<td></td>
<td>In 3d 3/2</td>
<td>453.297</td>
<td>1.52364</td>
<td>3.777</td>
<td>15789.83</td>
<td>2.484</td>
</tr>
<tr>
<td></td>
<td>N 1s</td>
<td>397.421</td>
<td>1.49639</td>
<td>0.477</td>
<td>22469.48</td>
<td>27.99</td>
</tr>
<tr>
<td></td>
<td>C 1s</td>
<td>284.542</td>
<td>1.88022</td>
<td>0.296</td>
<td>9298.21</td>
<td>18.66</td>
</tr>
<tr>
<td></td>
<td>Al 2p</td>
<td>71.4104</td>
<td>1.59534</td>
<td>0.193</td>
<td>10029.46</td>
<td>30.88</td>
</tr>
</tbody>
</table>

| 1% , 20 min APTES  | O 1s  | 533.661  | 2.62011 | 0.711  | 18311.31  | 13.08   |
|                    | In 3d 5/2 | 445.674  | 1.68436 | 3.777  | 29246.54  | 3.933   |
|                    | In 3d 3/2 | 453.315  | 1.57953 | 3.777  | 17956.81  | 2.415   |
|                    | N 1s a  | 397.492  | 1.60135 | 0.477  | 25286.82  | 26.93   |
|                    | N 1s b  | 400.043  | 1.60135 | 0.477  | 1008.3   | 1.074   |
|                    | C 1s   | 284.579  | 2.09345 | 0.296  | 11199.2  | 19.22   |
|                    | Si 2p a | 99.656   | 2.84812 | 0.283  | 888.43   | 1.595   |
|                    | Si 2p b | 103.284  | 2.68932 | 0.283  | 1037.14  | 1.862   |
|                    | Si 2p c | 107.384  | 3.13692 | 0.283  | 2063.46  | 3.704   |
|                    | Al 2p  | 71.4069  | 1.57763 | 0.193  | 9951.11  | 26.19   |
3.4 Growth and Characterization of Ion Sensing Monolayers on Si

3.4.1 Attachment of 2,4,5-Trifluorobenzaldehyde to APTES on Si

The addition of ion binding molecules to APTES is carried out by aldehyde attachment to the amine group of APTES. The chosen ion binding molecules, the crown ether-aldehyde and picolyaldehyde, mentioned in the introduction to this chapter do not have any uniquely identifiable atoms for XPS confirmation, when compared to what is already on the surface and in the XPS chamber. In order to confirm surface attachment, a fluorinated aldehyde was used. An APTES functionalized Si surface was soaked overnight (~14 hrs) in a 1% solution of 2,4,5-trifluorobenzaldehyde (Figure 3.26) in methanol. The sample was characterized by AFM imaging and XPS. No contact angle was taken.

![Figure 3.26 2,4,5-Trifluorobenzaldehyde.](image)

Figure 3.27 shows the AFM image of the surface after soaking in the fluorinated benzaldehyde solution. The image appears very similar to that of plain APTES, with small islands densely populating the surface. By AFM alone, it is difficult to prove that any aldehyde is attaching to the surface. However, the presence of an F 1s peak in XPS
would provide strong evidence of attachment. Figure 3.28 shows the XPS comprehensive survey scan of APTES on Si after the overnight trifluorobenzaldehyde deposition treatment. No fluorine signal (F 1s position is close to 700 eV) is present in the scan. Longer deposition times do not change this result. The unsuccessful Schiff base formation of the benzaldehyde with the APTES amine is most likely due to the electron deficiency in the trifluorobenzene ring. The 3 fluorine atoms, which are highly electronegative, are pulling electron density away from the carbon atoms, preventing further reaction chemistry.

Figure 3.27 AFM image of APTES on Si after a 14 hour soak in 1% 2,4,5-Trifluorobenzaldehyde in methanol. RMS roughness = 0.483 nm.
3.4.2 Attachment of 5-Bromo-2-hydroxy-3-methoxybenzaldehyde to APTES on Si

Due to the negative results obtained for trifluorobenzaldehyde, a more electron rich molecule, 5-bromo-2-hydroxy-3-methoxybenzaldehyde (bromobenzaldehyde, Figure 3.29) was used to confirm APTES binding chemistry. Similar to fluorine, bromine exhibits strong intensity peaks in XPS, but it is not present in the bare or APTES functionalized Si surfaces. Even if AFM imaging is inconclusive, the presence of bromine in XPS indicates surface presence. APTES (20 min, 1% deposition) on Si samples were soaked in 3 mM bromobenzaldehyde in methanol for varying times, with a maximum time point of 20 hours.
AFM imaging of the 20 hour bromobenzaldehyde exposed APTES sample again shows a surface that is similar to the plain APTES on Si surface. Figure 3.30 shows an AFM image of the surface of APTES on Si after soaking for 20 hours in 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in methanol. The RMS roughness for the 1 um x 1 um image is 0.411 nm, and RMS = 0.207 nm for the lower half of the image, where no large contamination particles are visible. AFM images of earlier time points, as well as a timed study of the deposition with the addition of a reducing agent, NaBH₃CN, can be found in Appendix A.1 and Appendix A.2, respectively.

Figure 3.29 5-Bromo-2-hydroxy-3-methoxybenzaldehyde.
Figure 3.30 AFM image of APTES on Si after 20 hrs soak in 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in methanol. RMS roughness = 0.411 nm (RMS = 0.207 for the smooth region/lower half of image).

X-ray photoelectron spectroscopy analysis was carried out on several different time points of the bromobenzaldehyde deposition on APTES on Si. Figure 3.31 shows the Br 3d region scans of the 0 min, 15 min, 30 min, 45 min, 1 hr, 2 hr, 4 hr, and 20 hr deposition time points. A full quantification report for all region scans on all samples can be found in Appendix B.7. It is clear that a Br 3d signal is present after soaking in the bromobenzaldehyde solution, and the signal grows in intensity with longer deposition times. Initially there are two Br 3d peaks, one at 66.38 eV and the other at 68.7 eV. As deposition time increases, the intensity of the higher energy peak increases in signal strength, while the lower energy peak decreases in signal. Upon reaching the 20 hour time point, the lower energy peak disappears, leaving a single Br 3d peak at 68.87 eV.
with a FWHM of 2.19 eV. For comparison, KBr was dropcast onto a Si wafer chip from a saturated solution in water. The XPS Br 3d peak (Appendix B.8) for this sample was found at 69.1 eV, with a minor peak resolved at 66.8 eV. The minor peak comprises 3.19% of the Br 3d peak area. The literature value for a Br 3d 5/2 peak is listed at 68.8 eV, with a delta of 1.05 eV between the 3d 5/2 and 3/2 peaks.43 Table 3.3 shows the change in percent concentration of the N 1s and Br 3d peaks with deposition time. It is clear that the ratio of bromine to nitrogen increases with increasing deposition time. The XPS data demonstrates successful addition of the bromobenzaldehyde to APTES.
Figure 3.31 Timed XPS Br 3d region scans of the attachment of 5-Bromo-2-hydroxy-3-methoxybenzaldehyde to APTES on Si.
3.4.3 Attachment of 4-Formylbenzo-15-Crown-5 to APTES on Si

After confirming the attachment chemistry of an aldehyde to APTES using the bromo-benzaldehyde, a similar benzaldehyde, with a crown ether functional group was attached to APTES on Si. The growth of 3 mM 4-Formylbenzo-15-Crown-5 (Figure 3.32) in methanol on APTES was monitored over time by AFM, XPS, and ellipsometry.
As mentioned earlier, crown ethers are selective for cations due to their electron rich oxygen centers. The pore diameter of the crown vs. the ionic radius of the cation dictates which ions will “fit” in the crown, and 15-crown-5 ethers are specifically selective for Na\(^+\), a biologically important ion. Initially, the growth of the crown-aldehyde was carried out without a reducing agent, leaving the Schiff bond, and allowing the attachment to be reversible. However, AFM imaging showed a surface similar to that of bare APTES with no change in surface roughness over time. Figure 3.33 shows a sample AFM image of the APTES surface after soaking in the crown overnight.

Figure 3.33 Sample AFM image of APTES on Si after soaking overnight in 3 mM 4-Formylbenzo-15-Crown-5 in MeOH, RMS roughness = 0.139 nm.
It is possible that the formation of the C=N bond was reversing over time due to the presence of water in solution, leaving the bare APTES on Si surface. Furthermore, XPS confirmation of attachment is difficult. The crown ether is composed of all carbon and oxygen atoms, which are elements consistently present in XPS spectra.

