MOCVD GROWTH OF GROUP-III NITRIDES ON SILICON CARBIDE:
FROM THIN FILMS TO ATOMICALLY THIN LAYERS

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by

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ABSTRACT

Group-III nitride semiconductors (AlN, GaN, InN and their alloys) are considered one of the most important class of materials for electronic and optoelectronic devices. This is not limited to the blue light-emitting diode (LED) used for efficient solid-state lighting, but other applications as well, such as solar cells, radar and a variety of high frequency power electronics, which are all prime examples of the technological importance of nitride based wide bandgap semiconductors in our daily lives. The goal of this dissertation work was to explore and establish new growth schemes to improve the structural and optical properties of thick to atomically thin films of group-III nitrides grown by metalorganic chemical vapor deposition (MOCVD) on SiC substrates for future novel devices.

The first research focus of this dissertation was on the growth of indium gallium nitride (InGaN). This wide bandgap semiconductor has attracted much research attention as an active layer in LEDs and recently as an absorber material for solar cells. InGaN has superior material properties for solar cells due to its wavelength absorption tunability that nearly covers the entire solar spectrum. This can be achieved by controlling the indium content in thick grown material. Thick InGaN films are also of interest as strain reducing based layers for deep-green and red light emitters. The growth of thick films of InGaN is, however, hindered by several combined problems. This includes poor incorporation of indium in alloys, high density of structural and morphological defects, as well as challenges associated with the segregation of indium in thick films. Overcoming some of these material challenges is essential in order integrate thick InGaN films into future optoelectronics. Therefore, this dissertation research investigated the growth mechanism
of InGaN layers grown in the N-polar direction by MOCVD as a route to improve the structural and optical properties of thick InGaN films.

The growth of N-polar InGaN by MOCVD is challenging. These challenges arise from the lack of available native substrates suitable for N-polar film growth. As a result, InGaN layers are conventionally grown in the III-polar direction (i.e. III-polar InGaN) and typically grow under considerable amounts of stress on III-polar GaN base layers. While the structure-property relations of thin III-polar InGaN layers have been widely studied in quantum well structures, insight into the growth of thick films and N-polar InGaN layers have been limited. Therefore, this dissertation research compared the growth of both thick III-polar and N-polar InGaN films grown on optimized GaN base layers. III-polar InGaN films were rough and exhibited a high density of V-pits, while the growth of thick N-polar InGaN films showed improved structural quality and low surface roughness. The results of this dissertation work thereby provide an alternative route to the fabrication of thick InGaN films for potential use in solar cells as well as strain reducing schemes for deep-green and red light emitters. Moreover, this dissertation investigated stress relaxation in thick N-polar films using in situ reflectivity and curvature measurements. The results showed that stress relaxation in N-polar InGaN significantly differed from III-polar InGaN due to the absence of V-pits and it was hypothesized that plastic relaxation in N-polar InGaN could occur by dislocation glide, which typically is kinetically limited at such low growth temperatures required for InGaN.

The second part of this dissertation research work focused on buffer free growth of GaN directly on SiC and on epitaxial graphene produced on SiC for potential vertical devices. The studies presented in this dissertation work on the growth of GaN directly on
SiC compared the stress evolution of GaN films grown with and without an AlN buffer layer. Films grown directly on SiC showed reduced threading dislocation densities and improved surface roughness when compared to the growth of GaN on an AlN buffer layer. The dislocations in the GaN films grown directly on SiC were predominantly of mixed-type dislocations. Films also contained basal plane stacking faults and \{1\overline{1}20\} prismatic stacking faults as revealed by transmission electron microcopy (TEM) near the GaN/SiC interface. Channeling cracks were also observed in the GaN films when the AlN buffer layer was not utilized. This was attributed to tensile stress induced from the thermal expansion coefficient mismatch, which was corroborated with in situ stress measurements collected during the growth process. The results provided in this dissertation showed the potential of growing GaN films directly on SiC for vertical power devices, where the use of an AlN buffer layer typically obstructs both electrical and thermal vertical transport in such devices.

Also in the second part of this dissertation, additional studies were performed to understand the nucleation behavior of GaN and AlN on epitaxial graphene produced directly on SiC. The use of graphene as a template layer for the heteroepitaxy of group-III nitrides has gained interest due to the hexagonal arrangement of the sp² hybridized carbon atoms being similar to the (0001) c-plane of wurtzite GaN. It was observed that the nucleation of AlN and GaN was preferential along the periodic graphene coated step edges of SiC and at defects sites on the (0001) terraces due to the enhanced chemical reactivity at those regions. The density of nuclei on the (0001) terraces of graphene increased with the unintentional incorporation of nitrogen defects into the graphene lattice via NH₃ exposure and intentional introduction of defects using oxygen plasma. Furthermore,
Raman spectral mapping showed that GaN selectively nucleates on regions of few-layered graphene as opposed to regions of multi-layered graphene. It was also revealed that though the graphene underlayers were highly defective in the region of GaN nucleation, the GaN nuclei were single crystalline, c-axis oriented and were free of threading dislocations. In contrast, polycrystalline islands of AlN were found to nucleate on graphene, but did not produce disorder to the underlying graphene.

Furthermore, to implement group-III nitrides in tunnel junctions for ultra-low voltage and steep-switching applications and single photon emitters for quantum communication and computing, extreme confinement of group-III nitrides into 2D layers must be realized. Confinement of this materials system in two-dimensions “i.e. 2D nitrides” leads to massive changes in the electronic properties. This brings to light an entirely new platform to tune the properties of group-III nitrides, such as the bandgap energy, without alloying.

Graphene has proven to be a remarkable material over the past decade. The third part of this dissertation research work showed that graphene can stabilize “2D” forms of traditionally “3D” binary compounds, launching a new platform to realize many other classes of materials that are not traditionally 2D, specifically on a technologically relevant substrate, like SiC. The growth process of 2D GaN utilized the mechanism of adatom intercalation from the vapor phase in an MOCVD growth environment into the interfacial region of graphene produced on SiC. The synthesis process developed in this dissertation work was termed as “Migration Enhanced Encapsulated Growth” (MEEG). Here the mechanism of 2D nitride formation was elucidated and the role of the interface of epitaxial graphene produced on SiC in providing sufficient stabilization of the direct bandgap 2D
buckled structure of GaN was discussed. The atomic structure was directly resolved from the nitrogen and gallium atomic columns using aberration corrected scanning TEM (STEM) in annular bright field (ABF) mode with supported ABF-STEM simulations. Density functional theory calculations predicted a bandgap for 2D GaN in the range of 4.79-4.89 eV which was corroborated with experimental results from UV-visible reflectance, absorption coefficient and low loss electron energy loss spectroscopy (EELS) measurements. Recognizing the impact of 2D nitrides, it can be expected that the addition of 2D GaN will enable new avenues for scientific exploration and novel optoelectronic device development.
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MY MOTHER ANGELLA M. AL BALUSHI

&

MY FATHER YAHYA R. AL BALUSHI
CHAPTER 1

INTRODUCTION

1.1 Motivation

Wide bandgap group-III nitride compound semiconductors, grown by metalorganic chemical vapor deposition (MOCVD), have been well established over the years as active layers in many electronic and optoelectronic devices. The most prominent application of these nitride semiconductors is in high-brightness light emitting diodes (LEDs) used for solid-state lighting. Today, these LEDs are vastly integrated in many residential and commercial settings. In fact, these solid-state white light sources are not only more efficient when compared to prior technology that relied on incandescent bulbs, but also inherit greater operating lifetimes. The U.S. Department of Energy estimates by 2035 that the widespread implementation of commercially available LEDs could result in ~75% reduction in energy consumption, a total savings of approximately $630 billion between 2015 to 2035 in avoided energy costs\(^1\). As a consequence of the technological advancements in the blue LED and its broad impact in providing efficient solid-state lighting, the 2014 Nobel Prize in Physics was awarded for this invention to Akasaki, Amano, and Nakamura. This was a result of their achievements in the aspects related to crystal growth, characterization and device fabrication that led to the development of the renowned blue LED and laser diode (LD) based on these wide bandgap semiconductors.

Usually, white light emission is obtained using a blue LED and converting part of the emitted light into the yellow and green spectral range using a phosphor material. The efficiency of LEDs follows what is known as Haitz’s law\(^2\), that is at a given wavelength of
light, the cost per lumen in LEDs should fall by a factor of 10 every decade, while the amount of light emitted should increase by a factor of 20. This metric, however, is an incomplete measure of efficiency in these devices. This is because the phosphor material used to convert part of the blue emission from InGaN/GaN LEDs to white light leads to significant energy loss that is on the order of ~25\%. This loss is referred to as Stokes loss in light emitters. Therefore, the partial conversion of the blue emitted light limits the highest attainable efficiency for solid-state white light emission. An obvious solution to this problem is to eliminate the phosphor material altogether and directly mix the emissions of blue, red and green LEDs. One of the major issues, however, that still remains an active area of research in LEDs is the issue of the so-called “green gap”. As illustrated in Figure 1.1, in comparison to the efficiency of blue LEDs based on InGaN/GaN quantum wells and red LEDs that are AlInGaP based, within the “green gap” there is a significant reduction in the efficiency of deep-green-to-yellow emitters that would be required to achieve true white light emission by the method of three color mixing. This is the critical issue that has hampered the realization of true efficient high-brightness LEDs for solid-state lighting, where the origin of the “green gap” still remains a topic of intense discussion.

There is a general consensus that the origin of the “green gap” is related to the challenges associated with the growth of InGaN. The strong localization effects on carriers, large strain and inhomogeneous distribution of indium that is common in the growth InGaN/GaN quantum wells leads to potential fluctuations in devices. Moreover, the strain driven piezoelectric polarization fields can lead to misalignments between the conduction and valence energy bands. This effect is referred to as the quantum confined Stark effect which leads to a reduction of the internal quantum efficiency and “droop” in
emitting devices\textsuperscript{7,8}. All of the cited origins of the “green gap” partially gleans from the choice of substrate utilized to fabricate these devices. The fabrication cost of LEDs is largely governed by the lack of native bulk substrates that are available for homoepitaxial growth, i.e. bulk GaN. As a result, heteroepitaxial growth on sapphire and silicon is typically used due to their relatively low cost and large available substrate diameters. The resulting grown materials, however, exhibit high dislocation densities that can also obstructs the efficiency of these light emitters. This has inspired efforts in the redesign of the LED and particularly the utilization of thick InGaN pseudo-substrates to serve as strain-reducing base layers to improve the efficiency of deep-green emitters.

\textbf{Figure 1.1} | The maximum external quantum efficiency (EQE) versus the emitted wavelength of commercially available nitride and phosphide based LEDs. Ref [5].

Furthermore, beyond light emitters, there has been interest in the growth of thicker InGaN layers to serve as absorber materials in multi-junction photovoltaics. InGaN has superior material properties for photovoltaic applications. This largely comes from its
direct bandgap tunability (from 0.64 eV to 3.42 eV) that nearly matches the entire solar spectrum for maximum efficiency\textsuperscript{9}. This was realized only after the re-evaluation of the InN optical bandgap energy from 1.9 eV to 0.64 eV\textsuperscript{10}. The modification of the absorption edge of InGaN is achieved by controlling the fraction of indium in the material. In order to utilize InGaN for photovoltaics, two design criteria must be considered: maximum optical absorption and minimum recombination of photo-carriers. The high absorption coefficient \( \sim 10^5 \text{cm}^{-1} \), high carrier mobility, good thermal conductivity and stability as well as superior resistance to radiation damage of InGaN, all prove advantageous for its integration into next generation multi-junction photovoltaics, based solely on a single material system\textsuperscript{11,12}. As a consequence, it has been theoretically envisioned that the InGaN materials system can be used to fabricate multi-junction photovoltaics with theoretical conversion efficiencies exceeding 60%\textsuperscript{13}. In addition, the possible bandgap alignment of InGaN with silicon offers new opportunities for its integration into hybrid photovoltaic architectures. For example, a triple-junction \( \text{In}_y\text{Ga}_{1-y}N/\text{In}_x\text{Ga}_{1-x}N/\text{Si} \) solar cell could offer energy conversion efficiencies exceeding 35%\textsuperscript{14}. Yet, the material performance and technological impact of InGaN as an absorber material for photovoltaics is hindered by several combined problems. These problems include poor incorporation of indium into the layers, high density of structural defects and challenges associated with the growth of high-quality thick layers beyond the critical thickness for stress relaxation. For photovoltaics, InGaN layers exceeding 100 nm in thickness are needed to maximize light absorption. Nevertheless, the growth of such thick layers is challenging. The large miscibility gap between InN and GaN in InGaN alloys leads to an inhomogeneous distribution of indium and/or clustering that can impact the strain state of the film and give rise to the formation of structural defects, such as V-pits.
The V-pits are energetically favorable to form at the apex of threading dislocations and increase in size and density with increasing layer thickness and indium content and also may act as pathways for leakage in devices. Overcoming these challenges is critical in order to pave the way for high performance InGaN photovoltaics. Therefore, for both LED and photovoltaic applications, developing new growth strategies to realize high quality thick films of InGaN are key issues that must be addressed.

Besides the application of wide bandgap group-III nitrides in optoelectronics, GaN is an excellent material for electron transport as a result of its high electron mobility that leads to low on-resistance (50 mΩ for 50 A device)\textsuperscript{15}, high electrical and thermal conductivities as well as high breakdown voltage that exceeds 1 kV. In fact, the first power device demonstrated was the AlGaN/GaN high electron mobility transistor (HEMT) back in 1993 and it is expected that the GaN power electronics market will exceed $1 billion by the year 2022\textsuperscript{15,16}. MOCVD growth of GaN on substrates with high breakdown voltages is of particular interest for high-frequency and power electronics such as inverters used for DC to AC conversion in photovoltaics and hybrid and electrical vehicle (HEV) systems\textsuperscript{17}. Generally, in GaN based power electronics, the choice of substrate is highly dependent on the application of interest. Most power inverters based on GaN are lateral structures formed on sapphire and/or Si substrates. These structures, however, suffer from high on-resistances and current collapse that can limit the efficiency of inverters to be used in photovoltaics and HEV applications\textsuperscript{18,19}. Alternatively, vertically conducting GaN based power devices are effective in suppressing current collapse and achieving much higher power densities\textsuperscript{20}. Such vertical device architectures require substrates that are highly conductive. Although recent research interest in vertically conducting GaN based power devices has been
catalyzed by the availability of high quality bulk GaN substrates grown by ammonothermal methods\textsuperscript{21}, the wide spread commercial implementation of such vertical devices has been limited by the small size and high cost of bulk GaN. Therefore, the search for other viable solutions to replace bulk GaN has been intensified. Vertical GaN-on-SiC devices can be an alternative to GaN-on-GaN for power electronics. The heteroepitaxial growth of GaN-on-SiC is, however, challenging due to the large lattice mismatch and poor wetting behavior of GaN on the surface of SiC. In addition, the thermal expansion mismatch can lead to large stress and cracking of films during cooling. Though AlN is commonly used as a buffer-layer for the epitaxy of GaN-on-SiC, it introduces a barrier at the interface, inhibiting carrier injection. Despite these challenges, high-quality buffer-free growth of GaN-on-SiC has been achieved\textsuperscript{22-26}. However, limited studies on understanding the stress evolution of the direct growth of GaN-on-SiC has been reported and are areas worth exploring in order to drive the technology forward.
1.2 Objectives

There are three major areas of research focus in this dissertation, with a commonality of integrating wide bandgap group-III nitride semiconductors specifically with SiC substrates. The first goal of this dissertation is to explore and establish new platforms for optoelectronic devices based on high quality thick InGaN thin films grown on SiC. In this dissertation, we present multiple comparative studies on the growth of thick InGaN films on III-polar and N-polar GaN base-layers and investigate the effect of polarity on the structural quality, surface morphology and optical properties of the MOCVD grown films. The results presented in this dissertation demonstrates thick N-polar InGaN films with improved structural and morphological quality compared to III-polar layers, thereby providing an alternative route to the fabrication of thick InGaN films for potential use in photovoltaics and strain reducing schemes for deep-green and red emitters.

The second major research objective of this dissertation is to explore the growth of GaN directly on SiC and on graphene-SiC for the purpose of using these heterostructures for vertical devices. In the case of the direct growth of GaN-on-SiC, we employ simultaneously in situ optical reflectance and wafer curvature measurements to monitor the evolution of surface morphology and stress during the growth of GaN-on-SiC. Our studies directly reveal significant differences in the stress state of the GaN during growth and the resulting surface morphology and microstructure of the films, when compared to conventional buffer assist growth approaches such as the use of AlN layers. Furthermore, the use of graphene as a pseudo-substrate for the growth of GaN has gained interest due to the hexagonal arrangement of the sp² hybridized carbon atoms being similar to the (0001) c-plane of wurtzite GaN. However, most studies have produced layers with surface
morphologies and structural qualities inferior to those produced on SiC and sapphire. This is due to the challenges associated with heteroepitaxy on the basal plane of pristine graphene due to the lack of dangling bonds. Despite the growing interest in the heteroepitaxy of GaN and AlN layers on graphene, there have been limited studies aimed at understanding the nucleation process. Therefore, this dissertation presents the first nucleation study of III-nitrides on graphene produced directly on SiC. These studies have provided the crystal growth community with new insight into the initial stages of the growth of nitrides on van der Waal surfaces. In these studies, we revealed the impact of the nucleation process on the structural properties of graphene, which is important to investigate in order to achieve the growth of high quality III-nitride films on graphene produced on SiC for the aforementioned applications.

The third major research focus of this dissertation is related to recent work in extending the properties of nitride semiconductors for next generation electronics. As discussed in the motivation section, wide bandgap group-III nitride semiconductors are emerging as the major candidate in providing diverse solid state solutions for a host of applications that span from LDs and LEDs, to power electronics and photovoltaics. However, in order for this materials system to potentially compete with silicon technology, it is imperative to implement group-III nitrides in a breath of new technologies that may not be feasible solely using silicon. These emerging technologies include tunnel junctions for ultra-low voltage and steep-switching applications, single photon emitters for quantum transport of information and polarization driven topological insulators for quantum computing. To realize these novel applications with group-III nitride semiconductors, new synthesis approaches and methods of bandgap engineering in this materials system must
be realized. To accomplish this, an alternative growth scheme was developed to realize two-dimensional growth of GaN on SiC, utilizing the mechanism of adatom intercalation from the vapor phase in an MOCVD growth environment into the interfacial region of graphene formed on SiC. The synthesis process that was developed in this dissertation, is referred to as “Migration Enhanced Encapsulated Growth” (MEEG)\(^27\) and establishes an entirely new platform to potentially realize tunable optoelectronics that may frame next-generation technology. In this dissertation, the growth process to realize two-dimensional GaN will be discussed. The results presented here show that thinning GaN to its atomic limit leads to massive changes to its bandstructure, most notable, the increase in the bandgap energy as a result of quantum confinement. Our demonstration of two-dimensional GaN establishes a novel route to transform traditionally three-dimensional crystal structures into two-dimensional layers that are stable in air, which will clearly establish new avenues of research in multiple scientific communities that includes nitride semiconductors, beyond graphene two-dimensional materials and computational materials discovery. This is further discussed in the chapter 6 regarding proposed future work.
1.3 Thesis organization

The research work presented in this thesis is divided into six parts:

- Chapter 1 (this chapter) provides a general introduction to the state of the field of group-III nitride semiconductors, some of the inherent materials growth challenges and areas that remain topics of research interest. Discussions continue by outlining the overall objectives of the dissertation and thesis organization.

- Chapter 2 provides a description of the experimental setup for the group-III nitride metalorganic chemical vapor deposition (MOCVD) reactor, its components and the growth process.

- Chapter 3 presents the results of the first research objective concerning the growth of group III-polar and N-polar thick InGaN films on SiC for potential use in photovoltaics and as strain reducing base layers for deep-green to red emitters. The discussions begin with introductions to the state of the field of thick InGaN growth by MOCVD. Discussions then follow with a detailed review of the literature on the challenges associated with MOCVD growth of thick InGaN and, the focus of the study and detailed experimental procedures used in the chapter. Results and discussions follow and the conclusions are summarized.

- Chapter 4 contains results on buffer free growth of GaN directly on SiC and nucleation studies of GaN and AlN on epitaxial graphene grown on SiC. Similarly, introductions are provided to motivate the reader on the
need for buffer free growth of III-nitride semiconductors, specifically for the realization of vertical devices and a review of the literature regarding the challenges associated with the direct growth of GaN on SiC and on the basal planes of pristine graphene are presented. The experimental procedures used in the chapter is then outlined. Results and discussions follow and the conclusions are also then summarized.

- Chapter 5 presents the third objective of this dissertation that relates to the realization of two-dimensional gallium nitride on SiC and the development of the MEEG scheme. The chapter begins with introductory material on the need of two-dimensional forms of wide bandgap semiconductors and a detailed review of the literature on the historical aspects and key information regarding graphite intercalation compounds and intercalation through graphene supported on solid substrates that are important for the reader. The focus of the study is discussed and a detailed description of the growth process and experimental procedure are then outlined. Finally, the results and discussions follow and the conclusions are summarized at the end of the chapter.

- Chapter 6 presents proposed future work that relates to the MEEG work outlined in chapter 5.
1.4 References


H. Li, X. Li, Z. Zhang, C. Yao, and J. Wang, in *Design consideration of high power GaN inverter*, 2016, p. 23.


CHAPTER 2

EXPERIMENTAL SETUP

In this chapter, we will describe the experimental methods that are commonly used throughout chapters 3 - 5 of this dissertation. First, a brief description is given of the reactor design, setup and components for gas delivery in the group-III nitride metalorganic chemical vapor deposition (MOCVD) system, as well as the precursors that were utilized for thin film growth. This system was located in room N-125A of the Millennium Science Complex. Basic information regarding the SiC substrates used, the general substrate preparation process and baseline growth recipes for the MOCVD are also given. Moreover, the system incorporates a multibeam optical stress sensor which will be reviewed in this chapter. Furthermore, the graphite hot zone furnace that was utilized for the growth of epitaxial graphene on SiC is also described with a general explanation of the system components. This system was located in room N-037 of the Millennium Science Complex.

There are a host of characterization techniques utilized throughout this dissertation. The details of those techniques are outlined in the experimental procedure section of chapters 3, 4 and 5. The characterization techniques presented in the chapters were done by the author of this dissertation, except for the following: chemical and surface analytical measurements using x-ray photoelectron spectroscopy (XPS) in chapters 4 and 5, were collected by Dr. Ganesh Bhimanapati (Department of Materials Science and Engineering – at Penn State) and Dr. Xiaoye Qin (University of Texas at Dallas), respectively; Transmission electron microscopy (TEM) shown throughout the chapters was performed by Dr. Ke Wang (Staff Scientist in the Materials Characterization Lab – at Penn State);
Cathodoluminescence measurements were performed in Lausanne, Switzerland at Attolight – École polytechnique fédérale de Lausanne; UV-Raman in section 3.4.4.1 of chapter 3 was performed by Mr. Vincent Larat in the application laboratory of HORIBA Scientific in Villeneuve-d’Ascq, France; Auger electron spectroscopy and mapping in section 5.4.2 of chapter 5 were taken by Mr. Dennis F. Paul at Physical Electronics, in Minnesota USA; Conductive atomic force microscopy measurements were collected by Mr. Yu-chuan Lin (Department of Materials Science and Engineering – at Penn State); UV-vis and ellipsometric measurements in chapter 5 were taken by Dr. Joshua D. Caldwell at the Naval Research Laboratory in Washington D.C. and secondary ion mass spectroscopy (SIMS) data were collected at Evans Analytical Group. Finally, density functional theory (DFT) calculations presented in chapters 4 and 5 were performed by Dr. Lazaro Calderin (Materials Research Institute – at Penn State) and Dr. Ram Krishna Ghosh (Penn State and University of Notre Dame), respectively. Assistance by other individuals that are not mentioned here are given special recognition in the acknowledgment section at the beginning of this dissertation and/or through published work.

All MOCVD growth experiments in the results thus presented were carried out by the author of this dissertation himself. In addition to the author, Mr. Rafael A. Vilá, Mr. Yu-Chuan Lin and Ms. Shruti Subramanian provided epitaxial graphene samples that were used in both chapters 4 and 5 of this dissertation.
2.1 Metalorganic chemical vapor deposition system

The group-III nitride MOCVD system shown in Figure 2.1, is a refurbished Thomas Swan CS0589 gas delivery system that was reconfigured and modified by CVD Equipment Corporation to incorporate a vertical cold-wall MOCVD reactor. This MOCVD system consists of three major sectors. These sectors are the process control computer, the reactor gas manifold cabinet and the reactor process chamber cabinet, which also houses the mounted multibeam optical stress sensor (MOS) and \textit{in situ} emissivity corrected pyrometry systems. These cabinets are exhausted and are monitored using integrated hydride and Midas toxic gas detectors from Neodym Technologies and Honeywell Analytics, respectively. The process control computer consists of relay logic, programmable logic controllers (PLCs) and an industrial computer with a pre-loaded CVDWinPrC\textsuperscript{TM} licensed software from CVD Equipment Corporation. The system operates in both manual and computer mode, where the software provides the capability of controlling and logging.

\textbf{Figure 2.1} | An image of the group-III nitride MOCVD system in N-125A MSC.
various grouped control loops throughout a growth process flow. Moreover, the MOCVD system also incorporates a Misonix XGC-30M scrubber for exhaust neutralization (not shown in Figure 2.1).

2.1.1 Reactor gas manifold cabinet

The reactor manifold cabinet regulates the delivery of seven process gases, one which is a dopant source, and up to seven different bubblers through a series of manual and pneumatic valves, mass flow controllers and pressure controllers that are plumbed, welded and VCR fitted throughout the gas cabinet with ¼ inch electropolished stainless steel tubing. From the seven process gasses delivered to the system, ultra-high purity hydrogen (purchased from Penn State general stores and delivered from Praxair), ultra-high purity nitrogen (in house boil-off from liquid nitrogen supplied by Air products) and ultra-high purity anhydrous ammonia (99.99995 % pure with < 50 ppb of O₂ and < 200 ppb of H₂O - Grade 6.5 from Praxair with DISS/K fitting/size) are passed through a MC3000 series ambient temp MicroTorr canister purifier from SAES. The purifier removes O₂, CO, H₂O, CO₂, organics and other impurities to < 1 ppb for reliable delivery of these sources into the MOCVD reactor process chamber. The ultra-high purity anhydrous ammonia and ultra-high purity hydrogen cylinders are placed in individual gas cabinets that are exhausted, while nitrogen was delivered directly from the building. In the discussed growth experiments, ammonia was used as the group-V source. Hydrogen was used as the carrier gas for the metalorganics and the reaction process background gas. Nitrogen was also used as the reaction process gas, however, only during the growth of InGaN. Furthermore, the other four process gasses that can be introduced into the reactor process chamber are 5% diborane in hydrogen, 5% germane in hydrogen, 10% silane in hydrogen and 0.01% silane
in hydrogen that is used as a dopant source. These later four gas sources were not utilized in any of the experiments discussed in this dissertation.

There are seven bubbler manifold that are available for use on the MOCVD system in order to deliver metalorganic precursor into the reactor process chamber. The metalorganic precursors used in the studies presented in this dissertation were trimethylgallium (TMGa), trimethylaluminum (TMAI) and trimethylindium (TMIn). Both SAFC and Epi Chem suppliers were used for the listed metalorganic sources. These bubblers were held in LAUDA Silver ECO Cooling thermostat circulating baths in order to produce the desired precursor equilibrium vapor pressure using the following equations:

$$\log_{10} P_{MO}(\text{Torr}) = A - \left( \frac{B}{T_{MO}} \right)$$ \hspace{1cm} \text{Eq. 2.1}

where, $P_{MO}$ is the equilibrium vapor pressure of the metalorganic source in Torr, $T_{MO}$ is the temperature of the circulating bath in Kelvin and the gas constants ($A$ and $B$) are obtained from the manufacturer. The table below summarizes the equilibrium vapor pressures utilized during the growth experiments presented in chapters 3-5 of this dissertation:

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>A</th>
<th>B</th>
<th>$P_{MO}$ (Torr)</th>
<th>$P_{total}$ (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa</td>
<td>-13 ± 0.1</td>
<td>8.07</td>
<td>1703</td>
<td>33.402</td>
</tr>
<tr>
<td>TMAI</td>
<td>25 ± 0.1</td>
<td>8.224</td>
<td>2134</td>
<td>11.655</td>
</tr>
<tr>
<td>TMIn</td>
<td>25 ± 0.1</td>
<td>10.52</td>
<td>3014</td>
<td>2.576</td>
</tr>
</tbody>
</table>

**Table 2.1** | Summary of the metalorganic bubbler conditions on the MOCVD system.

The stainless-steel tubing downstream of the bubblers, into the run lines and reactor process chamber were all heated above the temperature of the baths. This was done in order to
prevent condensation of the metalorganic sources on the walls of the tube, which can lead to build up of deposits and blockage of the lines. In addition, de-ionized (DI) water was used in the circulating baths to maintain the temperatures of the TMAI and TMIn bubblers, while an equal mixture of ethylene glycol and DI water was used to cool the TMGa bubbler to a temperature of -13°C. Moreover, as previously discussed, ultra-high purity hydrogen was used as the carrier gas in all of the metalorganic bubblers, where the flow of hydrogen gas was controlled up stream via mass flow controllers. The total pressure of the bubbler was also regulated downstream using a pressure controller in order to provide a desired molar flow rate of the metalorganic source to be introduced into the reactor process chamber. In the case of TMGa and TMIn, the molar flow rates \( n_{MO} \) in standard cubic centimeters per second (sccm) can be calculated using Equation 2.2. However, since TMAI exists as a dimer, the molar flow rate \( n_{TMAI} \) is be calculated using Equation 2.3:

\[
\begin{align*}
  n_{MO}(sccm) &= n_{H2} \times (P_{MO}/P_{total} \times (1 - P_{MO}/P_{total})) \\
  n_{TMAI}(sccm) &= 2 \times n_{H2} \times (P_{MO}/P_{total} \times (1 - P_{MO}/P_{total}))
\end{align*}
\]

Eq. 2.2

Eq. 2.3

where \( n_{H2} \) is the flow rate of H\(_2\) through the MFC in sccm and \( P_{total} \) is the pressure value set by the pressure controller downstream in Torr. The molar flow rates can be calculated in \( \mu \text{mol/min} \) using the following equation:

\[
  n_{MO}(\mu\text{mol/min}) = n_{MO}(sccm)/22400 \times 10^6
\]

Eq. 2.4

It is also common to report the ratio between the group-V molar flow rate (in this case the ammonia flow rate) and the group-III molar flow rate. This ratio is referred to as the V/III ratio. In the MOCVD system (Figure 2.2), the group-V and group-III sources are
Figure 2.2 | Schematic of the group-III nitride MOCVD reactor gas manifold.
separated before being introduced into the process chamber as a result of the two-make up configuration of the MOCVD reactor: The upper makeup with run and vent lines for ammonia, silane, germain, dimethylhydrazine, nitrogen and hydrogen gas sources, and a lower makeup with run and vent line configurations for six metalorganic precursors, diborane, hydrogen and nitrogen. As a result of the run/vent configuration, it is possible to switch in-and-out various precursors without disrupting steady state flow into the reactor process chamber. During a growth process flow, the lines are maintained under negative pressure through the use of a mechanical rotary vane vacuum pump (Leybold Trivac B series). This pump uses fomblin perfluorinated polyether (PFPE) grade oil.

2.1.2 Reactor process chamber setup

As illustrated in Figure 2.3.a-b, the MOCVD process chamber is a quartz vertical double-walled bell jar shaped reactor, where the inner walls are cooled using DI water circulating a bath that is connected to a heat exchange located in the back of the reactor cabinet (not shown). The inner walls of the reactor are protected during the growth process through the use of a quartz liner tube that can be exchanged and/or cleaned prior to each run. The liner tube is wiped-down with a cleanroom grade Kim-wipe coated with isopropanol and then N\textsubscript{2} blown. This is then followed by a high temperature hydrogen bake. Once the liner tube becomes significantly dirty from repetitive use, the liner tube is cleaned with hydrofluoric acid by the technical staff in the Penn State nanofabrication facility. Furthermore, the quartz reactor is sealed by stainless steel end caps. These end caps are also cooled, however, using the building centralized chilled water supply. The bottom end cap can be lowered for sample removal using a motor, while the top end cap contains the two optical ports and the injection gas inlets.
There are five gas inlets into the reactor. The first two inlets are purge gases for the optical ports. The purge gas prevents deposition from occurring onto the quartz windows. The third inlet is the purge gas between the liner tube and the reactor wall. This purge gas is to prevent material generated from gas phase and/or parasitic reactions from redepositing onto the bell jar reactor walls during the growth process. The final two inlet gases are from the upper run that contains the group-V source in the experiments presented in the dissertation (i.e. ammonia) and the other from the lower run that contains the group-III metalorganic precursors. Evident from the schematic in Figure 2.3.b are the two coaxial cones mounted from the top of the end cap, where the smaller diameter inner cone is
separated and centered in the larger diameter outer cone using a “centering spider”. The larger outer cone is the inlet used for group-V gas source delivery, while the inner smaller diameter cone is for group-III gas delivery. The inner group-III cone is placed closer to the surface of the susceptor (71 mm from the surface) in order to prevent pre-reactions between the group-III and group-V sources in the gas phase. The susceptors used in the growth experiments were made from high purity graphite and were coated with SiC. A 10 mm × 10 mm pocket was cutout into the susceptor in order to hold the SiC substrates used for growth. The susceptor sits on a rotating support quartz shaft that is held with the bottom end cap using a ferrofluid seal (Rigaku, Inc.). The support shaft rotation speed was set in all experiment at 30 rpm. The position of the support shaft was monitored using a triggering laser system from k-Space Associates (kSA) and is located in the bottom of the reactor cabinet. In addition, the quartz support shaft has an inner feed through for a thermocouple. This thermocouple was used to monitor the temperature of the susceptor that was inductively heated from the induction coils surrounding it from the outside of the bell jar reactor. Induction was carried out using a Lepel generator and a Eurotherm was used to control and regulate the susceptor temperature. Finally, there are two exhaust outlets that connect to a rotary vane mechanical pump and the pressure of the reactor was regulating using an MKS throttle valve. The exhaust is diluted with nitrogen and connect to a wet scrubber system. The scrubber system neutralizes the alkaline exhausted gases that was delivered downstream from the pump by periodically pulsing 1:1 dilution of sulfuric acid in DI water into the wet scrubber system.
2.1.3 Multibeam optical stress sensor

Seen in Figure 2.3.a.b are the enclosures that house the multibeam optical stress sensor (MOS) system developed and installed by kSA. This system was upgraded in the year of 2015 to enable 2D array MOS capability for in situ curvature measurements. The system also houses an emissivity corrected pyrometry system kSA ICE that allows for simultaneous collection of surface temperature with reflectivity and curvature data. The emissivity corrected pyrometer module consists of a 960 nm LED that can also be used for reflectivity measurements with the addition of the MOS 662 nm laser line. The capabilities were not available during the experiments presented in chapters 3 and 4, however, are mentioned here to inform the reader. Data is collected at each rotation of the susceptor using the laser triggering system - kSA trigger. This system provides the ability to synchronize data acquisition with sample rotation position and was also a recent upgrade to the system in the year of 2015. At the top end cap of the reactor, the two optical ports allow multiple spots of the 662 nm continuous wave (CW) AlGaInP laser line to enter and exit the reactor process chamber. These spots are generated by passing the laser line through two sequential etalons on the right housing of the system before entering the reactor process chamber (Figure 2.3.a-b). Once these laser spots enter the right optical port on the right side of the top end cap, the spots can reflect off the surface of the sample and exit via the left optical port on the top end cap. These laser spots are then steered into the CCD using a series of mirrors that are housed on the left side of the MOS system. The high-resolution CCD camera (2/3-inch, 1360 x 1040 pixels, 30 fps 8-bit / 15fps 12-bit) and motorized mirror optics allow for automatic tracking of the laser sport throughout the growth process using the kSA MOS preparatory software.
**Figure 2.4** A schematic demonstrating the MOS set up and the effect of substrate curvature and morphology on the reflected laser spots. (a) is during flat wafer condition or when film is stress/strain free. (b) during negative curvature or compressive stress/strain from in-plane mismatch. (c) during positive curvature or tensile stress/strain from in-plane mismatch. (d) shows the effect of surface morphology on the reflected laser spots, where surface roughness or 3D growth reduces laser reflectance.
Furthermore, the parallel laser beams that are reflected from the sample surface provides in-depth understanding of the growth stress evolution in the film. This stress is extracted from the changes in the curvature of the supporting substrate. The sensitivity of the MOS was quoted as $\sim 2 \times 10^{-5}$ m$^{-1}$ from the manufacturer. This sensitivity, however, is dependent on the thickness of the substrate utilized$^1$. The scheme in which the laser spots interact with the surface of the sample is best illustrated in Figures 2.4.a-d. As seen in Figure 2.4.a, the incoming laser spots are reflected from a presumed smooth sample surface at a normal incident angle of $\theta$. The parallel beam of laser spots is sensitive to the bow of the substrate. Therefore, the time dependent curvature of the substrate ($k(t)$) can be monitored from the following equation$^2$:

$$k(t) = (1 - (\delta d/d_0))(\cos \theta / 2L) \quad \text{Eq. 2.5}$$

where, $(\delta d/d_0)$ is differential change in the spacing between two laser spots ($\Delta$ in Figure 2.4.a) that was calibrated using a flat SiC reference and $(L)$ is the distance between the CCD camera and the substrate that was calibrated using a mirror of known curvature. The film thickness $h_f$ is determined from simultaneously collected oscillations in laser reflectance that results from Fabry–Perot constructive and destructive interferences during film growth which can also provide real-time monitoring of the morphological evolution and surface roughness of the films. The thickness oscillation period is dependent on the wavelength of the laser ($\lambda$) utilized and the refractive index of the material ($n_f$) at the laser wavelength as shown in the following equation:

$$h_f = \lambda / (2 \sqrt{n_f^2 - \sin^2 \theta}) \quad \text{Eq. 2.6}$$
The refractive index of GaN and AlN at 662 nm are ~2.3774 and ~2.1471, respectively. Therefore, the stress of the film ($\sigma_f$) can be related to the change in curvature of the substrate using Stoney’s equation:

$$\sigma_f = \frac{((\delta d/d_0)(M_s h_s^2 \cos \theta /12L))}{h_f} \quad \text{Eq. 2.7}$$

where ($\theta$) again is the normal incident angle of the reflected laser beams (10° in our current set-up), ($M_s$) is the biaxial modulus of the substrate and ($h_s$) is the substrate thickness. The biaxial modulus of the SiC substrate utilized during the growth experiments in chapters 3 and 4 was 602.2 GPa. The thickness of the SiC substrate utilized was ~360 μm.

In Figure 2.4.a, if we consider the case during the deposition of a thin film on a flat substrate and the in-plane lattice constant of the deposited film matches the in-plane lattice constant of the substrate, then the heterostructure consisting of the film and substrate should remain flat. Therefore, no differential change in the laser spots should be observed from MOS, i.e. stress-free growth state. This condition gives flat curvature during the growth process. If, however, the in-plane lattice constant of the film is larger than that of the substrate, such as in the example of Figure 2.4.b, then the film will grow under compressive stress due to the epitaxial lattice mismatch. The strain at the interface will result in the bending of the substrate and thus causes the film/substrate heterostructure to deform into a convex-up shape. This reduces the spacing between the reflected laser spots and thus providing negative curvature values. Alternatively, if the in-plane lattice content of the film is smaller than that of the substrate, such as in the case presented in Figure 2.4.c, then the film will grow under tensile stress due to epitaxial mismatch. The strain at the interface will transfer into the substrate, causing the film/substrate heterostructure to
deform into the concave-up shape. This leads to an increase in the spacing between the reflected laser spots and thus positive curvature values are obtained. In the three scenarios presented in Figure 2.4.a-c, we assume a flat starting substrate. If the substrate inherits an intrinsic bow or a bow is induced extrinsically due to thermal mismatch and/or from a temperature gradient in the substrate, then the overall curvature and bow of the film/substrate heterostructure is also affected.

In addition to film thickness, the reflectivity data that is collected provides qualitative information regarding the morphological evolution of the film during the length of the growth process (Figure 2.4.d). If the grown film exhibits high surface roughness, the laser spots are scattered from the surface leading to attenuation of the collected laser reflectance data over the length of the growth. Moreover, reflectivity data gives insight into the nucleation density and coalescence process during thin film growth. For example, during the growth of AlN on SiC, if the initial nucleation density is low, the reflectivity data will initially drop and then slowly recover as the lateral growth of the nuclei commences. The prolonged reflectivity gives insight into the rate of lateral growth of the nuclei-islands. Once the islands coalesce, the reflectivity saturates upon the initiation of step-flow growth. If, however, the initial nucleation density is high and rapid coalescence occurs, no prolonged recovery in the reflectivity data will be observed.

2.1.4 Substrate preparation and general growth process

2.1.4.1 Brief description of SiC substrates utilized in experiments

The SiC substrates used for the studies presented in chapters 3-5 were of 6H and 4H polytypes. For thin film growth, the SiC substrates were purchased from Cree, In., while
the SiC substrates utilized for the growth of epitaxial graphene in chapters 4 and 5 were from II-VI Advance Materials and Dow. The specifics of the substrate conductivity, orientation and degree of miscut are listed within the experimental procedure section of each chapter. All SiC substrate used in the experimental studies were \{0001\} oriented. In Figure 2.5.a-c, a general description of the principle crystallographic directions of the hexagonal system and the primary and secondary flats of SiC are presented to aid the reader in identifying the wafer face termination (silicon-face or carbon-face).

**Figure 2.5** | (a) Crystallographic direction for the hexagonal system. The \(<0001>\) direction is pointing out of the page. (b) are the orientations of the primary and secondary flats for epi-ready silicon-face SiC. (c) are the orientations of the primary and secondary flats for epi-ready carbon-face SiC.

All faces of the SiC substrates used for the growth studies were chemical mechanical polish (CMP) finished and epi ready. The samples were diced into \(\sim9.95\) mm \(\times\) 9.95 mm pieces using an ADT 7100 ProVectus dicing saw. Frist samples were mounted on UV-tape to protect the surface of interest from damage. After dicing, samples were then exposed to UV-light to release the tape from the substrate.
2.1.4.2 Substrate cleaning procedure

Prior to performing any growths in the MOCVD reactor, a 1–2 hour hydrogen bake was done. This insured the cleanliness of the reactor prior to any growth experiment. In addition, after SiC substrate dicing, the samples were then cleaned using the following procedure and then directly loaded into the reactor after the last step:

1. OptiClear solvent dip or heated PRS 3000 to remove residual resist.
2. Acetone scrub, then glacial acetic acid scrub, followed by an additional acetone scrub.
3. Ultrasonication in heated acetone.
4. Ultrasonication in heated 2-propanol (isopropanol).
5. De-ionized water rinse followed by N\textsubscript{2} blow dry.
6. Heated Nanostrip for 20 min – a stir bar was used to circulate the solution.
7. 10% hydrofluoric acid (HF) dip for 10 min.
8. Rinse in de-ionized water and N\textsubscript{2} blow dry.

In the following subsections, five baseline growth recipes are provided to the reader in order to reproduce the samples outlined in the chapters of this dissertation. In the first section, we will provide baseline recipes used in chapter 3 for the growth of III-polar InGaN and N-polar InGaN. Two other baseline recipes are provided for the direct growth of GaN on SiC via the two-step temperature growth process and buffer assisted growth of GaN on SiC with an AlN buffer layer. The final section provides the most updated growth recipe to produce two-dimensional GaN. The flow rates for the optical ports and liner tube in all of the five provided baseline recipes were 1 standard liter per minute (slm).
## 2.1.4.3 Recipe for III-polar and N-polar InGaN growth on SiC

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Table 2.2 | Baseline recipe for the growth of thick III-polar InGaN on the Si-face of SiC.

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Table 2.3 | Baseline recipe for N-polar InGaN growth on two-step GaN on C-face SiC.
2.1.4.4 Recipe for buffer and buffer-free growth of GaN on SiC

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Table 2.4 | Baseline recipe for the growth of GaN on AlN on the Si-face of SiC.

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<th>TMIn (sccm)</th>
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Table 2.5 | Baseline recipe for the direct growth of GaN on the Si-face of SiC via the two-step temperature growth process.
2.1.4.5 Recipe for 2D growth of GaN via the MEEG process

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Table 2.6 | Baseline recipe for the migration enhanced encapsulated growth (MEEG) process for 2D GaN. No sample rotation was performed in this recipe.

2.2 Graphite hot zone furnace

A graphite hot zone furnace from Thermal Technology LLC was used to perform epitaxial graphene growth on SiC. An image of the system is shown in Figure 2.6.a. The graphite hot zone furnace is pumped down using a combination of a mechanical pump and a diffusion pump. The details of the components of the system are outlined in the schematic shown in Figure 2.6.b. The process gases that are available on the system, include ultra-high purity hydrogen and ultra-high purity argon. Prior to epitaxial graphene growth, samples were cleaned using the procedure outlined in section 2.1.4.2. Samples are then loaded into a 2320 purified graphite enclosure aperture that contained a pinhole. The method of using an enclosure aperture for the production of epitaxial graphene on SiC is referred to as the “confinement controlled sublimation” method in the literature.
graphite enclosure consists of two parts. A 0.3-inch graphite stand with 10 mm × 10 mm pockets to mount the SiC substrates (Figure 2.7.a), and a crucible/lid to enclose the graphite stand (Figure 2.7.b). Complete details of the recipes used for epitaxial graphene growth are outlined in the experimental sections of chapter 4 and 5.

Figure 2.6 | (a) Image of the graphite hot zone furnace and (b) a schematic of the system’s components.

Figure 2.7 | (a) Image of the graphite stand and (b) crucible/lid enclosure unit.
2.3 References

CHAPTER 3

MOCVD GROWTH OF THICK III-POLAR AND N-POLAR INGAN ON SIC

3.1 Introduction

The extensive studies of pseudomorphically strained III-polar and N-polar InGaN quantum wells (QWs), grown by metalorganic chemical vapor deposition (MOCVD), has led to the realization of many optoelectronic devices, most notable the blue laser diode (LD) and light emitting diode (LED)\(^1,2\). For some applications, including absorber layers for photovoltaics and efficient deep-green to red emitters, the growth of thicker InGaN layers beyond pseudomorphic thicknesses is, however, essential. For example, in the case of photovoltaics, layers on the order of ~200 nm or more in thickness are needed to maximize absorption across the solar spectrum\(^3,4\). For solid-state lighting, the use of InGaN base-layers in place of GaN is desirable to reduce strain driven degradation of the internal quantum efficiency in emitters fabricated with high indium content QWs. The use of conventional GaN base-layers results in large lattice mismatch with the QWs, which leads to dislocation generation and piezoelectric polarization fields across the wells with increasing indium\(^5\). Such polarization fields give rise to the quantum-confined Stark effect and efficiency droop in conventional III-polar LEDs\(^6-8\). Efforts to reduce polarization effects in III-nitride emitters were demonstrated on non-polar and semi-polar substrates\(^9,10\), yet misfit strain in heterostructures still remains and consequently dislocations can form. As a substitute, the use of thick InGaN layers (>100 nm) as metamorphic-buffers and strain-reducing base-layers has been theoretically\(^11-17\) and experimentally\(^18\) shown to improve the performance of deep-green and red LDs and LEDs.
Despite the compelling interest in the replacement of the GaN base-layers with InGaN, the growth of layers beyond pseudomorphic thicknesses is, however, challenging. The high vapor pressure of indium reduces its incorporation into GaN with increasing growth temperatures. High growth temperatures are typically required to achieve high crystal quality group-III nitride films. Also, the large miscibility-gap between InN and GaN leads to indium clustering, which gives rise to surface roughening. Moreover, during heteroepitaxy of III-polar InGaN on GaN, layers grow under a considerable amount of compressive stress due to lattice mismatch. This mismatch between InGaN/GaN increases with increasing indium content. Since plastic relaxation via the formation of misfit dislocations by glide along the limited available slip systems is not easily activated at the typical MOCVD growth temperatures of InGaN, it has been suggested that layers of III-polar InGaN grown beyond pseudomorphic thicknesses tend to partially elastically relax via the formation of V-pits\textsuperscript{19}. These V-pits are energetically favored to form at the apex of threading dislocations and increase in size and density with increasing layer thickness and indium content\textsuperscript{20} and to some extent, these V-pits can be mitigated during semibulk growth of thick InGaN\textsuperscript{21,22}, but not entirely. Therefore, thick films of III-polar InGaN grown by MOCVD are plagued with composition inhomogeneity, poor crystal quality and high surface roughness. Consequently, the evolution of stress in these thick layers becomes complex, and as a result, the relaxation mechanisms of compressive stress in thick InGaN films have been largely unidentified.

Alternatively, growth in the N-polar direction offers several advantages that are attractive for thick InGaN films. N-polar InGaN can be grown at higher temperatures due to the increased stability of InN on the N-polar surface\textsuperscript{23}. This allows for higher indium
incorporation at elevated growth temperatures and therefore, improved structural quality in N-polar InGaN when compared to III-polar InGaN grown with the same indium content. Furthermore, due to the differences in surface energetics in N-polar InGaN\textsuperscript{24}, suppression of structural defects, such as V-pits, that inhibit the growth of thick layers, is possible. Therefore, growth in the N-polar direction provides a means to reduce defect densities, which thus enables the growth of thick InGaN layers for the aforementioned applications. As evidence of this, the growth of high-quality thick N-polar InGaN has been demonstrated \textit{via} molecular beam epitaxy and tri-halide vapor phase epitaxy\textsuperscript{25,26}. Metalorganic chemical vapor deposition (MOCVD) of atomically smooth N-polar InGaN beyond pseudomorphic thicknesses\textsuperscript{27,28}, however, has not come to fruition. This is due, in part, to the difficulty in producing high-quality MOCVD grown N-polar GaN base-layers for N-polar InGaN growth.

N-polar GaN grown by MOCVD typically exhibit a high density of hexagonal hillocks that form due to the low surface mobility of the group-III adatoms\textsuperscript{29}. This can be mitigated by using vicinal substrates which provide a higher density of atomic steps to promote step-flow growth and thus suppress the formation of hexagonal hillocks\textsuperscript{23,30-32}. Furthermore, it has been shown that by utilizing a two-step temperature growth process\textsuperscript{23}, nearly stress-free N-polar GaN base-layers can be obtained with good structural quality and low surface roughness\textsuperscript{33}. 
3.2 Literature Review

Recently, there has been interest in the growth of thicker InGaN layers to serve as absorber materials in multi-junction solar cells and as strain-reducing base layers for deep-green LEDs. InGaN has superior material properties for solar energy conversion. This largely comes from its direct bandgap tunability (from 0.64 eV to 3.42 eV) that nearly matches the entire solar spectrum for maximum efficiency (Figure 3.1)\(^34\). This was realized only after the re-evaluation of the InN optical bandgap energy from 1.9 eV to 0.64 eV as the growth of these materials improved\(^35\). The modification of the band edge of InGaN is achieved by controlling the indium fraction in the material. This is done in order to optimize solar cell device efficiency in multi-junction architectures. The InGaN material system has numerous advantages that make it an ideal candidate for ultra-high-efficiency photovoltaic

![Figure 3.1](image)

**Figure 3.1** | The bandgap of group III-nitride alloys as a function of the in-plane lattice constant, compared to the visible colors, solar cell spectrum and 1.55 μm wavelength. Ref [34].
In order to utilize InGaN for solar cells, two design criteria must be realized: maximum optical absorption and minimum recombination of photo-carriers. The high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$), high carrier mobility, good thermal conductivity and stability as well as superior resistance to radiation damage of InGaN, all prove advantageous for its integration into next generation multi-junction solar cells, based solely on a single material system$^{36,37}$. As a consequence, it has been theoretically envisioned that the InGaN material system can be used to fabricate multi-junction solar cells with theoretical conversion efficiencies exceeding 60%$^4$. In addition, the possible bandgap alignment of InGaN with silicon offers new opportunities for its integration into hybrid solar cells architectures. For example, a three-junction In$_y$Ga$_{1-y}$N/In$_x$Ga$_{1-x}$N/Si solar cell can offer energy conversion efficiencies exceeding 35%$^{38}$.

Although III-nitride materials, i.e. InGaN, can be considered one of the most important semiconductor systems, its material performance and technological impact as an absorber material for solar cells is hindered by several combined problems. These problems include poor indium incorporation, high density of material defects and challenges associated with the growth of high-quality thick layers. As a result of the high absorption coefficient in InGaN alloys, the growth of high quality III-polar InGaN layers, exceeding 120 nm in thickness, is needed to maximize light absorption. However, the growth of such thick layers is challenging as discussed in the introduction. Overcoming some of these materials challenges is important in order to pave the way for high performance InGaN solar cells.
3.2.1 Overview of the physical properties of InGaN

The stable wurtzite crystal structure of InGaN (Space group P63mc, point group 6mm) exhibits A-B stacking of In/Ga and N atoms along the [0001] direction of the hexagonal structure. The first growth of InGaN by MOCVD was reported by Nagatomo et al. in 1989\(^3\). Today, InGaN alloys are utilized in commercially available high efficiency blue LEDs. In its wurtzite form, a polar axis points from the N to the Ga atoms due to the lack of inversion symmetry (Figure 3.2)\(^4\). This anisotropy results in highly pronounced polarization-induced electric fields. These polarization-induced fields are prominent material properties that should be taken into consideration when designing optoelectronic devices such as LEDs and solar cells. In LEDs, it has been well established that the polarization-induced fields can modify the band edges and influence optical properties as

**Figure 3.2** | The crystal structure for both Ga-polar and N-polar GaN Ref [40] (a), the direction of the total polarization and its components for an InN/GaN junction. Ref [41].
a result of the quantum stark effect, where electron and hole wave-functions are not aligned\(^6\). Such an effect can reduce the internal quantum efficiency of the LED device.

### 3.2.1.1 Polarization-induced electric fields in InGaN

The polarization-induced fields in group III-nitride materials arise from two sources: the difference in spontaneous polarization within epilayers (AlN, GaN and InN) and piezoelectric polarization effects\(^41\). InGaN possesses non-vanishing spontaneous polarization due to the uniaxial nature of the strong ionicity between the A-B stacking of constituent atoms (Ga, In and N) in the stable hexagonal wurtzite crystal structure. This spontaneous polarization is forbidden in the cubic zinc-blend form of group III-nitride crystals due to the centrosymmetry of the crystal structure. For InGaN, the direction of the spontaneous polarization is from the nitrogen-atom to the closest metal-atom along the ±c direction, which is the conventional direction for MOCVD growth of group-III nitrides films. From here on out, the polarity growth direction of the III-nitride film shall be denoted as N-polar or III-polar depending on if the spontaneous polarization is “in” or “opposite” to the [0001] growth direction, respectively. Moreover, due to the coordination nature of the metal-atom in group-III nitride materials, the growth surface can be thought of being terminated with three nitrogen atoms in N-polar materials, as oppose to one nitrogen atom in III-polar materials. The spontaneous polarization for ternary compounds can be calculated via a combination of the mole fraction of the binary constituents using a modified version of Vegard’s law. For InGaN, the spontaneous polarization is expressed\(^42\):

\[
P_{sp}^{In_{x}Ga_{1-x}N}(x) = xP_{sp}^{InN}(x) + P_{sp}^{GaN}(x)(1 - x) - b_{In_{x}Ga_{1-x}N}x(1 - x) \quad \text{c/m}^2
\]

Eq. 4.1
where \( x \) is the indium mole fraction and \( b \) is the bandgap energy bowing parameter for InGaN. The bowing parameter for InGaN alloys ranges between 1.4 eV – 2.8 eV and is dependent on the indium content and the stress state of the film\(^{43}\). In addition, piezoelectric polarization effects in InGaN can be sizable. This effect arises from stress-induced polarization charge in the hexagonal wurtzite crystal structure. The stress-induced polarization has two components. One is due to the misfit stress as a result of the lattice mismatch between InGaN and the underlying substrate. The other is due to thermal stress caused by the difference in thermal expansion coefficients of the epitaxial InGaN layer and the underlying substrate\(^{42}\). The piezoelectric polarization is defined in terms of the elastic moduli. In group III-nitride semiconductors, the piezoelectric polarization along the [0001] direction can be expressed as Eq. 4.2 and by using Vegard’s law, the piezoelectric polarization for InGaN can be calculated (Eq. 4.3)\(^{42}\):

\[
P_{pz}^{[0001]} = 2(e_{31} - e_{33}c_{13}^2)\epsilon_1 \tag{Eq. 4.2}
\]

\[
P_{pz}^{In_xGa_{1-x}N} = xP_{pz}^{InN}(\varepsilon) + P_{pz}^{GaN}(\varepsilon)(1-x) \tag{Eq. 4.3}
\]

where \( e_{ij} \), \( c_{ij} \) and \( \epsilon_1 \) are the piezoelectric moduli, the elastic coefficients and the in-plane strain respectively. One can relate piezoelectric polarization to strain and stress coefficients in a crystal, with the following equation\(^{41}\):

\[
P_{pz,l} = e_{ijk}\epsilon_{jk} = d_{ijk}\sigma_{jk} \tag{Eq. 4.4}
\]

Given the sensitivity of polarization fields to the indium mole fraction and strain of InGaN, it is thus necessary to investigate and understand the growth stress state of the InGaN film not only as a function of thickness, but also as a function of indium content. Figure 3.2.b
shows how the spontaneous and strain induced piezoelectric polarization can arise during the heteroepitaxy of InN on GaN. For conventional growth in the III-polar [0001] direction, the polarization-induced field is along the [000\bar{1}] direction. This can have negative effects on many optoelectronic devices, more specifically in solar cells.

3.2.1.2 Consequences of polarization-induced fields in InGaN for solar cells

The total electric field in III-nitride based photovoltaic devices depends on the built-in electric field, the forward bias and the total polarization-induced field\textsuperscript{44}. Reports have shown that high polarization-induced fields can degrade photovoltaic action in solar cells\textsuperscript{45,46}. The large difference between the bandgap energies of GaN and InGaN can result in potential barriers and surface charge states. In addition, polarization charges can lead to internal electric fields that can reduce the band bending necessary for carrier drift, leading to carriers only being collected through diffusion and therefore, reducing the overall device efficiency\textsuperscript{47}. For this reason, the polarization-induced field produced in the p-GaN/i-InGaN/n-GaN heterostructure for films grown in the III-polar [0001] direction, hinders the separation of free carriers in the active region generated by light absorption and enhances parasitic recombination\textsuperscript{48}. This is because the spontaneous polarization field points in the opposite direction of the built-in electric field, hindering band bending and potentially reversing the free carrier motion. Such polarization-induced fields can be large enough to cancel and even reverse the electric field of the space charge region\textsuperscript{49}. In order to develop multi-junction solar cells based solely on the InGaN materials system, these challenges must be addressed and solved.
If the polarization induced electric field is reversed, it can be advantageous in solar cell devices in separating electron-hole pairs and reducing recombination efficiency\textsuperscript{47}. As seen in Figure 3.3.a-b, the behavior of the polarization induced fields is quite different in N-polar InGaN p-i-n solar cells. This is because the spontaneous polarization is in the direction of the built-in electric field. As a result, the polarization field favors the separation of the generated electron-hole pairs by enhancing the overall electric field. Therefore, the carrier recombination rate is found to be much less than the generation rate. As a result, N-polar InGaN based solar cells are more capable of operating across the entire InGaN composition range. In simulations of N-polar InGaN p-i-n solar cells performed by Balushevich et al., fill factor exceeding 80-85\% at carrier lifetime longer than 1-20 ns was demonstrated\textsuperscript{48}.

![Diagram](image.png)

**Figure 3.3** | Direction of total polarization field in, metal-polar InGaN (a) and N-polar InGaN (b) p-i-n solar cell. Adapted and modified from Ref [44].

Moreover, in solar devices, photovoltaic action is affected by the material quality. It has been demonstrated that the conversion efficiency is impacted with increasing indium content due to the increase in the piezoelectric fields and degree of strain relaxation through the generation of extended material defects\textsuperscript{50}. As the strain in the material relaxes, the
degree of piezoelectric polarization is reduced, while the spontaneous polarization in the material remains. However, a higher degree of relaxation leads to inferior crystal quality at the expense of reducing the piezoelectric polarization, due to the generation of dislocations and defects in the film. Such defects have an effect on the recombination life time of carriers in the solar cell device. Therefore, in III-polar InGaN based solar cells, it is difficult to maintain high material quality while reducing the piezoelectric polarization. However, with N-polar InGaN, the effect of polarization enhances photo-carrier generation. In N-polar InGaN growth, the polarization-induced field is reversed from that of the III-polar growth and is in the direction of the built-in potential. Therefore, the total electric field is larger than the original built-in electric field. This can enhance photo-carrier collection. In addition, with increasing indium fraction, the band offset between InGaN/GaN expands. This band offset expansion can inhibit carrier transport across the interface. However, with the enhanced electric field in N-polar InGaN, an increase in the probability of carriers to drift to overcome the potential barrier at the interface is possible. Therefore, maintaining good crystal quality and high polarization-induced fields is possible and beneficial in N-polar InGaN growth.

The growth of N-polar InGaN films will enable development of high performance solar cells with improved conversion efficiencies. However, there has been no demonstration to date of N-polar InGaN solar cells. This is due to the challenges associated with the growth of high-quality layers. Therefore, understanding the growth kinetics of N-polar InGaN and the mechanisms responsible for stress relaxation and defect generation is important, as it has a direct impact on solar cell device performance.
3.2.2 Understanding the challenges for the realization of high indium content thick InGaN films

During MOCVD growth, InGaN layers grow on GaN base-layers under compressive stress due to the epitaxial lattice mismatch. However, due to increasing lattice mismatch with increasing indium content in InGaN, the InGaN layer relaxes via defect-related mechanisms such as the formation of hexagonal V-pits, phase separation, dislocation loops and misfit dislocations. To avoid the formation of such misfit dislocations, InGaN must be pseudomorphically strained or grown on strain reducing base-layers. In addition, due to the large compressive stress, indium incorporation is reduced due to the composition pulling effect. To incorporate more indium, growth temperatures are typically reduced. However, this leads to a decrease in the surface mobility of the adatoms, leading to compositional inhomogeneity, a higher density of defects and rough surfaces. Such effects can increase the incorporation of impurities such as carbon and oxygen as well as increase structural defect densities from indium clustering.

3.2.2.1 Nucleation and Growth of InGaN

The majority of the InGaN growth studies reported in the literature focus on the initial stages of thin quantum well layers. For solar cells, thicker layers are necessary in order to maximize absorption. However, there are challenges associated with the growth of high-quality thick layers with high indium content. Such challenges include crystal quality degradation with increasing indium content that originates from phase separation. Phase separation occurs in InGaN due to the large solid-phase miscibility gap that results from the large lattice mismatch between InN and GaN in the alloy as shown in Figure 3.4.

Phase separation in InGaN can create recombination channels and potentially pin open-circuit voltages in solar cell devices\textsuperscript{53}. Theoretical calculations predict that phase separation is not only dictated by indium fraction, but also by the strain state of the film\textsuperscript{54}. Phase separation can be suppressed and kinetically controlled not only by optimizing growth conditions such as V/III ratio, growth rate and temperature, but also by mitigating stress in the film\textsuperscript{53}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4.png}
\caption{Solid and dashed lines are calculated binodal and spinodal decomposition curves for the InGaN, assuming a constant solid phase interaction parameter. Ref [52].}
\end{figure}

In addition, composition and strain inhomogeneity can occur in InGaN films and originate from a coupled effect of compressive stress from the large lattice mismatch, surface morphology and kinetic effects during growth. The correlation between surface morphology and compositional instability has been reported in the literature\textsuperscript{55}. Rough surface morphologies can promote relaxed high indium InGaN growth, while smooth surface morphologies promote pseudomorphic strained layers with lower indium content.
Such inhomogeneities can lead to indium clustering that can give rise to localized states that act as carrier traps\textsuperscript{55}. These traps can limit diffusion of carriers in solar cell devices.

During the growth of InGaN, two types of phase separation have been observed in epitaxial layers. The first type is InGaN microstructures and/or inclusions that are rich in indium, located within the InGaN matrix and the other being macroscopic InGaN phase instabilities related to the difference in InGaN growth rates on different available crystallographic growth planes\textsuperscript{56}. Typically, phase separation can be observed from secondary on-axis and off-axis peak reflections in high-resolution x-ray diffraction measurements and multiple peaks in photoluminescence measurements performed at room temperature. In addition to high resolution x-ray diffraction and photoluminescence, Atom Probe Tomography (ATP) can provide phase analysis with part per million sensitivity and sub-nanometer spatial resolution in three dimensions.

**3.2.2.2 Stress evolution during the growth of thick InGaN**

The high incorporation efficiency of indium into the InGaN layers is necessary for the realization of multi-junction solar cells with theoretical efficiencies >60%. As a result, InGaN layers typically grow under considerable amounts of stress due the lattice mismatch that accompanies high-indium fractions in the material. For solar cells, developing strategies to mitigate stress relaxation in InGaN is important in order to produce layers with good crystal quality and surface morphologies. The importance of understanding stress evolution comes from its inherent importance in defect formation \textit{via} relaxation during growth. Stress relaxation, particularly in thick InGaN films, is not well understood. This is because typical mechanisms of stress relaxation during heteroepitaxy, such as plastic
relaxation *via* the formation of misfit dislocation by glide along available slip systems in the wurtzite crystal structure, as seen in Figure 3.5, is kinetically limited. Therefore, relaxation by other mechanisms typically dominate. This includes the commonly observed V-pit formation in III-polar InGaN films with high dislocation densities as seen in Figure 3.6. It is known that V-pits open up at the apex of threading dislocations and are formed due to the surface energy of the indium terminated (10\overline{1}1) pyramidal planes being lower than that of the (0001) surface. Therefore, investigating the relaxation mechanism specific to InGaN is necessary in order to improve MOCVD grown films for solar cell devices. There are three physical mechanisms to relax the compressive stress in these films: misfit dislocation generation at interfaces which impacts the crystal quality, three-dimensional growth (Stranski-Krastanow mode) transformation which impacts the surface morphology and dislocation bending (inclination) which allows...
threading dislocation to interact and potentially annihilate. Pantzas et al. investigated the evolution of stress in III-polar InGaN using \textit{ex situ} measurement techniques\textsuperscript{60}. During the growth of thick layers, Pantzas et al. reported that two distinct InGaN phases were present. The first phase was fully strained to the underlying GaN base-layer and the other was fully relaxed beyond a critical thickness\textsuperscript{60}. When the thickness of the InGaN layer grows beyond its critical thickness, compressive stress is partially relaxed through the generation of misfit dislocations or through a transition in the growth mode. This critical thickness is dependent on the indium fraction and is controlled by growth conditions such as temperature, TMIn flow rate, growth rate and reactor pressure. As seen in Figure 3.7, the critical thickness for dislocation generation and growth mode transition decreases with increasing indium fraction\textsuperscript{61}. The results show that three-dimensional growth mode transition is induced more easily than dislocation generation for indium fractions less than 27%. The distinct layers reported by Pantzas et al. resulted from a transition in the growth mode from 2D to 3D\textsuperscript{60}.

\textbf{Figure 3.6} | 3D projection of an AFM scan of the surface of III-polar InGaN and highlighting the formation of a V-pit in the center schematic. The image on the right is a transmission electron micrograph showing an isolated V-pit opening up at the apex of a threading dislocation (TD).
In addition, Huag et al. showed a degradation in the InGaN material property that was correlated to a change in the growth mode from step-flow growth to three-dimensional island nucleation induced by the reduction in growth temperature from 760°C to 640°C (an increase in indium composition)\textsuperscript{56}. This resulted in an increase in the RMS roughness from 0.7 nm to 5.6 nm. However, for indium fractions greater than 27%, as seen in Figure 3.7, plastic relaxation \textit{via} the formation of misfit dislocations is the predominant mechanism for compressive stress relaxation at such high indium fractions. It is possible to relax part of the stress through extended dislocations generated from the GaN template into the InGaN layer. This partial relaxation of the InGaN layer results in an increase in its critical thickness for stress relaxation beyond that predicted by theory\textsuperscript{61}. Iida \textit{et al.} showed that two characteristic thicknesses where observed by \textit{in situ} x-ray rocking curve measurements of

\textbf{Figure 3.7} | Critical thicknesses of dislocation generation and three-dimensional growth versus indium composition in InGaN with different density of dislocation in the film. Ref [61].
the (0002) reflection during the growth of thick layers of III-polar InGaN$^{52}$. They observed from \textit{in situ} x-ray rocking curves that the quality of the InGaN slightly improved with layer thickness. This was attributed to dislocation bending and annihilation by dislocations interacting with each other. The connection between stress relaxation and threading dislocation bending has been modeled by Romanov and Speck$^{63}$. For the case of [0001] oriented growth of hexagonal structures such as group III-nitride materials, threading dislocations usually have a pure edge character (a-type dislocation). The (1$\overline{1}$00) prismatic glide planes for a-type dislocations are normal to the biaxial stress plane. However, shear stress is absent in the glide planes. Therefore, relaxation mechanisms based on dislocation glide are not accessible. Romanov and Speck established that stress relaxation \textit{via} the inclination of threading dislocations was assisted through an effective dislocation climb process of edge dislocations directed out of the (1$\overline{1}$00) glide planes.

Moreover, from the \textit{in situ} x-ray results of Iida \textit{et al.}, two critical thicknesses for stress relaxation \textit{via} dislocation generation were observed. The first was related to the formation of V-pits from extended threading dislocations that have propagated from the GaN template. Threading dislocations in c-oriented InGaN consist of three types. These threading dislocations are edge, screw and mixed type dislocations with burgers vector a, c and a+c, respectively. Threading dislocations lead to anisotropic broadening of diffraction peaks. Through analyzing rocking curves of symmetric and asymmetric peaks, the density of threading dislocations can be extracted using the mosaic model$^{64}$. Some of these threading dislocations bend and improve the crystal quality; others propagate and open at the surface \textit{via} the formation V-pits. The second critical thickness for stress relaxation occurs with the generation of (a+c)-type misfit dislocations. These dislocations
generate additional threading dislocations and are mainly responsible for the additional V-pit formation at the III-polar InGaN surface. Iida et al. showed that a network of misfit dislocations was generated along the \(<1\overline{1}00>\) direction close to the interface. Such dislocations may be induced via slip along the \(<1\overline{2}3>\) direction in the \((1\overline{1}22)\) plane system\(^62\).