To permanently fix the crown attachment, a full reductive amination of the Schiff base was carried out by adding 6 equivalents of NaBH₃CN to the 3 mM solution of crown ether in MeOH. The surface was monitored by AFM over a period of 12 hours (Figure 3.34). Unfortunately, AFM imaging showed the surface to be very rough with overly large particles covering the surface, even at the lowest time points.

Figure 3.34 AFM time study of APTES on Si after soaking in 3 mM 4-Formylbenzo-15-Crown-5 in MeOH, with 6 eq. NaBH₃CN.
Excess reducing agent in solution most likely did not completely dissolve or has aggregated into large particles which physisorbed onto the surface. Contamination with these particles increases with time. To avoid this issue, the reducing agent was scaled back to 2-3 equivalents from 6 equivalents. The amount of APTES used was also decreased. Typical APTES growth conditions used for the aldehyde attachment were a 1% solution of APTES in water, for 20 mins. However, for this time study, APTES growth was carried out in a 0.5% solution in water for 25 mins. This was done in an attempt to minimize as much hydrolysis of the APTES as possible and achieve a smoother monolayer. Figure 3.35 shows the AFM images of the growth of the crown on a 0.5% APTES on Si surface. All RMS roughness values are given in Table 3.4.
Figure 3.35 AFM time study of 0.5 % APTES on Si after soaking in 3 mM 4-Formylbenzo-15-Crown-5 in MeOH, with 2-3 eq. NaBH₃CN.
TABLE 3.4

AFM RMS ROUGHNESSES FOR THE TIME STUDY OF 0.5 % APTES ON SI
AFTER SOAKING IN 4-FORMYL BENZO-15-CROWN-5 IN METHANOL, WITH 2-3
EQ. SODIUM CYANOBOROHYDRIDE

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si</td>
<td>0.106 nm (excluding large particles)</td>
</tr>
<tr>
<td>APTES</td>
<td>0.118 nm (excluding large particles)</td>
</tr>
<tr>
<td>1 hr crown growth</td>
<td>0.192 nm</td>
</tr>
<tr>
<td>3 hr crown growth</td>
<td>0.201 nm</td>
</tr>
<tr>
<td>6 hr crown growth</td>
<td>0.259 nm</td>
</tr>
<tr>
<td>12 hr crown growth</td>
<td>0.792 nm</td>
</tr>
</tbody>
</table>

The AFM images show a clear increase in roughness with time, which is a good indication that the crown is attaching. Image J was used to obtain coverage information for the crown attachment. The 1 hr time point coverage was 6.81 ± 0.71%, 3 hrs was 8.50 ± 0.80%, 6 hr coverage was 19.18 ± 1.35%, and 12 hr was 26.76 ± 2.07%.

Thickness measurements of the crown on APTES were obtained by ellipsometry. Thickness measurements were repeated 7 to 8 times for all samples, over various locations on the chip. The ellipsometer measurement parameters, N and K, used were taken from a standard table provided in the instrument’s user manual. The angle of incidence and the analyzer angle were set at 70º. The thickness of the native SiO$_2$ layer on a freshly cleaned Si chip was found to be 18.88 ± 0.34 Å, by using the following parameters:

Oxide overlayer: N = 1.55, K = 0, est. thickness = 10.00 Å

Si Substrate: N = 3.87, K = 0.018
In order to determine SAM thickness, 2 methods of obtaining measurements were used. A “single layer method” was performed by estimating the thickness of the overlayer (the siloxane SAM w. aldehyde) and underlayer (the oxide) separately. The resulting thickness obtained by the instrument was only due to the SAM. This method was carried out using with the following parameters:

Siloxane overlayer: \( N = 1.45, K = 0 \), est. thickness = 14.00 Å

Oxide underlayer: \( N = 1.55, K = 0 \), est. thickness = 18.88 Å

Si Substrate: \( N = 3.87, K = 0.018 \)

A “subtraction method” was performed by estimating the thickness of the overlayer to include the oxide thickness. The oxide layer thickness of 18.88 Å was then subtracted from the thickness obtained by the instrument to give the thickness of the siloxane SAM alone. For the subtraction method, the following parameters were used:

Siloxane overlayer: \( N = 1.45, K = 0 \), est. thickness = 32.88 Å

Si Substrate: \( N = 3.87, K = 0.018 \)

Table 3.5 lists the averages and standard deviations for the thicknesses obtained by ellipsometry (both methods) for the timed growth of the crown on APTES.
### TABLE 3.5

ELLIPSOMETRIC DATA FOR THE TIMED STUDY OF 4-FORMYL BENZO-15-CROWN-5 ON 0.5% APTES ON SILICON (ALL VALUES ARE IN Å)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Single Layer Method</th>
<th>St. Dev.</th>
<th>Thickness on top of APTES:</th>
<th>Subtraction Method</th>
<th>St. Dev.</th>
<th>Thickness on top of APTES:</th>
<th>Difference in Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr Crown-ald (APTES)</td>
<td>4.09</td>
<td>0.31</td>
<td>n/a</td>
<td>5.75</td>
<td>0.32</td>
<td>n/a</td>
<td>1.66</td>
</tr>
<tr>
<td>1 hr Crown-ald</td>
<td>6.94</td>
<td>0.60</td>
<td>2.85</td>
<td>8.60</td>
<td>0.58</td>
<td>2.85</td>
<td>1.66</td>
</tr>
<tr>
<td>3 hr Crown-ald</td>
<td>10.65</td>
<td>0.91</td>
<td>6.56</td>
<td>12.32</td>
<td>0.92</td>
<td>6.57</td>
<td>1.66</td>
</tr>
<tr>
<td>6 hr Crown-ald</td>
<td>9.92</td>
<td>0.60</td>
<td>5.83</td>
<td>11.56</td>
<td>0.59</td>
<td>5.81</td>
<td>1.64</td>
</tr>
<tr>
<td>12 hr Crown-ald</td>
<td>10.34</td>
<td>0.43</td>
<td>6.25</td>
<td>12.00</td>
<td>0.44</td>
<td>6.25</td>
<td>1.66</td>
</tr>
</tbody>
</table>

The subtraction method used with the ellipsometer generally resulted in thicknesses about 1.66 Å greater than the single layer method. The low standard deviations obtained from measuring multiple locations on each sample indicate uniform thickness across the surface. The thickness of APTES was measured at 4.09 ± 0.31 Å for the single layer method and 5.75 ± 0.32 Å for the subtraction method. If the APTES molecules stand perpendicular to the surface, the monolayer thickness would be approximately 7 Å. The lower thickness indicates the molecules are tilted at an angle. Between 3-12 hours of crown deposition, the thickness on top of APTES did not
significantly change. The average thickness from all 3 times points (data averaged from both methods) is $6.21 \pm 0.33 \text{ Å}$. The approximate length of the benzaldehyde crown is about $8 \text{ Å}$ (determined using ChemOffice). The orientation when bound to APTES can also be tilted, resulting in a reduced thickness.

X-ray photoelectron spectroscopy data (Mg-Kα source) was obtained for the 0 hr, 1 hr, 6 hr, and 12 hr benzaldehyde crown samples used in the AFM and ellipsometer study. Each sample was calibrated against its own maximum C 1s peak, which was set to 284.5 eV. A survey scan and individual region scans for the maximum time point (12 hrs) can be found in Appendix B.9. The full quantification report for all samples is in Appendix B.10. The ratios of the % concentrations for O 1s, N 1s, and C 1s vs. Si 2p were evaluated, and the results are presented in Table 3.6. The addition of the crown was anticipated to cause an increase in % concentration of oxygen and carbon, however, the effect should be minimal, considering that the monolayers are thin. The bulk of the surface sampled by XPS is still Si and its native oxide.