If threading dislocation densities and therefore V-pits can be reduced, plastic relaxation via slip should become the more predominant stress relaxation mechanism. This will allow for a more complete understanding of the mechanism responsible for stress relaxation where V-pits are not present. With the reduced V-pit densities, mechanisms such as bending and annihilation of threading dislocations, such as that proposed by Zhu et al. and observed in cross section TEM by Srinivasan et al., can be possible\(^65\)\(^57\). Dislocation bending of misfit dislocations by effective climb has been observed in the AlGaN systems, where V-pits do not form\(^66\). Therefore, stress relaxation should be different in the absence of V-pits on N-polar surfaces, particularly since the \((10\overline{1}0)\) facets and therefore V-pits are energetically unfavorable to form.

3.2.2.3 The impact of defect and impurities

Defects are the main cause for poor solar cell device performance, particularly at high indium content. High defect densities can lead to lower open-circuit voltage values\(^67\). Stress relaxation due to lattice mismatch results in extensive generation of extended defects such as V-pits and other dislocations that originate from the increased strain energy. These defects can act as leakage paths to the metal contacts and conductive channels that can lead to shunting of the p-n junctions, reducing the open circuit voltage and degrading the fill
factor of the device. Carrier lifetime can also be impacted by the variety of defects that are particularly present in III-polar InGaN, reducing carrier lifetimes and device efficiency. Zhang et al. showed that the photovoltaic action in p-i-n InGaN/GaN solar cells was influenced by the dislocation density. A decrease in the dislocation density from $5 \times 10^9$ to $5 \times 10^8$ cm$^{-2}$ enhanced the external quantum efficiency of the device by three times. Balushevich et. al. showed when V-pit density increased from $10^6$ to $10^8$ cm$^{-2}$, a dramatic reduction in $V_{oc}$ from $\sim 2$ to $< 1$ V was observed.

Moreover, during MOCVD growth, sources of impurities can arise from the precursor and carrier gases such as the metalorganics/ammonia and hydrogen, leaks and air exposure. The high n-type carrier background concentration that is commonly observed in InGaN films is caused by nitrogen vacancies and high oxygen concentration. With decreasing growth temperatures to increase indium incorporation, the decomposition efficiency of ammonia is reduced and therefore, there are less N atoms available. This increases the likelihood of forming nitrogen vacancies. Furthermore, the high oxygen background concentrations exhibited in N-polar GaN films grown by MOCVD makes the film highly n-type, since oxygen acts as a shallow donor. Oxygen incorporation is higher in N-polar GaN films in comparison to III-polar films. Lin et al. showed that by decreasing the growth temperature to increase indium incorporation, an increase in carbon and oxygen incorporation occurs. Oxygen incorporates onto nitrogen sites through bonding with neighboring Ga atoms. Oxygen impinging onto nitrogen sites will only form single bonds to Ga in III-polar GaN films. However, in N-polar GaN films, oxygen impinging onto nitrogen sites will form three bonds to Ga atoms as shown in Figure 3.8. This leads to higher oxygen incorporation in N-polar GaN films.
The high residual oxygen donors can be compensated for through doping with Mg acceptors. However, it is difficult to obtain high p-type doping in InGaN due to the high activation energy of 0.2 eV for Mg acceptors\textsuperscript{71}. The reason for the high activation energy for Mg acceptors comes from the Mg-H complexes that form. Since H\textsubscript{2} is the carrier gas in the MOCVD process and typically getters at defects and dislocations, high defect densities may partially contribute to the low efficiency of activating Mg acceptors. Before Mg can act as an acceptor, the Mg-H complex bond must be broken. This can be achieved through annealing and low energy electron beam irradiation. But by mitigating defects and dislocations in InGaN, it may be possible to reduce the H impurity incorporation and thus increase the efficiency of activating Mg acceptors. Therefore, it is crucial to improve the crystal quality of InGaN to achieve higher p-type doping necessary for solar cells.

**Figure 3.8** | In the case of the III-polar surface, no screening of the single polar Ga-O bond leads to strong repulsion of oxygen (left), whereas in the case of the N-polar surface (right), the 3 bonds for oxygen to subsurface Ga leads to a screening of the repulsion forces and relaxation of oxygen into the lattice. Adapted from Ref [70].
Moreover, carbon acts as a deep acceptor that can compensate residual donors. An increase in carbon incorporation arises from the incomplete decomposition of NH₃ in which the hydrogen radicals are needed to react and remove methyl groups from the surface by converting it to methane.

3.2.3 Growth of N-polar InGaN films

3.2.3.1 Advantages of N-polar growth to produce thick InGaN

The N-polar orientation offers several advantages that make it attractive for high-quality growth of InGaN layers. First, N-polar InGaN can be grown at higher temperatures due to the higher stability of InN in the N-polar direction. The higher stability of indium on the N-polar face comes from the difference in bonding between the N-polar and III-polar surface, where indium adatoms on the N-polar surface can be more effectively trapped at the step-edges due to the number of available bonds, where in the case on the III-polar surface, indium can bond at the terraces, leading to 2D island growth which gives more time for indium to be replaced by gallium. This allows higher indium incorporation at elevated growth temperatures which is necessary to improve the structural quality of the III-nitride film. Therefore, improved material quality with higher indium fractions is achievable in N-polar InGaN in comparison to the III-polar growth. In InGaN, there are differences in the available dangling bonds for group-III metal incorporation between III-polar and N-polar surface. Such difference can enhance the adatom mobility and influence growth kinetics. As observed in N-polar growth of InGaN, as seen in Figure 3.9.b, the number of dangling bond at the surface is less than that at the step-edges. This enhances the indium adatom’s mobility; incorporating at the step-edges. As a result, promotion of
step flow growth and smooth surfaces can be achieved for N-polar growth. Furthermore, incorporation of indium adatoms at the step edges increases the incorporation of indium in the film, particularly when the growth rate is increased.

**Figure 3.9** | Schematic proposed for the incorporation of indium into InGaN on (a) III-polar and N-polar surface. Ref [73].

Second, the direction of the polarization field in N-polar InGaN is reversed from that of III-polar InGaN. The strength of this polarization field increases with indium content in InGaN. Presence of high polarization fields across the active regions in the III-polar growth direction can dramatically reduce carrier collection and degrade solar cell efficiencies. The growth in the N-polar direction allows higher efficiencies to be obtainable in solar cell devices due to the enhancement of the electric field. Lastly, with the differences
in surface energetics in N-polar InGaN, suppression of structural defects, such as V-pits, that inhibit the growth of thick layers is possible. Therefore, the growth in the N-polar direction provides a route to reduce defect densities and therefore enable thick InGaN layers for solar energy conversion.

3.2.3.2 Mitigating hexagonal hillocks in N-polar GaN

Studies on the growth stress evolution of thick N-polar InGaN films have not been reported in the literature. This is largely due to the absence of high-quality N-polar GaN base-layers for N-polar InGaN growth. N-polar GaN films grown by MOCVD typically exhibits a high density of hexagonal hillocks that originate from inversion domains (Figure 3.10.a). These hillocks arise due to the difference in growth rates between the III-polar and N-polar domains, where III-polar GaN grows faster (Figure 3.10.b)\textsuperscript{29}. This is attributed to the difference in nucleation sites that facilitates adatom diffusion. During III-polar GaN growth, the Ga-Ga bonds on the terraces are weak. This results in Ga adatoms desorption.

![Figure 3.10](image.png)

**Figure 3.10** | Differential interference contrast (DIC) optical micrograph of homoepitaxial MOCVD grown N-polar GaN exhibiting a high density of hexagonal hillocks (a) and a cross-section TEM (b) highlighting the inversion domain within the hexagonal hillock and in the N-polar GaN film. Ref [29].
at the terraces and transport to step-edges which results in smooth surfaces from the step flow growth. However, during N-polar GaN growth, the Ga-N bond at the terraces is rather strong. When Ga adatoms impinge on to the terraces, there is a higher activation barrier for desorption. This reduces the likelihood of Ga adatoms to be transported to the steps and results in an increase in the likelihood of multiple domains to nucleate on the terraces\textsuperscript{29}.

This low adatom surface mobility on the N-polar surface can be mitigated through the utilization of vicinal substrates. Increasing the misorientation of vicinal substrates allows for a higher density of micro-steps to be available. This promotes step flow growth and can suppress the formation of hexagonal hillocks. However, utilizing vicinal substrates gives rise to surface undulations and increased surface roughness. It has been shown that by using a two-step GaN temperature growth process, surface roughening \textit{via} step bunching as a result of GaN growth of vicinal substrates can be reduced\textsuperscript{74}. 
3.3 Focus of This Study

This chapter explores the growth of thick InGaN films on III-polar and N-polar GaN base-layers, to investigate the effect of polarity on the structural quality, surface morphology and optical properties of the MOCVD grown films. Our results demonstrate thick N-polar InGaN films with improved structural and morphological quality compared to III-polar layers thereby providing an alternative route to the fabrication of thick InGaN films for potential use in photovoltaics and strain reducing schemes for deep-green and red emitters.

Furthermore, it is well known that during heteroepitaxial growth of InGaN, the magnitude of the strain-induced piezoelectric polarization is rather large\textsuperscript{75}. Understanding stress evolution in thick InGaN layers grown on GaN base layers is essential given the sensitivity of the piezoelectric polarization fields to the indium content and strain state of GaN. Though few studies employing \textit{in situ} measurements during the growth of III-polar InGaN films have been reported\textsuperscript{62,76-78}, the majority of studies investing the growth stress evolution in InGaN have, however, concentrated on the use of \textit{ex situ} characterization techniques. The use of \textit{in situ} stress measurements, provides significant insight into the relation between indium incorporation, morphological evolution and defect formation in thick III-polar and N-polar InGaN films that is unattainable using \textit{ex situ} characterization techniques alone. Therefore, this chapter also present a comparison study on the evolution of stress in InGaN films grown by MOCVD, with emphasis on the heteroepitaxy of thick layers of N-polar InGaN on optimized N-polar GaN base layers grown \textit{via} a two-step temperature growth process. The two-step temperature growth process consists of an initial low temperature layer followed by a thick main high temperature layer of N-polar GaN.
The impact of changing the growth temperature of the initial layer in the two-step growth process for N-polar GaN on the final stress state of the GaN base layer, and the incremental growth stress and optical properties in the sequentially grown N-polar InGaN film was investigated. To further investigate the optical properties of InGaN films, both steady state and time-resolved cathodoluminescence (TRCL) mapping of the III-polar and N-polar films were performed at room and liquid helium temperatures.
3.4 Experimental Procedure

3.4.1 MOCVD growth conditions for III-polar and N-polar InGaN on SiC

MOCVD growths were carried out in a customized vertical cold-wall reactor with a rotating (60 rpm) induction heated SiC-coated graphite susceptor, where the temperature was monitored using a thermocouple. The precursors used during growth were trimethylgallium (TMGa), trimethylaluminum (TMAI), trimethylindium (TMIn) and ultrahigh purity NH$_3$. Here, n-type SiC (4H and 6H polytypes) from Cree was chosen as the supporting substrate for the growth of thick III-polar and N-polar InGaN films. In contrast to conventional sapphire substrates, both III-polar and N-polar films can be obtained respectively on the Si-face and C-face of SiC without the need for pre-growth nitridation or polarity inversion schemes$^{79-81}$. Thick films (140 nm) of III-polar and N-polar InGaN were grown under identical conditions of temperature (780°C), reactor pressure (300 Torr) and V/III ratio (2449.5) on respective III-polar and N-polar GaN base layers. Though H$_2$ was used as the carrier gas to transport TMGa (3.039 μmol/min) and TMIn (6.074 μmol/min), the growth environment of InGaN was in N$_2$ and NH$_3$ (22.321 mmol/min). For III-polar InGaN growth, 90 nm of AlN (TMAI = 13.799 μmol/min, NH$_3$ = 89.286 mmol/min - V/III ratio: 6470) was initially grown on the Si-face of (0001) 6H-SiC at 1100°C and 100 Torr, followed by ~1 μm GaN (TMGa = 7.934 μmol/min, NH$_3$ = 62.500 mmol/min - V/III ratio: 7877) grown at 1100°C and 100 Torr. H$_2$ was used as the carrier gas for AlN and GaN growth.

In the case of N-polar InGaN, films were grown n-type vicinal C-face 4H-SiC substrates, misoriented in the <10\overline{1}0> direction from the (000\overline{1}) by 4°. First 30 nm of AlN
(TMAI = 5.520 μmol/min, NH₃ = 89.286 mmol/min - V/III: 16176) was initially grown at 1150°C under 100 Torr followed by the N-polar GaN base layer grown via a two-step temperature growth process. The use of vicinal substrates and high V/III ratio for AlN promotes step-flow growth, as it increased the probability of group-III adatoms to reach the SiC step-edges, reducing adatom clustering within the terrace regions and thereby inhibiting the formation of hexagonal hillocks²³,³⁰-³². Reducing the density of hexagonal hillocks improves the crystallinity in the successive GaN base layer. The two-step temperature growth process of N-polar GaN consisted of an initial 140 nm N-polar GaN layer (TMGa = 7.934 μmol/min, NH₃ = 35.714 mmol/min - V/III: 3846.4) grown at 900°C and 100 Torr on AlN. This was followed by a main 960 nm high temperature N-polar GaN layer (TMGa = 9.285 μmol/min, NH₃ = 35.714 mmol/min - V/III: 4501.1) grown at 1100°C and 100 Torr. H₂ was used as the carrier gas for AlN and GaN growth. In subsequent studies, the temperature of the initial layer was varied between 875°C and 925°C. Using a two-step temperature growth process for N-polar GaN, smooth films with RMS roughness of 1.3 nm over a 20 μm x 20 μm area were obtained.

3.4.2 Experimental step-up for in situ stress measurements

To monitor the stress evolution in the films, a k-Space Associates (kSA) multi-beam optical stress sensor (MOS) was employed for in situ measurements of the films during the growth process. The MOS system is based on laser reflectance and is used to monitor differential changes in the wafer curvature⁸². As illustrated in Figure 3.11, this is achieved from the array of laser spots that are reflected off of the growing film surface, where the differential change ∆ = δd/d₀ of the spacing (d) between laser spots corresponds to a change in the curvature in the sample. This differential change can be
related to a film stress ($\sigma_f$) × film thickness ($h_f$) product using a modified version of Stoney’s equation\textsuperscript{83}:

$$\sigma_f h_f = \left[ \frac{d d_0}{12 L} \right] \frac{\delta d (M_s h_s^2 \cos \theta)}{h_s} \quad \text{Eq. 4.5}$$

where ($\theta$) is the incident angle of the reflected laser beams, ($L$) is the distance between the substrate and CCD camera, ($M_s$) is the biaxial modulus of the substrate and ($h_s$) is its thickness. The film thickness $h_f$ is determined from simultaneously collected oscillations in laser reflectance that results from Fabry–Perot constructive and destructive interferences during film growth which can also provide real-time monitoring of the morphological evolution and surface roughness of the films.

**Figure 3.11** | A schematic of the experimental set-up of a multi-beam optical stress sensor (MOS) for in situ curvature and reflectivity measurements (left) during MOCVD growth of III-polar and N-polar heterostructures (right).
3.4.3 Post MOCVD growth microstructural and surface characterization

For microstructural analysis with transmission electron microscopy (TEM), cross-sectional specimens were first prepared using conventional manual thinning and argon ion milling procedures, then imaged with a JEOL 2010F field-emission TEM operated at 200 kV. For high-resolution imagining at the interface of epilayers, an FEI Titan aberration corrected TEM operating at 300 keV with a SuperX energy dispersive x-ray (EDX) detector for elemental mapping was utilized. Furthermore, high resolution X-ray diffraction (HR-XRD) measurements was used to investigate the crystal quality of the GaN base layer through the use of a Philips X’Pert PRO MRD four-circle diffractometer with a Cu Kα 0.15406 nm radiation source, while atomic force microscopy (AFM) in a Bruker Dimension 3100 system operated at a scan rate of 1.00 Hz was used to determine surface roughness.

3.4.4 Post MOCVD growth spectroscopic characterization

To investigate the composition, impurity levels and optical properties of the InGaN films, secondary ion mass spectroscopy (SIMS), Raman spectroscopy, photoluminescence (PL) and cathodoluminescence (CL) measurements were utilized. SIMS measurements and analysis were performed by EAG Laboratories services.

- A few notes on SIMS measurements for impurity level detection in III-polar films:

  I. C and Si are considered real throughout the epilayers profiled.

  II. H in the depth ~150-980 nm is considered detection limit for the analysis.
III. O is the depth ~150-860 is considered at a high background due to high concentration/contamination < 150nm.

IV. Detection limits in GaN (in atoms/cc): H \( \sim 5 \times 10^{17} \), C \( \sim 0.8-1 \times 10^{16} \), O \( \sim 1 \times 10^{16} \), and Si \( \sim 1 \times 10^{16} \).

- A few notes on SIMS measurements for impurity level detection in N-polar films:

I. C was affected by surface contamination that lead to the tailing into the sample. This contamination likely raised the background of C as well.

II. H is considered real <~130nm in depth. >130nm it is at background levels (although they are slightly higher than expected, likely due to high H preceding that depth).

III. O and Si are considered real throughout the sample.

IV. Detection limits in GaN (in atoms/cc): H \( \sim 0.1-1 \times 10^{18} \), C \( \sim 1-2 \times 10^{16} \), O \( \sim 1 \times 10^{16} \), and Si \( \sim 1 \times 10^{16} \).

Furthermore, Raman spectroscopy was performed over a 10 µm x 10 µm area, on the InGaN films with a 325 nm laser (Horiba-LabRAM: 2400 g×mm\(^{-1}\) grating) operated at 4 mW power density, 500 µm confocal hole and 40x NUV objective at room temperature. Furthermore, room temperature band-edge emission in the InGaN samples was investigated using PL measurements with a 266 nm wavelength (4th harmonic of the Nd:YAG 1064 nm output), 100 Hz pulsed laser excitation source with < 10 mW average power.
Moreover, electron excitation with CL-SEM allows one to probe a variety of semiconductors over a wide spectral range which is typically difficult to achieve with laser excitation (i.e. photon) by conventional optical means. The combination of picosecond spectroscopy with SEM enables to correlate detailed study of carrier dynamics to the surface morphology. Therefore, this technique was utilized to study the impact of V-pits and hexagonal hillocks in III-polar and N-polar InGaN, respectively, on the carrier dynamics and thus the generated photoemission. Therefore, spatially and time resolved CL measurements were carried out at Attolight in École Polytechnique Fédérale de Lausanne on a Alalin Chronos 4027 CL-scanning electron microscope at an acceleration voltage of 6 kV. Both room temperature (298 K) and liquid helium temperature (13 K) measurements were performed. Time-resolved CL (TRCL) measurements were also performed with a ~1 ps electron pulsed excitation source at repetition rate of 80 MHz. This excitation source was generated by illuminating a 20 nm thick gold photocathode deposited on a quartz plate using a 266 nm ultraviolet mode-lock laser at 200 fs and 80.7 MHz repetition rate. The collected CL signal was evaluated with a Jobin-Yvon (iHR320) spectrometer with a Synapse CCD camera and a Hamamatsu streak camera synchronized with the electron pulses. The slits and diffraction grating of the CL system were set at 2000 μm and (600/300 and 150/500) lines/mm, respectively. Light emission was recorded at center peak emissions between 370 nm to 500 nm.

The spatial and temporal resolutions of the TRCL system was 50 nm and 30 ps. Several factors control the spatial resolution in CL measurements. These factors include the interaction volume of the electron beam, the probe size and the diffusion length of free carriers in the sample. However, the spatial CL resolution is predominantly determined by
the interaction volume that is controlled by the applied accelerating voltage. This gives CL the advantage of probing different depths of the film to which can be modeled using Monte Carlo simulations. Furthermore, the field of view (FOV) of the coupled SEM was 300 μm with a spatial resolution of 10 nm using a 0.71 (f/0.5) numerical optical aperture. The working distance used for all measurements was ~ 3 mm and the probe emission and EH current of 105 μÅ and 10 μÅ, was respectively used.

In TRCL measurements at room temperature, the effective decay time ($\tau_{CL}$) is defined by both the radiative ($\tau_R$) and nonradiative ($\tau_{NR}$) components of the carrier lifetime:

$$\tau_{CL} = (\tau_R - 1 + \tau_{NR} - 1) - 1 \quad \text{Eq. 4.6}$$

When the temperature of the sample is at liquid helium temperatures, the nonradiative component of the lifetime becomes so long that effectively the $\tau_{CL} = \tau_R$, granted that the transient is a single exponential. Furthermore, TRCL at cryogenic temperatures reduces the widths of emission lines and therefore reduces overlap between different peaks associated with different optical processes. Therefore, measurements at liquid helium temperatures allows the ease of distinguishing between different spectral lines associated with various localized states. Moreover, low temperature TRCL reduces carrier diffusion across the sample and consequently, the carrier dynamics in the sample can be measured locally within the spatial resolution of the SEM.
3.5 Results and Discussion

3.5.1 Investigating the effect of polarity on the incorporation of indium and structural quality of thick InGaN

The growth structures used to realize high quality III-polar and N-polar GaN base layers for the sequential growth of thick InGaN are outlined in Figure 3.12.a. For III-polar InGaN, a III-polar GaN base layer grown on SiC with an AlN buffer layer was utilized. In the case of N-polar InGaN, the use of a two-step temperature growth process was necessary in order to produce N-polar GaN base layers with comparable structural quality to that of III-polar GaN for sequential N-polar InGaN growth. From high-resolution x-ray diffraction (XRD) measurements (Figure 3.12.b), a higher incorporation of indium in N-polar InGaN is observed. This is evident from the down shift of the (000\(\bar{2}\)) reflection of InGaN with respect to the (0002) reflection of III-polar InGaN. Since the N-polar films are grown on a vicinal substrate, N-polar InGaN is susceptible to triclinic deformation\(^85\). As a result, SIMS was performed to determine the indium content in the layer. From SIMS, the initial indium content near the InGaN/GaN interface was \(\sim\)11\%, which gradually increased to \(\sim\)15\% with increasing thickness (an average indium content of \(\sim\)13\%). Generally, compositional instabilities commonly reported in InGaN are not only dictated by the miscibility-gap, but also by the strain state of the film\(^86\)\(^-\)\(^88\). This gradual up-climb of indium observed in our layers has been attributed to compressive stress relaxation, referred to as “compositional-pulling”\(^89\). In the case of the III-polar InGaN, the indium content was determined from XRD\(^90\) (outlined by Morales et al. in Ref [90]). We find that the average indium content in III-polar InGaN was \(\sim\)7.5\%, however, a slight asymmetry in the (0002) reflection of InGaN is observed (Figure 3.12.b). This asymmetry is indicative of compositional inhomogeneity.
Furthermore, the overall reciprocal space map (RSM) around the asymmetric [10\bar{1}5] reflections of III-polar and N-polar InGaN (Figure 3.12.c-d), shows only a small amount of relaxation in the layers. The vertical broadening in the RSM is suggestive of compositional change in indium, while horizontal broadening is indicative of partial strain relaxation\(^91\). The slight deviation towards lower reciprocal lattice values \((\mathbf{q}_z)\) in III-polar InGaN suggests some degree of relaxation, whereas in the RSM of N-polar InGaN, strain relaxation is more pronounced and an overall higher indium incorporation into the film is clearly observed.

Furthermore, x-ray rocking curve (XRC) measurements were performed to assess the crystal quality of these GaN base layers and the sequential grown InGaN. From the XRC of the symmetric [0002] reflections, the full-width-at-half-maximum (FWHM) of III-polar GaN was 309 arcsecond, while N-polar GaN had a FWHM of 531 arcsecond. For the XRC FWHM of the [10\bar{1}5] skew symmetric reflections, the III-polar and N-polar GaN base layers had a FWHM of 445 arcsecond and 532 arcsecond, respectively. Although the structural quality and surface roughness of the III-polar GaN base layer is better than that of the N-polar GaN base layer, the structural quality of the InGaN layers from XRC are rather comparable. From the XRC of the symmetric reflections for the respective InGaN film polarities, FWHM were both \(~486\) arcsec, indicating comparable levels of mosaic tilt. The XRC FWHM of the [10\bar{1}5] skew symmetric reflection, however, revealed lower extent of twist in N-polar InGaN. XRC FWHMs of 1236 arcsec and 946 arcsec were measured for III-polar and N-polar InGaN films, respectively. This reduction in the mosaic twist in N-polar InGaN may arise from the absence of V-pits and the use of vicinal SiC\(^92\).
From AFM measurements, a significant improvement in the surface morphology is observed for N-polar InGaN in comparison to III-polar InGaN. Clearly visible, in Figure 3.13.a, are V-pits on the surface of III-polar InGaN, which exhibits an RMS roughness of 2.3 nm. The N-polar InGaN films grown on the N-polar GaN base-layers are free of hexagonal hillocks and show an RMS roughness of 0.7 nm (Figure 3.13.b). This improvement in the surface morphology partially arises from the absence of morphological
defects (hillocks and V-pits) as well as potential differences in the growth mode between the two polarities. The undulations that appear in the N-polar InGaN surface in Figure 3.13.b are a result of the compressive stress induced step-bunching from the underlying GaN base-layer. Within the N-polar GaN base-layer, these steps increase the probability of gallium adatoms reaching the step-edges which reduces gallium clustering on the terrace, thereby inhibiting the formation of hexagonal hillocks and promoting step-flow growth. While atomic steps help promote step-flow growth in InGaN, excessive bunching of these steps is not desired. The influence of step-bunching, particularly on the surface roughness of the N-polar films, is controlled by optimizing the growth temperature of the initial layer in the two-step temperature growth process of the N-polar GaN base-layer, which is discussed in the following section.

**Figure 3.13** | Comparison of the surface morphology of III-polar (a) and N-polar (b) InGaN, revealing an RMS roughness of 2.3 nm and 0.7 nm, respectively, over a 2 µm × 2 µm area. The scale bars are 500 nm.
3.5.2 The evolution of stress during the growth of III-polar and N-polar InGaN

*In situ* stress measurements provide significant insight during the growth of thin films. A comparison of the overall reflectivity and curvature data collected *in situ* using MOS during the growth of the III-polar and N-polar films are illustrated in Figure 3.14.a-b. Evident from the reflectivity data is the constant growth rate for both III-polar and N-polar InGaN layers which were measured to be 85 nm/hour (growth rate calculations discussed in section 2.1.3 of chapter 2). The growth rates for the GaN base layers, however, different due to the variances in the V/III ratio used to optimize the respective film polarities. In the case of III-polar GaN (Figure 3.14.a, the growth rate was 0.45 nm/second, providing a base layer with an RMS roughness of ~0.70 nm. In the case of the N-polar GaN base layers grown *via* the two-step temperature growth process (Figure 3.14.b), the growth rate for the initial low temperature layer was 0.19 nm/second, while the growth rate of the high temperature layer was 0.40 nm/second. The RMS roughness of the N-polar GaN base layers were ~1.3 nm.

![Figure 3.14](image)

**Figure 3.14** | A comparison of the overall reflectivity and curvature data collected *in situ* using MOS during the growth of the III-polar (a) and N-polar (b) InGaN/GaN/AlN films on the Si-face and C-face of 6H-SiC, respectively.
The most prominent difference in the III-polar and N-polar heterostructures are the variances in the overall curvature of each respective layer. As a general rule, compressive (tensile) film stress causes convex (concave) substrate bowing, i.e. negative (positive) curvature values. The bowing of the substrate that results from the lattice mismatch between the group-III nitride layers and SiC at the growth temperature leads to the overall observed compressive stress in the layers. Comparing the two heterostructures, it is clear that for both the III-polar and N-polar films, a constant accumulation of compressive stress is occurring with thickness due to the continual decrease in the curvature from the start of growth. Based on the changes in curvature for the III-polar film, the 90 nm layer of AlN first initiates growth on SiC under compressive stress that begins to relax prior to the deposition of the III-polar GaN layer, which also grew under compressive stress that slightly relaxes with thickness. Similarly, in the N-polar heterostructure, 30 nm of AlN grows under compressive stress with slight relaxation as well. However, during the two-step temperature growth process of N-polar GaN, the low temperature layer initially grows under compressive stress but considerably relaxes before the growth of the main high temperature GaN layer which is nearly stress free before N-polar InGaN growth. Under these conditions for N-polar GaN, the two-step temperature growth process intentionally increases the wafer bow (concave) before N-polar InGaN growth.

Figure 3.15 compares the stress-thickness product as a function of layer thickness for the III-polar and N-polar InGaN films, calculated from the curvature data using a modified version of Stoney’s Equation. The slope of the stress-thickness vs. thickness curve provides the incremental growth stress in the film. Evident are significant differences in the evolution of growth stress in the respective film polarities. The III-polar InGaN layer
grew under a constant compressive stress of -3.87 GPa on a compressively strained GaN base layer. In the case of N-polar InGaN, the layer grew initially under a low stress value of +0.972 GPa for ~20-30 nm on a low stress N-polar GaN base layer (+0.04 GPa). The low incremental stress transitioned to a compressive stress of -6.27 GPa that was relatively constant throughout the remainder of the layer growth. The larger magnitude of the constant compressive stress observed in N-polar InGaN (-6.27 GPa) compared to III-polar InGaN (-3.87 GPa) arises from the enhanced indium incorporation in the N-polar epilayer.

As discussed in the previous section, the indium content for III-polar InGaN determined by XRD was ~7.5%, while in N-polar InGaN, the average indium content, determined using secondary ion mass spectroscopy (SIMS), was ~13%. SIMS was used to measure the

Figure 3.15 | Stress-thickness versus thickness curves collected during the growth of III-polar (top-blue) and N-polar (bottom-red) InGaN with in situ stress measurements. The slopes of the dashed black lines are the extracted layer incremental stress values.
indium content in N-polar InGaN layers as a result of the susceptibility of the films to deformation due to use of high degree miscut substrates that can obscure lattice parameter measurements by XRD\textsuperscript{85,90}. As illustrated in Table 3.1, the magnitude of the constant incremental compressive stress measured \textit{in situ} during III-polar and N-polar InGaN growth correlates well with the predicted epitaxial misfit stress at the growth temperature for the different compositions of InGaN, where the high temperature elastic constants for GaN and InN used in these calculations were extracted from prior literature\textsuperscript{94,95}. As seen in Table 3.1, with the exception of the initial region of low stress for N-polar InGaN, these results indicate that there is no appreciable relaxation of the compressive epitaxial growth stress in the InGaN layers for both the III-polar and N-polar films.

<table>
<thead>
<tr>
<th>Polarity of InGaN</th>
<th>Indium content</th>
<th>Film growth stress at growth temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated theoretical misfit stress</td>
</tr>
<tr>
<td>III-polar</td>
<td>~ 7.5% (XRD)</td>
<td>-3.54 GPa</td>
</tr>
<tr>
<td>N-polar</td>
<td>~ 13% (SIMS)</td>
<td>-6.00 GPa</td>
</tr>
</tbody>
</table>

\textbf{Table 3.1} | The magnitudes of the constant incremental stress measured \textit{in situ} during III-polar and N-polar InGaN growth and the predicted epitaxial misfit stress at the growth temperature for the respective film polarity compositions.

It has been reported that the indium-induced changes in the surface energetics leads to the stabilization of the (10\overline{1}1) facets of V-pits at the apex of threading dislocation\textsuperscript{24}. The formation of these V-pits in III-polar InGaN, as seen in the AFM of Figure 3.13.a, has been reported to result from elastic stress relaxation\textsuperscript{19}. In fact, Won et al. investigated the effect
of indium surfactant on stress relaxation in III-polar GaN layers and found that not only does indium promote step flow growth, but with increasing indium, the (10\bar{1}1) facets of V-pits are stabilized and the incremental compressive stress of the layers is reduced\textsuperscript{96}. Though V-pits were suggested to be a mechanism of elastic relaxation of thick III-polar InGaN, the constant incremental stress observed from \textit{in situ} measurements (Figure 3.15) indicates that any relaxation of compressive stress that occurs during growth is relatively small and below the sensitivity of the measurement technique. In the case of N-polar InGaN, energy calculations have shown that these (10\bar{1}1) facets on the (000\bar{1}) surface of InGaN are not energetically favorable to form\textsuperscript{24}. If V-pits are reduced however, such as in the case of N-polar growth, it can be hypothesized that plastic relaxation should become more pronounced during epitaxy of InGaN/GaN heterostructures. Consequently, the appearance of the layer of initial low stress in N-polar InGaN may be indicative that the formation energy for plastic relaxation in InGaN is indeed reduced in the absence of V-pits. This is similar to the reported formation of misfit dislocations \textit{via} slip in the absence of TDs at the interface of III-polar InGaN grown \textit{on} epitaxial lateral overgrown GaN (ELOG)\textsuperscript{57}. Therefore, differences in the stress evolution observed from \textit{in situ} measurements are likely to originate from the type and density of defects within the epilayers.

### 3.5.3 Examining the impact of polarity on the microstructure of InGaN using TEM

We investigate the microstructure of InGaN from cross-section specimens in an aberration-corrected scanning TEM (STEM, 300 kV), with a SuperX energy dispersive x-ray (EDX) detector. Evident from the high-angle annular dark field (HAADF) STEM image in the III-polar InGaN film (Figure 3.16.a) is the extensive formation of V-pits at the apex of TDs. These V-pits form ~50 nm from the III-polar InGaN/GaN interface. The
growth of high indium content III-polar InGaN beyond pseudomorphic thicknesses leads to large compressive misfit stress at the InGaN/GaN interface\textsuperscript{97}. This misfit stress is partially elastically relaxed by the formation of V-pits\textsuperscript{19}, and an increase in indium content in the film with thickness is reported to occur upon relaxation of the compressive stress via the “compositional-pulling” effect\textsuperscript{96}. An increase in the indium content of the film reduces the formation energy of V-pits by stabilizing (10\overline{1}1) facets. In Figure 3.16.b, our EDX map of the III-polar InGaN film reveals an accumulation of indium near the (10\overline{1}1) facets of the V-pits and compositional inhomogeneity within the bulk of the film, seen in the overlaid indium elemental line scan, \~50 nm from the III-polar InGaN/GaN interface. The compositional fluctuations in the III-polar InGaN film may be an effect of partial stress relaxation as observed in the RSM (Figure 3.12.c)\textsuperscript{62}.

Stress relaxation during heteroepitaxy of thick InGaN, in general, is not well understood. This is because, plastic relaxation via the formation of misfit dislocation by glide along available slip planes, is kinetically limited at typical MOCVD growth temperatures for InGaN. Therefore elastic relaxation, such as the formation of V-pits, tends to dominate with increasing indium content in the film\textsuperscript{19}. V-pits are, however, absent in the cross-section of N-polar InGaN, and even at the apex of TDs propagating from the GaN base-layer (Figure 3.16.c). In addition, the EDX map (Figure 3.16.d) confirms a higher incorporation of indium in the N-polar film. The results from EDX are consistent with our observation from the RSM in Figures 3.12.c-d. For both polarity cases, we find in EDX a gradual increase in indium with increasing layer thickness. This observation is more pronounced in N-polar InGaN due to the lack of lateral compositional variations across the
Figure 3.16 | HAADF STEM images (top) and corresponding EDX maps (bottom, with overlaid % indium line scans) of III-polar (a-b) and N-polar InGaN/GaN (c-d). The arrow in (c) is highlighting the propagation of a TD from the GaN base layer into InGaN. The scale bar is 100 nm.
cross-section specimen. A gradual increase in indium with thickness as seen in our EDX and SIMS results has previously been attributed to the compositional-pulling effect\cite{89}, although our results from RSM and \textit{in situ} stress measurements do not show significant compressive stress relaxation in the InGaN. Further studies are needed to unambiguously identify the origin of the thickness variation of the indium content.

We also performed cross-section TEM of the N-polar InGaN films under different imaging conditions to assess the dislocation microstructure in the epilayers (Figure 3.17). In Figure 3.17.a, micrographs were collected with multi-beam diffraction condition near the GaN $\langle 1\bar{1}00 \rangle$ zone axis to reveal all types of TDs, while Figures 3.17.b and 3.17.c are weak beam dark field micrographs collected within the same region using $g = \langle 0002 \rangle$ and $g = \langle 1\bar{1}20 \rangle$ diffraction conditions, respectively. Under $g = \langle 0002 \rangle$ pure screw (c type) and mixed (a+c type) dislocations are visible, where $g = \langle 1\bar{1}20 \rangle$ reveals dislocations with a pure edge (a type) component in addition to mixed (a+c type) dislocations. In the N-polar films, dislocations were predominantly mixed (a+c type) with a small number of dislocations with a pure edge component. These TDs are mostly annihilated in the initial low temperature layer of N-polar GaN (Figure 3.18.c) which significantly reduces the overall TDs that propagate into the N-polar InGaN film. Consequently, relaxation of the misfit stress observed from \textit{in situ} curvature measurements of N-polar GaN (Figure 3.14.b) occurs mostly in the initial low temperature layer via the formation of dislocation loops and annihilation of TDs through their interactions with stacking faults\cite{33}. Moreover, the dislocation microstructure in the main high temperature N-polar GaN layer exhibits TDs with low inclination angles (Figure 3.18.c). The inclination of TDs is a mechanism of compressive stress relaxation in many group-III nitride epilayers,\cite{63} such as in the case of
**Figure 3.17** | TEM analysis of the N-polar InGaN dislocation microstructure on an N-polar GaN base layer grown via the two-step temperature growth process on N-polar AlN/C-face 6H-SiC substrate: (a) micrograph collected using a multi-beam diffraction condition near the N-polar GaN $<1\overline{1}00>$ zone axis to reveal all types of TDs. (b-c) weak beam dark field micrograph collected in the same region as (a) using diffraction conditions $g = <0002>$ (b) and $g = <1\overline{1}20>$ (c). (d) weak beam dark field micrograph revealing a region of bright contrast near the N-polar InGaN/GaN interface. (e) high resolution TEM image of an edge type dislocations running parallel to the basal plane N-polar InGaN/GaN interface.
high TD density AlGaN where the inclination of these TDs is assisted by an effective dislocation climb process directed out of specific glide planes. The inclination of TDs is also the source of partial compressive stress relaxation observed in the III-polar GaN base layer (Figure 3.18.a). Though most TDs that end up propagating from the N-polar GaN base layer into N-polar InGaN show little to no deflection nor change in their inclination angles, their overall density in N-polar InGaN is relatively low and therefore should not significantly contribute to relaxation of the initial low stress layer observed from in situ stress measurements. Such observations are similar to the growth of thick AlGaN epilayers, where films can be grown pseudomorphically on bulk AlN substrates with thickness values exceeding the Matthew and Blakeslee model.

The difficulty of relaxing compressive stress during the heteroepitaxy of AlGaN on bulk AlN may be reconciled by the low density of preexisting TDs in bulk AlN, where typically their propagation and inclination are mechanisms of stress relaxation. Therefore, it is suspected that the lack of significant relaxation of compressive stress in both III-polar and N-polar InGaN films (i.e. the layers of constant incremental stress in Figure 3.15 is due to the overall lower density of TDs in the layers. In the case of N-polar InGaN, however, the subsequent larger build-up in strain energy as a consequence of the higher misfit stress compared to III-polar InGaN (due to the enhanced incorporation of indium, Table 3.1) perhaps is partially relieved via plastic relaxation near the InGaN/GaN interface.

In fact, weak beam TEM near the N-polar InGaN/GaN interface revealed a region of bright contrast (Figure 3.17.d and 3.18.c). The thickness of this region of bright contrast aligns well with the layer of initial low stress observed from in situ stress measurements. This region of bright contrast indicates the presence of defects and local differences in
strain which is supported by high resolution TEM (HR-TEM, Figure 3.17.e) at the interface. From HR-TEM, no regular array of misfit dislocations was observed, however, edge type dislocations running parallel to the basal plane were located near the N-polar InGaN/GaN interface and corroborates with the initial low temperature layer seen from in situ stress measurements. These defects have been reported to nucleate from the step edges when high degree miscut substrates are utilized\textsuperscript{102}, however, further studies are needed to identify the origin of these dislocations.

**Figure 3.18** | Additional TEM analysis of the III-polar InGaN (a-b) and N-polar InGaN (c) dislocation microstructure using weak beam dark field mode.
3.5.4 Comparison studies on the optical properties of III-polar and N-polar InGaN

3.5.4.1 Raman and photoluminescence measurements with UV excitation sources

UV-Raman was performed, over a 10 µm x 10 µm area, on the InGaN films with a 325 nm laser (Horiba-LabRAM: 2400 gr×mm−1 grating) and room-temperature macrophotoluminescence (macro-PL) measurements using a 266 nm laser. Figure 3.19.a shows the E2(high) and A1(LO) spectra for III-polar and N-polar InGaN. Though all spectra are red-shifted towards the E2(high) and A1(LO) of bulk InN103 and exhibit a low frequency shoulder, this shift is larger in the case of N-polar InGaN. The Raman positions for the E2(high) and A1(LO) modes of III-polar and N-polar InGaN after peak deconvolution are listed in Table 3.2. The asymmetric broadening of the E2(high) and A1(LO) modes in InGaN has been attributed to compositional gradient and inhomogeneity104-106 as well as regions with distinct strain states within the film107.

In fact, from macro-PL measurements of the III-polar and N-polar films (Figure 3.19.b), we find two distinct peak emissions: one peak originating from a lower indium content region (III-polar peak-(i) at 424.7 nm and N-polar peak-(iii) at 432.0 nm) and the other from a higher indium content region (III-polar peak-(ii) at 439.5 nm and N-polar peak-(iv) at 451.6 nm). In the case of the III-polar InGaN film, the region surrounding the V-pits (ii) likely contributes to the observed peak emission at 439.5 nm as a result of the high accumulation of indium and the peak at 424.7 nm originates from the bulk of the layer (i). In the case of the N-polar InGaN film, the absence of V-pits precludes lateral inhomogeneities as the source of the two emission peaks. The heteroepitaxy of InGaN beyond the critical thickness is commonly reported to result in the formation of two distinct
**Figure 3.19** | UV-Raman spectra, collected over a 10 µm x 10 µm area, of the $E_2$(high) and $A_1$(LO) phonon modes for III-polar and N-polar InGaN in (a). Raman peak deconvolution (Table 3.2) was performed using a Gaussian fitting function. Macro-PL spectra of III-polar (top blue) and N-polar (bottom red) InGaN films illustrating the near band edge emissions from different regions of the thick layers (b). The peak positions from (i-iv) are: 424.7 nm, 439.5 nm, 432.0 nm and 451.6 nm, respectively. The black dashed curves are deconvolution of major peaks in the respective macro-PL spectrum performed using a Gaussian fitting function.
regions with different strain states that can impact the optical properties of the film. Therefore, the peak originating from the region of lower indium content (iii) at 432.0 nm is likely to originate near the N-polar InGaN/GaN interface. This region is at a significantly different strain state than the bulk of the film which contains a higher fraction of indium resulting in a peak emission at (iv) 451.6 nm. Nonetheless, macro-PL further supports the enhancement in the incorporation of indium in N-polar InGaN. Interestingly, however, the separation between the peak emissions from region (iii) and region (iv) in N-polar InGaN is ~28% larger than that of region peak-(i) and region peak-(ii) from III-polar InGaN. This observation may arise from the observed differences in lateral and vertical variations in composition and/or strain within the respective film polarities.

<table>
<thead>
<tr>
<th>vibrational modes</th>
<th>III-polar InGaN</th>
<th>N-polar InGaN</th>
</tr>
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<tbody>
<tr>
<td>E₂(high)</td>
<td>565.11 cm⁻¹</td>
<td>563.94 cm⁻¹</td>
</tr>
<tr>
<td>E₂(high)</td>
<td>558.58 cm⁻¹</td>
<td>547.40 cm⁻¹</td>
</tr>
<tr>
<td>A₁(LO)</td>
<td>730.74 cm⁻¹</td>
<td>724.64 cm⁻¹</td>
</tr>
<tr>
<td>A₁(LO)</td>
<td>704.23 cm⁻¹</td>
<td>694.71 cm⁻¹</td>
</tr>
</tbody>
</table>

Table 3.2 | Raman shift positions after peak deconvolution of the E₂(high) and A₁(LO) phonon modes for the III-polar and N-polar InGaN spectra in Figure 3.19.a.

Evident in Figure 3.19.b is the higher photoemission intensity from the region of peak-(i) of III-polar InGaN in comparison to the region of peak-(i). As evident in cross-section STEM (Figure 3.16.a), the region associated with peak-(ii) is where V-pits reside. The accumulation of indium near these V-pits (Figure 3.20.a-b) may act as localization
centers for carriers\textsuperscript{108,110}. These centers prevent pathways for nonradiative recombination and thus increase the efficiency of radiative emission. In the absence of these indium rich clusters, such as in the case of our N-polar InGaN films, the macro-PL intensity from the region of peak-(\textit{iv}) is lower than the region of peak-(\textit{iii}). Moreover, the observed quenching of the overall luminescence in N-polar InGaN when compared to the III-polar film\textsuperscript{70,111}, arises from the enhanced incorporation of oxygen into the N-polar films\textsuperscript{69}. From SIMS analysis (Figure 3.21), the oxygen concentration in N-polar InGaN was $\sim 1.1 \times 10^{20}$ cm$^{-3}$.

\textbf{Figure 3.20} | Microstructure analysis of III-polar (a-d) and N-polar (e-f) InGaN with high angle annular dark field (HAADF) STEM (a, c and e) and corresponding EDX mapping of the intensity of indium distributed in the cross-section specimen (b, d and f). Clearly evident in the case of the III-polar InGaN cross-section specimen (a and c) is the accumulation of indium around the (10\overline{1}1) facets of the V-pits (b) and within the bulk of the layer (d). In the case of the N-polar InGaN films (e), the accumulation of indium within the layers is not observed in our EDX map (f). The scale bar in (a-f) are 50 nm.
Though the oxygen concentration in the III-polar InGaN film cannot be accurately obtained from SIMS due to the high density of V-pits, the oxygen concentration in the III-polar GaN base-layer was $\sim 3.2 \times 10^{16} \text{cm}^{-3}$, while in N-polar GaN, the oxygen concentration was $\sim 1.1 \times 10^{19} \text{cm}^{-3}$.

Figure 3.21 | SIMS depth profiles for (a) III-polar and (b) N-polar films. Note that only in the N-polar films are the concentration of indium correctly calibrated in these measurements. The indium content from SIMS for the III-polar films are not accurate and is shown in this plot only to distinguish the InGaN layer from GaN.
3.5.4.2 The effect of residual misfit stress on the optical properties of N-polar InGaN

To further investigate the stress evolution in thick N-polar InGaN films, the strain state of the N-polar GaN base layer was modified \textit{in situ} prior to InGaN growth. This was achieved by varying the growth temperature of the initial GaN layer during the two-step temperature growth process, while keeping the temperature of the main N-polar GaN layer constant at 1100°C. As shown in Figure 3.22.a, increasing the growth temperature of the initial layer from 875°C to 900°C resulted in the reduction of the incremental tensile stress in the main high temperature GaN layer from + 0.21 GPa to + 0.04 GPa, respectively. Further increase in the temperature of the initial layer to 925°C followed a transition of the stress state of the main high temperature layer from tension to compression, where the resulting magnitude of the incremental compressive stress was - 0.04 GPa. The increase in the observed compression in the main high temperature GaN layer with increasing initial layer temperature arises from the change in temperature between the initial and main GaN layers. The lattice mismatch between GaN and the 6H-SiC substrate with an AlN buffer layer leads to compressive stress. As the temperature difference between the initial low and main high temperature GaN layers increases, the tensile stress that is generated from a positive increase in curvature as the sample is ramped to the growth temperature of the main high temperature GaN layer (1100°C) partially offsets the compressive epitaxial stress. Consequently, increasing the temperature of the initial GaN layer (i.e. reducing the temperature change) leads to a reduction of the compensating tensile stress and as a result, the transition of the high temperature GaN layer from tensile to compressive stress occurs. Thus, the two-step temperature growth provides an effective route to strain engineer the base layer for InGaN growth.
Figure 3.22 | (a) Stress-thickness versus thickness curves highlighting the incremental stress in the main high temperature layer of N-polar GaN (1100°C) on different initial low temperature N-polar GaN layers that varied in growth temperature. The compressive stress in the N-polar InGaN layer increased with increasing growth temperature of the initial low temperature layer in N-polar GaN. It should be noted that the undulations observed in the stress-thickness versus thickness curves are artifacts of the measurement that result from small film thickness variations across the sample. (b) PL near band-edge emission from the N-polar InGaN/GaN heterostructures under different magnitudes of incremental stress. In the case of N-polar InGaN, two peak emissions are observed.
The evolution of stress in the sequentially grown thick N-polar InGaN on GaN base layers, where the initial GaN layer varied in temperature, showed similar stress-thickness vs. thickness behavior as was previously discussed. First, an initial low stress layer grew for ~30 nm which gradually transitioned to a layer of constant compressive stress throughout the remainder of the layer growth. The constant incremental stress in these layers, was however, influenced by the strain state of N-polar GaN. The constant compressive incremental stress in N-polar InGaN increased with increasing compression in the N-polar GaN (Figure 3.23). The magnitude of the constant incremental stress in N-polar InGaN was measured at - 6.10 GPa, - 6.37 GPa and - 6.82 GPa when a temperature of 875°C, 900°C and 925°C, respectively, was utilized for the growth of the initial low temperature N-polar GaN layer. What was also conspicuous in these samples is a blue shift in the wavelength of the PL spectra as the compressive stress increased in the N-polar InGaN. Evident in Figure 3.22.b are the near band-edge emissions from the N-polar GaN and InGaN layers. In the case of N-polar InGaN, two peak emissions are observed. As outlined in Section 3.5.4.1, the observation of two peaks in thick N-polar InGaN was attributed to the co-existence of two distinct regions with different strain states as a function of layer depth in the N-polar InGaN film. In each spectrum, the peak seen at shorter wavelengths (i.e. lower indium content) is likely to originate from the region of initial low stress near the N-polar InGaN/GaN interface, while the peak at longer wavelengths (i.e. higher indium content) is likely to arise from the thicker compressively strained InGaN layer on top of it. Two factors can contribute to the observed overall blue shift in the PL spectra with increasing incremental compressive stress in InGaN. The first factor is associated with the influence of compressive stress on the incorporation of indium. Yi et
al. investigated the incorporation efficiency of indium in 100 nm InGaN layers grown AlGaN templates by MOCVD and observed that the indium incorporation was reduced in compressively strained films\textsuperscript{112}. In our case, x-ray $2\theta - \omega$ measurements of the symmetric [0002] and asymmetric [10\(\overline{1}5\)] reflections of the N-polar InGaN films do not indicate any significant changes in the incorporation of indium, partially precluding this as the dominate factor in our PL observations. The factor that may contribute to the blue shift that is observed in PL is residual strain in the bulk of the N-polar InGaN film. This dependence of PL luminescence on applied biaxial strain has been reported in InGaN/GaN QWs using a pressure cell\textsuperscript{113}. Further investigation is, however, necessary to preclude the

Figure 3.23 | Stress-thickness versus thickness curves highlighting the incremental stress in the N-polar InGaN on different N-polar GaN base layers, where the initial low temperature N-polar GaN layers in the two-step temperature growth varied in growth temperature (875°C top-green, 900°C middle-blue and 925°C bottom-red).

al. investigated the incorporation efficiency of indium in 100 nm InGaN layers grown AlGaN templates by MOCVD and observed that the indium incorporation was reduced in compressively strained films\textsuperscript{112}. In our case, x-ray $2\theta - \omega$ measurements of the symmetric [0002] and asymmetric [10\(\overline{1}5\)] reflections of the N-polar InGaN films do not indicate any significant changes in the incorporation of indium, partially precluding this as the dominate factor in our PL observations. The factor that may contribute to the blue shift that is observed in PL is residual strain in the bulk of the N-polar InGaN film. This dependence of PL luminescence on applied biaxial strain has been reported in InGaN/GaN QWs using a pressure cell\textsuperscript{113}. Further investigation is, however, necessary to preclude the
influence of impurities and segregation of indium on the stress-dependent band edge PL signature observed in the films.

3.5.5 Spatio-time resolved cathodoluminescence studies of InGaN

Similar to photoluminescence (PL), cathodoluminescence (CL) is an optical spectroscopic technique. This process involves the creation of free electron-hole pairs with an electron beam instead of using lasers, the recombination of these electron-hole pairs and subsequent detection of the optical emission that results from this process. In this section, we combine the use of CL-SEM to spatially resolve the various optical transitions that occur in thick InGaN as a function of film polarity. Both room temperature (RT) and liquid helium temperature measurement were performed in order to provide an in-depth analysis of the spatial distribution of luminescence across the surface of III-polar and N-polar InGaN. We also investigate the concentration and distribution of morphological defects from SEM, such as V-pits, hexagonal hillocks and other defect structures that are created due to step-bunching and/or step-meandering induced from growth front instabilities. In addition, we combined our measurements with time resolved CL analysis in order to understand the different carrier transients that are involved in the optical process in pristine areas of the sample as well as on and in the vicinity of the aforementioned defects. The spatial and temporal resolution of our analysis provides insight on how the polarity of the InGaN films effects the surface recombination velocity and carrier diffusion length, but more importantly, the origin of the quenching of the luminescence in N-polar InGaN. This section is split into two parts. First, we will discuss results on III-polar InGaN and associated transients, then focus our discussion on N-polar InGaN and summarize.
3.5.5.1 CL continues-wave excitation of III-polar InGaN at RT and 13 K

The CL response in semiconductors arises from the spontaneous emission associated with specific energy transitions. These transitions result from the absorption of secondary electrons created by the high energy electron bombardment of the samples, i.e. an electron beam. In these studies, an accelerating voltage of 6 keV was utilized. When high energy electrons bombard the samples, a cascading effect of secondary electrons are created in the first few nanometers from the surface. The cascade of secondary electrons increase in number while decreasing in energy as they penetrate into the sample, depending on the accelerating voltage utilized. Therefore, this process creates a thin positively charged region near the surface and a thicker negatively charge region within the depth of the sample. At the final stages of the multiplication process of secondary electrons, the collisions that occur between the incident electrons and atoms leads to detachment of

![Integrated CL spectra of III-polar InGaN collected over 4.65 μm areas at room temperature (RT, red curve) and cryogenic temperature (13 Kelvin). The peak maximum for the spectra at RT and 13 K are positioned at 418.9 nm and 415.8 nm, respectively and were extracted using a Gaussian fit.](image)

**Figure 3.24** Integrated CL spectra of III-polar InGaN collected over 4.65 μm areas at room temperature (RT, red curve) and cryogenic temperature (13 Kelvin). The peak maximum for the spectra at RT and 13 K are positioned at 418.9 nm and 415.8 nm, respectively and were extracted using a Gaussian fit.
valence electrons and thus the generation of free electron-hole pairs that can recombine radiatively and non-radiatively via Shockley-Read-Hall and Auger recombination processes. Unlike PL, which only requires the bandgap energy for efficient photoemission, the incident electron energy required for efficient CL is several times that of the bandgap energy ($E_g$) of the semiconductor due to requirements of both energy and momentum conservation in the solid. This minimum threshold energy in the solid is described as the effective ionization energy ($E_{eff}$):

$$E_{eff} = 2.8 \times E_g + r(h\omega_r)$$

Eq. 4.7

where ($r$) is the average number of phonons per generated electron-hole pairs from the collision process (i.e. impact ionization) and ($h\omega_r$) is the highest-frequency zero-wave-vector phonon. Despite the number of studies on the optical properties of thick InGaN films using CL, comprehensive understanding of the recombination mechanisms in these alloys is far from complete and hence the in-depth analysis presented in this dissertation.

Clearly evident in the integrated spectrum of III-polar InGaN at RT (Figure 3.24) are multiple optical transitions that are occurring beyond the near band edge peak emission located at 418.9 nm (the broad band-tail highlighted with the black arrow). These optical transitions are less prominent in low temperatures measurements as seen in the spectra collected at 13 K (Figure 3.24). In addition, a blue shift in the CL near band edge emission for III-polar InGaN at 415.8 nm was detected. This blue shift in wavelength is likely to arise due to changes in the carrier dynamics in InGaN as a function of temperature. Similar observations have been reported extensively in the literature, specifically in low temperature PL measurements of InGaN/GaN quantum wells and is attributed to potential variations across the films due to an inhomogeneous distribution of indium. Such potential
fluctuations in the film leads to filling of band-tail localized states in III-polar InGaN and screening of the internal polarization fields that are strain driven\textsuperscript{115}.

To fully understand these effects in our thick III-polar InGaN films, we performed spatial examination of our samples. Local investigation of the optical properties of III-polar InGaN at room temperature is shown in Figure 3.25. Evident in the SEM image (Figure 3.25.a) is the high density of V-pits on the surface of III-polar InGaN and as discussed previously, these V-pits open up at the apex of threading dislocations that predominantly have either a mixed and/or pure edge component. Moreover, a few threading dislocations
with a pure screw component were observed from weak-beam TEM in our samples and therefore should be representative in the observed density of V-pits seen in the micrograph. The corresponding fully integrated CL spectrum at each spatial position in SEM is presented in the panchromatic CL intensity map in Figure 3.25.b and for visual clarity in the superimposed panchromatic CL + SEM image in Figure 3.25.c. Variations in the intensity of the photoemission across the sample can be seen from the panchromatic CL intensity map. In a few areas of the sample (dark purple colored regions), almost no light emission can be observed. From SEM, these areas of low luminescence seem to occur within large clusters of V-pits that may contain threading dislocations with a pure screw component that are known to impair radiative emission\textsuperscript{116}. In addition, when comparing the SEM image to the panchromatic CL intensity map, almost no luminescence is seen in the core of individual V-pits, however, most of the luminescence across the sample (green colored regions) appear to arise throughout the dense network of V-pits, where in the vicinity of the network of V-pits are also hot spots of high luminescence (yellow/orange colored regions).

As discussed previously, the large miscibility gap between InN and GaN leads to InGaN films with compositional inhomogeneity and therefore potential fluctuations should be immensely present in these films. In general, such potential fluctuations observed in alloys are strongly correlated to the optical properties of the material, specifically localization of electron-hole pairs, i.e. excitons. These sites of localization can vary in energy depth and can be randomly distributed across the sample. Sites of exciton localization in InGaN commonly appear in two forms\textsuperscript{117}: The first being indium rich clusters in the bulk of the film that may act like quantum dots and specifically the
accumulation of indium in the periphery of V-pits. The second contributing factor is associated with the resulting in-plane stain inhomogeneity across the sample due to the presence of these morphological defects. Furthermore, carrier diffusion at room temperature allows these electron-holes pairs to migrate across the potential landscape, typically from sites of shallow localization to sites of strong localization. The critical energy that separates a localized state from a delocalized state is known as the mobility edge\textsuperscript{118}. If the site that the exciton resides in has a larger energy than the mobility edge, the exciton will diffuse to a site of reduced energy through the emission of phonons. In the case that the energy of the site is lower than the mobility edge, these excitons would decay by radiative processes\textsuperscript{119}. Since the efficiency of luminescence in our InGaN films is determined by the competition between radiative and non-radiative optical processes, one should expect through the confinement of these excitons at such strongly localized sites (regions of indium clustering), that the rate of radiative recombination should increase and thus CL intensity.

In fact, the monochromatic CL maps (Figure 3.25.e-g) that were extracted from hyperspectral maps provide insight into the variance in CL intensity observed from the panchromatic map in Figure 3.25.b-c. The CL map at 3.36 eV reveals some of the photoemission extracted from the underlying GaN layer, most prominently at the center of individual V-pits. Light emission from the underlying GaN layer occurs due to the depth resolution of CL at the accelerating voltage utilized and therefore our results insures that the complete depth of the III-polar InGaN layer was fully profiled at RT. Furthermore, the CL map in Figure 3.25.e was extracted at the maximum peak emission observed from the integrated spectra collected over the entire field of view at RT (Figure 3.24). Clearly
evident in the CL map at 2.96 eV is the lack of CL emission at the V-pits. At lower energies, however (i.e. increasing incorporation of indium), CL emission is clearly visible around individual V-pits seen in the CL map extracted at 2.77 eV (Figure 3.25.f). If we extract a monochromatic CL map from the regions of highest intensity seen in the panchromatic map (Figure 3.25.c), we find that the peak emission resides at even lower energies as illustrated in the CL map extracted at 2.54 eV (Figure 3.25.g). Therefore, the regions of bright contrast are expected to have higher accumulation of indium that may act as sites for carrier localization and therefore, lead to the observed bright emission in the panchromatic CL maps. We can also conclude from our CL measurements at RT that almost no emission at the core of the V-pits where threading dislocations terminate originates from the III-polar InGaN layer. Therefore, these V-pits in thick III-polar InGaN are likely centers for non-radiative recombination.

Pozina et al. observed similar results in CL-SEM measurements of InGaN/GaN quantum wells in an LED structure\textsuperscript{120}. In their results, regions of dark contrast appeared across the surface of the LED structure when operated at high injection currents. The regions were attributed to threading dislocations that were active non-radiative recombination centers, where typically these dislocations are inactive. These threading dislocations reduced the radiative efficiency and therefore limited the light output from the LED structure at high injection current. This effect in LEDs is referred to as efficiency “droop”. Similarly, Yoshikawa et al. observed a variation in the CL peak position across V-pits in a InGaN quantum well\textsuperscript{121}. This variation in the peak position was attributed mainly to a change in indium. In addition, they also observed an abnormal change in the CL peak position at the apex of threading dislocations the terminate V-pits. Despite the
role of these threading dislocations at the apex of V-pits in the non-radiative recombination process, the blue LED that was first demonstrated in 1994 was relatively efficient at the time. A common explanation to the success of these InGaN/GaN MQW heterostructures in achieving high efficiency light emission is the random localization of excitons in the InGaN alloys due to composition fluctuations as discussed previously.

Moreover, we investigated our III-polar InGaN samples at 13 K. As discussed in the previous integrated spectra at 13 K in Figure 3.24, the carrier dynamics and therefore localization effects can be rather different. At low temperature, the dominant recombination process is thought to be localized excitons. However, in Figure 3.26, when the dense network of V-pits from the SEM image (Figure 3.26.a) are compared to the corresponding CL panchromatic image collected at 13 K (Figure 3.26.b), significant difference in the local distribution of CL luminescence can be clearly pointed out from previous measurements taken at RT. First, most of the areas of less luminescence (dark purple regions) arises from the surroundings of the V-pits, where at the core of the V-pits, relatively bright CL emission is clearly evident. The effect in the luminescence is reversed at RT measurements. Therefore, the reduced luminescence surrounding the V-pits at 13 K is most likely due to relative changes in the overall luminescence in different regions of the sample. This may potentially be attributed to a reduction of exciton localization in some regions surrounding the V-pit, where at RT these excitons were highly localized, as well as an increase in the overall luminescence from the surrounding areas. Moreover, the panchromatic CL map shows that most of the CL emission arises from the areas of the III-polar InGaN layer that are free of V-pits (green colored regions). In addition, spots of bright luminescence (yellow/orange colored regions) are also observed in these low temperature
measurements in larger areas across the field of view. Results from the monochromatic CL maps collected at 13 K (Figure 3.26.d-g) are somewhat similar to those obtain at RT, however, carrier localization of the CL emission at 2.77 eV and 2.54 eV where clustering of indium is expected seem to be less pronounced.

Figure 3.26 | Spatially resolved CL measurements of III-polar InGaN at 13 K: (a) secondary electron SEM image of the surface and corresponding (b) panchromatic CL intensity map and (c) superimposed SEM + panchromatic CL image. (d-g) are monochromatic CL maps extracted from the collected hyperspectral map at (d) 3.36 eV; (e) 2.96 eV, (f) 2.77 eV and (g) 2.54 eV. The scale bare is 1 μm.

Furthermore, similar observations of CL emission close to the cores of the threading dislocation in V-pits, as seen in our panchromatic CL maps in Figures 2.36.b-c, have been reported in InGaN/GaN quantum wells. Massabauau et al. used a combination of spatial resolved CL measurements and plan view TEM to demonstrated that carriers can be
localized in the vicinity of the cores of threading dislocations through formation of In-N chains condensates\textsuperscript{122}. These In-N chains hinder carrier diffusion to the cores of these threading dislocations which act as centers for non-radiative recombination. Moreover, these In-N chains around the cores of threading dislocations are a consequence of strain fields of the individual dislocation and vicinity of neighboring threading dislocations. To further understand the carrier dynamics in the vicinity of these dislocations in thick III-polar InGaN, we performed both spatial and time resolved CL (TRCL) measurements at 13 K.
3.5.5.2 TRCL studies of III-polar InGaN at 13 K

In Figure 3.27.a, the distribution of indium, seen from the EDX intensity map from a cross-sectional TEM prepared specimen, shows the accumulation of indium in the periphery of the V-pit. Such defect structures are investigated with TRCL at 13 K, performed with a ~1 ps electron beam pulsed excitation source at a repetition rate of 80 MHz. The panchromatic CL map in Figure 3.27.b, which was acquired from a pulsed excitation source, illustrates weak luminescence from the areas of the V-pits. In fact, in a magnified panchromatic CL map (Figure 3.27.c), most of the CL luminescence arises from

![Image]

**Figure 3.27** TRCL of III-polar InGaN at 13 K in the vicinity of a V-pit: (a) EDX map of indium in a cross-sectional prepared TEM specimen (b) panchromatic CL intensity map acquired from pulsed excitation CL ~1 ps at 80 MHz and (c) a magnified panchromatic CL image from the area highlighted in b. (d-h) TRCL streak maps acquired from the areas of the panchromatic CL map in c. The scale bars for (a), (b) and (c) are 50 nm, 1 μm and 100 nm, respectively.
the surroundings of the V-pit with some areas of very high luminescence (purple colored regions). In the vicinity of the V-pit, however, a significant reduction in the CL intensity is clearly evident and almost no luminescence can be seen at the core of the dislocation. Unlike the panchromatic map acquired via continuous-wave CL excitation in Figure 3.26.b, the pulsed excitation source in these measurements show no significant distinguishable luminescence in the vicinity of the threading dislocation core and perhaps is a result of reduced carrier confinement at these regions in this particular pulsed excitation CL mode. Nonetheless, several TRCL streak maps were extracted from the areas highlighted in Figure 3.27.c. These TRCL streak maps are shown in Figures 3.27d-h. In addition, transients were extracted from these TRCL streak maps at the peak maxima over a spectral range of 20 nm. The corresponding transients to the streak maps, shown in Figure 3.28, have mono-exponential decays. Such decays are suggestive that radiative recombination are the predominant optical transitions that are occurring at 13 K. The time constants for each TRCL decay transient are listed within Figure 3.28.

The streak maps at Figures 3.28.d-e were acquired in the area outside of the V-pit and at the center of the V-pit, respectively. The streak maps show very broad spectral transients, however, at the center of the V-pit, the lifetime of the carriers is reduced. The carrier lifetime extracted from transients in the respective streak maps showed a time constant of 539.8 ps outside the area of the V-pit, while within the V-pit a time constant of 479.1 ps was observed. The reduced carrier lifetime observed in the center of the V-pit confirms our observations that the threading dislocation core at the apex of the V-pit are centers for non-radiative recombination and thus obstructs carrier lifetime. Furthermore, we compare the carrier dynamics in the areas of high luminescence observed in the vicinity
of the V-pit as seen in our panchromatic CL map. The streak maps in Figure 3.27.f and 3.27.g show a much narrow spectral bandwidth for the transients than those extracted from regions (d) and (e). Moreover, significant improvement in the carrier lifetime is clearly evident form the streak maps. In addition, transient extracted from the streak map collected closer to the V-pit (Figure 3.27.f) is shifted towards lower wavelengths (i.e. higher indium) then that extracted much farther away from the V-pit (Figure 3.27.g). This is an expected result, as we discussed previously, the accumulation of indium in the periphery of the V-pits is quite conspicuous, and as we observed in RT measurements, carriers are more likely to be localized in these areas as a result. In fact, the carrier lifetime extracted closer to the

**Figure 3.28** | TRCL transients extracted from the streak maps in Figure 2.28 (d-h).

The extracted lifetimes from the mono-exponential decays are listed as well.
V-pit (region-(f)) showed a time constant of 801.4 ps, while away from the V-pit, the extracted carrier lifetime was 693.6 ps. Therefore, the improvement in the panchromatic CL luminescence from these areas are a result of the increased carrier localization, and thus carrier lifetime and radiative recombination. The final streak map (Figure 3.27.h) showed a similar transient behavior and carrier lifetime as that extracted from region-(d), giving an overall average carrier lifetime across the field of view of III-polar InGaN to be on the order of ~ 0.5-0.7 nanoseconds, however, further studies to understand the local variances in the carrier lifetime in our sample are necessary.