**TABLE 3.6**

XPS % CONCENTRATION RATIOS OF OXYGEN, NITROGEN, AND CARBON VS. SILICON FOR THE TIMED GROWTH OF 4-FORMYL BENZO-15-CROWN-5 ON APTES ON SILICON

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 1s : Si 2p</th>
<th>N 1s : Si 2p</th>
<th>C 1s : Si 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr Crown</td>
<td>$1.092 \pm 0.115$</td>
<td>$0.035 \pm 0.008$</td>
<td>$0.446 \pm 0.098$</td>
</tr>
<tr>
<td>1 hr Crown</td>
<td>$1.071 \pm 0.112$</td>
<td>$0.035 \pm 0.008$</td>
<td>$0.493 \pm 0.108$</td>
</tr>
<tr>
<td>6 hr Crown</td>
<td>$1.146 \pm 0.120$</td>
<td>$0.051 \pm 0.011$</td>
<td>$0.591 \pm 0.130$</td>
</tr>
<tr>
<td>12 hr Crown</td>
<td>$1.191 \pm 0.125$</td>
<td>$0.064 \pm 0.014$</td>
<td>$0.643 \pm 0.141$</td>
</tr>
</tbody>
</table>
The oxygen and carbon ratios increased slightly as the deposition time increased, however, their ranges overlap. The nitrogen to silicon ratio also increased. There is no nitrogen contained in the benzaldehyde crown, and therefore it should not cause an increase in N content in the sample. However, the increase in N 1s signal can be explained by residual cyanide nitrogen from the reducing agent being present on the surface. The plain APTES sample has 2 N 1s peaks, one at 400.27 eV and the other at 402.32 eV, which are assigned to the APTES amine nitrogen and protonated amine nitrogen, respectively. The 1, 6, and 12 hr crown samples each have 3 nitrogen peaks, at approximately the same locations. For the maximum time point, the peaks are at 398.69 eV, 400.76 eV, and 402.69 eV. The highest energy peak is still assigned to the protonated amine nitrogen, the 400 eV peak to the APTES amine, and the 398 eV peak to leftover cyanide nitrogen from the reducing agent. Figure 3.36 shows the peak fittings for the XPS N 1s region scans of the plain APTES and 12 hr crown samples.
Figure 3.36 XPS N 1s peak for APTES on Si (0 hr Crown) and 12 hr 4-Formylbenzo-15-Crown-5 growth on APTES on Si.
3.4.4 Attachment of Dipicolylamine to APTES on Si

In order to create an anion binding SAM, dipicolylaldehyde (see previous Figure 3.3) was attached to an APTES monolayer on Si via reductive amination with NaBH$_3$CN. The reduction attaches 2 picolyl groups to an APTES amine, forming a dipicolylamine ligand (DPA, also in previous Figure 3.3). The growth of 3 mM picolylaldehyde in methanol with 2-3 eq. NaBH$_3$CN was monitored over time by AFM, XPS, and ellipsometry. For this study, APTES growth was carried out in a 0.5% solution in water for 25 mins. Figure 3.37 shows AFM images of 1 hr, 3 hr, 6 hr, and 12 hr times points of APTES in the dipicolylaldehyde/reducing agent solution. Bare Si and APTES can be viewed in Figure 3.35.
Figure 3.37 AFM time study of 0.5 % APTES on Si after soaking in 3 mM picolylaldehyde in methanol with 2-3 eq. NaBH₃CN.
After the picolylaldehyde deposition, it was difficult to distinguish possible DPA on APTES from plain APTES. Due to this complication, % coverage data was not obtained for the full image series. There was a slight increase in surface roughness, although it was not as distinct as what was seen with the crown aldehyde. Table 3.7 lists the RMS roughness values for the different time points during the deposition. A 1 µm x 1 µm AFM image of APTES was found to have an RMS roughness of 0.118 nm. With the exception of the 3 hr time point, RMS roughnesses obtained were within less than 0.05 nm of the APTES RMS. The large particles seen in the images, particularly the 3 hr time point, are most likely due to undissolved reducing agent. When measuring the RMS of smooth areas of the images (excludes the large particles), the 1 hr time point is the only image with a higher RMS than APTES. However, Image J coverage data for the 1 hr time point only yields a coverage of 3.94 ± 1.21%.

**TABLE 3.7**

AFM RMS ROUGHNESSES FOR THE TIME STUDY OF 0.5 % APTES ON Si AFTER SOAKING IN PICOLYLALDEHYDE IN METHANOL, WITH 2-3 EQ. SODIUM CYANOBOROHYDRIDE

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS Roughness (Whole Image)</th>
<th>RMS Roughness (Smooth Patch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hr picolylaldehyde soak</td>
<td>0.161 nm</td>
<td>0.151 nm</td>
</tr>
<tr>
<td>3 hr picolylaldehyde soak</td>
<td>0.279 nm</td>
<td>0.109 nm</td>
</tr>
<tr>
<td>6 hr picolylaldehyde soak</td>
<td>0.122 nm</td>
<td>0.113 nm</td>
</tr>
<tr>
<td>12 hr picolylaldehyde soak</td>
<td>0.164 nm</td>
<td>0.0896 nm</td>
</tr>
</tbody>
</table>
Using AFM to prove DPA attachment to APTES was inconclusive. Thickness measurements of DPA on APTES were obtained by ellipsometry. As with the crown aldehyde (see Section 3.4.3), 2 different measurement methods, single layer and subtraction, were used. Table 3.8 lists the measurements made on the picolylaldehyde timed samples.

**TABLE 3.8**

**ELLIPSOMETRIC DATA FOR THE TIMED STUDY OF DIPICOLYLAMINE ON 0.5% APTES ON SILICON (ALL VALUES ARE IN Å)**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr DPA (APTES)</td>
<td>4.09</td>
<td>0.31</td>
<td>n/a</td>
<td>5.75</td>
<td>0.32</td>
<td>n/a</td>
<td>1.66</td>
</tr>
<tr>
<td>1 hr DPA</td>
<td>9.16</td>
<td>0.69</td>
<td>5.07</td>
<td>10.82</td>
<td>0.67</td>
<td>5.07</td>
<td>1.66</td>
</tr>
<tr>
<td>3 hr DPA</td>
<td>7.40</td>
<td>0.63</td>
<td>3.31</td>
<td>9.05</td>
<td>0.63</td>
<td>3.30</td>
<td>1.65</td>
</tr>
<tr>
<td>6 hr DPA</td>
<td>6.49</td>
<td>0.48</td>
<td>2.40</td>
<td>8.14</td>
<td>0.47</td>
<td>2.39</td>
<td>1.65</td>
</tr>
<tr>
<td>12 hr DPA</td>
<td>6.46</td>
<td>1.18</td>
<td>2.37</td>
<td>8.12</td>
<td>1.16</td>
<td>2.37</td>
<td>1.66</td>
</tr>
</tbody>
</table>

The pyridine rings of the DPA ligand may be oriented vertically, horizontally (flat and parallel to the surface), or anywhere in between. If the rings are oriented vertically (as shown in Figure 3.4), the height on top of APTES would be approximately 7.4 Å (determined using ChemOffice). If the APTES is also oriented perpendicular to the
surface, the height of APTES + vertical DPS would be ~14.7 Å. This configuration would result in the maximum thickness that could be obtained for a monolayer. For the 1 hour deposition sample, the height on top of APTES was found to be ~ 5.07 Å, indicating that the rings are not completely vertical. For the longer time points, the height actually decreased, with the 12 hour time point resulting in a height on top of APTES at ~ 2.37 Å. Although, qualitatively speaking, the ellipsometer results indicate that something has grown on APTES, it is important to note that the accuracy of the Gaertner ellipsometer is listed by the manufacturer as ± 3 Å.

X-ray photoelectron spectroscopy data (Mg-Kα source) was obtained for the 0 hr (bare APTES), 1 hr, 3 hr, 6 hr, and 12 hr picolylaldehyde samples used in the AFM and ellipsometer study. Each sample was calibrated against its own maximum C 1s peak, which was set to 284.5 eV. A survey scan and individual region scans for the maximum time point (12 hrs) can be found in Appendix B.11. The full quantification report for all samples is in Appendix B.12. The ratios of the % concentrations for O 1s, N 1s, and C 1s vs. Si 2p were evaluated, and the results are presented in Table 3.9. The addition of the DPA ligand was anticipated to cause an increase in % concentration of nitrogen and carbon, as these are the components of the pyridine rings. However, the XPS results show only a slight increase in the nitrogen to Si ratio, and a similar result was seen for the crown aldehyde, which has no nitrogen in the molecule. As was seen with the crown aldehyde, the N 1s spectrum was resolved into 3 peaks, at 398.43 eV, 400.53 eV, and 402.61 eV. The carbon to silicon ratio fluctuated, and the highest ratio was actually seen for the APTES sample without any exposure to picolylaldehyde.
### TABLE 3.9

% CONCENTRATION RATIOS OF OXYGEN, NITROGEN, AND CARBON VS. SILICON FOR THE TIMED GROWTH OF DIPICOLYLAMINE ON APTES ON SILICON