3.5.5.3 CL continuous-wave excitation of N-polar InGaN at RT and 13 K

As discussed in section 3.4.4.1 of this chapter, PL measurements of N-polar InGaN films at RT showed approximately 100× reduction in the luminescence intensity when compared to InGaN grown in the III-polar direction. We also observed particularly high background of oxygen in our N-polar InGaN samples which could be the source of luminescence quenching that has been commonly discussed in the literature. However, the origin of luminescence quenching has only been discussed in the context of N-polar GaN layers or N-polar InGaN/GaN quantum well structures, generally with poor crystal and morphological quality. Our two-step temperature growth process for N-polar GaN enables the fabrication of not only high crystal quality N-polar GaN base layers but also thick N-polar InGaN films with improved structural quality and therefore our films are ideal platforms to identify the origin of luminescence quenching in N-polar InGaN. To the best of our knowledge, no previous reports have identified the origin of luminescence quenching in thick N-polar InGaN. In this section, we make use of CL-SEM to spatially provide in-depth analysis on the optical properties of our N-polar InGaN films.
Similar to III-polar InGaN, multiple optical transitions are evident in the integrated spectra of N-polar InGaN collected at RT over a field of view of 4.65 μm (Figure 3.29). Specific spectral features can be pointed out. First a doublet in the near band edge peak emission can be observed. As discussed previously in PL measurements of N-polar InGaN, the observation of two peaks arise from luminescence from two district regions of depth within the InGaN layer. The peak located on the lower wavelength side originates from the lower indium content layer that resides near the N-polar InGaN/GaN interface, while the other peak at longer wavelengths originates from the residual bulk of the film that is not only at a different strain state but also contains a higher content of indium. Also, evident in the CL spectrum at RT are spectral shoulders on both sides of the peak maxima and a broad band-tail emission at longer wavelengths. The CL spectra at 13 K shows less of these spectral features, however, the doublet around the peak associated with the near band edge

![Figure 3.29](image)

**Figure 3.29** | Integrated CL spectra of N-polar InGaN collected over 4.65 μm areas at room temperature (RT, red curve) and cryogenic temperature (13 Kelvin). The peak maximum for the spectra at RT and 13 K are positioned at ~436.6 nm and ~439.7 nm, respectively and were extracted using a Gaussian fit.
emission shows that the peak at lower wavelength side becomes more prominent. Though the CL peak positions in N-polar InGaN provides additional evidence of the enhanced incorporation of indium into the layers when compared to III-polar InGaN, the overall CL luminescence in N-polar InGaN was \( \sim 100\times \) less than that of III-polar InGaN.

There are several effects that can contribute to quenching of the luminescence in N-polar InGaN. The first factor may arise from carrier diffusion to threading dislocations that act as non-radiative recombination centers like in our III-polar InGaN samples. However, from weak-beam TEM, both our III-polar and N-polar InGaN samples have relatively similar dislocation densities and if we assume that the in-plane carrier diffusion lengths in both polarities are similar, then threading dislocations should not be the major source for non-radiative recombination and thus luminescence quenching in our samples. In addition to being centers for non-radiative recombination, threading dislocations also provide pathways for leakage and can create deep levels through impurity-defect complexes that form around their dislocation core\(^{123}\). This brings us to the second possible factor contributing to the quenching of the luminescence in N-polar InGaN, which is related to impurities in our sample and in the case of N-polar growth the high incorporation of oxygen. Impurities are commonly present in group-III nitride films grown by MOCVD. Substitutional O on the nitrogen (\(O_N\)) and Si on the gallium (\(\text{Si}_{Ga}\)) are the most extensively studied shallow donors in GaN. The binding energies for the O and Si donors in GaN are 7.0 meV and 6.2 meV, respectively\(^{124,125}\). Oxygen can also form a complex with gallium vacancies, resulting in a \(V_{Ga}-O\) deep acceptor complex that is stable in GaN up to 1250°C\(^{126,127}\). In addition, interstitial oxygen can also occur in GaN thin films, creating a deep level acceptor. In GaN, these shallow donors are easily detected by low
temperature PL and CL measurements as neutral donor bound excitons. The peak position of the A exciton bound to neutral O donors in GaN is $\sim 3.4714$ eV$^{124}$. In the case of InN, donors are expected to be very shallow according the effective mass model. This is because the effective mass of the electron is much smaller in InN compared to GaN and AlN$^{128}$. The optical properties of shallow donors in InN have not been identified experimentally, largely due to poor quality of the films that inherit high density of microstructural defects and thus potential fluctuations. Moreover, InN films grown by MOCVD typically exhibit higher carrier concentrations that typically exceed the limit of degenerate doping. As a result, the Fermi level is pinned to the surface, $\sim 1.6$ eV above the conduction band, leading to near band edge emissions that are usually broad$^{129}$. One would expect that the high oxygen background in our N-polar samples measured by SIMS should increase the associated bound exciton spectral lines. However, like InN, the peak position of donor bound excitons in InGaN also have been largely unidentified in the literature as a result of challenges associated with the growth of high quality films.

A third important factor that should be considered as a mechanism of non-radiative recombination in our sample is the depletion of free carries at the surface. This phenomenon arises in group-III nitrides as a result of the large effective polarization fields that can develop due to the non-centrosymmetric crystal structure, particularly when these fields are not screened. In N-polar InGaN/GaN, both the spontaneous and piezoelectric fields are pointed in the same direction towards the surface of the sample which as a result can lead to an accumulation of free carriers. Since the surface can be decorated with various amounts of dispersed morphological defects and adsorbates, these free carriers can be easily captured and hence reduce the radiative efficiency from the bulk of the InGaN film.
To obtain insight into potential sources for quenching of the overall luminescence observed in our thick N-polar InGaN, we begin our analysis of our films with spatially resolved continuous-wave CL at RT. SEM of the N-polar InGaN in Figure 3.30.a shows a smooth mostly featureless surface at the current magnification. The panchromatic CL intensity maps in Figures 3.30.b-c, however, shows a variance in the luminescence across the surface of N-polar InGaN. Some relatively large areas of the sample seen in the panchromatic CL maps display almost no luminescence (areas with bright purple color), while other small hot spots of bright luminescence can also be seen in the maps (areas with

Figure 3.30 | Spatially resolved CL measurements of N-polar InGaN at RT: (a) secondary electron SEM image of the surface and corresponding (b) raw panchromatic CL intensity map and (c) colorized panchromatic CL image. (d-g) are monochromatic CL maps extracted from the collected hyperspectral map at (d) 3.35 eV; (e) 3.06 eV, (f) 2.84 eV and (g) 2.58 eV. The scale bare is 1 μm.

To obtain insight into potential sources for quenching of the overall luminescence observed in our thick N-polar InGaN, we begin our analysis of our films with spatially resolved continuous-wave CL at RT. SEM of the N-polar InGaN in Figure 3.30.a shows a smooth mostly featureless surface at the current magnification. The panchromatic CL intensity maps in Figures 3.30.b-c, however, shows a variance in the luminescence across the surface of N-polar InGaN. Some relatively large areas of the sample seen in the panchromatic CL maps display almost no luminescence (areas with bright purple color), while other small hot spots of bright luminescence can also be seen in the maps (areas with
yellow/orange colors). The monochromatic CL intensity maps (Figure 3.30.d-g) extracted from the hyperspectral map correlates the regions of luminescence observed in Figure 3.30.b-c rather well. Evident at 3.35 eV (Figure 3.30.d), are some of the CL intensity escaping from the underlying N-polar GaN base layer as a result of the depth resolution of the CL technique. Interestingly before the peak maxima at 3.06 eV, are striations features (Figure 3.30.e) that are parallel to the miscut direction of the SiC substrates utilized for our N-polar film growth. These striations observed from CL may arise from step-bunching and/or step-meandering during the growth of N-polar InGaN as a result of possible instabilities during the growth that are stress introduced during the two-step growth process of the N-polar GaN base layer.

Furthermore, at the peak maxima corresponding to the near band edge emission (2.84 eV), the monochromatic CL intensity map shown in Figure 3.30.f illustrates rather uniform luminescence within the field of view. This is a significant improvement from III-polar InGaN, as the dense network of V-pits obstructed the luminescence across the sample. Most of the regions that lacked luminescence at 2.84 eV in Figure 3.30.f correlates well to features observed in the monochromatic CL intensity map in Figure 3.30.g, which was extracted at 2.58 eV. Note that the hot spots of bright contrast observed from the panchromatic CL intensity maps in Figures 3.30.b-c corresponds to the features in at 2.58 eV (Figure 3.30.g). These bright spots may arise due to carrier localization along the step-edges and perhaps similar to the trench like features observed by Sonderegger et al. that also showed localized carriers from time resolved CL measurements and thus enhanced radiative recombination in those trenches\textsuperscript{130}. A second possibility is associated with partial screening of the internal polarization fields. Since these atomic step-edges likely reside on
semi-polar atomic planes, the quantum confined stark effect should be reduced and result in changes in the carrier recombination dynamics\textsuperscript{131}. An additional possibility to the bright luminescence is the accumulation of indium at the step-edges, however, no conclusive evidence of indium clustering was observed in our samples from AFM, but we cannot rule this out. What we can conclude that these regions of bright luminescence do not play any significant role in the overall light emission from the N-polar InGaN sample.

\textbf{Figure 3.31} | (a) AFM of the N-polar InGaN surface. The boxes placed on the image highlights the possible striations observed in the monochromatic CL intensity map seen in Figure 3.30.e, while the circled regions highlight the potential structures from the areas that lacked luminescence from the panchromatic CL maps in Figures 3.30.b-c. (b) are locally extracted CL spectrum from the hyperspectral map on the region of uniform luminescence (top blue curve) and from the region that lacked luminescence (bottom red curve). The scale bare is 1 \( \mu \text{m} \).
Moreover, the CL energies associated with the regions that lacked luminescence in the overall panchromatic CL intensity map were largely unidentified. This is suggestive that the regions that lacked luminescence must exhibit a broad spectral emission band from that of pristine areas of the N-polar InGaN sample. The various luminescence features from the monochromatic CL maps were correlated to the surface morphology of the N-polar InGaN film using AFM. Evident in Figure 3.31.a are the striations (highlighted within the dashed boxes) parallel to the miscut directions of SiC. Furthermore, the morphological features that are believed to be associated with the regions that lacked luminescence are circled in Figure 3.31.a. Also, evident in Figure 3.31.b, the extracted CL spectra from the area of uniform CL intensity is compared to the spectra extracted from the region that showed no CL signal. The peak ratio between the near band edge emission to what is presumed to be the yellow luminescence (YL) band is significantly reduced on the region that lacked luminescence (bottom red spectra) from a region of uniform luminescence (top blue spectra). The observation of yellow luminescence (YL) is common in GaN. This band appears in the range of ~2.3 - 2.2 eV\textsuperscript{132}. The YL band is a deep level and usually observed as a broad spectral band in GaN as a result of strong coupling between electrons and phonons in the solid\textsuperscript{133,134}. The observation of the YL band is not specific to a particular impurity type in GaN but rather attributed to a transition from the conduction band or shallow donor to a deep acceptor. The YL band may also result from specific point defects in the sample\textsuperscript{135,136}, however, this band has been commonly attributed in the literature to gallium vacancies in GaN\textsuperscript{126,137,138}. Several gallium vacancies related defects have been identified in the literature and theory predicts that generally the formation energies for isolated gallium vacancies and gallium vacancies that are complexed with O are rather low.
Figure 3.32 | Spatially resolved CL measurements of N-polar InGaN at 13 K: (a) secondary electron SEM image of the surface and corresponding (b) raw panchromatic CL intensity map and (c) colorized panchromatic CL image. (d-g) are monochromatic CL maps extracted from the collected hyperspectral map at (d) 3.39 eV; (e) 3.06 eV, (f) 2.82 eV and (g) 2.63 eV. (h, left) panchromatic CL intensity map acquired from pulsed excitation CL in the same area as the stripe in g with, (h, right) corresponding TRCL streak maps from the indicated positions in (h, left). The scale bare is 1 μm.
and therefore should be favorable to form and thus lead to the emission of a strong YL band\textsuperscript{132}. Since our N-polar samples contain relatively high concentrations of oxygen, the observation of the YL band in the areas the lacked luminescence in the panchromatic CL map perhaps is a result of optical non-radiative transitions between the conduction band edge or oxygen shallow donor state to a deep acceptor gallium vacancy that is complex with oxygen.

In addition to CL measurements at RT, low temperature spatially and time resolved CL measurements were collected at 13 K. Similar areas of N-polar InGaN, seen in SEM (Figure 3.32.a), which were flat and defect free were studied in CL-SEM. Evident in the panchromatic CL maps shown in Figures 3.32.b-c are areas of relative uniform CL intensity as well as spots of bright luminescence (labeled (i)). Unlike the panchromatic CL intensity maps collected at RT, regions that clearly lacked luminescence are not as pronounced. This could be a result of the increase in the overall luminescence intensity from the entirety of the sample at 13 K. Nonetheless, the monochromatic CL intensity maps in Figure 3.32.d-g show similar features to those seen at RT (Figure 3.30). The CL map at 3.39 eV (Figure 3.32.d) represents some of the luminescence extracted from the underlying N-polar GaN base layer. At 3.06 eV (Figure 3.32.e), similar striations that were parallel to the miscut direction of the SiC substrate at RT, are also clearly visible at 13 K. Furthermore, Figure 3.32.f shows the monochromatic CL intensity map near band edge emission at 2.82 eV. The luminescence intensity seen at 2.82 eV is fairly uniform, where the regions that lacked luminescence correlate well to the luminescence in the monochromatic CL map at 2.63 eV and are believed to reside at the step-edges of the film.
Moreover, in order to understand the features of high luminescence seen in the panchromatic CL intensity map (labeled as (i)), we investigated these regions with time resolved CL using a ~1 ps pulsed excitation source at 80 MHz repetition rate (Figure 3.32.h). The features of high luminescence are fairly visible in the panchromatic CL intensity map collected with pulsed excitation (Figure 3.32.h (left)). Various TRCL streak maps were collected to understand the carrier dynamics at these regions of high luminescence from the rest of the N-polar InGaN film (Figures 3.32.h (right)). The TRCL map collected on the bright spot (point (i)) clearly shows longer carrier lifetime than the TRCL maps at point (ii) and (iii) outside of the region with bright luminescence. Unlike the mono-exponential transient decay behavior for the carrier lifetime observed in the III-polar InGaN films, TRCL transients extracted for N-polar InGaN exhibit bi-exponential decay. At low temperature, radiative emission tends to dominate and therefore, the transient is usually mono-exponential. The observation of bi-exponential decay is characteristic of capture processes in a multilevel system that result from deeper non-radiative centers either in the bulk or the surface/interface of the film. The transient with a bi-exponential decay exhibits an initial fast component followed by a slow component. Therefore, the time constants of a bi-exponential decay cannot purely represent radiative and non-radiative processes, as both optical transitions contribute to the time constants, specifically if the sample is not highly uniform, i.e. exhibits potential fluctuations in the layers. Usually, however, the faster component of the decay is dominated by non-radiative recombination while the slower component is dominated by radiative optical transitions that are occurring. The carrier lifetime constants extracted from the transients are listed in Figure 3.32.h, where \( t_1 \) represents the fast component of the decay and \( t_2 \) represents the slower component.
In the case of the region of high luminescence (point (i)), the fast and slow components of the lifetime extracted from the transient were 64.1 ps and 230.4 ps, respectively. Outside the region of bright luminescence, a significant reduction in the lifetime of the slow component of the decays at point (ii) and (iii) is observed. Therefore, it is possible that the lifetime of the carriers in the regions of bright contrast are enhanced due to exciton localization in those regions, however, more work is needed to fully understand the optical transitions that are occurring in N-polar InGaN, particularly in the vicinity of the aforementioned spectral features.

From these TRCL measurements, a few things can be concluded. First, the lifetime of the carriers in the case of N-polar InGaN is on the order of ~50-200 ps, while in the case of III-polar InGaN, carrier lifetime is on the order of ~0.5-0.7 ns. From a first approximation, this explains the large differences in the luminescence intensity between the two polarities. Second, since the decay behavior of the transient in N-polar InGaN is bi-exponential, we can suspect that the high concentration of oxygen in our samples plays a predominant role in quenching the luminescence and most likely through forming deep levels when complexed with gallium vacancies. These deep levels with the addition to shallow oxygen donors should obstruct radiation emission. This is not the case in our III-polar InGaN films, where the decay behavior of the transient is mono-exponential. Finally, the enhanced YL band luminescence to the near band edge emission in N-polar InGaN of regions that lacked luminescence in our panchromatic CL intensity maps further supports the notion that oxygen plays a big role in quenching the overall luminescence in N-polar InGaN.
3.5.5.4 TRCL studies of morphological defects in N-polar InGaN at 13 K

Microstructural defects such as stacking faults and threading dislocations are common in heteroepitaxial grown group-III nitrides films. These microstructural defects can impact the electronic and optical properties of the materials. As demonstrated in CL-SEM of III-polar InGaN, threading dislocations were suggested to be centers for non-radiative recombination. These microstructural defects in the panchromatic CL intensity maps exhibited dark contrast, however, it is still unclear if the intrinsic dislocation itself, the point defects and/or impurities that may decorate the dislocation core are the sources of non-radiative recombination. In N-polar InGaN, morphological defects can also obstruct radiative emission. In this section, two particular morphological defects of interest are studied with CL-SEM.

The first defects of investigation are the hexagonal hillocks that originate from the N-polar GaN base layer. Since the InGaN layer is only 130-140 nm in thickness, the N-polar InGaN film will essentially overlay these hexagonal hillocks. In Figures 3.33.a-c are the SEM and corresponding panchromatic continuous-wave intensity map collected for an individual hexagonal hillock at RT. From SEM, the hexagonal hillock exhibits semi-polar facets with a flat top. When we compare the SEM to the panchromatic CL intensity map in Figure 3.33b, we find relatively high luminescence from the semi-polar planes of the hexagonal hillock with relatively low to no luminescence from the planar top of the defect. Similarly at 13 K (Figures 3.33.c-d), the hexagonal hillock shown in the SEM in Figure 3.33.c also exhibits a planar top that revealed very low overall luminescence in the panchromatic CL intensity map shown in Figure 3.33.d. We examine the carrier dynamics in the vicinity of the hexagonal hillock more closely at 13 K using TRCL. Two points of
interest were examined from the SEM in Figure 3.33.e. The first region labeled (i) on the flat plane of the hexagonal hillock and the other region labeled (ii) away from the hillock on a pristine part of the sample. Both TRCL streak maps in Figure 3.33.f, collected on and off the hexagonal hillock, revealed a bi-exponential behavior in the transient shown in Figure 3.33.g, where $t_1$ represents the fast component of the transient and $t_2$ represents the slow component of the bi-exponential decay. The streak maps between the two collected
regions are dramatically different, however, additional measurements are needed in order to truly understand and explain the lifetime behavior of the carrier in the vicinity of these defects.

The second defect that was investigated are stripe features highlighted in the SEM shown in Figure 3.34.a. This feature seen in the panchromatic CL intensity map collected at 13 K was not highly luminescent (Figure 3.34.b), however, small features on this defect appear to exhibit high CL intensity compared to the rest of the field of view. This again is probably due to carrier localization. Interestingly, however, the CL spectrum extracted on the stripe and outside of the stripe clearly show that the stripe feature exhibits a strong YL band. This could suggest that these stripe features are sources of oxygen accumulation in the film. Furthermore, Figures 3.34.d-g are monochromatic CL intensity maps extracted from the hyperspectral map at 13 K. In Figure 3.34.d, CL intensity at 3.39 eV highlights some of the emission escaping from the underlaying N-polar GaN base layer. Similar to previous CL maps, the monochromatic CL intensity map at 3.09 eV in Figure 3.34.e shows the features of luminescence that are parallel to the miscut of the SiC substrate. Moreover, Figure 3.34.f reveals a mostly uniform CL emission across the field of view where the near band edge emission is expected at around 2.81 eV. The feature on the stripe that lacked luminescence appears to emit around 1.80 eV near the YL band shown in CL map in Figure 3.34.g. Finally, TRCL measurements were performed on and off the stipe feature in the SEM (Figure 3.34.a). Evident form the TRCL streak maps in Figure 3.34.h and extracted transient decays in Figure 3.34.i are significant difference in the carrier lifetimes, where the decay behavior observed on and off the stipe feature was bi-exponential.
Figure 3.34 | CL-SEM of a stripe defect structure in N-polar InGaN at 13 K: (a) is an SEM image of the stripe defect structure with, (b) the corresponding panchromatic continuous wave intensity map. (c) are extracted CL spectrum from the region on the defect structure (i) and away from the structure (ii) labeled in the SEM. (d-g) are monochromatic CL maps extracted from the collected hyperspectral map at (d) 3.39 eV; (e) 3.09 eV, (f) 2.81 eV and (g) 1.80 eV. (h) are TRCL streak maps collected at corresponding regions labeled in the SEM in a. (i) are the associated transients extracted from the streak maps in h. All scale bars are 10 μm.
3.6 Conclusions

In this chapter, we investigated the effect of polarity of the GaN base-layer on the structural quality, surface morphology and optical properties of MOCVD grown thick InGaN films. Our results demonstrate that thick N-polar InGaN films can be grown free of V-pits and hexagonal hillocks, without significant compositional inhomogeneity as observed in III-polar InGaN. Moreover, our results from XRD, SIMS, EDX, UV-Raman, macro-PL and CL-SEM demonstrate an enhancement in the indium incorporation efficiency in N-polar InGaN. UV-Raman and macro-PL measurements show the existence of regions with different composition and/or strain for both III-polar and N-polar InGaN. In the case of III-polar InGaN, the differences are attributed to lateral compositional variations arising from the presence of V-pits. In the case of N-polar InGaN which lacks V-pits, the regions likely arise from variations in both composition and strain over the layer thickness as evidenced by RSM.

Furthermore, the evolution of stress was investigated using in situ curvature measurements during MOCVD growth. Our results showed that the initial low temperature layer used in the two-step temperature growth process for N-polar GaN not only mitigates the overall dislocation density in the films through the formation of dislocation loops and TD annihilation with stacking faults, but also establishes an effective approach to control and engineer strain (tensile or compressive) in the main high temperature N-polar GaN and subsequent N-polar InGaN epilayers. Unlike III-polar InGaN that grew under a constant compressive stress, N-polar InGaN films grew initially under low stress which gradually transitioned to a state of constant compressive stress for the remainder of the film thickness. The overall lower density of TDs in N-polar InGaN and the absence of V-pits in the films
appeared to promote partial plastic relaxation of the misfit stress in the initial layer thickness during the growth of N-polar InGaN as corroborated with the dislocation microstructure analyzed in HR-TEM and in situ stress measurements. Furthermore, as the compressive stress increased in the N-polar InGaN by increasing the growth temperature of the initial low temperature layer in N-polar GaN, blue shifts in the band-edge emissions of InGaN were observed. This blue shift observed in PL is likely to originate from residual strain that resides in the bulk of the N-polar InGaN layer. This corroborates well with in situ stress measurements and reciprocal space maps, which all show little relaxation in the thick InGaN films during growth and after sample cooldown. Further investigation is, however, necessary to preclude the influence of impurities and segregation of indium on the stress-dependent band edge PL signature observed in the films. Finally, the large differences in the luminescence intensity between the III-polar InGaN and N-polar InGaN is a result of significant difference in the carrier lifetimes of the respective polarities. Our TRCL measurements showed the lifetime of the carriers in the case of N-polar InGaN is on the order of ~50-200 ps, while in the case of III-polar InGaN, carrier lifetime is on the order of ~0.5-0.7 ns. Since the decay behavior of the transient in N-polar InGaN is bi-exponential, we suspect that high concentration of oxygen in our samples play a predominant role in quenching the luminescence and most likely through forming deep levels when complexed with gallium vacancies. These deep levels with the addition to shallow oxygen donors should obstruct radiation emission. Moreover, the enhance YL band luminescence to the near band edge emission in N-polar InGaN on regions that lacked luminescence in our panchromatic CL intensity maps further supports the notion that oxygens plays a significant role in quenching the overall luminescence in N-polar films.
3.7 References


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CHAPTER 4

BUFFER FREE GROWTH OF GAN ON SILICON CARBIDE

4.1 Introduction

Part of the success in the industrialization of many group-III nitride based optoelectronics such light emitting diodes (LEDs)\textsuperscript{1,2}, laser diodes (LDs)\textsuperscript{3} and ultraviolet emitters\textsuperscript{4} arrives from the wide spread implementation of MOCVD in the device fabrication process. More recently, as highlighted in Figure 4.1, there has been interest in the use of this growth process for the fabrication of new power electronics\textsuperscript{5,6}, specifically in the development of efficient high power modules and inverters for hybrid and electric vehicle (HEV) systems\textsuperscript{7-9}. Currently, these systems primarily rely on Si-based power devices such as insulated gate bipolar transistors (IGBTs) and metal-oxide-semiconductor field effect transistors (MOSFETs), where the performance of these devices is limited by the inherent properties of the Si material\textsuperscript{10}. The main issue with high power modules is the

![Figure 4.1](image.png)

**Figure 4.1** | Schematic highlighting the use of III-nitrides for high power density electronics.
large heat generation, resulting in poor high-temperature operation and thus requiring complex cooling systems\textsuperscript{11}. Devices with high power operation and low on-resistance are essential for the future of inverters in HEVs.

![Schematic of a generic lateral (left) and vertical (right) III-nitride based power device structure.](image)

**Figure 4.2** Schematic of a generic lateral (left) and vertical (right) III-nitride based power device structure.

GaN is an attractive material for the use in power electronics due to its high electron mobility and high saturation velocity that can withstand high-temperature operation\textsuperscript{5}. Traditionally, GaN-based power electronics are lateral structures (Figure 4.2), where current flows from the source to the drain near the surface. Such lateral device structures suffer from dynamic on-resistance (during rapid switching from ‘on’ to ‘off’ states during device operation, electrons remain trapped at the channel) and current collapse due to surface states, limiting the device performance\textsuperscript{12,13}. Furthermore, in order to increase the breakdown voltage in lateral devices necessary for high power modules in HEVs, an increase in the distance between the source and drain is needed, which leads to larger overall chip size\textsuperscript{14}. Vertically conducting GaN-based power devices offer many advantages over lateral structures which are reaching their limits\textsuperscript{15,16}. In a vertical device, the current flows in all areas of the device, consequently, current collapse is suppressed which allows for better device operation\textsuperscript{9}. In addition, the vertical device configuration is more effective.
in realizing low on-resistance and high breakdown voltages, achieving much higher power density over lateral device structures. However, the development of vertically conducting GaN-based power devices has been limited due to the absence of viable substrates that exhibit both high thermal and electrical conductivity (such as degenerately doped bulk diamond substrates) that are available at economical costs. More recently, the fabrication of vertical GaN-based power devices has been reported on bulk GaN substrates (GaN-on-GaN)\textsuperscript{17,18}, however, bulk GaN substrates are still limited in terms of size, cost and availability.

As a result, group-III nitride films are conventionally grown heteroepitaxially on a variety of foreign substrates such as silicon, sapphire and silicon carbide (SiC). The wide spread availability of SiC (up to 8-inch wafers from \textit{II-VI ADVANCED MATERIALS}) has enabled the realization of high-frequency devices, i.e. AlGaN/GaN high-electron mobility transistors (HEMTs), operating at high power density, owing to its superior thermal conductivity that provides efficient pathways for heat dissipation\textsuperscript{19-21}. Vertically conducting GaN-based devices on SiC (GaN-on-SiC) can be a viable alternative to GaN-on-GaN devices. Nonetheless, the heteroepitaxial growth of GaN on SiC by MOCVD is challenging. This arises from the large lattice and thermal expansion coefficient mismatch between group-III nitride alloys and the substrate, as well as the poor wetting behavior of GaN on the surface of SiC, which significantly impacts film quality\textsuperscript{22}. To overcome these challenges, AlN, which has a smaller lattice mismatch to SiC compared to GaN and improved wettability, is commonly employed as a buffer layer to promote epitaxial growth of GaN on SiC. However, due to the insulating nature of AlN (6.1 eV), a potential barrier is introduced at the GaN/SiC interface which inhibits current flow between the GaN film
and substrate in vertical devices. In addition, MOCVD growth of AlN is typically defective. Therefore, AlN can also act as a thermal barrier that can prevent efficient dissipation of heat in devices. As a result, there is significant interest in the growth of GaN directly on SiC or indirectly on SiC with highly conductive buffer layers that do not impair with vertical transport between GaN and the SiC substrate.

4.1.1 Examining the growth evolution of buffer free growth of GaN-on-SiC

From prior literature, MOCVD growth of high-quality GaN directly on SiC has been demonstrated using multi-step growth processes to transition typical three-dimensional growth of GaN on SiC that arises due to difference in the surface energies and large lattice mismatch, to a two-dimensional growth mode. Despite the potential of this approach for vertical devices, there is limited information on the structural properties of GaN on SiC layers and the evolution of film stress in this growth process. In this chapter, we employ in situ optical reflectance and wafer curvature measurements to monitor and understand the growth evolution (nucleation, coalescence and growth stress) during heteroepitaxy of GaN on SiC with an insulating AlN buffer layer to that grown directly on SiC using a two-step temperature growth process. The studies in the first part of this chapter reveals that there are significant differences in the microstructural, morphological and stress evolution of GaN with and without the use of an AlN buffer layer that has not been identified from prior literature.

4.1.2 Investigating alternative buffers for vertical GaN-on-SiC power devices

More recently, there has been significant attention to the use of layered materials, specifically graphene, to assist in the heteroepitaxial growth of group III-nitrides on a
variety of foreign substrates, like SiC$^{27-32}$. Graphene is a two-dimensional and layered material of hexagonally arranged sp$^2$ hybridized carbon atoms. An advantage in the use of graphene for the epitaxy of III-nitride films is that graphene has a hexagonal arrangement of atoms similar to (0001) c-plane of wurtzite GaN. On the basis of the in-plane lattice parameters of graphene and group-III nitrides like AlN and GaN (2.461 Å, 3.111 Å, 3.189 Å, respectively)$^{33-35}$, the in-plane lattice mismatch between AlN or GaN and graphene can be significant (Figure 4.3). However, this high lattice mismatch may be less important during heteroepitaxy due to the potential for van der Waals bonding at the III-V/graphene interface, which can relax the lattice mismatch requirements$^{36}$. In addition, the low migration barrier of group-III metals on graphene allows adatoms to diffuse readily on the surface at reduced growth temperatures$^{37}$. Therefore, pristine graphene can enable large

**Figure 4.3** | Density Functional Theory (DFT) simulations using Local Density Approximation (LDA) of fully relaxed superimposed (a) AlN/graphene and (b) GaN/graphene slabs, illustrating significant in-plane lattice mismatch at the heterointerface.
adatom diffusion lengths during nucleation which may promote the formation of large two-dimensional islands that can coalesce into films with reduced dislocation densities.

Graphene can be formed by several different methods. Epitaxial graphene (EG) can be produced directly on SiC by selective thermal decomposition of silicon from the surface of the substrate at elevated temperatures, leaving a carbon rich surface that can reconstruct under appropriate conditions to form sp² carbon networks of graphene. Graphene is also commonly grown directly on copper foil by the thermal decomposition of methane (referred to as polycrystalline CVD grown graphene) which is typically then followed by transfer of the graphene monolayer to other substrates. The advantage of EG grown from SiC is that the surface of EG follows the morphology of the underlying SiC substrate, which consists of (1\(\overline{1}0\))n step edges with wide (0001) terraces, and provides large areas of pristine and highly oriented graphene. This, in addition to exhibiting a surface that is free of residual polymer and contaminants (often present on the surface of CVD graphene after the transfer process from the host metal foil) would be key to high quality growth of GaN on graphene with low impurity incorporation.

The growth of GaN by MOCVD on the basal plane of pristine graphene is challenging. This is largely due to the absence of dangling bonds which leaves the graphene surface chemically inert. Therefore, most attempts to grow GaN on CVD graphene have relied on buffer assisted epitaxy, where thin AlN layers or ZnO nanowalls deposited on graphene at low temperature were used to promote GaN nucleation and growth. However, the quality of the films produced was inferior to GaN layers grown on conventional substrates. Recently, Kim et al. demonstrated the direct growth of GaN on EG under typical MOCVD growth conditions with very low nucleation density of GaN on
the terraces of graphene. Instead, GaN nucleates at the periodic EG coated step edges and grew laterally over the SiC terraces resulting in a coalesced film with threading dislocation densities in the range of ~1x10^9 cm^-2 which are comparable to results obtained for GaN growth on SiC using an AlN buffer layer. Despite the growing interest in the heteroepitaxy of group III-nitride films on graphene, there have been limited studies aimed at understanding the nucleation process. In the second part of this chapter, the nucleation of AlN and GaN by MOCVD on EG was investigated with the goal of studying the effect of growth temperature and the role of step edges and defects in the graphene lattice on the nucleation process. Using a combination of growth experiments and structural and chemical analysis, the studies presented here provide important insight into the initial stages of group-III nitride growth on graphene that can impact the coalescence process of these films on SiC for potential application of graphene as a conductive buffer layer for future GaN-on-SiC power devices.
4.2 Literature Review

4.2.1 Important properties of SiC in the scope of power devices

As a substrate material, SiC has many favorable properties for the fabrication of group-III nitride based power devices, most notable are its high thermal conductivity and low lattice mismatch with GaN. Historically, however, SiC was not widely utilized due to their high cost and size limitations. Today, large diameter substrates are readily available in both conducting (p- and n-type) and high resistivity forms. As a result, the most efficient group-III nitride based LEDs and power devices that are commercially available are produced on SiC. The crystal structure of non-centrosymmetric wurtzite SiC has a basic unit cell of tetrahedrally coordinated C atoms, covalently bound to silicon in the center of the tetrahedron. The two most important polytypes of SiC, as illustrated in Figure 4.4, are the 4H and 6H polytypes. In the 4H polytype, the stacking sequence is ABACAB, etc., while in the 6H polytype, the is stacking ABCABC. These two polytypes belong to the same P63mc space group symmetry, where the bandgap energy for 4H- and 6H-SiC
polytypes are 3.27 eV and 3.02 eV, respectively. The in-plane $a$ lattice parameter is 3.08 Å and is constant in all polytypes. The out-of-plane $c$ lattice constant for the 4H polytype is 10.053 Å, while the 6H polytype $c$ lattice constant is 15.1173 Å. Compared to conventionally used sapphire, SiC has superior thermal conductivity. The thermal conductivity at room temperature for 4H- and 6H-SiC are 370 W m$^{-1}$K$^{-1}$ and 380 W m$^{-1}$K$^{-1}$, respectively. The in-plane and out-of-plane crystalline alignment for GaN, AlN and InN on SiC is much more simplified compared to the 30 degree in-plane rotation requirement with respect to sapphire. In the case of c-plane 6H-SiC, the epitaxial relationship is $[0 0 0 2]_{\text{GaN}}/[0 0 0 6]_{\text{SiC}}, [1 1 \bar{2} 0]_{\text{GaN}}/[1 1 \bar{2} 0]_{\text{SiC}}$. The one caveat of the epitaxy of GaN on SiC is that the thermal mismatch is tensile. The tensile stress generated from the coefficient of thermal expansion (CTE) mismatch between the GaN and SiC is approximately 0.4 GPa upon cooldown from $1100^\circ$C to $25^\circ$C.

4.2.2 The impact of the interface structure of SiC on GaN nucleation

It is important to discuss the nature of the interface between group-III nitrides and SiC. Unlike the 4H and 6H stacking sequences of SiC, GaN (as well as AlN, InN and their alloys) comprises a 2H stacking sequence and in this vein, nucleation can be obstructed and defects are prone to form at such interfaces. The surface atomic structure in the vicinity of a step in SiC is illustrated in Figure 4.5.a. Two distinct terrace terminations, labeled terrace 1 and terrace 2 are highlighted in the figure. These terraces are related to each other via a displacement vector $\vec{d}$. If this displacement vector does not correspond to one of the crystallographic symmetry operations in group-III nitrides, stacking faults can form. If we also consider the possibility of both the zinc blende and wurtzite crystal structures of GaN to possibly nucleate during MOCVD heteroepitaxy (Figure 4.5.b), either individually
on each SiC terrace or in combination, the event of forming a stacking fault is more likely.

Table 4.1 provides a summary of stacking faults found in group-III nitrides\textsuperscript{45}. Both intrinsic (I) and extrinsic (E) basal plane stacking faults (BSFs) can form at the GaN/SiC interface. I\textsubscript{1}-type BSFs have the lowest formation energy and form through the insertion of a \((\frac{1}{2}[0001])\) atomic plane with a \(\frac{1}{3} < 1\overline{1}00 >\) displacement\textsuperscript{46}. The I\textsubscript{3}-type BSF has the second lowest formation energy and appears as double of a I\textsubscript{1}-type BSF. Furthermore, I\textsubscript{2}-type BSFs involve a shift in \(\frac{1}{3} < 1\overline{1}00 >\) displacement vector and are bound to partial dislocations. These BSFs are higher in energy than I\textsubscript{1}-type and I\textsubscript{3}-type BSFs, therefore they rarely form. Extrinsic type BSFs on the other hand have the highest formation energy and are formed through precipitation of point defects\textsuperscript{47}. In addition to BSFs, prismatic stacking faults emanating from the steps of SiC can also form\textsuperscript{48}. These prismatic stacking faults are usually bound by two I\textsubscript{1}-type BSFs with a stair-rod dislocation insertion at the juncture of the BSFs and the PSF.

**Figure 4.5** | (a) The formation of two distinct terrace regions on SiC in the vicinity of a step-edge. (b) the stacking sequence between SiC and Zinc blend (left) and Wurtzite (right) GaN. Images are from Ref [44] with modifications.
The formation of the stacking faults can be mitigated through the assurance that the number of layers adjacent to a step-edge on the surface of 4H-SiC and 6H-SiC consist of four and six bilayers, respectively. The formation of steps on SiC with mixed stacking sequences is inevitable during heteroepitaxy of group-III nitrides\textsuperscript{49}. In addition to stacking faults, inversion domain boundaries and double domain boundaries can initiate during epitaxy of GaN on SiC as a result of stacking mismatch\textsuperscript{50}. In short, though SiC shows good promise in achieving buffer free growth of GaN on SiC for vertical devices, a host of possible defects can be generated at the interface and understanding ways to control the formation of such defects are of great importance.

<table>
<thead>
<tr>
<th>Stacking fault type</th>
<th>Displacement vector</th>
<th>Stacking sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>I\textsubscript{1}</td>
<td>$\frac{1}{6} &lt; 20\bar{2}3 &gt;$</td>
<td>ABABCBCBC</td>
</tr>
<tr>
<td>I\textsubscript{2}</td>
<td>$\frac{1}{3} &lt; 1\bar{1}00 &gt;$</td>
<td>ABABCACAC</td>
</tr>
<tr>
<td>I\textsubscript{2}</td>
<td>none</td>
<td>ABABCBABA</td>
</tr>
<tr>
<td>E</td>
<td>$\frac{1}{2} &lt; 0001 &gt;$</td>
<td>ABABCABAB</td>
</tr>
<tr>
<td>Prismatic</td>
<td>$\frac{1}{2} &lt; 10\bar{1}1 &gt;$</td>
<td>along (12\bar{1}0) planes</td>
</tr>
</tbody>
</table>

\textbf{Table 4.1} | List of stacking faults in the wurtzite structure of group-III nitrides. Ref [45].

\textbf{4.2.3 Heterogeneous integration of graphene with group-III nitrides}

Group-III nitrides provide excellent materials properties for next generation high frequency power devices. The two-dimensional electron gas (2DEG) that forms at the
interface of AlGaN/GaN exhibit carrier mobilities exceeding 1000 cm$^2$ V$^{-1}$ s$^{-1}$, which combined with the high electron saturation velocity and high critical field of GaN has enabled the production of high electron mobility transistors (HEMTs) operating well into the GHz range$^{51}$. Despite the compelling properties of group-III nitrides, the wide spread use of these materials in devices operating at extremely high power densities have been hampered by poor dissipation of heat the is generated during device operation. Such poor heat dissipation in these devices will ultimately impact device reliability. Moreover, the high fields that develop at the gate edge during the operation of these devices can lead to non-uniform distribution of power which can increase gate leakage and degrade drain current$^{52}$. In the interest of these issues in pushing the limits of GaN based high frequency power devices, there has been renewed interest in the heterogeneous integration of graphene with group-III nitrides as a result of the superior thermal, optical, electrical and mechanical properties of these the sp$^2$ bound carbon layered crystals. The thermal conductivity in graphene exceeds 5000 W m$^{-1}$ K$^{-1}$, which is well suited in providing significant improvement in the thermal management of group-III nitride based devices$^{53}$. Unlike metals, the thermal conductivity in graphene is governed by phonon transport, even at the monolayer limit. In the case of metals, however, thermal conductivity is governed by electron transport and therefore when the thickness of metal layers on the order of the mean free path of electrons, the thermal conductivity can be significantly reduced$^{54}$.

There are several areas of interest in the integration of graphene with group-III nitrides. One area of interest is the use of graphene as a transparent conductive electrode (TCEs) in group-III nitride based LEDs$^{55}$. The most important attributes in any transparent electrode are high optical transparency, low sheet resistance and low contact resistance, all
of which graphene can provide when integrated with group-III nitrides. In fact, the renowned roll-to-roll process of nitrogen doped graphene, produced by chemical vapor deposition (CVD) on catalytic metal foils, has led to the development of graphene based TCEs with optical transparencies that exceed conventional indium tin oxide (ITO) TCEs\textsuperscript{56}. These TCEs exhibited sheet resistances and optical transparency in the range of $\sim 30 - 125 \ \Omega/\square^{-1}$ and $\sim 90 - 97.4\%$, respectively. However, the residual polymer and/or metal that

![Schematic representation of the band alignment between graphene and n-type GaN before (a) and after (b) junction formation. In addition, the band alignment between graphene and p-type GaN before (c) after contact (d) is presented. Ref [52, 57].](image)

**Figure 4.6**
remain after the transfer process of CVD graphene onto these group-III nitride surfaces can impact transport in heterojunctions.

This is best exemplified in Figure 4.6\textsuperscript{52,57}, where the band alignments and hence transport mechanism between graphene and p-type as well as n-type GaN are illustrated. Graphene contacted to GaN exhibits rectifying behavior. In both cases before contact, the Fermi level of graphene coincidences with the Dirac point. When contact between graphene/group-III nitrides occurs, charge transfer of electrons occurs which induces a shift in the Fermi level in graphene. In the case of p-type GaN, electrons are pulled out of the graphene into GaN resulting in a shift of the Fermi level into the valance band. In the case of n-type GaN, electrons are transferred into graphene, rising the Fermi level into the conduction band. Any residual contaminants from the transfer process of CVD graphene can be represented at the graphene/group-III nitride interface as an ultrathin insulating layer, which ultimately impacts the Schottky barrier height. As a result, there are discrepancies presented in the literature on the behavior of graphene contacts to group-III nitrides. For example, in publications discussing metal/graphene/AlGaN/GaN heterostructures reported by Park et al., the graphene insertion provided an Ohmic contact to AlGaN, while in a report by Fisichella et al., the graphene insertion in a similar heterostructure provided a Schottky contact\textsuperscript{58,59}. Therefore, in order to form reliable contacts of graphene to III-N, i.e. pristine interfaces, strategies for direct integration of graphene with III-N must first be realized.

In addition to contacts, graphene is of great interest for local thermal management, particularly in the interest of vertical devices and devices with drastically confined dimensions. As discussed previously, the poor thermal conductivity in sapphire at room
temperature (~30 W m^{-1} K^{-1}) has led to the replacement of these substrates with SiC for power devices. However, group-III nitride/SiC devices can also suffer from self-heating which imposes limitation on the operation of these devices. There are a number of efforts used to manage self-heating in GaN power devices. Some examples include flip-chip bonding with epoxy underfill\textsuperscript{60} and the use of heat sinks, however, further improvements are necessary in order to operate devices at higher power densities. An example exploiting graphene in the thermal management of an AlGaN/GaN power devices was demonstrated by Yan et al. using few layers of graphene\textsuperscript{61}. Using graphene heat spreaders, they demonstrated from spectroscopy a significant reduction in the temperature of hotspots during device operational by ~ 20°C. Such improvements correspond to an order-of-magnitude increase in the lifetime in these devices. They also showed an improvement in the output current in these devices as a result of better device thermal management.

Moreover, the integration of graphene with group-III nitrides has led to the development of new vertical device concepts, the most promising of these devices includes the hot electron transistor. Illustrated in Figure 4.7 is the band alignment associated with a generic graphene based hot electron transistor. Hot electron transistors are three-terminal devices that consist of a graphene base layer sandwiched between an emitter-base barrier and a base-collector barrier that separates the graphene base from the emitter and collector terminals. Historically, the emitter-base and base-collector barriers utilized in these devices were SiO\textsubscript{2} and/or other high-k dielectrics. In the off-state, the barriers inhibit electrons from flowing through into the collector. During the on-state, the emitter-base and base-collector barriers are reduced and electrons can tunnel through or pass over the emitter-base barrier \textit{via} thermionic emission and thus contribute to the on-current. These electrons
will have energies above the Fermi level of graphene, hence the term “hot electrons”. The terminals in initial devices consisted of a silicon emitter, graphene base-emitter and a metal collector. These devices however suffer from poor collector current densities. Other semiconductors have been considered to replace silicon in the hot electron transistor device architecture. The most promising alternatives to Si are wide bandgap semiconductors such group-III nitrides and SiC. Graphene based hot electron transistors that make use of group-

Figure 4.7 | Schematic representation of the band alignment in a graphene base layer hot electron transistor operating in the off-state (a) and in the on-state (b). EB barrier is the emitter-base barrier, while BC barrier is the base-collector barrier. Ref [52].
III nitride emitter layers have been demonstrated by many groups\textsuperscript{62,63}. For large scale production of these devices, however, direct growth of the nitride semiconductors on graphene must be realized.

### 4.2.4 Growth of group-III nitrides on graphene

The growth of group-III nitrides on the basal plane of pristine graphene is rather challenging. The reason for this is largely due to the absence of dangling bonds to promote nucleation and growth of overlayers. As a result, the graphene surface is chemically inert. In order to provide sites for nucleation of deposited adatoms on graphene, a change in hybridization of the carbon atoms in graphene, from sp\textsuperscript{2} to sp\textsuperscript{3}, must first be realized in order to provide dangling bonds for nucleation. This change in the hybridization of the bound carbon atoms in the hexagonal layered crystal is rather energy intensive, since it requires breaking bonds and/or knocking off carbon atoms. Therefore, there is a higher barrier associated with forming a bond with adatoms onto graphene.

The MOCVD growth of III-nitride materials directly and indirectly on graphene have been reported extensively in literature. Chung et al. was first to report the growth of GaN films by MOCVD on highly oriented ZnO nanowalls produced on CVD graphene\textsuperscript{27,28}. Using this process, they obtained highly c-oriented GaN films with six-fold symmetry, however, the FWHM in x-ray rocking curve of the (0002) reflection of GaN was 2880 arcsec, where typically GaN grown with an AlN buffer layers on SiC is < 400 arcsec. Also, the RMS roughness of the film over a 5 µm x 5 µm area was 11 nm, which is inferior to GaN produced on both sapphire and SiC. Later on, Baek et al. also reported MOCVD growth of GaN microdisks on a low-temperature GaN buffer layers grown ZnO/CVD
graphene templates. There films, however, had a high density of threading dislocations and were polycrystalline. Moreover, Choi et al. grew GaN directly on few layered graphene produced via diffusion assisted synthesis. They showed that GaN tends to nucleate along naturally formed ridges and not on the basal plane of graphene. This was because the graphene ridges contained a considerable amount of dangling bonds that act as nucleation sites. The crystal quality of their films, however, were poor. Gupta et al. grew semi-polar group-III nitrides on CVD graphene. Their GaN films were grown on CVD graphene using a two-step temperature grown AlN buffer layer (800°C/1040°C). The films produced by Gupta et al. were polycrystalline and very rough, however, they showed that by increasing the V/III ratio, semi-polar planes could be effectively isolated. One of the most important works on the growth of GaN on graphene for the purpose of fabrication of hot electron transistors was demonstrated by Nepal et al. For the epitaxial growth of group-III nitrides, they used fluorine-functionalization epitaxial graphene. Epitaxial graphene was produced on the Si-face of SiC via high temperature selective sublimation of silicon, leaving a carbon rich surface that can reconstruct under appropriate conditions to form sp² carbon networks of graphene. The epitaxial graphene layers were pristine and highly crystalline as opposed to polycrystalline CVD graphene. Fluorination of graphene was achieved using XeF₂ gas and resulted in formation of semi-ionic F-C functional sites on the surface of graphene. These functional groups served as nucleation sites for III-nitride growth. These functional groups, however, were not stable under conventional high temperature MOCVD growth conditions. To get around this problem, Nepal et al. used atomic layer epitaxy to deposit a low temperature AlN buffer layer prior to the growth of GaN by MOCVD. The FHWM of the x-ray rocking curve for the (0002) reflection of GaN.
was reported to be 544 arcsec and the Raman spectra showed that graphene remained. Finally, Kim et al., demonstrated the direct growth of GaN on epitaxial graphene produced on SiC without an AlN buffer layer\textsuperscript{32}, however the nature of chemical reactions that occur at the interface during MOCVD growth was not clear, hence the studies presented in this chapter.
4.3 Experimental Procedure

4.3.1 MOCVD growth conditions and experimental setup

Nucleation and growth studies of GaN and AlN were carried out in a customized vertical cold-wall MOCVD reactor on a SiC-coated graphite susceptor that is inductively coupled to RF coils. The precursors used for the studies in this chapter were trimethylaluminum (TMAI), trimethylgallium (TMGa), and ultra-high purity ammonia (NH₃) gas for Al, Ga, and N, sources, respectively. Ultra-high purity hydrogen was used as the carrier gas during all experiments. Furthermore, the MOCVD reactor was equipped with a k-Space Associates (KSA) multi-beam optical stress sensor (MOS). This in situ optical measurement technique allows the evaluation of film stress during growth based on changes in the curvature of the sample from laser reflectance. The simultaneously collected laser reflectance from the growth front of the epilayers also provides real-time monitoring of film thickness, morphological evolution and surface roughness throughout the growth experiments. More details on the operation of MOS can be found in Chapter 3.

To complement experimental observations, Density Functional Theory (DFT) simulations were also carried out, in collaboration with Dr. Lazaro Calderin (Materials Research Institute – Penn State) to elucidate the structure at the interfaces of the materials using the local density approximation (LDA) ⁶⁷, with dispersion corrections according to Ortmann et al. ⁶⁸. We used norm-conserving pseudopotentials for all the elements, as well as grid of k-points and cutoff-energies that guaranteed errors in total energies below 0.1 meV/atom and errors in the forces less than 0.1 meV/Å.
4.3.1.1 Direct growth of GaN-on-SiC

Prior to growth, n-type Si-face (0001) 6H-SiC substrates were cleaned using standard solvents (1 hour opticlear soak or heated PRS 3000 to remove resist after dicing, acetone scrub, glacial acetic acid scrub, acetone scrub, 5 minutes of acetone sonication in a heated bath, 5 minutes of isopropyl alcohol (IPA) sonication in a heated bath, 6× DI rinse, heated Nanostrip with a stir bar for 10 minutes) followed by a 10:1 HF dip and high-temperature H₂ etch at 1100°C to ensure the removal of the native oxide from the surface. For the direct growth of GaN on SiC, a two-step temperature growth process was utilized. The two-step GaN consisted of an initial (650 nm) low-temperature layer grown at 900°C and 100 Torr, followed by a thick main (2.5 µm) high-temperature layer of GaN grown at 1100°C and 100 Torr. The molar flow rates used for the initial low-temperature and main high-temperature GaN layers were fixed at 7.95 µmol/min and 62.50 mmol/min for TMGa and NH₃, respectively.

4.3.1.2 Indirect growth of GaN-on-SiC via an AlN buffer layer

To understand the difference in growth stress, GaN growth was also carried out with an AlN buffer layer, in addition to the direct growth of GaN on SiC via the two-step temperature growth process. For the growth of GaN on SiC with a AlN buffer layer, 100 nm of AlN was first grown on SiC at 1100°C and 100 Torr with the molar flow rates of 13.80 µmol/min and 80.25 mmol/min for TMAI and NH₃, respectively. Following the growth of AlN, a thick (2.5 µm) layer of GaN was grown at 1100°C and 100 Torr under the aforementioned molar flow rates used for the direct growth of GaN on SiC.
4.3.1.3 Indirect growth of AlN- and GaN-on-SiC via epitaxial graphene intermediate layers

The growth of EG was performed on the Si-face of 6H-SiC semi-insulating substrates via sublimation of silicon from (0001) surface at 1700°C for 30 min under 600 Torr argon (Ar) pressure. Prior to graphene growth, a pre-hydrogen (H₂) etch of the surface was performed at 1500°C for 15 min under 700 Torr in a 10% H₂/Ar mixture. In addition to EG growth on (0001) 6H-SiC, samples were also grown on vicinal 4H-SiC n-type substrates (Dow Chemical), misoriented in the <1120> direction by 4° from the c-axis to increase the step edge density. Selected EG samples grown on (0001) 6H-SiC substrates were treated with an O₂ plasma (TePla M4L Barrel plasma etch system) for 90 sec at 100 W and 500 mTorr total pressure, to increase the point defect density in the EG.

Prior to the nucleation of GaN and AlN, EG samples were held at 1100°C in 9.2 sLM of H₂ under 100 Torr total pressure for 30 min. This pre-nucleation anneal step was performed in order to passivate the graphene buffer layer with hydrogen at the graphene/(0001) SiC interface. This hydrogenation process produces quasi-free standing epitaxial graphene (QFEG)\(^69\). The nucleation of AlN and GaN on EG was performed under 50 Torr and 100 Torr total pressure, respectively. The molar flow rates used for nucleation of AlN on EG were 24.15 µmol/min and 89.30 mmol/min for TMAI and NH₃, respectively. For the nucleation of GaN, the molar flow rates for TMGa and NH₃ were 7.93 µmol/min and 62.50 mmol/min, respectively. H₂ was used as the carrier gas and the temperatures used for the nucleation study of both AlN and GaN were 500°C, 700°C and 900°C.
4.3.2 Post MOCVD nucleation and growth surface characterization

Tapping mode atomic force microscopy (AFM) was performed on the samples using a Bruker Dimension Icon system operated at a scan rate between 0.5 - 1.00 Hz. Furthermore, a systematic investigation of the sample surface topography with field-emission scanning electron microscopy (FE-SEM) was performed using a LEO 1530 instrument operated at 3 kV. In addition, surface chemical analysis of the samples was evaluated with X-ray photoelectron spectroscopy (XPS Kratos Axis Ultra) using an Al Kα x-ray source which had a binding energy of 1486 eV and an energy resolution of 0.1 eV. Finally, Raman spectra and mapping of samples were measured with a WITec Confocal Raman system operated at room temperature using a 488 nm laser excitation source to evaluate the post-growth residual stress of the GaN film and the point defect density in graphene.

4.3.3 Post MOCVD nucleation and growth microstructural characterization

High-resolution x-ray diffraction (HR-XRD) measurements were employed using a Philips MRD four-circle diffractometer with a Cu Kα 0.15406 nm radiation source to investigate the crystallinity and crystallographic orientation of the nuclei of AlN and GaN. Moreover, transmission electron microscopy (TEM) analysis was performed on cross sectional specimens. These site specific cross sectional specimens were prepared by focused ion beam (FIB) milling using an “in situ lift-out” technique. Prior to cross sectional milling, a protective carbon layer was first deposited over the region of interest by electron-beam deposition. The starting FIB milling voltage was 30 kV to create a membrane of the cross-sectional sample and thin the sample to electron transparency. The final milling
voltage was stepped down to 2 kV to further thin the samples and minimize sidewall damage. High-resolution transmission electron microscopy (HR-TEM) analysis was performed on the cross-sectional samples with a FE-2010F scanning/TEM (S/TEM) instrument operated at 200 kV and a FEI Titan3 dual aberration corrected S/TEM instrument operated at 300 kV that was equipped with a SuperX Energy Dispersive Spectrometry (EDX) system for elemental analysis.
4.4 Results and Discussion

4.4.1 The evolution of stress during MOCVD growth of GaN-on-SiC

The evolution of stress during the growth of III-nitride films is a complex process that depends on the interacting surface and growth conditions. With in situ measurements, both a qualitative and quantitative understanding of the growth process and stress evolution, from the initial stages of nucleation and islanding through coalescence and lateral growth into continuous films, can be achieved.

4.4.1.1 Investigating the growth and morphological evolution of GaN-on-SiC

Differences in the growth mode evolution of GaN were observed when the film was grown directly on SiC compared to growth with an AlN buffer layer. This is evident from in situ optical reflectance versus thickness data, collected with MOS during the growth of the main high-temperature GaN layer on 6H-SiC with an AlN buffer (Figure 4.8.a), and with an initial lower-temperature GaN layer (Figure 4.8.b). Oscillations in the reflectance versus thickness data provide information on the morphological evolution during the growth of GaN\textsuperscript{70,71}. During growth, the intensity of the reflected laser beam off of the film surface can diminish as a result of surface roughing which scatters the laser light. Therefore, qualitative information on the density and aspect ratio of the GaN nuclei can be gleaned from a measurement of the intensity of the reflectance as a function of thickness. In addition, the time required for the laser intensity to recover following nucleation provides insight into the island coalescence process and the transition from a three-dimensional island growth mode to a two-dimensional step flow mode.
The reflected laser intensity as a function of layer thickness measured during the growth of the main high-temperature GaN layer is plotted in Figure 4.8.a and 4.8.b for growth on the AlN buffer layer and the lower temperature GaN layer on SiC, respectively.

**Figure 4.8** | Reflectance versus thickness data collected during the growth of: (a) the high-temperature GaN layer grown on 6H-SiC with an AlN buffer layer, and (b) the high-temperature GaN layer grown on 6H-SiC with an initial low-temperature GaN layer (highlighting I and II growth stages). Stress-thickness versus thickness curves collected during the growth of: (c) the main high-temperature GaN layer grown on 6H-SiC with an AlN buffer layer, and (d) the main high-temperature GaN layer grown on 6H-SiC with an initial low-temperature GaN layer.
In the case of the growth on an AlN buffer layer (Figure 4.8.a), the intensity of the reflected laser decreases only slightly at the start of the GaN growth and remains nearly constant throughout the growth process. This implies that during the initial growth of the main high-temperature GaN layer on the AlN buffer layer, rapid coalescence of the GaN nuclei occurs and two-dimensional step flow growth initiates during early stages of the growth process.

In contrast, the growth of the main high-temperature GaN layer on 6H-SiC consists of two stages when a lower-temperature GaN layer is utilized. As seen from the reflectance versus thickness data of the high-temperature GaN layer in Figure 4.8.b (stage I), the reflected intensity diminishes initially and gradually recovers with increasing thickness.

Figure 4.9 | Reflectivity and stress measurements during the growth of the initial layers.
During the growth of the initial lower-temperature GaN layer (Figure 4.9), the intensity of the reflectance diminished without recovery due to incomplete coalescence of the truncated GaN islands and surface roughness that arise from the poor wettability of GaN on SiC. Therefore, the prolonged recovery of the reflectance during the nucleation of the high-temperature GaN layer implies an initial low density of GaN nuclei that eventually form into large islands. This leaves the surface rough and hence results in a decrease in the intensity of the reflectance initially. These islands laterally overgrow and coalesce with increasing growth time. When the GaN islands coalescence, the reflectance begins to recover. Once the reflectance saturates, as seen in Figure 4.8.b (state II), two-dimensional step flow growth commences and continues with increasing thickness.

4.4.1.2 The relationship between island coalescence and growth stress of GaN-on-SiC

The initial stages of island coalescence can impact the stress evolution during the growth process. The growth of the initial lower-temperature GaN layer on SiC leads to the formation of large truncated islands as a result of the poor wettability of GaN on the surface of SiC. Therefore, a two-step temperature growth process was utilized in order to overcome the challenge of the coalescence of islands into a continuous film. In the other case, the observation of the rapid coalescence of GaN on the AlN buffer layer, comes from the improved wettability of GaN on the surface of AlN. This leads to a high nucleation density of GaN, as well as a reduction in the lattice mismatch (~2.4%). In addition, the morphological evolution (from three-dimensional growth to two-dimensional step-flow) that results from the coalescence of the islands into a film, creates a transition point in the evolution of the film stress.
This is clearly evident in the stress-thickness versus thickness curves in Figure 4.8.c and 4.8.d, collected during the growth process with the MOS. As seen in Figure 4.8.c and 4.8.d, the slope in the stress-thickness versus thickness curve represents the incremental stress in the film. Here, the negative and positive slopes in the stress-thickness versus thickness curve signifies compressive and tensile stress, respectively. With the use of an AlN buffer layer, which grew under an initial incremental compressive stress of -2.10 GPa and gradually relaxed to -0.338 GPa (Figure 4.9), the high-temperature GaN layer grows under an initial compressive stress of -1.04 GPa (Figure 4.8.c). This compressive stress gradually relaxes with thickness to a final incremental stress is -0.17 GPa. In the case of GaN grown directly on SiC with a lower-temperature GaN layer (Figure 4.8.d), the high-temperature GaN grows initially under a compressive stress value of -0.35 GPa. This compressive stress transitioned into a tensile stress around ~300 nm and then grew under an approximately constant incremental tensile stress of +0.27 GPa.

There is a dynamic interplay between growth related stresses that arise from the evolving film morphology and the mechanisms for stress relaxation. During initial nucleation, the film can be under compression due to capillary forces between islands\textsuperscript{72,73}. However, the growth of GaN on AlN leads to compressive stress largely due to epitaxial mismatch. This compressive stress is observed in the case of the growth of the high-temperature GaN layer on SiC with an AlN buffer layer (Figure 4.8.c). As the islands grow laterally, the capillary forces can decrease to some extent, resulting in partial relaxation of the compressive stress.

Furthermore, the gradual relaxation of the compressive may also result from the inclination of edge-type TDs in the microstructure. The inclination of TD with increasing
thickness has been reported during the growth of AlGaN on SiC\textsuperscript{43}. Details on the mechanism of compressive stress relaxation due to the inclination of TDs have been discussed by Romanov and Speck\textsuperscript{74}. In the case of the high-temperature GaN layer grown after the initial lower-temperature GaN layer on SiC (Figure 4.8.d), the initial observed compressive stress of - 0.35 GPa likely arises from the morphological evolution of the high-temperature GaN on the truncated and rough surface of the initial lower-temperature layer. During the growth of the high-temperature GaN layer, adatoms diffusing across the surface can incorporate in-between ledges and grain boundaries. It is suggested that this mechanism of the attachment of adatoms can induce compressive stress during growth of polycrystalline films\textsuperscript{75,76}. However, tensile stress can also develop in films during the early stages of the growth, through the mechanism of island “zipping”\textsuperscript{77}. Initially during the growth of the high-temperature GaN layer on SiC with a low-temperature GaN layer, islands nucleate and laterally grow from favorable sites. A continuous film is formed by islands impinging on each other, reducing the interfacial energy by forming grain boundaries. The elastic deformation of the islands as they are “zipping” together levies a cost of an increase in strain energy. Therefore, the induced tensile stress transition point observed in the stress-thickness versus thickness curve (Figure 4.8.d) in the high-temperature GaN layer may be the result of this island “zipping up” process. This observation of compressive-to-tensile stress transition during early stages of growth have been reported in Volmer-Weber growth of GaN on Si\textsuperscript{78,79}.

After island coalescence and surface roughness saturation, a transition to two-dimensional step-flow growth occurs. The stress behavior of the film during this stage of the growth process highly depends on the mobility of the adatoms. In low adatom mobility
growth of films, such as the MOCVD process presented experimentally here, the diffusion of adatoms on the surface is lower compared to the impingement rate. This consequently leads to the subsequent epitaxial growth of films in the strained state of the previous template layer. This growth effect was pointed out by Abermann and Koch in the growth of metal films with low adatom mobility$^{80,81}$. The growth of the high-temperature GaN layer remains compressive, when grown on a compressively strained AlN buffer layer (incremental stress = - 0.74 GPa), primarily due to epitaxial mismatch. However, in the case of the growth of the high-temperature GaN layer on SiC with an initial low-temperature GaN layer, tensile stress is sustained during two-dimensional growth after the tensile stress transition (induced from the island zipping-up process), primarily as a result of the low adatom mobility.

Residual stress is present post-growth in the GaN layers grown on 6H-SiC. This is evident from the Raman spectra of the GaN layers (Figure 4.10) collected after the growth process and cool down of the sample to room temperature. The residual stress in the GaN films after cool down is a combination of the intrinsic growth stress and extrinsic stress that results due to differences in the coefficient of thermal expansion (CTE) mismatch. The residual biaxial compressive and tensile stress in the GaN films can be determined respectively from the upward and downward frequency shift of specific Raman modes, relative to unstrained bulk GaN. Measurements of the GaN layers were done in a backscatter $z(x,x)\bar{z}$ configuration, with an excitation source (488 nm) and power density that insured that the GaN layer was completely probed. In c-plane wurtzite GaN, there are six active Raman modes$^{82}$. For the $z(x,x)\bar{z}$ configuration, the $E_2$(high) and $A_1$(LO) modes are only observed. This selection rule of the Raman mode occurs in wurtzite GaN as a
result of the optically anisotropic uniaxial crystal. The $E_2^{\text{(high)}}$ mode for bulk GaN is centered at 568.0 cm$^{-1}$ and is most sensitive to biaxial stress in the film$^{82,83}$. As evident in Figure 4.10, the Pseudo-Voigt fit of the $E_2^{\text{(high)}}$ mode of GaN revealed a downward shift in frequency ($566.1 \pm 0.3$ cm$^{-1}$), i.e. residual biaxial tensile stress, in the case of the growth of GaN on SiC with an AlN buffer layer. However, in the case of the growth of GaN on SiC via the two-step temperature growth process, a much larger downward shift in frequency ($563.6 \pm 0.3$ cm$^{-1}$), i.e. residual biaxial tensile stress, is observed. Employing the linear stress coefficient of $+4.2$ cm$^{-1}$/GPa for the $E_2^{\text{(high)}}$ mode, the residual biaxial stress ($\sigma$) can be calculated from the deviation in frequency ($\omega$) with respect to stress-free bulk GaN (568.0 cm$^{-1}$)$^{82,84}$.

**Figure 4.10** | Raman spectra collected at room temperature with a 488 nm excitation source in backscatter geometry of $z(x,x)\overline{z}$ for: GaN grown on 6H-SiC with an AlN buffer layer (top blue) and GaN grown directly on 6H-SiC via the two-temperature growth process (bottom red).
\[ \sigma = \frac{\Delta \omega}{4.3} \text{ (cm}^{-1}\text{GPa}^{-1}) \] 

We find in the case of the growth of GaN on an AlN buffer layer, a residual biaxial tensile stress value of + 0.46 GPa is observed and in the case for the growth of GaN on SiC via the two-step temperature growth process, a residual biaxial tensile stress value of + 1.05 GPa is observed. The caveat with the growth of GaN on SiC is that thermal expansion mismatch induced tensile stress is generated during post-growth cool down. The calculated tensile stress as a result of cool down from 1100°C – 25°C for GaN and AlN on SiC are ~ + 0.40 GPa and ~ + 0.80 GPa, respectively\(^4\). Therefore, the observed differences in the residual stress is attributed to the degree of the thermal expansion mismatch induced stresses in overcompensating the final stress state of the film after the cool down process.

### 4.4.1.3 The impact of stress on the surface morphology of GaN-on-SiC

The tensile stress induced from the thermal expansion mismatch with SiC can lead to cracking of the GaN film. This is evident in the Nomarski optical contrast micrographs of the GaN surface displayed in Figure 4.11.a and 4.11.b. The growth of the high-temperature GaN layer on SiC with an AlN buffer layer (Figure 4.11.a) leads to a crack-free surface of GaN. In the case of the growth of GaN on SiC with a lower-temperature GaN layer (Figure 4.11.b), the micrograph shows a low density of cracks across the surface. As observed from MOSS during the growth of GaN on SiC with the low-temperature GaN layer (Figure 4.8.d), the incremental stress of the film remained tensile after ~300 nm. Upon cool down, the additional generated tensile stress as a result of thermal expansion mismatch can lead to the observed cracking in the GaN film. This is consistent with the residual biaxial tensile stress observed in Raman (Figure 4.10) for the growth of the two-step GaN
on SiC, where the growth of GaN with an AlN buffer layer indicates a smaller residual biaxial tensile stress, below the critical stress for cracking, thus producing crack-free GaN after post-growth cool down.

![Nomarski optical contrast micrographs of the surface of: (a) GaN grown on 6H-SiC with an AlN buffer layer, and (b) GaN grown directly on 6H-SiC via the two-temperature growth process (arrows indicate channeling cracks on the GaN surface). AFM images of the height (c-d) and amplitude (e-f) collected with tapping mode over a 20 × 20 µm² area of: (c-e) GaN grown on 6H-SiC with an AlN buffer layer, and (d-f) GaN grown directly on 6H-SiC via the two-temperature growth process. The insets in (c-d) are AFM images of the height collected over a 2 × 2 µm² area.](image)

**Figure 4.11** | Nomarski optical contrast micrographs of the surface of: (a) GaN grown on 6H-SiC with an AlN buffer layer, and (b) GaN grown directly on 6H-SiC via the two-temperature growth process (arrows indicate channeling cracks on the GaN surface). AFM images of the height (c-d) and amplitude (e-f) collected with tapping mode over a 20 × 20 µm² area of: (c-e) GaN grown on 6H-SiC with an AlN buffer layer, and (d-f) GaN grown directly on 6H-SiC via the two-temperature growth process. The insets in (c-d) are AFM images of the height collected over a 2 × 2 µm² area.

Although the compressive incremental stress observed in the GaN layer grown on SiC with the AlN buffer layer (Figure 4.8.c) mitigates cracking that results from the thermal expansion induced tensile stress, the use of the AlN buffer layer can lead to an increase in surface roughness. AFM images of the height (Figure 4.11.c-d) and amplitude (Figure
were collected with tapping mode AFM. The macroscale RMS roughness of the high-temperature GaN surface was examined by AFM over a 20 × 20 μm² area. An improvement in the macroscale surface roughness of GaN is observed for the direct growth of GaN on SiC via a two-step temperature growth process (RMS = 1.44 nm), in comparison to the growth of GaN with an AlN buffer-layer (RMS = 4.09 nm). This improvement in the RMS roughness may arise from a reduction in compressive stress-induced surface roughing in the case of the growth of GaN on SiC via the two-step temperature growth process. This is similar to what was observed in the growth of AlGaN on bulk AlN and the growth of N-polar GaN via two-step temperature growth process on SiC. Moreover, the prolong recovery of the reflectance during the nucleation of the high-temperature GaN layer on the lower-temperature GaN layer (Figure 4.8.a) leads to large island coalescence and two-dimensional step flow growth with terraces relatively wider (Figure 4.11.f) than terraces resulting from the growth of GaN on the AlN buffer layer (Figure 4.11.e). The wider observed terrace width during two-dimensional step-flow growth may also contribute to the improved macroscale roughness of GaN grown on SiC via the two-step temperature growth process.