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 1s : Si 2p</th>
<th>N 1s : Si 2p</th>
<th>C 1s : Si 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr DPA</td>
<td>1.092 ± 0.078</td>
<td>0.035 ± 0.008</td>
<td>0.446 ± 0.107</td>
</tr>
<tr>
<td>1 hr DPA</td>
<td>1.034 ± 0.073</td>
<td>0.033 ± 0.008</td>
<td>0.316 ± 0.076</td>
</tr>
<tr>
<td>3 hr DPA</td>
<td>1.025 ± 0.073</td>
<td>0.042 ± 0.010</td>
<td>0.367 ± 0.088</td>
</tr>
<tr>
<td>6 hr DPA</td>
<td>1.039 ± 0.074</td>
<td>0.047 ± 0.011</td>
<td>0.433 ± 0.103</td>
</tr>
<tr>
<td>12 hr DPA</td>
<td>0.854 ± 0.061</td>
<td>0.057 ± 0.014</td>
<td>0.371 ± 0.089</td>
</tr>
</tbody>
</table>

3.5 Growth and Characterization of Ion Sensing Monolayers on AlGaN/GaN

3.5.1 Attachment of 5-Bromo-2-hydroxy-3-methoxybenzaldehyde to APTES on AlGaN/GaN

The deposition procedure for the bromine benzaldehyde on APTES on Si was also carried out on APTES on AlGaN/GaN. The brominated aldehyde was used for attachment confirmation purposes, and therefore, deposition was only evaluated by XPS. An APTES on AlGaN/GaN wafer was placed in 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in methanol with 2 eq. of NaBH₃CN for 20 hours (the maximum time point used in the Si study). The XPS survey scan, region scans, and quantification report for this sample can be found in Appendix B.13. The Al 2p and Br 3d regions overlap one another, and are presented in Figure 3.38.
After 20 hours in the Br-aldehyde solution, 2 peaks appear in the Al 2p region, one at 71.46 eV with a FWHM of 1.805 eV, and the other at 68.18 eV with a FWHM of 2.55 eV. The previous Br-aldehyde study on Si showed a strong peak for Br 3d at 68.8 eV after a 20 hr deposition, and for a dropcast KBr sample, a strong peak was located at 69.1 eV. The peak at 68.18 eV in the AlGaN/GaN sample can be assigned to bromine, indicating positive attachment. The peak at 71.46 eV, is assigned to Al. However, this peak position is rather low for an Al 2p peak, which usually appears around 74 eV. For comparison, bare APTES (20 min, 1%) on AlGaN/GaN gives a single Al 2p peak (Figure 3.39) at 73.82 eV with a FWHM of 1.62 eV.
3.5.2 Attachment of 4-Formylbenzo-15-Crown-5 and Dipicolylamine to APTES on AlGaN/GaN

The crown aldehyde and picolylaldehyde were also deposited on APTES on AlGaN/GaN following the procedures outlined for Si. APTES samples were soaked in 3 mM 4-formylbenzo-15-crown-5 in methanol and 3 mM picolylaldehyde in methanol with 2 eq. NaBH$_3$CN for 12 hours. The samples were imaged by atomic force microscopy and 1 µm x 1µm scans of both can be found in Figure 3.40. The RMS roughness for the crown image is 0.630 nm, with the smoother dotted line inset at 0.212 nm. The roughness for the picolylaldehyde image is 0.491 nm with the dotted line inset at 0.251 nm. Both surfaces appear to have large contamination particles on them, which can be the result of undissolved reducing agent or aldehyde. The images have no distinct features on them that indicate crown or DPA attachment.
Figure 3.40 APTES on AlGaN/GaN after 12 hour soak in a.) 3 mM 4-formylbenzo-15-crown-5 in methanol with 2 eq. NaBH$_3$CN and b.) 3 mM picolylaldehyde in methanol with 2 eq. NaBH$_3$CN.
3.6 Evaluation of Ion Binding Monolayers by XPS

3.6.1 Cation Binding of 4-Formylbenzo-15-Crown-5 in Chloride Salts

Cation binding of 15-crown-5 treated APTES on Si (12 hour deposition in 3 mM 4-Formylbenzo-15-Crown-5 in MeOH) was evaluated by X-ray photoelectron spectroscopy (Mg-Kα source) after soaking wafers in various chloride solutions. As mentioned earlier, 15-crown-5 is selective for sodium ions. Samples were first scanned for possible Na⁺ binding from the reducing agent, NaBH₃CN. During crown attachment, deposition solutions include roughly 9 mM NaBH₃CN. The Na 1s region was scanned in XPS for the 6 hour and 12 hour crown on APTES deposition times. Additionally, bare APTES on Si was soaked for 12 hours in a 12 mM NaBH₃CN solution in MeOH (no crown-aldehyde) and scanned for Na 1s. For comparison, a dropcast NaBH₃CN on Si sample was also prepared from a saturated solution in MeOH and scanned for sodium. The Na 1s region scans for all 4 samples can be found in Appendix B.14.

The dropcast sample gave a strong Na 1s peak at 1071.83 eV. The literature value for Na 1s (NaCl) is listed at 1072.1 eV. The APTES in 12 mM NaBH₃CN sample as well as both the 6 hour and 12 hour crown deposition samples show a minor noisy bump in the Na 1s region at approximately 1072 eV. This indicates some sodium is residing on the surface, but it may be physisorbed onto the APTES. The bump is not present in a scan of piranha/RCA cleaned silicon. Figure 3.41 shows the Na 1s spectra of a.) piranha/RCA cleaned Si and b.) the 12 hr crown-aldehyde on APTES on Si sample.
Figure 3.41 Na 1s XPS region scan for a.) piranha/RCA cleaned Si and b.) 12 hr crown-aldehyde on APTES on Si.

To test ion capture by the crown, as well as test for selectivity, 12 hr crown-aldehyde on APTES samples, as well as plain APTES samples, were soaked in 1 mM aqueous solutions of LiCl, NaCl, KCl, and MgCl₂ for 1 hour. Overlays of the Na 1s, K 2p, and Mg 2p region scans for both the plain APTES and 12 crown samples can be found in Appendix B.15. Additionally, Li 1s/Mg 2p and K 2p region scans for piranha/RCA cleaned Si (no ion exposure) are in Appendix B.16. The Na 1s region for both samples still presents as a noisy bump at approximately 1072 eV, and the 12 hr
crown scan looks almost identical to the bare APTES scan. If sodium is selectively binding, there should be a more intense peak for the crown sample. No peak was seen in either sample for the K 2p region, indicating potassium is not binding to either surface. The Li 1s (55.6 eV) and Mg 2p (49.8 eV) regions overlap one another. Both APTES samples soaked in LiCl and in MgCl$_2$ show a broad and noisy peak around 48.6 eV that extends and slopes down to 56 eV. The same peak/slope shape is present for the clean Si wafer. However, both crown samples from LiCl and MgCl$_2$ show the appearance of a second peak at 52.6 eV (Figure 3.42).

![Mg 2p/Li 1s Overlay](image)

Figure 3.42 Overlay of the Li 1s and Mg 2p region scans for LiCl and MgCl$_2$ soaked 12 hr crown-aldehyde on APTES samples.

This second peak is very broad and the entire Li 1s/Mg 2p region (for the LiCl soaked sample) was actually resolved into 3 peaks (Figure 3.43) at 48.79 eV with a FWHM of 3.18 eV, 52.25 eV with a FWHM of 2.97 eV, and 54.60 eV with a FWHM of...
It is unclear if the emergence of the 2 higher energy peaks is due to the presence of Li on the samples, especially since the MgCl$_2$ sample should not contain lithium.

Figure 3.43 Component break down of the Li 1s / Mg 2p region for 12 hour crown-aldehyde on APTES soaked in LiCl.

3.6.2 Coordination of Zn$^{2+}$ to DPA via Zinc Nitrate

The coordination of zinc to dipicolylamine on APTES on Si was evaluated by X-ray photoelectron spectroscopy (Mg-K$\alpha$ source). APTES monolayers were treated for 12 hours with 3 mM picolylaldehyde in MeOH + 2 eq. NaBH$_3$CN to attach DPA ligands to APTES. These samples, along with plain, non-DPA treated APTES samples, were soaked in 30 mM Zn(NO$_3$)$_2$ in water for approximately 6 hours, and scanned for zinc on the surface. Figure 3.44 shows an overlay of the Zn 2p region scans for both the APTES
control and DPA-APTES. A full quantification report for all region scans can be found in Appendix B.17.