4.4.1.4 The influence of island coalescence on the microstructure of GaN-on-SiC

X-ray rocking curve (XRC) measurements in HR-XRD were also performed to further understand the interrelationship between the growth stress evolution and structural quality of the GaN films. As observed from the reflectance-thickness data (Figure 4.8.b) and AFM (Figure 4.11.c and 4.11.e), the delayed coalescence of GaN, when grown on SiC with a lower-temperature GaN layer, leads to larger island size and improved surface morphology. Therefore, the delayed coalescence of the islands in turn should also give rise
to a reduction in the density of TDs. There is a strong correlation between TD density and the mosaicity of the film. During the growth of GaN, TDs are generated to accommodate the misorientation of the sub-grains, i.e. mosaic tilt and twist. The tilt and twist represent misorientation of the mosaic out-of-plane and in-plane, where they relate to screw (c-type) with \( b = [0001] \) and edge (a-type) \( b = 1/3 <11\bar{2}0> \) TD components, respectively. From the XRC FWHM of the (0002) and (10\bar{1}0) reflections of c-plane GaN, the angle distribution of the respective mosaic tilt and twist, which characterizes the TDs density in the film, is measured. However, the XRC FWHM of the (10\bar{1}0) reflection cannot be measured directly in a standard ‘four-circle’ diffractometer geometry. In order to estimate

**Figure 4.12** | A series of measured x-ray rocking curve FWHM reflections of GaN as a function of inclination angle to estimate twist (\( \chi = 90^\circ \)) and TD density in the GaN films using a model developed by Srikant et al., for the growth of GaN on 6H-SiC: with an AlN buffer layer (diamonds, dashed line fit), and via the two-step temperature growth process (squares, solid line fit).
the TD density in the GaN layers, a model developed by Srikant et al. was utilized. The model considers crystallite rotations and convolutions of two Pseudo-Voigt functions. Therefore, by measuring a series of XRC FWHM as a function of inclination angle ($\chi$) as seen in Figure 4.8, the XRC FWHM of the (10$\overline{1}$0) reflection at $\chi = 90^\circ$, i.e. twist in the film, can be estimated. Once twist is estimated, then the screw and edge TD density ($\rho$) is calculated using the classical model for the distribution of random dislocations:

$$\rho_{\text{screw}} = \frac{r_{\text{tilt}}^2}{4.36 \times b_{\text{screw}}^2} \quad \text{Eq. 5.2}$$

$$\rho_{\text{edge}} = \frac{r_{\text{twist}}^2}{4.36 \times b_{\text{edge}}^2} \quad \text{Eq. 5.3}$$

where $r_{\text{tilt}}$ and $r_{\text{twist}}$ are the XRC FWHMs of the (0002) and (10$\overline{1}$0) respectively. Burgers vectors along [0001] $b_{\text{screw}}$ and $1/3 < 11\overline{2}0 > b_{\text{edge}}$ are 5.1850 Å and 3.1888 Å, respectively. Figure 4.12 illustrates the fitted XRC FWHM as a function of inclination angle for the GaN layers grown on SiC via the two-step temperature process and with the AlN buffer layer. Evident in Table 4.1, a reduction in the total $\rho_{TD}$ of GaN grown via the two-step temperature process is observed, as compared to the growth of GaN with the AlN buffer layer. This reduction in the TD density in the case of the growth of GaN on SiC via the two-step temperature growth is attributed to larger island size and delayed coalescence of the high-temperature GaN layer, when the AlN buffer layer is not utilized.

<table>
<thead>
<tr>
<th>GaN on SiC with AlN buffer layer</th>
<th>Edge $\rho_{TD}$ (cm$^{-3}$)</th>
<th>Screw $\rho_{TD}$ (cm$^{-3}$)</th>
<th>Total $\rho_{TD}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN on SiC with AlN buffer layer</td>
<td>$2.24 \times 10^9$</td>
<td>$4.97 \times 10^7$</td>
<td>$2.29 \times 10^9$</td>
</tr>
<tr>
<td>GaN on SiC via two-step temp. growth</td>
<td>$1.91 \times 10^9$</td>
<td>$3.27 \times 10^7$</td>
<td>$1.94 \times 10^9$</td>
</tr>
</tbody>
</table>

Table 4.2 | Estimated TD densities of GaN as calculated by HR-XRD
TEM was used to investigate the microstructure of FIB cross-sectional specimens of GaN grown directly on SiC via the two-step temperature growth process. Figure 4.13.a shows a bright-field image collected near the GaN <10̅10> zone axis using multi-beam diffraction conditions to reveal all types of TDs in the GaN layer. The TDs are primarily confined within the lower-temperature GaN layer, where the diffraction pattern (Figure 4.13.a inset) shown in that region reveals single crystalline wurtzite GaN. The topmost part of the high-temperature GaN layer reveals a lower density of TDs propagating to the surface, where STEM shows a flat surface of GaN. In order to evaluate the different type of dislocations confined in the lower-temperature GaN layer, weak-beam dark-field TEM images were collected at the <10̅10> zone axis, tilted towards \( \mathbf{g} = <0002> \) (Figure 4.13.c) and \( \mathbf{g} = <11̅20> \) (Figure 4.13.d) to reveal, c- and (a+c)-type and a- and (a+c)-type dislocations, respectively, in the film. Weak-beam TEM shows predominant (a+c)-type dislocations in both \( \mathbf{g} \) conditions. However, TEM also reveals the presence of both basal plane stacking faults (BSFs) and 11̅20 prismatic stacking faults (PSFs). When \( \mathbf{g} = <11̅20> \) (Figure 4.13.d-e), the observed vertical fringes within the first 500 nm from the GaN/SiC interface are related to PSFs. They are invisible under \( \mathbf{g} = <0002> \) (Figure 4.13.c) since \( \mathbf{g} \cdot \mathbf{R} = 0 \), where \( \mathbf{R} \) is the stacking fault displacement vector.

The formation of PSFs are likely to originate from the nature of the island coalescence of the initial lower-temperature GaN layer, as a result of the poor wetting behavior of GaN on SiC. The observation of 11̅20 PSFs near the GaN/SiC interface was also reported in the molecular beam epitaxy (MBE) growth of GaN on vicinal 6H-SiC\(^{89}\). Furthermore, the presence of BSFs may prevent the propagation of TDs into the topmost part of the GaN, thus reducing the total \( \rho_{TD} \) as observed from HR-XRD.
4.4.2 Nucleation studies of III-nitride layers on epitaxial graphene grown on SiC

The use of graphene as a pseudo-substrate for the growth of GaN and AlN has gained interest due to the hexagonal arrangement of these $sp^3$ hybridized carbon atoms being similar to the (0001) c-plane of wurtzite GaN. However, most studies have produced...
layers with surface morphologies and structural qualities inferior to those produced on SiC and sapphire. This is due to the challenges associated with heteroepitaxy on the basal plane of pristine graphene due to the lack of dangling bonds and thus nucleation sites. Despite the growing interest in the heteroepitaxy of GaN and AlN layers on graphene, there have been limited studies aimed at understanding the nucleation process. In the second part of this chapter, we will address the challenges of the heteroepitaxy of III-nitrides on graphene through nucleation studies of AlN and GaN on epitaxial graphene formed on SiC, to therefore provide new insight into the initial stages of the growth of potential thin films on such van der Waal surfaces. Furthermore, we reveal the impact of the nucleation process on the structural properties of graphene, which is of important understanding in order to tailor growth conditions and/or engineering the graphene pseudo-substrate in a matter that could be favorable for sequential growth of GaN epilayers with high structural quality.

4.4.2.1 Nucleation of AlN on epitaxial graphene on SiC

The chemical reactivity of graphene significantly impacts the nucleation of group III-nitride layers. This is evident from our investigation of the effect of temperature on the size and density of AlN nuclei on EG. The FE-SEM images (Figure 4.14.a-c and its insets) indicate that the nucleation of AlN on the (1̅10$n$) EG coated step edges of SiC and (0001) terraces has occurred for all growth temperatures. The nucleation of AlN primarily occurs along the EG coated step edges at 500°C and 700°C (Figure 4.14.a-b) with the terraces exhibiting a low density of AlN nuclei. An increase in the size of the AlN nuclei on the terraces of EG occurs at 700°C (Figure 4.14.b and inset), where this increase in the nuclei size is attributed to the enhancement of the adatom mobility with increasing temperature.
Moreover, a dramatic increase in the density of AlN nuclei on the terraces of EG occurs when the nucleation temperature is increased to 900°C (Figure 4.14.c and inset). The observed differences between the nucleation density of AlN on the EG coated step edges and terraces may arise from the differences in their respective chemical reactivity. Lin et al. demonstrated with surface potential force microscopy (SPFM) measurements of EG, that a reduction in the surface potential occurs across the EG coated step edges of SiC. This difference in the surface potential modifies the chemical reactivity of graphene at

**Figure 4.14** | FE-SEM images following the nucleation of AlN at (a) 500°C, (b) 700°C and (c) 900°C. Preferential nucleation of AlN on (110n) EG coated step edges are indicated in the image, where the insets illustrates the size and density of the AlN nuclei on the (0001) terrace region. The scale bar of the insets is 400 nm.
the step edges compared to that of the basal plane terraces. In addition, the $sp^2$ carbon $\pi$-bonds that reside on highly curved surfaces inherit high localized strain that can increase the surface chemical reactivity of graphene at the step edges and therefore influence the nucleation of subsequent deposited materials onto the surface. In fact, Speck et al. demonstrated preferential nucleation of aluminum oxide, deposited by atomic layer deposition (ALD), on the EG coated step edges in comparison to the terraces. A similar
selective growth is also observed on highly-oriented pyrolytic graphite (HOPG) and exfoliated graphene at the step edges and particularly at defects.\(^{95}\)

Defects play a critical role in the nucleation and growth of AlN on graphene. This is evidenced when comparing the nucleation of 12 nm of AlN at 500°C on EG produced under different conditions. Investigated samples varied in step edge density (Figure 4.15a and 4.15.b) and defect density (Figure 4.15.c). Clearly evident in Figure 4.15.a and 4.15.b, the increased step edge density leads to no additional nucleation of AlN on the terraces itself, but EG treated with an O\(_2\) plasma, to intentionally introduce defects into the graphene lattice, exhibits a significant increase in AlN nucleation density on the terraces. The point defect density in the graphene layers is confirmed in Raman spectroscopy (Figure 4.15.d), where an increase in the defectiveness of EG after plasma treatment leads to an increase in the \(I(D)/I(G)\) ratio (\(I\) is the peak intensity). The G peak in graphene corresponds to the high-frequency \(E_{2g}\) phonon which signifies sp\(^2\) hybridized graphene, whereas the D peak signifies disorder due to defects induced on the sp\(^2\) hybridized graphene lattice.\(^{96-98}\)

Following Cançado et al.\(^{99}\):

\[
 n_D^2 (cm^{-2}) = 7.3 \times 10^{-9} \times E_L^4 (eV^4) \times [I(D)/I(G)]
\]

Eq. 5.4

where \(E_L\) is the energy of the laser excitation source (2.54066 eV). The defect density \((n_D)\) in EG before and after O\(_2\) plasma treatment (quantified from the \(I(D)/I(G)\) ratio) was \(n_D = 1.42 \times 10^9\) cm\(^2\) and \(n_D = 2.48 \times 10^{11}\) cm\(^2\), respectively. The ~200x increase in EG defect density correlates strongly with the significant increase in AlN nucleation density across EG. This provides evidence that the increase in the nuclei density observed for the nucleation of AlN at 900°C (Figure 4.15.c) is likely due to the introduction of defects
during the nucleation process. The increase in defect incorporation with increasing temperature is likely to originate from the precursors used during the AlN nucleation process - such as NH₃, increasing available nucleation sites for AlN and resulting in the high density of AlN nuclei present across the entire surface of the sample.

4.4.2.2 Nucleation of GaN on epitaxial graphene on SiC

![Figure 4.16](image)

**Figure 4.16** | FE-SEM images following the nucleation of GaN at (a-c) 500°C, (d-f) 700°C and (g-i) 900°C, indicates preferential nucleation of GaN: (b), (e) and (h) along the (1̅1̅0n) EG coated step edges and (c), (f) and (i) defects in regions of few-layered EG (lighter contrast) on the (0001) terrace as compared to regions of multi-layered EG (darker contrast) due to the enhanced chemical reactivity of EG at those regions. The scale bar on the right column is 400 nm.
Temperature has a direct effect on the faceting and crystallographic orientation of the GaN nuclei grown directly on graphene. The FE-SEM images (Figure 4.16.a-i) show the nucleation of GaN on the (1\overline{1}0n) EG coated step edges of SiC and (0001) terraces as a function of temperature. At 500°C (Figure 4.16.a-c), the nucleation of GaN, which is observed to be polycrystalline, occurs only along the EG coated step edges (Figure 4.16.b) and no further nucleation of GaN is observed on the terraces (Figure 4.16.c). The occurrence of polycrystalline GaN arises from the low decomposition efficiency of NH\textsubscript{3} at 500°C as well as the low surface adatom mobility of Ga at such reduced temperatures. The increase in the nucleation temperature to 700°C and 900°C (Figure 4.16.d-f and 4.16.g-i, respectively), shows GaN primarily nucleating along the EG coated step edges with an increase in the density of the GaN nuclei on the terraces with increasing temperature. Similar to AlN, the preferred nucleation of GaN along the EG coated step edges is attributed to the enhanced chemical reactivity at those regions due to surface potential differences and/or localized strain\textsuperscript{91,93}. The increase in the density of the GaN nuclei on the terraces of EG with increasing temperature, provides evidence that the density of the GaN nuclei on the terraces is correlated to density of defects in EG introduced during the nucleation process. This is clearly evident when comparing the nucleation of GaN at 500°C (Figure 4.16.a) and 900°C (Figure 4.16.g). Furthermore, an increase in the faceting of the GaN nuclei is seen with increasing temperature (Figure 4.16.a-i), where HR-XRD measurements confirmed that the peak intensity of the [0002] reflection of GaN increased with an increase in the nucleation temperature (supporting information, Figure 4.17). No other orientation of GaN was observed from HR-XRD measurements, which indicates that
under current growth conditions, c-axis orientation is the preferred crystallographic orientation of the GaN nuclei on EG at high temperatures.

![HR-XRD of GaN layers as a function of the nucleation temperature.](image)

**Figure 4.17** | HR-XRD of GaN layers as a function of the nucleation temperature.

Layer thickness of EG plays an important role in the nucleation selectivity of the III-nitride layers on the (0001) terraces. This is clearly apparent for the case of GaN nucleation in all of the samples, where two distinct regions of contrast are observed within each terrace (Figure 4.16.a, 4.16.d and 4.16.g). The difference in contrast along each terrace is related to the number of layers ($n$-layers) of graphene, with the lighter regions corresponding to few-layered EG ($n \leq 3$) and the darker regions corresponding to multi-layered EG ($n > 3$). GaN only nucleates on the lighter regions (few-layered EG) and no nucleation of GaN occurs on the darker regions (multi-layered EG), as is evident in Figure 4.16.g. The surface properties of graphene, such as the work function\textsuperscript{100}, surface potential\textsuperscript{101}, and oxidation\textsuperscript{102}, are known to be dependent on the $n$-layers of EG. Therefore, we speculate that the role of the $n$-layers of EG on selectively nucleating GaN on district
regions within each terrace may be attributed to differences in the surface potential and/or chemical reactivity.

**Figure 4.18** | FE-SEM image following the nucleation of GaN (a) at 900°C of a selected area for Raman spectral mapping of the (b) GaN $E_2^{\text{high}}$ peak and (c) EG D peak, indicating that GaN nucleates on regions of few-layered EG and these regions are highly defective as confirmed from (d) the Raman spectra $I(D)/I(G)$ and $I(2D)/I(G)$ ratio, respectively, taken at corresponding locations (marked 1, 2 and 3) seen in (b).

Raman spectral mapping of the GaN $E_2^{\text{high}}$ peak (Figure 4.18.b) confirms the selectivity of the GaN nuclei towards the EG coated step edges and regions of lighter contrast on the terraces (Figure 4.18.a). Correlating the FE-SEM image (Figure 4.18.a) to the graphene D peak Raman spectral map (Figure 4.18.c), it can be seen that the lighter
regions are very defective when compared to the regions of darker contrast. This is revealed from the enhanced graphene D peak intensity (Figure 4.18.c) and further confirmed from the $I(D)/I(G)$ ratio of the Raman spectra (Figure 4.18.d) collected at corresponding locations (marked 1, 2 and 3) in Figure 4.18.b. In the case of spots 1 and 2, subtraction of the SiC substrate from the spectra was performed and their corresponding $I(D)/I(G)$ ratio was obtained to be 0.05 and 1.2, respectively. Furthermore, the intensity of the 2D peak, which is the D peak overtone and occurs due to a double resonance Raman process\textsuperscript{103}, diminishes with respect to the G peak with increasing graphene layer thickness\textsuperscript{104}. From the $I(2D)/I(G)$ ratio of spot 2, the $n$-layers of EG where preferential nucleation of GaN occurs on the terrace (i.e. region of lighter contrast) exhibit fewer layers of EG in comparison to the region of darker contrast at spot 1. Therefore, GaN nucleates on regions of few-layered EG that are highly defective (spot 2) in comparison to the regions of multi-layered EG (spot 1). The increased defectiveness of graphene in the terrace regions where the GaN nuclei are found is believed to be due to the enhanced chemical reactivity at those regions and potential bonding at the III-nitride/graphene interface which we further investigated with XPS and HR-TEM.

4.4.2.3 Surface chemical analysis of AlN and GaN on epitaxial graphene on SiC

XPS measurements reveal potential chemical reaction of the III-nitride layers grown on EG. This is seen from the systematic analysis of the core-level spectra observed in each sample (Figure 4.19.a-j). The binding energy scale was calibrated to the spectral component of $sp^2$ carbon in the $C1s$ core-level spectra for charge correction. Figure 4.19.a-g illustrates high-resolution XPS spectra collected from the AlN and GaN samples, where their respective nucleation temperatures are indicated within each figure. The $Al2P$ (Figure
4.19.a) and Ga2P (Figure 4.19.b) core-level spectra indicates predominant Al-N and Ga-N bonding, respectively. However, the slight asymmetry in the Al2P core-level peak center to higher binding energies is indicative of potential Al-Al metallic bonding at the surface. Similarly, the Ga2P3/2 and Ga2P1/2 peaks in the Ga2P core-level spectra, with binding energies of 1117.0 eV and 1144.0 eV, respectively (Figure 4.19.b), shows a slight shift to elemental Ga, indicating potential Ga-Ga metallic bonding on the surface. The metallic bonding observed from high-resolution XPS analysis likely arises from clustering of Ga and Al atoms on the surface of EG. Furthermore, the doublet in the C1s core-level spectra seen for AlN (Figure 4.19.c) and GaN (Figure 4.19.d) indicates both sp² C-C bonding at 284.5 eV and Si-C bonding from the SiC substrate. The slight variation in the Si-C binding energies in the C1s core-level spectra for AlN and GaN is likely due to differences in the extent of hydrogenation of the graphene buffer due to variation in the n-layers of graphene across the terraces of EG. Furthermore, the O1s core-level spectra from AlN and GaN (Figure 4.19.e and 4.19.f, respectively) show a small amount of Al-O and Ga-O bonding. This metal-oxygen bonding is likely to originate from the native oxide on the surface of the AlN and GaN nuclei.

Additionally, XPS indicates that significant sp² and sp³ C-N bonding is present following the nucleation of the III-nitride layers on EG. This is evident in the slight asymmetry in the N1s core-level spectra position towards C-N bonding for both AlN (Figure 4.19.g) and GaN (Figure 4.19.h), where strong Al-N and Ga-N bonding is seen in their respective samples. The deconvolution of the C1s (Figure 4.20.c) core-level spectrum for the ~12 nm AlN sample grown at 900°C (Figure 4.19.i) reveals three spectral components with binding energies of 282.7 eV, 284.5 eV and 284.7 eV. These binding
Figure 4.19 | XPS surface chemical analysis of the (a) Al2p, (b) Ga2p, (c-d) C1s, (e-f) O1s and (g-h) N1s for (a), (c), (e) and (g) AlN and (b), (d), (f) and (h) GaN core-level spectra at respective growth temperatures, where (i) and (j) are deconvolutions of the C1s and N1s core-level spectrum, respectively for AlN grown at 900°C, illustrating significant sp² and sp³ C-N bonding.
energies are attributed to Si-C (possibly from the substrate), sp$^3$ C-C (graphene) and C-N bonding, respectively. Furthermore, the deconvolution of the N1s core-level spectrum for the AlN sample grown at 900°C (Figure 4.19.j), reveals two additional spectral components, beyond the Al-N bonding at 397.5 eV, with binding energies of 398.9 eV and 400.7 eV. These two spectral components are attributed to C-N bonding in the AlN sample. As is evident from the observations of Marton et al. from XPS measurements of carbon nitride films$^{105}$, both sp$^3$ C-N bonding around ~398.0 eV and sp$^2$ C-N bonding around 400.0 eV were observed. Also, Lv et al. attributed the N1s deconvoluted peaks with binding energies of 400.6 eV and 398.6 eV, from XPS measurements of nitrogen doped graphene sheets, to substitutional and pyridine-like nitrogen dopants in graphene, respectively$^{106}$. Similarly, Bertóti et al. revealed in RF N$_2$ plasma treated multi-wall carbon nanotubes and HOPG, three chemical bonding states at 398.3 ± 0.3 eV, 399.7 ± 0.3 eV and 400.9 ± 0.3 eV from XPS$^{107}$. These binding energies were assigned to pyridine-like, melamine-like and substitutional nitrogen bonding, respectively. Therefore, our analysis of the spectral components of the deconvoluted N1s core-level spectrum (Figure 4.19.j) provides evidence that both sp$^3$ C-N at 400.7 eV and sp$^3$ C-N at 398.9 eV bonding are present following the nucleation of AlN on EG. The sp$^2$ C-N bonding that is observed from XPS measurements is likely to originate from nitrogen incorporation into the graphene lattice. This is a result of the increasing decomposition efficiency of NH$_3$ with increasing temperature. Therefore, XPS confirms that the dramatic increase in the density of nuclei observed across the surface of the sample for the nucleation of AlN at 900°C (Figure 4.14.c), is likely due to the introduction of nitrogen defects into the graphene lattice via NH$_3$ during the nucleation process. In comparison to the nucleation of AlN at 500°C and
700°C (Figure 4.14.a and 4.14.c, respectively), the decomposition efficiency of NH₃ is reduced and therefore, the density of nuclei on the terraces decreases.

Nitrogen defects in the graphene lattice play a critical role in providing nucleation sites on the pristine EG terraces, where potential sp⁢³ like bonding can occur via NH₃ exposure. The sp⁢³ C-N bonding observed from XPS measurements indicates potential chemical reaction between AlN and graphene beyond van der Waals bonding. No C-N bonding is observed from the XPS spectral deconvolution of the N1s core-level spectrum for the nucleation of GaN at 900°C, since the thickness of the GaN nuclei (~150 nm) was beyond the penetration depth (100 Å) for XPS analysis. However, we suspect that the increase in the nucleation density on the terraces of EG with increasing temperature (Figure 4.16.a-i) is attributed to the increase in nitrogen defects in the graphene lattice similar to the case of AlN nucleation on EG. To understand the influence of such chemical reactions on the structural properties of graphene, we investigated the interfaces of AlN and GaN nuclei on EG with high-resolution S/TEM.

### 4.4.2.4 Microstructural analysis of AlN and GaN on epitaxial graphene on SiC

The nucleation of the III-nitride layers significantly impacts the structural properties of the underlying EG. This is apparent from aberration corrected Z-contrast/high angle annular dark field (HAADF) STEM and HR-TEM images of cross sectional AlN (Figure 4.20.a-c) and GaN (Figure 4.21.a-c) samples, both grown at 900°C. Evident in Figure 4.20.a, STEM analysis confirms that AlN nucleates along the (1\̅0n) EG coated step edges of SiC and (0001) terraces, where the graphene gap (layer of dark contrast) is
clearly discernable at the interface of AlN and SiC. A change in the contrast of the graphene gap is observed along the terrace region (Figure 4.20.a) and likely corresponds to a transition from multi-layered EG to few-layered EG. This confirms that AlN nucleates from the surface of EG rather than the SiC substrate. Furthermore, HR-TEM imaging reveals that AlN indeed grows on multi-layered EG at the step edges of SiC (Figure 4.20.b) as well as few-layered EG on the (0001) terrace (Figure 4.20.c), where the AlN is observed to be polycrystalline with large grain size. Though the EG is observed to not be defective in the terrace region, the EG at the kink of the SiC step edge (Figure 4.20.b) exhibits signs of disorder. The increase in the defectiveness of the graphene at the kink of the step edge may arise from the enhanced chemical reactivity of graphene due to additional strain when
under curvature\textsuperscript{92,93}. Additionally, high magnification EDX mapping (Figure 4.20.d) with its counterpart HAADF STEM image of the AlN/EG/(0001) SiC interface at the terrace region (Figure 4.20.e) further confirms the presence of a graphene gap (the dark region) between the AlN (highlighted in red) and the SiC substrate (highlighted in green).

Furthermore, STEM imaging of GaN in the terrace region of EG (Figure 4.21.a) reveals that the GaN nucleus exhibits (11\overline{2}2) semi-polar faceted side walls with a (0002) faceted top. The graphene on the periphery of the nucleus is highly defective, as is evident in HR-TEM (Figure 4.21.b), confirming Raman findings (Figure 4.18.b-c) that indicate GaN nucleates on regions of EG that are highly defective. HR-TEM images of the GaN/EG/(0001) SiC interface at the terrace region confirms that the graphene below the GaN nucleus is extremely defective (Figure 4.21.c), especially when compared to AlN (Figure 4.20.c). Nonetheless, HR-TEM demonstrates that the GaN nuclei are single crystalline, oriented in the [0002] direction and free of threading dislocations. Prior work on the growth of GaN on graphene relied on buffer assisted epitaxy using thin AlN layers\textsuperscript{30,31}, where the resulting GaN films were inferior to films produced directly on common bulk crystalline substrates. The quality of the films reported may relate directly to the crystallinity of the AlN buffer grown on graphene which is revealed to be polycrystalline from our HR-TEM observations. Therefore, the growth of GaN directly on graphene may produce films of higher quality.

The HR-TEM results demonstrate that the nucleation of GaN on the terraces of EG leads to a significant increase in the defectiveness of the graphene. This is in contrast to the nucleation of AlN, where the graphene remained largely preserved. The increase in the defectiveness of graphene at the GaN/EG/(0001) SiC interface, following nucleation, may
arise from differences in heteroepitaxial strain energies and/or bonding. The in-plane lattice mismatch between AlN and GaN on graphene, from the reported lattice constants$^{33-35}$, are 26.4% and 29.6%, respectively. Such comparable high strain energies may lead to structural deformation of the graphene layers thereby increasing its defectiveness. First-principles calculations from Density Functional Theory (DFT), as reported by Gohda et al.$^{108}$, revealed that the GaN/graphene system can partially break sp$^2$ C-C bonds and form C-N-C bonding upon expansion of the graphene lattice in order to relax the in-plane strain. However, in the AlN/graphene system, the graphene lattice was retained, due to the in-

Figure 4.21 | Low magnification Z-contrast STEM of a (a) GaN nucleus grown on EG at 900°C with (11\$reve{2}$2) semi-polar and (0002) faceted side walls and top, respectively, showing that GaN nucleates on regions of few-layered EG on the (0001) terrace that are highly defective seen in (b) HR-TEM at the periphery of the GaN nucleus and (c) HR-TEM of the GaN/EG/(0001) interface, where GaN is shown to be single crystalline, [0002] oriented and free of dislocations.
plane strain not being large enough to induce structural transformation to the graphene, as suggested by Gohda et al.\textsuperscript{108}. Additionally, the polycrystalline nature of AlN, as is observed from HR-TEM (Figure 4.20.c), may reduce the strain in the graphene layers and therefore, allows that graphene to remain intact following nucleation in comparison to the case of single crystalline GaN (Figure 4.21.c).

\textbf{4.4.2.5 AlN-graphene and GaN-graphene interfaces investigated using DFT}

We further investigated the origin of the defectiveness of graphene with DFT modeling of AlN and GaN on graphene (0001) interfaces \textsuperscript{67,68}. To model the system, we begin with two sets of previously relaxed “slabs”, one of AlN or GaN and the other one of graphene, ensuring that the pieces of the graphene layers are completely included in the supercell containing either the AlN or the GaN slabs. Next, and in contrast to what was done by Gohda et al.\textsuperscript{108}, we allowed the composite structures to fully relax without geometric constraints. Under such conditions, the AlN produces very little distortion to the graphene layers as compared with GaN (Figure 4.22.a-b), confirming the experimental HR-TEM results (Figure 4.20.c and 4.21.c). This also suggests strong bonding signaled by the disordering of the graphene layers in the presence of GaN. In addition, we observed that the strain of the AlN and GaN layer closest to the graphene layers show an in-plane strain or distortion with respect to the solids of -3.9\% and -3.3\% respectively, while the inter-plane strain reaches levels of -2.4\% and -3.9\% respectively.

We show in Figures 4.18.c-d, projected density of states (pDOS) calculations of the AlN/graphene and GaN/graphene interfaces. The pDOS calculations clearly predict bonding between the layer of nitrogen atoms and the graphene layer at the interface in both
The strength of the s-s and p-p bonding is higher for GaN/graphene, particularly for the nitrogen-carbon s-orbitals. The gallium d-state, as compared to the aluminum s- and p-states, localizes the nitrogen s- and p-states in energy, draws the density of states deeper down and opens up a gap isolating the band at the Fermi level (E_F) and therefore reducing its density of states. These results demonstrate that the bonding between AlN/graphene (Figure 4.22.a) and GaN/graphene (Figure 4.22.b) is not due to van der Waals forces alone, but also has contributions from chemical bonding. Given that the strains between AlN/graphene and
GaN/graphene are not very different, the higher degree of disorder of the graphene layer in the presence of GaN in comparison to AlN may be due to the differences in bonding strength at the interface.
4.5 Conclusions

In the first half of chapter 4, we investigated the morphological and stress evolution during the growth of GaN on 6H-SiC with \textit{in situ} optical reflectance and wafer curvature measurements, respectively. With the AlN buffer layer, GaN grew under an initial compressive stress of -1.04 GPa which gradually relaxed with thickness (-0.17 GPa). In the case of GaN grown directly on SiC via a two-step temperature growth process, the high-temperature GaN layer grew initially under compressive stress (-0.36 GPa) which evolved into tensile stress (0.27 GPa) above ~300 nm. This transition into tensile stress occurs when islands laterally overgrow and impinge on each other, i.e. zip-up. As a result, a reduction in the interfacial energy occurs by forming grain boundaries, levitating an increase in the strain energy. The growth of GaN directly on SiC showed a reduction in the TD density and an improvement in the macroscale roughness as a result of the prolonged coalescence of the high-temperature GaN layer. However, cracking of the GaN film was observed when AlN was not utilized. Film cracking observed in GaN is largely a result of the difference in CTE between GaN and SiC, inducing tensile stress during post-growth cool down. The film cracking may be reduced by utilizing low Al content AlGaN in the low temperature layer and/or optimizing the temperature change in the two-step temperature growth process in order to introduce sufficient amounts of compressive stress into the GaN film before cool down. Weak-beam TEM revealed predominant (a+c)-type dislocations with few BSFs and 1120 PSFs, all confined within the initial low-temperature GaN layer. These BSF may block the propagation of threading dislocation into the high-temperature GaN layer and result in an improvement in the film quality.
The second half of chapter 4 investigates the impact of graphene properties on the nucleation of AlN and GaN. We found that preferential nucleation of AlN and GaN occurs primarily along the EG coated step edges of SiC and at defects in EG due to potential enhanced chemical reactivity in those regions. In the case of AlN, the nucleation density on the terraces of EG increased with the introduction of intentional defects into the graphene lattice via O₂ plasma treatment or nitrogen incorporation into the graphene lattice via high temperature NH₃ exposure. However, aberration corrected S/TEM reveals that AlN grown on EG was polycrystalline with large grains without significant distortion of the graphene layers. In the case of GaN nucleation on the terraces of EG, Raman spectral mapping confirms that GaN nucleates on regions of few-layered EG, where these regions were observed to be highly defective as confirmed from the \( I(D)/I(G) \) ratio and HR-TEM. Finally, HR-TEM reveals that the GaN nuclei were single crystalline, c-axis oriented and free of threading dislocations. However, the graphene underlayer was highly defective on the terraces of EG possibly due to enhanced strain energy resulting from the large in-plane lattice mismatch between GaN and the graphene layers and differences in bonding strength at the III-nitride/graphene interface.
4.6 References


CHAPTER 5

TWO-DIMENSIONAL GROWTH OF GAN ON SILICON CARBIDE

5.1 Introduction

Gallium nitride (GaN) is considered one of the most important semiconducting material since the discovery of silicon. The properties of this semiconductor include bandgap tunability that spans from the infrared into the ultraviolet, high dielectric breakdown and high electron mobility. These extensive properties were key in the emergence of many disruptive technologies that now have become truly ubiquitous. This is not limited to the blue light emitting diode used for efficient solid-state lighting, but other applications as well, such as power devices used in radar as well as photodetectors. These devices have been extensively investigated for many years, yet in order to shape next generation technologies, innovative research must be undertaken to extend the intrinsic properties of group-III nitride semiconductors. For example, to implement GaN in tunnel junctions for ultra-low voltage and steep-switching applications\(^1\), single photon emitters for quantum communication\(^2\) and polarization-driven topological insulators for quantum computing\(^3\), the growth of highly stoichiometric crystalline monolayers with wide bandgap energies extending into the deep ultraviolet must be realized.

Bandgap engineering in GaN for electronic and photonic devices is achieved via alloying with indium and/or aluminum. Alloying, however, can lead to local fluctuations in composition due to the large miscibility gaps, phase separation and poor dopant activation, specifically in Mg p-type doping with increasing indium and/or aluminum content. Therefore, other methods to engineer the bandgap of GaN are desirable. An
effective approach to do so is through extreme geometric confinement of this material system, such as in the case of two-dimensional confinement of nitride semiconductors into atomic sheets “i.e. 2D nitrides”. Generally, spatial confinement of semiconducting materials tends to lead to massive changes in the electronic bandstructure, most notable an increase in the bandgap energy via the phenomena known as quantum confinement\(^4\). Modulating the bandstructure via geometrical confinement brings to light an entirely new approach to tune the properties of group-III nitride materials. Tuning the bandstructure in semiconductors through 2D vertical confinement exists in many conventional materials that are naturally layered: transition metal dichalcogenides being the most studied example. This class of materials consist of monolayer units free of dangling bonds, held together in a bulk layered crystal by van der Waals forces. Inspired by the exotic properties of semi-metal graphene\(^5\), the vast interest in semiconducting two-dimensional and layered materials (2DLMs) has been driven by the compelling properties of monolayer films compared to their bulk layered film counterparts. Such properties include the emergence of the direct bandgap in monolayers as well as the valley hall effect and large exciton binding energy. Ultimately, 2DLMs offers the ultimate scaling factor in the vertical direction for device miniaturization and a remarkable platform to study new exotic phenomena in condense matter physics. Cleaving atomic sheets from bulk layered crystals is easily achieved through mechanical exfoliation. In the case of the group-III nitride materials system, the only naturally layered material is hexagonal boron nitride (hBN). Also referred to as ‘white graphene’, hBN is an atomically flat and smooth 2DLM that offers unique properties that are not collectively recognized in other semiconducting 2D crystals. This includes a wide bandgap energy (5.97 eV), high optical transparency and
exceptional in-plane thermal conductivity. Consequently, hBN has quickly established itself as a prominent material component in the design of many novel 2D electronic devices\textsuperscript{6}. The bandgap energy of hBN is, however, indirect and as a result, there has been a large need to synthesize new 2D nitrides that exhibit both wide and direct bandgap energies for optoelectronic devices\textsuperscript{7}.