Both samples show the presence of zinc on the surface, however, the DPA sample shows more intense Zn 2p peaks. For comparison, zinc does not show up at all in the 2p region scan for piranha/RCA cleaned Si (Figure 3.45). The 2p 3/2 peak is located at 1028.37 eV with a FWHM of 2.102 eV and the 2p 1/2 peak is located at 1051.69 eV with a FWHM of 2.323 eV. This gives a peak Δ of 23.32 eV. The literature value for Zn 2p 3/2 is 1021.8 eV with a Δ of 22.97 eV. The peak position for the APTES and DPA samples is approximately 6.5 eV higher than the literature value, but this can be attributed to the positive charge on zinc.
The % concentration ratio of Zn : N is $0.15 \pm 0.042$ for the APTES sample and $0.37 \pm 0.104$ for the DPA sample. The presence of zinc on the non-DPA treated APTES control means that some zinc is physisorbed onto the surface. The fact that the zinc signal is more intense for the DPA sample does show that zinc is more attracted to this surface, even with the error range in consideration. This is the first positive confirmation that some DPA ligands have successfully attached to the APTES layer.

Ligand behavior of DPA was also tested with iron, a different divalent metal cation. A plain APTES on Si sample and a DPA-APTES on Si sample were soaked in 30 mM FeCl$_2$ in water for approximately 2 hours, and scanned by XPS for Fe on the surface. Figure 3.46 shows an overlay of the Fe 2p region scan for APTES and DPA-APTES after soaking in iron solution. A full quantification report for all region scans of both samples can be found in Appendix B.18.
The result after soaking in iron solution was similar to that of soaking zinc, where both the APTES and DPA samples have iron present on the surface, but the signal intensity is slightly greater for the DPA sample. The Fe : N % concentration ratio for the APTES sample is $0.13 \pm 0.036$, and it is $0.29 \pm 0.081$ for the DPA sample.

3.6.3 Anion Binding of Zn-DPA in Phosphate Solution

With positive confirmation of the presence of zinc on the DPA surface, anion binding of the Zn$^{2+}$-coordinated DPA ligand was tested with monopotassium phosphate, KH$_2$PO$_4$. A Zn-DPA-APTES on Si sample (12 hr DPA, 6 hr Zn$^{2+}$) was soaked in 1 mM KH$_2$PO$_4$ in water for 1 hour. A plain APTES sample was also placed in phosphate solution for 1 hour. The samples were scanned by XPS for phosphate content (via P 2p region scans) on the surface. Being as the oxygen content of each sample is very high, it
is difficult to tell if an increase in oxygen signal is due to phosphate oxygen. Figure 3.47 shows an overlay of the P 2p region scans for the APTES control and Zn-DPA-APTES samples. A full quantification report for all region scans for both samples can be found in Appendix B.19.

![Figure 3.47 XPS P 2p region scan for APTES and Zn-DPA-APTES after soaking in 1 mM KH₂PO₄ for 1 hour.](image)

Both samples show a broad noisy peak centered at ~ 131.5 eV. However, when comparing the region to a scan performed on piranha / RCA cleaned Si (see Figure 3.48, quantification report in Appendix B.20) this broad peak also appears. The peak is actually due to a silicon plasmon band. The P : Si % concentration ratios for clean Si, APTES, and Zn-DPA-APTES are 0.066 ± 0.016, 0.051 ± 0.011, and 0.060 ± 0.013, respectively. Since there is no increase in the ratio, this peak is solely due to the Si plasmon, and phosphate is not binding to the Zn-DPA-APTES surface.
In addition to the lack of phosphate binding, analysis of the Zn 2p region (Figure 3.49) shows that the surface Zn content for the Zn-DPA-APTES sample has actually been reduced after soaking in the phosphate solution. This is illustrated by the loss of the once sharp Zn 2p peaks, and the reduction of the Zn : N % concentration ratio to 0.035 ± 0.010 from 0.37 ± 0.104 before placement in the phosphate solution. This result suggests that Zn$^{2+}$ coordination to DPA is reversible in solution.
3.6.4 DNA Binding of Zn-DPA

DNA binding of the Zn$^{2+}$ coordinated DPA ligand was tested using DNA origami obtained from Valerie Goss (University of Notre Dame, Dept. of Chemistry). The DNA origami are nanoscale rectangles. They are approximately 70 nm x 90 nm x 2 nm in size, and kept in a 10X TAE/Mg$^{2+}$ buffer solution (400 mM Tris-HCL, 200 mM acetic acid, 20 mM EDTA, and 125 mM magnesium acetate, pH =8). DNA is negatively charged and thus should attach to the Zn$^{2+}$ coordinated DPA on APTES. Since it was noticed that Zn coordination is reversible in solution, DNA binding was performed both with and without a zinc spike added to the DNA sample. DNA samples were spiked by adding 2 µL of 30 mM Zn(NO$_3$)$_2$ to 10 µL of 2 nM DNA.
For deposition, a Zn-DPA-APTES sample was treated with 6 µL of unspiked DNA and another was treated with 6 µL spiked DNA. Treatments were performed by placing a sample in a 1" wafer container, dispensing the DNA on the surface, closing the container to prevent evaporation, and allowing the DNA to remain on the surface for 30 mins. Samples were gently rinsed with ultra-pure water, N₂ dried, and taken for AFM imaging. Figure 3.50 and Figure 3.51 show the unspiked and Zn spiked images respectively.

Figure 3.50 AFM image of DNA origami on Zn-DPA-APTES on Si.
The % coverage of DNA on the unspiked sample is 25.47 ± 0.90 %. For the spiked sample it is 7.89 ± 1.30 %. The lower coverage for the spiked sample may be due to DNA aggregating in solution with zinc. The aggregates, being fairly neutral, would not bind to the surface, and are removed during the rinsing step. Additionally, the process of spiking the sample does dilute the 2 nM DNA down to 1.67 nM.

In both images, it is also difficult to distinguish the rectangular morphology of the origami. Most of the rectangles appear to have folded edges. Overall, the DNA origami do appear to be sticking to the Zn-DPA-APTES on Si surface. For comparison, a Zn-
DPA-APTES on AlGaN/GaN sample was exposed to 6 µL of 2 nM DNA for 30 mins. AFM imaging of this sample (Figure 3.52, 5 µm x 5 µm and Figure 3.53, 1 µm x 1 µm) also shows DNA origami adhering to the surface. Due to the heavy contamination in the 5 µm x 5 µm image, coverage data could not be obtained. For the 1 µm x 1 µm image, 8 individual origami can be seen on the surface. In addition to the origami being present, they have mostly maintained their rectangular shape. A few origami appear to have rolled edges.

Figure 3.52 AFM image of DNA origami on Zn-DPA-APTES on AlGaN/GaN.
Figure 3.53 1 μm x 1μm AFM image of DNA origami on Zn-DPA-APTES on AlGaN/GaN.

3.7 Discussion

APTES monolayer formation on AlGaN/GaN was confirmed by contact angle, AFM and XPS. Just as with the GaN study in Chapter 2, the monolayer grows by island formation. AFM imaging shows an initial increase in RMS roughness that drops as the islands become a continuous monolayer. XPS shows attenuation of the gallium signal with monolayer formation as well as the appearance of a Si 2p peak after functionalization. Unlike the GaN study, the monolayers on AlGaN/GaN are stable in
pH = 7 buffer solution after 20 hours. The contact angle before the buffer soak was mid to high 60°'s and was ~ 61° after soaking in buffer. This result shows that the oxide layer on AlGaN has greater stability than that of GaN, which may be due to aluminum diffusion through the GaN cap to the topmost surface during annealing. This reinforces the gallium oxide with aluminum oxide. The positive stability of the monolayer and underlying oxide in aqueous solution means that AlGaN/GaN will withstand use in biosensor applications.

InAlN/GaN is unfortunately not a usable material for functionalization in solution. After APTES treatment, the material does not appear to be functionalized, as seen by AFM imaging and XPS analysis. Further negating the usage of the material, the surface is easily damaged and etched after typical semiconductor cleaning treatments. Even when simple solvent rinses are used, the surface morphology of the material still changes after monolayer treatment in aqueous APTES solution. A recent study on the wet etching of InAlGaN nitride, which has a similar grainy surface morphology to InAlN, has shown that the etch rate of the material is dependent upon the homogeneity of the surface. InAlGaN layers with higher RMS roughnesses (AFM) were found to etch faster. It is possible that less grainy, more continuous InAlN films could withstand short aqueous surface treatments for usage in applications other than biosensors.

XPS analysis of the timed deposition of 5-bromo-2-hydroxy-3-methoxybenzaldehyde to APTES on Si shows a steady increase in signal from bromine with time. The % concentration ratio of bromine to nitrogen increases from 0 for plain APTES (no Br detected by XPS) to $0.690 \pm 0.193$ after a 20 hour deposition. The coverage of the Br-APTES monolayer on Si can be estimated by comparing it to the
coverage of APTES on Si. Moon et. al. previously determined that the coverage of APTES on SiO$_2$ is 3.9 molecules per 100 Å$^2$.\textsuperscript{84}

A 20 min, 1% APTES deposition on Si has a nitrogen to silicon % concentration ratio of 0.059 ± 0.013. This ratio is close the 0.066 ratio previously obtained by the Lieberman group for a full APTES SAM.\textsuperscript{85} After the 20 hour Br-aldehyde deposition, the N to Si ratio drops to 0.038 ± 0.008, which is 57.6% of a full SAM. This drop indicates some of the monolayer is lost after soaking in solution for so long. The shorter Br-benzaldehyde deposition time points have a higher ratio, ranging from 0.045 ± 0.010 to 0.057 ± 0.013. A partial monolayer of 57.6% equates to a coverage density of APTES on Si (for the 20 hr Br-aldehyde sample) of 2.25 APTES molecules per 100 Å$^2$. If one Br-benzaldehyde molecule were to bind to each APTES molecule, the Br to N ratio would be 1 to 1, however, it is 0.690 ± 0.193 for this sample, meaning 69% of the APTES amines have a brominated benzene ring attached. This yields a coverage of 1.55 Br-benz-APTES molecules per 100 Å$^2$.

Given that the crown aldehyde molecule does not contain any elements not found on the APTES surface, coverage data by XPS could not be obtained. Surface coverage was visually analyzed by Image J for the AFM image series of the growth of the crown, which was measured at 26.76 ± 2.07\% for a 12 hour deposition.

The DPA ligand also does not contain any elements not found on the APTES surface. However, the addition of DPA to APTES does add 2 additional N atoms to the APTES. The APTES samples used for the DPA study were grown from a 0.5 % solution for 25 mins. The XPS N to Si ratio obtained for a plain APTES sample in this study is 0.035 ± 0.008, which is 53.0\% of a full SAM, or an APTES on Si coverage of 2.07
molecules per 100 Å². After a 12 hour deposition of picolylaldehyde with reducing agent, the N to Si ratio increased to 0.057 ± 0.014, which is a little more than 1.5x the plain APTES ratio. If 1 DPA were to bind to every APTES, the ratio would triple. Although coverage of DPA cannot be quantified, it is clear that not every APTES molecule has a DPA attached.

For the coordination of zinc to the DPA-APTES, a separate APTES growth and DPA deposition was performed. After soaking in 30 mM Zn(NO₃)₂, a plain APTES sample had a N to Si ratio of 0.050 ± 0.011, which is 75.75% of a full monolayer, or a coverage of 2.95 molecules per 100 Å². The Zn to N ratio for this sample was 0.15 ± 0.042. A 12 hr DPA-APTES sample had a N to Si ratio of 0.070 ± 0.015, which is 1.4x that of the plain APTES SAM. The zinc to nitrogen ratio was 0.37 ± 0.104. The fact that both the N:Si and Zn:N ratios are higher for the DPA-APTES sample indicates that not only is DPA present on the surface, but zinc is preferentially sticking to the DPA surface. Zinc coordination was found to be reversible in solution.

DNA origami was successfully bound to Zn-DPA-APTES modified surfaces of both Si and AlGaN. For the silicon surface, the all rectangular origami appear to have folded or rolled edges, yet for the AlGaN surface, only a few of the origami have a rolled edge. This effect may be caused by differences in charge density on the Si surface vs. the AlGaN surface which is related to the coverage of APTES, vs. DPA APTES, vs Zn-DPA-APTES.

Ion binding by the crown and DPA modified APTES surfaces could not be proven by XPS. However, it is still possible that ion capture can be analyzed by electrical measurements with AlGaN/GaN. Successful electrical measurements detecting changes
in enzyme concentrations have been made by immobilizing the enzyme on aldehyde modified APTES in the gate region of an AlGaN/GaN HEMT device. Baur et. al. grew an APTES monolayer in the gate region of the AlGaN/GaN HEMT and soaked the for 1 hour in 20 mM glutaraldehyde in water with NaBH₃CN reducing agent. The modified APTES was then exposed to penicillinase. The authors were able to detect the presence of the enzyme on the surface by fluorescence microscopy with Alexa Fluor 488 labeled penicillinase. No additional proof of enzyme surface attachment was provided. The authors then characterized electrical response of the HEMT in a three-electrode measurement cell with a Ag/AgCl₂ reference electrode, and changes in the electrical response of the device were observed with changing enzyme concentration. The results were compared to the response of the HEMT to physisorbed penicillinase on an unfunctionalized gate region. They found that the unfunctionalized HEMT showed large variations in signal for all concentrations measured, while the functionalized HEMT exhibited a reproducible response. This study is promising for the future potential of proving the ability of ion capture by the crown and DPA modified APTES layers.

3.8 Summary

APTES functionalized surfaces of Si and AlGaN/GaN can be modified with aldehyde treatments through reductive amination using NaBH₃CN as a reducing agent. Successful attachment of 5-bromo-2-hydroxy-3-methoxybenzaldehyde can be seen by XPS with the emergence of Br 3d peaks at 68.8 eV and 68.18 eV for Si and AlGaN surfaces, respectively. The Si modified surface has a coverage density of 1.55 Br-benz-APTES molecules per 100Å². The APTES on Si attachment of 4-formylbenzo-15-
crown-5 with 2-3 equivalents of reducing agent can be seen by AFM with an increase in surface roughness from 0.118 nm up to 0.259 nm for a 6 hour deposition and 0.792 nm for a 12 hour deposition. Ellipsometry measurements also show an increase in thickness on top of APTES of 5.83 Å for a 6 hr deposition and 6.25 Å for 12 hours. XPS measurements show an increase in the oxygen to silicon and carbon to silicon ratios due to the presence of the crown on the surface.

AFM and ellipsometry analysis for the deposition of dipicolylamine (DPA) via picolylaldehyde and reducing agent is less conclusive than for the crown. However, XPS does show an increase in the nitrogen to silicon ratio after a 12 hour deposition. XPS also shows the successful attachment of zinc to the DPA modified surface with a Zn : Si ratio increase (from 0) to 0.37 ± 0.104 for DPA, which is greater than that of a plain APTES control (0.15 ± 0.042). Additionally, DNA origami was successfully bound to the Zn-DPA modified surfaces for both Si and AlGaN/GaN. Zinc coordination, however, was found to be reversible in solution.

Although the results for XPS analysis of cation and anion binding of the crown and Zn-DPA modified surfaces were inconclusive, future electrical testing of the modified surfaces as the gate region of a HEMT structure (with metal contacts) may prove changes in the electrical (I/V) characteristics of the sample when exposed to various ionic solutions of different concentrations.
3.9 Experimental

3.9.1 Sample Preparation

All glassware and tweezers were rinsed with acetone, then boiled in ethanol (absolute) for 30 minutes and given a final rinse with ultra-pure (18 MΩ, milli-Q) H₂O. Si wafers, p-type,[100], were commercially purchased and diced with a diamond tip pen to approximately 10 mm × 10 mm chips. Aluminum gallium nitride/gallium nitride and indium aluminum nitride/gallium nitride samples were provided by Dr. Huili Grace Xing, Department of Electrical Engineering, University of Notre Dame. The layered composition of the AlGaN/GaN samples is as follows: 3 nm GaN cap / 19 nm Al₀.₂₈Ga₀.₇₂N / 2 μm GaN buffer / Sapphire substrate. The layered composition of the InAlN/GaN samples is as follows: 10 nm In₁₇Al₈₃N / 0.5 nm AlN / 2 μm GaN Buffer / Sapphire substrate. AlGaN/GaN structures were grown by metal organic chemical vapor deposition (MOCVD) and InAlN/GaN structures were grown by molecular beam epitaxy (MBE). All samples were approximately 10 mm × 10 mm chips.

All chips were rinsed with acetone, ethanol, and followed by a final rinse with ultra-pure 18MΩ H₂O, then N₂ dried. It was discovered during this research that InAlN/GaN can only be cleaned with solvents, as is described in Section 3.2.2.

After solvent cleaning, the Si and AlGaN/GaN chips were etched for 20 minutes with a piranha acid solution of 1:3, 30% H₂O₂:H₂SO₄ (concentrated), rinsed with 18MΩ H₂O, and dried with N₂ gas. After piranha treatment, Si wafers were etched in 10% HF for 25 seconds, followed by a 10 min treatment in an RCA 1 bath (1:1:5, NH₄OH:30% H₂O₂:H₂O ) at 70 ºC, then a 10 min treatment in an RCA 2 bath (1:1:5, HCl:30%
H₂O₂; H₂O) at 70 °C. The wafers were rinsed with 18MΩ H₂O after each treatment, and
dried with N₂ gas after the final rinse.

3.9.2 Monolayer Deposition

To avoid excess surface contamination, samples were immediately used after
cleaning. All monolayer solutions were made in 20 ml glass scintillation vials which
were cleaned by the procedure mentioned above and dried in an oven. Each chip was
placed in its own vial to avoid sample contamination.

APTES (3-Aminopropyltriethoxysilane) monolayers were grown by soaking a
chip in 5-10 mL of 0.5-2% APTES in 18 MΩ H₂O for a maximum time of 30 mins.
Because APTES tends to hydrolyze over time due to moisture from lab ambient, a fresh
supply of APTES (less than 6 months old) was used for making solutions in water. After
growth, the samples were rinsed with 18 MΩ H₂O and N₂ dried.

F-TES monolayers (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane were
grown by soaking a chip in 5-10 mL of 1% F-TES in toluene for 1.5 hrs. The toluene
was not dried prior to making the F-TES solution. After deposition, samples were rinsed
with toluene, and N₂ dried.

Fluorinated benzaldehyde treatments were carried out on APTES functionalized
surfaces. The APTES was grown from a 1% solution in water for 20 mins. The APTES
samples were soaked for 14 hrs in a 1% solution of 2,4,5-trifluorobenzaldehyde in
methanol. Samples were rinsed with methanol and N₂ dried.

Bromine aldehyde treatments were also carried out on APTES grown from a 1%
solution in water for 20 mins. The APTES samples were soaked for varying time points
in a 3mM solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde in methanol. Samples
were rinsed with methanol and N\textsubscript{2} dried. The maximum time point used was 20 hours. Br-aldehyde deposition was also carried out using NaBH\textsubscript{3}CN as a reducing agent, with 6 equivalents of reducing agent added directly to the deposition vial. Some undissolved reducing agent remained and the deposition solutions were syringe filtered with a 0.45 μm polypropylene filter.

Crown aldehyde treatments were carried out on APTES grown from a 0.5% solution in water for 25 mins. The APTES samples were soaked for varying time points in a 3 mM solution of 4-formylbenzo-15-crown-5 in methanol with 6 eq. of NaBH\textsubscript{3}CN. Samples were rinsed with methanol and N\textsubscript{2} dried. The maximum time point used was 12 hours. The reducing agent was scaled back to 2-3 equivalents after it was noticed by AFM that the excess of NaBH\textsubscript{3}CN left large contamination on the sample surface, even after syringe filtering.

Dipicolylamine (DPA) attachment was carried out on APTES grown from a 0.5% solution in water for 25 mins. The APTES samples were soaked for varying time points in 3 mM picolylaldehyde in methanol with 2-3 eq. NaBH\textsubscript{3}CN. Samples were rinsed with methanol and N\textsubscript{2} dried. The maximum time point used was 12 hours. Zinc and iron coordinations of the DPA were performed by taking a 12 DPA sample and soaking in either 30 mM Zn(NO\textsubscript{3})\textsubscript{2} in 18 MΩ H\textsubscript{2}O for 6 hours or 30 mM FeCl\textsubscript{2} in 18 MΩ H\textsubscript{2}O for 2 hours. Samples were rinsed with 18 MΩ H\textsubscript{2}O and N\textsubscript{2} dried.

3.9.3 Ion and DNA Binding Studies

Cation binding of the 15-crown-5 treated APTES on Si was carried out by soaking samples in 1 mM solutions of LiCl, NaCl, KCl, and MgCl\textsubscript{2} in 18 MΩ H\textsubscript{2}O. The samples used were 12 hour depositions of 3 mM 4-formylbenzo-15-crown-5 in methanol
on APTES. Each sample was in a separate vial of each chloride solution for 1 hour. Samples were rinsed with 18 MΩ H₂O and N₂ dried.

Anion and DNA binding was carried out on APTES samples after a 12 hour, 3 mM dipicolylamine in methanol treatment (2 eq. NaBH₃CN), with a 6 hour 30 mM Zn(NO₃)₂ treatment. For anion binding, the Zn-DPA-APTES samples were soaked in 1 mM KH₂PO₄ in 18 MΩ H₂O for 1 hour. Samples were rinsed with 18 MΩ H₂O and N₂ dried. DNA binding was carried out on the Zn-DPA-APTES samples with 70 nm x 90 nm x 2 nm DNA origami rectangles. The DNA origami were obtained from Valerie Goss (University of Notre Dame, Department of Chemistry). The concentration of the origami was 2 nM in 10X TAE/Mg²⁺ buffer solution (400 mM Tris-HCL, 200 mM acetic acid, 20 mM EDTA, and 125 mM magnesium acetate, pH =8).

DNA binding was performed both with and without a zinc spike added to the DNA sample. DNA samples were spiked by adding 2 µL of 30 mM Zn(NO₃)₂ to 10 µL of 2 nM DNA. Zn-DPA-APTES samples were treated with either 6 µL of unspiked DNA or 6 µL of spiked DNA. Treatments were performed by placing a sample in a 1” wafer container, dispensing the DNA on the surface, closing the container to prevent evaporation, and allowing the DNA to remain on the surface for 30 mins. Samples were gently rinsed with 18 MΩ H₂O, N₂ dried.

3.9.4 Instrumentation

Contact angle measurements were taken using a Krüss G10 goniometer. All measurements were taken using ultra-pure, 18MΩ H₂O and an advancing drop. Reported values are an average of 4 locations on a single chip. Ellipsometry measurements were obtained on a Gaertner Scientific automated ellipsometer. The measurement parameters,
N and K, were taken from a standard table provided in the instrument’s user manual. For the silicon substrate, \( N = 3.87 \) and \( K = 0.018 \). For the native oxide on Si, \( N = 1.55 \) and \( K = 0 \). The angle of incidence and the analyzer angle were set at 70° and measurements were repeated approximately 8 times for all samples, over various locations on the chip. Monolayer thickness estimates were made by using the theoretical thickness of the SAM molecule, and assuming no tilt angle of the molecule (SAM is oriented perpendicular to the surface).

Atomic force microscopy was performed using a Nanoscope IIIa Multimode Instrument (Digital Instruments) in tapping mode. Silicon cantilevers were used (spring constant = 40 N/m, resonant frequency = 300 KHz, Vista Probes). Image analysis was performed using the Nanoscope III software. X-ray photoelectron spectroscopy was performed using a Kratos XSAM800 instrument with an Mg-Kα source, and a 0° take off angle. Samples were mounted via carbon tape to the instrument’s metal sample slugs. Data acquisition was carried out at high \( x10^{-8} \) Torr. Data analysis was performed using CasaXPS software (version 2.3.16). All peaks were calibrated against the C 1s (284.5 eV) peak. Relative standard deviations were applied to all % concentrations and % conc. ratios. RSD's were obtained from the averages and standard deviations of % N, % O, % C, and % Si for multiple APTES on Si depositions.
APPENDIX A:
SUPPLEMENTAL ATOMIC FORCE MICROSCOPE IMAGES

A.1 Earlier time points of the growth of 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in MeOH on APTES (on Si)

Figure A.1 One hour growth of 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in MeOH on APTES (on Si).
Figure A.2 Five hour growth of 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in MeOH on APTES (on Si).
A.2 Separate time study of the growth of 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in MeOH on APTES (on Si), with NaBH$_3$CN reducing agent.

Figure A.3 Timed growth of 3 mM 5-bromo-2-hydroxy-3-methoxybenzaldehyde in MeOH on APTES (on Si), with NaBH$_3$CN reducing agent.
APPENDIX B:

SUPPLEMENTAL X-RAY PHOTOELECTRON SPECTROSCOPY DATA

B.1 Piranha Etched GaN Region Scans and Quantification

Figure B.1 Ga 2p region scan of piranha etched GaN.
Figure B.2 Ga 3p region scan of piranha etched GaN.

Figure B.3 O 1s region scan of piranha etched GaN.
Figure B.4 N 1s region scan of piranha etched GaN.
## TABLE B.1

**QUANTIFICATION REPORT FOR PIRANHA ETCHED GaN**

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B.2 Piranha Etched AlGaN/GaN Region Scans and Quantification

Figure B.5 Ga 2p region scan of piranha etched AlGaN/GaN.
Figure B.6 O 1s region scan of piranha etched AlGaN/GaN.

Figure B.7 N 1s region scan of piranha etched AlGaN/GaN.
Figure B.8 C 1s region scan of piranha etched AlGaN/GaN.

Figure B.9 Ga 3p region scan of piranha etched AlGaN/GaN.
Figure B.10 Al 2p region scan of piranha etched AlGaN/GaN.
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<th>Sample Identifier</th>
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B.3 Solvent Cleaned InAlN/GaN Region Scans and Quantification

Figure B.11 O 1s region scan of solvent cleaned InAlN/GaN.
Figure B.12 In 3d region scan of solvent cleaned InAlN/GaN.

Figure B.13 N 1s region scan of solvent cleaned InAlN/GaN.
Figure B.14 C 1s region scan of solvent cleaned InAlN/GaN.

Figure B.15 Al 2p region scan of solvent cleaned InAlN/GaN.
### TABLE B.3

QUANTIFICATION REPORT FOR SOLVENT CLEANED INAlN/GAN

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B.4 APTES on AlGaN/GaN Survey Scan, Region Scans, and Quantification

Figure B.16 Survey scan of APTES on AlGaN/GaN.
Figure B.17 Ga 2p region scan of APTES on AlGaN/GaN.

Figure B.18 O 1s region scan of APTES on AlGaN/GaN.
Figure B.19 N 1s region scan of APTES on AlGaN/GaN.

Figure B.20 C 1s region scan of APTES on AlGaN/GaN.
Figure B.21 Ga 3p / Si 2p region scan of APTES on AlGaN/GaN.

Figure B.22 Al 2p region scan of APTES on AlGaN/GaN.
## TABLE B.4

QUANTIFICATION REPORT FOR APTES ON ALGAN/GAN

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B.5 F-TES on AlGaN/GaN and Si Region Scans, Si Survey Scan, and Quantification

Figure B.23 Ga 2p region scan of F-TES on AlGaN/GaN.
Figure B.24 F 1s region scan of F-TES on AlGaN/GaN.

Figure B.25 O 1s region scan of F-TES on AlGaN/GaN.
Figure B.26 N 1s region scan of F-TES on AlGaN/GaN.

Figure B.27 C 1s region scan of F-TES on AlGaN/GaN.
Figure B.28 Ga 3p region scan of F-TES on AlGaN/GaN.

Figure B.29 Al 2p region scan of F-TES on AlGaN/GaN.
Figure B.30 Survey scan of F-TES on Si.

Figure B.31 F 1s region scan of F-TES on Si.
Figure B.32 O 1s region scan of F-TES on Si.

Figure B.33 C 1s region scan of F-TES on Si.
Figure B.34 Si 2p region scan of F-TES on Si.
### TABLE B.5

**QUANTIFICATION REPORT FOR F-TES ON ALGAN/GAN AND SILICON**

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B.6 APTES on InAlN/GaN Region Scans

Figure B.35 O 1s region scan of APTES on InAlN/GaN.
Figure B.36 In 3d region scan of APTES on InAlN/GaN.

Figure B.37 N 1s region scan of APTES on InAlN/GaN.
Figure B.38 C 1s region scan of APTES on InAlN/GaN.

Figure B.39 Si 2p region scan of APTES on InAlN/GaN.
Figure B.40 Al 2p region scan of APTES on InAlN/GaN.
B.7 Quantification Report of the Timed Growth of 5-Bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on Si

TABLE B.6

QUANTIFICATION REPORT FOR THE TIMED GROWTH OF 5-BROMO-2-HYDROXY-3-METHOXYBENZALDEHYDE ON APTES ON SILICON

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B.8 Br 3d for KBr Dropcast on Si

Figure B.41 Br 3d region scan of dropcast KBr on Si.
B.9 Survey and Region Scans of 12 hr growth of 4-Formylbenzo-15-Crown-5 on APTES on Si

Figure B.42 Survey scan of 12 hr grown 4-formylbenzo-15-crown-5 on APTES on Si.
Figure B.43 O 1s region scan of 12 hr grown 4-formylbenzo-15-crown-5 on APTES on Si.

Figure B.44 N 1s region scan of 12 hr grown 4-formylbenzo-15-crown-5 on APTES on Si.
Figure B.45 C 1s region scan of 12 hr grown 4-formylbenzo-15-crown-5 on APTES on Si.

Figure B.46 Si 2p region scan of 12 hr grown 4-formylbenzo-15-crown-5 on APTES on Si.
B.10 Quantification report of 0 hr, 1 hr, 6 hr, and 12 hr growth of 4-Formylbenzo-15-Crown-5 on APTES on Si

TABLE B.7

QUANTIFICATION REPORT FOR THE TIMED GROWTH OF
4-FORMYL BENZO-15-CROWN-5 ON APTES ON SILICON

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B.11 Survey and Region Scans of 12 hr growth of Dipicolylamine on APTES on Si

Figure B.47 Survey scan of 12 hr grown dipicolylamine on APTES on Si.
Figure B.48 O 1s region scan of 12 hr grown dipicolylamine on APTES on Si.

Figure B.49 N 1s region scan of 12 hr grown dipicolylamine on APTES on Si.
Figure B.50 C 1s region scan of 12 hr grown dipicolylamine on APTES on Si.

Figure B.51 Si 2p region scan of 12 hr grown dipicolylamine on APTES on Si.
B.12 Quantification report of Bare Si, 0 hr, 1 hr, 3 hr, 6 hr, and 12 hr growth of Dipicolylamine on APTES on Si

### TABLE B.8

**QUANTIFICATION REPORT FOR THE TIMED GROWTH OF DIPICOLYLAMINE ON APTES ON SILICON**

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B.13 Survey Scan, Region Scans, and Quantification Report for 20 hr, 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN

Figure B.52 Survey scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.
Figure B.53 O 1s region scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.

Figure B.54 N 1s region scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.
Figure B.55 C 1s region scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.

Figure B.56 Ga 3p region scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.
Figure B.57 Al 2p region scan of 20 hr grown 5-bromo-2-hydroxy-3-methoxybenzaldehyde on APTES on AlGaN/GaN.
TABLE B.9

QUANTIFICATION REPORT FOR THE 20 HR GROWTH OF 5-BROMO-2-
HYDROXY-3-METHOXYBENZALDEHYDE ON APTES ON ALGAN/GAN

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B.14 Na 1s XPS Spectra for Dropcast NaBH$_3$CN, Plain APTES in 12 mM NaBH$_3$CN, and 6 and 12 hr Crown-benzaldehyde on APTES on Si

Figure B.58 Na 1s region scan of dropcast NaBH$_3$CN on Si.
Figure B.59 Na 1s region scan of plain APTES in 12 mM NaBH$_3$CN.

Figure B.60 Na 1s region scan of 6 hr grown crown-benzaldehyde (with reducing agent) on APTES on Si.
Figure B.61 Na 1s region scan of 12 hr grown crown-benzaldehyde (with reducing agent) on APTES on Si.
B.15 Cation Region Scans for Ion Soaked Bare APTES and 12 hr Crown-benzaldehyde on APTES on Si

Figure B.62 Na 1s region scan of plain APTES and 12 hr. crown on APTES after soaking both samples in 1 mM NaCl for 1 hour.
Figure B.63 K 2p region scan of plain APTES and 12 hr. crown on APTES after soaking both samples in 1 mM KCl for 1 hour.

Figure B.64 Li 1s region scan of plain APTES and 12 hr. crown on APTES after soaking both samples in 1 mM LiCl for 1 hour.
Figure B.65 Mg 2p region scan of plain APTES and 12 hr. crown on APTES after soaking both samples in 1 mM MgCl$_2$ for 1 hour.
Figure B.66 Li 1s / Mg 2p region scan of piranha / RCA cleaned Si.
Figure B.67 K 2p region scan of piranha / RCA cleaned Si.
B.17 Quantification Report for APTES and 12 hr DPA on APTES Soaked in Zn(NO$_3$)$_2$

TABLE B.10

QUANTIFICATION REPORT FOR PLAIN APTES AND 12 HR DPA ON APTES
AFTER SOAKING IN ZINC NITRATE FOR 6 HOURS

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B.18 Quantification Report for APTES and 12 hr DPA on APTES Soaked in FeCl₂

TABLE B.11

QUANTIFICATION REPORT FOR PLAIN APTES AND 12 HR DPA ON APTES
AFTER SOAKING IN IRON CHLORIDE FOR 2 HOURS

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B.19 Quantification Report for APTES and Zn-DPA on APTES Soaked in KH$_2$PO$_4$

**TABLE B.12**

**QUANTIFICATION REPORT FOR PLAIN APTES AND ZN-DPA ON APTES**

**AFTER SOAKING IN POTASSIUM PHOSPHATE FOR 1 HOUR**

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### TABLE B.13

**QUANTIFICATION REPORT FOR PIRANHA / RCA CLEANED SILICON**

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