Thinning conventional bulk group III-nitrides, such as GaN, AlN and InN to their atomic limits opens up new opportunity not only for bandgap engineering via quantum confinement, but also creating a new class of wide bandgap 2D materials beyond hBN for 2D optoelectronic devices. Along similar lines to initial theoretical discovery and subsequent experimental synthesis of “beyond graphene” 2D materials (such as silicene and borophene), the wurtzite structure of bulk GaN is predicted to reconstruct into a 2D nitride graphitic structure when thinned to a few atomic layers\textsuperscript{8-11}. The scaling of these nitride semiconductors in the vertical direction leads to a thickness-dependent energy bandgap ($E_g$) via quantum confinement\textsuperscript{4}. A gap, however, remains between the theoretical prediction of 2D nitrides “beyond hBN”\textsuperscript{8,11} and experimental realization of such structures. Despite the extensive computational discovery of 2D materials\textsuperscript{12}, the experimental realization of large-area 2D nitrides on technologically relevant substrates, however, still remains elusive\textsuperscript{13,14}. The plausibility of experimental synthesis of 2D nitrides from 3D covalently bounded crystals is quite challenging. First, the energy required to mechanically exfoliate a monolayer from a tetrahedral coordinated bulk crystals is extremely large. This is due to the strong bonding between the group-III metal and nitrogen (i.e. the large cohesive energy)\textsuperscript{15}. Second, even if cleaving a tetrahedral coordinated bulk crystal was experimentally possible, the resulting polar atomic layer will exhibit unsaturated dangling
bonds on the surface, making the 2D nitride energetically unstable\textsuperscript{16}. The unstable cleaved polar monolayer would be terminated with group-III metal cations on one side and nitrogen anions on the other. Therefore, to satisfy the electrostatic criterion and alleviate the surface states, it is proposed that these unstable cleaved polar monolayers take on trigonal-planar coordinated graphitic structures, driven by several combined mechanisms. This includes charge compensation through surface reconstruction, electron redistribution and/or adsorption of charged species\textsuperscript{17}. Though charge compensation in cleaved atomic layers of group-III nitrides may be reached through electron redistribution, the resulting surface energy, in most cases, is high. Therefore, other pathways to efficiently stabilize the graphitic structure of group-III nitrides should be considered. In this chapter, we discuss the use of the interface between epitaxial graphene formed on SiC as a means of confining and stabilizing the growth of traditionally three-dimensional binary compound semiconducting crystals, like GaN, into a two-dimensional crystalline form, specifically on technologically relevant substrates like SiC.

Graphene has proven to be a remarkable material over the past decade. Our studies show that quasi-free standing epitaxial graphene grown on SiC provides a pristine interface of reduced energy to promote Frank–van der Merwe two-dimensional growth of metastable crystalline solids. To realize 2D GaN at this pristine interface, we developed a novel growth scheme known as “Migration Enhanced Encapsulated Growth” to confine the synthesis chemistry at the extreme interface of graphene and SiC. Unlike monolayers of material synthesized by molecular beam epitaxy (MBE) in ultrahigh vacuum, MEEG occurs within a low pressure MOCVD environment using conventional metalorganic precursors for group-III elements and ultrahigh purity ammonia as a nitrogen source. Here, graphene also
establishes a potential platform to address challenges associated with creating clean, atomically abrupt \textit{in situ} vertical heterostructures, protected from air and thus stable for conventional \textit{ex situ} characterization.

This chapter will discuss the development of this new synthesis route to experimentally realize 2D forms of conventional compound semiconductors \textit{via} the mechanism of adatom intercalation from the vapor phase through the lattice of graphene. The effect of confinement of these 2D semiconductors on their electrical and optical properties from that of their bulk counter parts is also discussed. We also theoretically predict and experimentally validate that the atomic structure of 2D GaN grown \textit{via} MEEG is notably different from reported theory\textsuperscript{8,9,11}. Moreover, we establish that graphene plays a critical role in stabilizing the 2D buckled structure which exhibits a direct bandgap (nearly 5.0 eV) due to quantum confinement. Our results provide a foundation for discovery and stabilization of 2D nitrides that are difficult to prepare \textit{via} traditional synthesis. In the next section, we will review some key concepts from the literature that relates to intercalation of 2DLMs which will assist the reader in understanding the main ideas outlined in the results section of this chapter.
5.2 Literature Review

5.2.1 An outlook on intercalation in the scope of graphite intercalation compounds

Unlike the tetrahedral covalent bonding in bulk GaN, AlN and InN, two-dimensional and layered materials (2DLMs), like wide bandgap hBN, consists of atomic sheets that are held together by van der Waals forces. Analogous to graphene, a monolayer of these sp² bonded sheets can be isolated using top-down approaches such as mechanical or chemical exfoliation, like in the case of graphene derived from graphite, or synthesized from the bottom-up. Essentially, 2DLMs are extreme surfaces that are susceptible to physical and/or chemical modulation on one or both sides. It is rather common to modulate the properties of these 2D layers (i.e. surfaces) by chemical functionalization, alloying and/or doping. Another approach to modulate these surfaces is through the mechanism of intercalation. This approach is rather an old topic which was first demonstrated in 1841 by C. Schafhäutl in the swelling of graphite crystals submerged in sulfuric acid. In this instance, graphite is the “host” medium for the intercalation of “guest” species. Therefore, the concept of intercalation in graphite is defined as a reversible topotactic reaction that occurs through the injection of mobile guest species between the crystalline layers of the host. Graphite is an excellent host for intercalation due to its high crystalline anisotropy, that is, strong in-plane bonding within the layers and weak out-of-plane bonding between them. The major types of guest species used in graphite intercalation compounds (GICs) are metals, solvated metals and molecular ions. A unique, yet important property of graphite that is critical in the intercalation process is that it is amphoteric. This stems from its unique bandstructure were the magnitude of the ionization potential and electron affinity are equal. The amphoteric property of graphite allows both donor and acceptor ionic guest
species “i.e. intercalants” to be accommodated within the ABAB stacked layers shown in Figure 5.1.a-b.

Figure 5.1 | (a) Schematic of ABAB stacking in graphite. (b) an illustration of layer stage ordering of the intercalated species within graphite. The stage ordering number is defined as the number of \( n \) adjacent layers of graphite separating the guest intercalated layer.

The intercalants provide free carriers to the host \((G)\) material via charge transfer. For example, in graphite, alkali metal intercalants are donors \((D)\), whereas halogen intercalants are acceptors \((A)\). Therefore, a verity of charge transfer complexes can arise in GICs. This is shown in the following intercalation reactions:

\[
xG + D \rightarrow D^+ G_x^+
\]

\[
xG + A \rightarrow G_x^+ A^-
\]  

Eq. 5.1  

Eq. 5.2
There are several methods used for intercalation. These methods can be categorized into chemical intercalation and electrochemical intercalation. For chemical intercalation, both vapor-phase and wet-chemical methods have been utilized. In the case of vapor-phase intercalation, the guest intercalant source and the host medium are placed separately in a two-zone closed ampule or other enclosed configurations. The over pressure and temperature gradient between the intercalant source and host medium controls the intercalation reaction. Vapor-phase transport is the most popular intercalation method in forming GICs. Some of the first studies in the 1980’s using this method were on potassium intercalation into graphite. Typically, the intercalations of similar alkali metal donors occur at a temperature range of 200°C - 550°C. Vapor-phase transport accommodates a wide variety of intercalants and is fairly scalable. The process, however, is irreversible and requires relatively high temperatures which may not be suitable for host materials that can thermally decomposes at low temperatures. In the case of wet-chemical intercalation, the host medium is immersed into a solvent containing the guest intercalant and the intercalation process proceeds via chemical reactions. Unlike chemical vapor-phase transport, this process is reversible, however, the kinetics can be very slow, difficult to control and lead to swelling and damage of the host medium. For electrochemical intercalation, the use of both liquid and solid electrolytes is common. In both cases, an externally biased electrode controls the intercalation of ions into the host medium. This process is highly reversible and the kinetics are much faster in the liquid electrolyte case. However, limited number of intercalants are available in electrolyte form.

For the intercalation techniques discussed, there are a few parameters of significance that should be considered when designing an intercalation experiment. In the
case of GICs, small thin host materials are generally used in order to improve intercalation efficiency and therefore promote the formation of homogenous staging of intercalants between the graphite layers\textsuperscript{21}. Furthermore, both the reaction temperature and the vapor pressure of the guest intercalant source are critical in the intercalation process. For example, Young et al. showed for graphite intercalation compounds with bromine using the vapor-phase transport method, that a critical over pressure of Br\textsubscript{2} was necessary to initiate the intercalation process on the exposed basal surfaces of graphite\textsuperscript{22}. Beyond these discussed parameters, the size and ionization potential of the intercalant guest specie with respect to the electron affinity of host medium are important considerations to drive intercalation. For the case of a metal intercalant, like an alkali donor, the ionization potential is defined as the energy required to remove an electron from a neutral atom, where the electron affinity in the graphite host medium is defined as the energy produced by taking an electron from the vacuum level to the $\pi^*$-band edge. For intercalation to occur, the ionization potential of the intercalant guest specie should be lower than the electron affinity of the graphite host medium ($\sim 4.6$ eV)\textsuperscript{23}. Therefore, the lower the ionization potential, the more easier electrons can be transferred to the graphite host medium and consequently the energy gain is minimized. There are however a few caveats. For example, the intercalation of intercalation of K, Na and Li into graphite. As illustrated in Figure 5.2\textsuperscript{24}, K has an ionization potential of 4.34 eV and is below the electron affinity of graphite, which explains the ease of its intercalation into graphite as reported extensively in the literature. For Na and Li, the story is more complicated. The ionization potential for Na and Li are 5.14 eV and 5.39 eV, respectively. However, as the ionization potential increases, the ionic diameter decreases. Though Li should be more difficult to intercalate
into graphite than Na based on the ionization potential, due to its smaller ionic diameter with respect to Na, Li intercalates easier into graphite and has been experimentally demonstrated in the literature. While in the case of Na, intercalation into graphite has been more difficult. Moreover, it is possible to modulate the electron affinity of the host in order to promote reactions of intercalants that inherit high ionization potentials. For example, doping graphite with boron to create BC$_2$N can increase the electron affinity from 4.6 eV (graphite) to ~ 6.6 eV (BC$_2$N).

**Figure 5.2** | Relationship between ionization potentials of metals and the electron affinities of graphite and BC$_2$N. Ref [24].

When guest species intercalate into graphite, an increase in the separation distance between layers occur. This distance is on the order of ~ 0.5 nm for alkali metal ions from the initial separation distance of 0.335 nm (Figure 5.1.a). In addition, staged structures can initiate in GICs (Figure 5.1.b), where the staging number $n$ is defined as the number of graphite layers in the host that separates the intercalant layer. Staging energetics in GICs
is mainly governed by three factors\textsuperscript{25}. The first is the charge transfer between the guest species and host medium on the onset of intercalation. As discussed previously, this energetically drives the intercalation process and is the origin of effective repulsion between intercalated layers. The second governing factor arises from the elastic strain that is exerted on the graphite layers due to incorporation of the intercalants. The third factor is the electrostatic interactions that occur between the guest species within the layers. The staging and resulting structural ordering observed in GICs has led to interesting properties that includes magnetism and superconductivity. Therefore, intercalation ultimately provides a powerful means of tuning the properties of graphite for a novel application.

5.2.2 Intercalation of graphene on supporting substrates

Graphene is one-to-few layers of graphite and similarly, intercalation of graphene on supported solid substrates is also possible with a verity of intercalant guest species. The
elements that are highlighted in red, illustrated in Figure 5.3, represent the various guest species that have been successfully reported to intercalate over layers of graphene supported on a variety of substrates. This is mostly for the case of graphene grown epitaxially on SiC or on metal substrates like Ir(111), Pt(111), Rh(111) and Ni(111). The intercalation of these graphene over layers on supported substrates can be energetically favorable if the energy cost to decouple the graphene from the surface is offset by the energy gained from the intercalant’s interaction and possible passivation of the dangling bonds on the substrate. Therefore, the confined interface between graphene and the substrate provides plenty of room for new chemistry. In fact, when two kinds of species intercalate under graphene, chemical reaction can occur. This has been demonstrated during CO oxidation and hydrogen oxidation, when CO and oxygen molecules intercalate, or when both hydrogen and oxygen intercalate graphene formed on Pt(111). Moreover, Lizzit et al. reported the formation of SiO$_2$ under graphene formed on Ru(0001) via a two-step intercalation process. First, Si was deposited on graphene and annealed to drive Si through the graphene lattice. After Si intercalation, the sample was then exposed to O$_2$ to transform the intercalated Si layer between graphene and Ru(0001) into SiO$_2$.

From our previous discussion, adatoms with low ionization potentials generally tend to intercalate graphene more efficiently. An intriguing question that may arises is the origin of the driving force for intercalation of atoms with high ionization potentials, such as the intercalation of Si between graphene and Ru(0001) in the previous example. This can be best explained by the role of the supporting substrate in the intercalation process. Li et al. studied the influence of the substrate in the intercalation process of Si through graphene grown on Ru(0001). They used a climb nudged elastic band method to simulate...
and compare the energy barriers in the intercalation of Si on free standing graphene, to graphene supported on a Ru(0001) slab. As illustrated in Figure 5.4.a-b, the energy barrier for the intercalation of Si for free standing graphene is 0.66 eV and hence, the barrier is too large for the process to proceed efficiently. However, when graphene is supported on Ru(0001), a significant reduction in the barrier height from 0.66 eV to 0.33 eV occurs. This suggests the significance of the substrate in driving the intercalation process, even though the ionization potential of Si (8.15 eV) is much higher than the electron affinity of graphene. This is a powerful advantage that graphene produced on supporting substrates inherit over bulk graphite, as the electron affinity of the graphene host layers (i.e. the work function) can be advantageously modulated with ease to enhance the intercalation process. This phenomenon is best exemplified in layers of graphene grown epitaxially on the Si-face of SiC.

![Figure 5.4](image)

**Figure 5.4** | Energy barrier calculations of Si intercalation through graphene (a) without a Ru supporting substrate and (b) with a Ru supporting substrate. Ref [26-62].

The growth of epitaxial graphene occurs by thermal decomposition of silicon from the surface of SiC. This leaves a carbon rich surface that can spontaneously reconstruct to form sp² bonded graphene. The growth initiates with an initial carbon-rich ($6\sqrt{3} \times 6\sqrt{3}$)
R30° reconstruction of the surface, known as the graphene buffer layer, which is partially bonded to the SiC substrate. The growth then is followed by the formation of sequential layers of graphene that are bonded to each other by van der Waals forces. As a result of the partially covalently bonded graphene buffer layer, a significant amount of dangling bonds (surface states) remains unpassivated on SiC and can significantly impact the mobility of graphene. Therefore, these dangling bonds in epitaxial graphene (EG) are typically passivated with hydrogen by intercalation. As a result of hydrogen intercalation, the graphene buffer layer also decouples from the SiC substrate creating an additional layer of EG. When the graphene buffer layer is decoupled from the SiC substrate, the graphene layers in this case are refer to as quasi-free standing epitaxial graphene (QFEG).

One of the unique features of the EG grown on SiC is that the work function (i.e. the electron affinity)\textsuperscript{67-69} can be modulated with ease. The dangling bonds that are present at the interface prior to hydrogen intercalation leads to the transfer of electrons into graphene and thus shifting its Fermi level. Moreover, spontaneous polarization of the SiC substrate leads to the transfer of holes into graphene. This effect dominates the work function of graphene once the dangling bonds at the interface are passivated via hydrogen intercalation and QFEG is formed. These effects on EG grown on SiC are best illustrated in Figures 5.5\textsuperscript{70}. In Figure 5.5, not only can we modulate the work function of graphene as a function of layer number, but also, we can significantly increase the work function (i.e. the electron affinity) of graphene through the passivation of the interface dangling bonds and forming QFEG. This is a powerful concept in EG, as we can modulate the electron
affinity of the host to potentially promote the intercalation of atoms with high ionization potentials, such as in Si in the previously discussed example.

**Figure 5.5** | Work function of epitaxial graphene (denoted as EG in the red symbols) and quasi-free standing epitaxial graphene (denoted QFG in the blue symbols, instead as QFEG throughout this chapter) as a function of number of layers. The data is referenced to the work function of highly oriented pyrolitic graphite (HOPG). Ref [70].

5.2.3 The role of defects in graphene intercalation

Defects play a significant role in providing pathways for intercalation. However, the role of the defect size, coordination, orientation and density on the energy barrier for intercalation is rarely discussed in the literature. This is partially due to the difficulty in correlating the defects responsible in the intercalation process. Energy calculations may, however, provide valuable insight into the nature of defects that are necessary to promote
intercalation. Therefore, it is worth mentioning calculations by Song et al.\textsuperscript{71}, where they investigated the penetration of the first two row elements through a monolayer of graphene using density functional theory and nudged elastic band methods. In their studies, the penetration of these elements into graphene can be classified into three main categories of events and/or energy barriers. These events are “bonding” to the graphene lattice, “doping” of the graphene lattice and “intercalation” through graphene. As seen in Figure 5.6, depending on the element of interest, the size and configuration of the defect, a transition between the different events can occur. This is prominent in the case of Al, where by increase the defect size, a transition from bonding, to doping, to intercalation through graphene can occur.

**Figure 5.6** | The energy barriers for atoms penetrating various defects in free standing graphene. Each row corresponds to a certain defect. The three penetration events are highlighted with following colors: bonding is red, doping is yellow and intercalation is green. More details of this figure can be found in Ref [71].
5.3 Experimental Procedures

5.3.1 Ab initio density functional theory simulations

Through collaboration with Prof. Suman Datta’s group at University of Notre Dame, ab initio calculations were performed to complement and explain many of our experimental observations. The calculations of binding energy and different electronic properties for 2D nitrides (GaN, AlN and InN) are performed using ab initio DFT as implemented in the Atomistic-ToolKit (ATK) version 2014.3 QuantumWise A/S (www.quantumwise.com). In our calculations, we optimize different structural forms by the Broyden–Fletcher–Goldfarb–Shannon (BFGS) scheme until all the forces acting on atoms are mitigated to less than 0.01 eV/Å and the stress is less than 0.01 eV/Å³. A well conserved Monkhorst-Pack grid (21×21×21) is used with a mesh cutoff energy of 10 Hartree for the bulk cases whereas we use a sampling of 21×21×1 for the 2D structures. To make isolated 2D nitride layers from the cleaved [0001] bulk structure, we used a supercell having a thick vacuum region (15 Å) along the c-axis (while retaining the same lattice parameters ‘a’ and ‘b’ as in the bulk). Moreover, the vdW force between the different layers also has a significant effect in determining the interlayer distance for GaN. To incorporate the vdW interactions, we add a semi-empirical dispersion potential term to the conventional Kohn-Sham DFT energy through the Grimme’s DFT-D2 method for all exchange correlation energies. We use generalized gradient approximation (GGA) functional in our DFT scheme to calculate the binding energies, whereas meta-GGA functional for the $E_g$ corrections $^{72}$. Furthermore, hybrid functional HSE06 DOS calculations were also performed under FHI-aims function. It is computationally heavy for periodic systems. Therefore, we used a low k-point grid of 6×6×1. All other numerical
parameters were the same as the meta-GGA functional approach. The lattice parameters used for the rhombohedral unit cell of GaN with the R3m space group were $a = 3.183 \AA$ and $c = 23.38 \AA$. The overall structure was optimized between bilayer graphene and non-passivated 6H-SiC. All surface states were saturated between 2D GaN and SiC after optimization. The DFT calculated binding energy of R3m 2D GaN was $-2.2224 \text{ eV/\AA}^2$.

5.3.2 Synthesis of quasi-free standing epitaxial graphene and measurements

Both semi-insulating (vanadium doped) on-axis silicon-face 6H-SiC (II-VI Incorporated) and n-type (nitrogen doped) on-axis silicon-face 6H-SiC (Cree Incorporated) were cleaned by sonication in acetone and isopropanol followed by a heated bath in a piranha solution (Nanostrip) and then subjected to an oxygen plasma etch ($\text{Plasma-Therm 720: 150 W, 10 mTorr, 45 sccm oxygen}$) for 2 minutes. Graphene growth conditions were adjusted in order to improve the uniformity of graphene on respective substrates (semi-insulating and n-type 6H-SiC). Substrates were annealed at 1400-1500°C (200 or 700 Torr, 5-10% $\text{H}_2$, 90-95% argon, respectively) for 30 minutes in order to obtain atomically flat terraces. The growth chamber was then evacuated and allowed to dwell at ultra-high vacuum ($< 1 \times 10^{-9}$ Torr) for 10 minutes. The growth of epitaxial graphene commenced on the silicon-face of SiC(0001) via sublimation of silicon in 100% argon at 1575°C or 1625°C under 700 or 200 Torr total pressure, respectively. In addition to the graphene-buffer layer, the resulting graphene is primarily monolayer along the (0001) terraces with some bi- and tri-layer graphene near the (1\overline{1}0n) step edges of 6H-SiC. Growth quality and wrinkle density of graphene were examined using Raman spectroscopy and atomic force microscopy (AFM), respectively. Raman spectra were collected using a WITec Confocal Raman system operated at room temperature using a 488 nm laser.
excitation source. Atomic force microscopy (AFM) of graphene was performed in tapping mode using a *Bruker Dimension Icon* system (probe resonance frequency ~320 kHz) with a scan rate of 1.00 Hz. Hydrogenation of graphene was then performed for 30 minutes at 900-1100°C in 9.20 slm total flow of ultrahigh purity hydrogen under 100 Torr total pressure. The graphene-buffer layer is converted to an additional layer of graphene (QFEG) resulting in primarily bilayer graphene along the (0001) terraces of 6H-SiC.

5.3.3 Synthesis of 2D GaN *via* migration-enhanced encapsulated growth (MEEG)

The growth of 2D GaN was realized in a customized vertical two-flow (group-III and group-V) showerhead cold-wall reactor on a graphite susceptor heated through induction. After *in situ* hydrogenation of graphene to form QFEG, samples were held at 550°C in 9.2 slm total flow of ultrahigh purity hydrogen under 50 Torr total pressure. The intercalation of gallium commenced with 60 cycles of 7.93 μmol/minute of trimethylgallium (TMGa). Each cycle consisted of a 2 second pulse of TMGa and a 3 second purge in hydrogen. Following gallium intercalation, samples were ramped to 675°C and held for 5 minutes. Ammonolysis of intercalated gallium was performed for 15 min *via* decomposition of ultrahigh purity ammonia (62.5 mmol/min) at 675°C, also in ultrahigh purity hydrogen and 50 Torr total pressure. Samples were then cooled naturally to room temperature in ultrahigh purity nitrogen. Since the quintuple structure of 2D GaN has an R3m space group symmetry, we would like to note that the nomenclature (GaN) reported here refers to the binary compound semiconductor “gallium nitride” and not the 1:1 stoichiometry.
5.3.4 Post synthesis characterization of the as-grown 2D GaN samples

The patchwork regions of 2D GaN under graphene were investigated using a *Carl Zeiss Merlin* field emission scanning electron microscope (SEM) operated at 1.0 kV. In addition, regions of intercalated gallium and nitrogen were analyzed by Auger electron spectroscopy (AES) in the *PHI 720 Scanning Auger Nanoprobe*. SEM images with FOV of 1.0 µm were collected under 25.0 kV and 1.0 nA. Elemental maps (128×128 pixel) were then collected in AES, operated at 25.0 kV, 5.0 nA current with the sample normal to the electron gun. We compared the growth of 2D GaN *via* MEEG to bulk GaN grown directly on 6H-SiC. The conditions for the growth of bulk GaN directly on 6H-SiC are outlined in the experimental section of Chapter 4, where buffer free growth of III-polar GaN was achieved directly on SiC\(^{73}\). Moreover, Raman spectra and mapping of the graphene/2D GaN/6H-SiC heterostructure were collected with a *Horiba LabRAM HR Evolution* confocal Raman system operated at room-temperature using (633 nm “max at 16 mW”, 532 nm “max at 48 mW”, 364 nm “max at 50 mW”) excitation sources. For electrical measurements, 2D GaN was grown *via* MEEG using epitaxial graphene grown on n-type 6H-SiC. Site specific regions of the graphene/2D GaN/6H-SiC heterostructure were isolated using focus ion beam (FIB), in order to probe consistent vertical transport measurements without shorting *via* graphene. Measurements were performed under PeakForce TUNA mode in a *BRUKER Dimension* conductive AFM (C-AFM) using a platinum AFM tip. Current-voltage (I-V) characteristics of the heterostructure were investigated by sweeping the voltage from the conductive tip between -2.5 V to 2.5 V, under a loading force and sensitivity of 5 nN and 1 nA/V, respectively. For bandgap measurements, reflectance of samples were collected with UV-visible spectroscopy using
a 60 mm integrating sphere on a *PerkinElmer LAMBDA 1050 UV/Vis/NIR* spectrophotometer (resolution of spectral bandwidth ≤ 0.05 nm) operated at room temperature. UV-Vis ellipsometry measurements were performed using a *J.A. Woolam Co., Inc. V-VASE* spectroscopic ellipsometer. Data was collected over the spectral range from 1.55 eV to 6.42 eV at 40, 50, 60 and 70 degrees.

5.3.5 High resolution electron microscopy preparation, imaging and measurements

Cross-section transmission electron microscope (TEM) specimens of regions of 2D GaN were prepared by *in situ* lift out via milling in a *FEI Helios NanoLab DualBeam 660* FIB. Prior to milling, thick protective amorphous carbon was deposited over the region of interest by electron beam deposition. The FIB-TEM membrane was fabricated with a starting milling voltage of 30 kV and then stepped down to 2 kV to minimize sidewall damage and thin the specimen to electron transparency. The thickness of the samples was < 30 nm, as measured by EELS. During dual-EELS measurements, a source electron monochromator was used to improve the signal-to-noise and reduce spectral delocalization at 80 kV. The energy spread full width at half maximum (FWHM) of the monochromator was setup to be < 0.2 eV. Prior to milling of specimens for $E_g$ measurements of 2D GaN via low loss EELS, samples were first prepared for TEM after MEEG by mechanical exfoliation of graphene layers from the surface, followed by the deposition of 30 nm of SiO$_2$ using thermal evaporation *Kurt J. Lesker Lab 18*.

Moreover, high resolution electron microscopy of regions of 2D GaN (STEM at 300 kV and monochromated TEM at 80 kV) was performed in a *FEI* dual aberration corrected *Titan$^3$ G2 60-300 S/TEM* equipped with a SuperX energy dispersive x-ray (EDX)
spectrometry system. STEM conditions were 50 pA for beam current, C2 aperture of 70 µm and camera length of 115 mm. Elemental mapping with EDX in STEM mode was performed at 300 kV with acquisition times of up to 5 minutes. The spatial resolution of aberration corrected STEM in annular bright field (ABF) mode makes it possible to directly image the position of nitrogen and gallium in the 2D GaN R3m structure. In the wurtzite structure of bulk GaN, the displacement of projected atomic pairs, referred to as dumbbells, can be resolved along the [11̅20] zone axis. The local polarity of the dumbbells indicates the structural nature of 2D GaN (planar or buckled). If the 2D structure is buckled, the polarity of the dumbbell, given by the terminating (gallium or nitrogen) atom facing SiC(0001) can be directly imaged. As a result, we captured simultaneous high angle annular dark field (HAADF) and ABF images at 200kV. The HAADF detector (Fischione) had a collection angle of 51-300 mrad for Z-contrast imaging, while the ABF detector (FEI DF4) had a collection angle of 7-40 mrad for atomic column displacement imaging (nitrogen and gallium dumbbells). Microscope conditions for ABF-STEM were 50 pA for beam current, C2 aperture of 70 µm and camera length of 145 mm. Optimal contrast conditions to image the nitrogen atoms in the ABF images was achieved using a negative defocus of approximately -100 Å. Fast Fourier transform (FFT) bandpass filtering and Gaussian blur function were applied to select ABF-STEM images to improve visualization of atomic columns of lighter elements. Features of small and large structures were filtered up to 6 and 60 pixels, respectively and with a Gaussian blur radius of up to 2 pixels. Finally, ABF-STEM images were simulated using the multislice method implemented in a MATLAB code, following the methods given by Kirkland74. The simulations were performed with a 200 kV probe, a probe illumination semi-angle of 28.9 mrad, and an ABF
collection semi-angle of 7-40 mrad. A probe spacing of 0.15 Å was used, which is below the high-resolution STEM information limit at 200 kV, to ensure accuracy of the images. The finite probe size was accounted for by convolving the simulated image with a 0.9 Å FWHM Gaussian.

5.3.6 Stability assessment of 2D GaN analyzed using XPS

The graphene/2D GaN/semi-insulating 6H-SiC sample was loaded into an ultra-high vacuum (UHV) system which consists of multiple UHV chambers. The UHV system includes a remote plasma source in a plasma-enhance atomic layer deposition (PEALD) chamber (Picosun PR200) and an x-ray photoelectron spectroscopy (XPS) chamber. These chambers are interconnected with a UHV transfer tube all maintained at < 3.75 × 10⁻¹⁰ Torr, as described elsewhere. For stability studies of 2D GaN in vacuum and air, graphene was first etched off the sample with in situ remote plasma, without any damage or modifications to the 2D GaN surface as confirmed by angled resolved XPS. A forming gas (FG) plasma (90% N₂ and 10% H₂) at flow of 150 sccm was ignited at 2000 W for 120 seconds with the substrate temperature maintained at 200°C. The XPS measurements were carried out during all steps (as-grown, after graphene FG plasma etch and after exposure to air) in order to monitor the stability of 2D GaN. The XPS system was equipped with a monochromated Al kα (hv = 1486.7 eV) x-ray source and a 7 channel analyzer with a pass energy of 15 eV. All high resolution XPS measurements were collected at 45° with respect to the sample normal and at same sample position. High resolution core level spectra were collected for the C 1s, Si 2p, O 1s, N 1s, Ga 2p₃/₂ and Ga 3d regions with detailed peak deconvolution and fitting carried out with the AAnalyer software after appropriate charge correction to compensate any shifts in the peak core level positions.
5.4 Results and Discussions

5.4.1 Properties of 2D nitrides from ab initio hybrid density functional theory

**Figure 5.7** | (a) binding energy calculations of freestanding planar and buckled 2D nitrides (N: nitrogen, M: group-III metal element and H: hydrogen atoms), as a function of layer number (L), showing increased stability of the buckled structure gleaned from their decreasing binding energies relative to planar 2D nitrides. (b) bandstructure calculations via DFT meta-GGA of freestanding planar and buckled 2D monolayer GaN, illustrating buckled 2D GaN with a direct bandgap ($E_g$) of 5.28 eV and planar 2D GaN with indirect $E_g$ of 4.12 eV, both larger than the direct $E_g$ of wurtzite bulk GaN (3.42 eV) due to quantum confinement. (c) diagram of bandgap energy versus in-plane lattice parameter for bulk and buckled 2D nitrides, establishing the possibility of probing deep into the ultraviolet with monolayers of group-III nitrides. The dashed lines are to illustrate the potential for $E_g$ tunability via alloying of 2D buckled monolayers. The $E_g$ as a function of number of atomic buckled layers is included as an inset in (c). The overlaid color band corresponds to the visible range of the energy spectrum.
The stability of cleaved wurtzite surfaces is affected by surface passivation. Two types of freestanding monolayer hexagonal group-III nitride structures, planar and buckled (Figure 5.7.a), are predicted to be stable from our binding energy calculation performed using Ab initio density functional theory (DFT) simulations. Based on DFT, when unsaturated states are not properly passivated, a planar structure is obtained; however, when two layers of planar 2D nitrides come into contact, bonding beyond van der Waals (vdW) occurs, leading to a semi-metallic behavior as reflected in the density of states (Figure 5.8). Alternatively, when unsaturated states are properly passivated, using partially charged pseudo-hydrogen\textsuperscript{78}, the structure is most stable in the buckled form. To identify the most stable structure, the binding energy of the 2D planar and buckled structures as a function of layer number was investigated. Evident from Figure 5.7.a, the freestanding buckled structure exhibits a more negative binding energy when compared to the planar structure, and therefore is considered the preferred configuration for 2D nitrides, regardless of the number of layers. Such variations in atomic configuration lead to significant differences in the electronic structure.

Perhaps most immediately notable in freestanding monolayer 2D GaN is the prominent increase in bandgap ($E_g$) compared to bulk GaN (3.42 eV) due to quantum confinement\textsuperscript{4}. More importantly, we find that the planar structure (Figure 5.7.b) exhibits an indirect $E_g$ of 4.12 eV, while the buckled structure maintains a direct $E_g$ of 5.28 eV. This is a critical difference between the predicted 2D GaN layers (direct \textit{versus} indirect $E_g$), as it has significant impact on the realization of light emitting devices. More importantly, our binding energy calculations demonstrate that the direct $E_g$ buckled structure is the most
thermodynamically stable, indicating that 2D nitrides (and alloys) are viable candidates for tunable optoelectronics (Figure 5.7.c).

Figure 5.8 | (a-b), structure simulation of planar 2D bilayer GaN before (a) and after (b) structure relaxation within a bilayer graphene/6H-SiC(0001) heterostructure. (b-c), after optimization, clear bonding between the initial van der Waals (vdWs) separated planar layers is evident and clearly reflected in its DOS (c). (c), DOS calculations after relaxation of planar 2D bilayer GaN in the supercell (b), revealing surface states near the Fermi level ($E_F$) and therefore, semi-metallic behavior of the 2D GaN structure that prefers buckling over remaining planar.
5.4.2 2D GaN formation *via* migration-enhanced encapsulated growth (MEEG)

Direct growth of wurtzite GaN on SiC(0001) conventionally results in three-dimensional (3D) island formation due to surface energy constraints and large lattice mismatch. If one, however, is able to passivate sites of high surface energy to promote Frank–van der Merwe growth, 2D GaN can be realized. Here, we introduce a “migration-enhanced encapsulated growth” (MEEG) process to enable the growth of 2D GaN. A schematic of the proposed MEEG process is shown in Figure 5.9.a-c. The starting substrate consists of epitaxial graphene formed by sublimation of silicon from the surface of SiC(0001) (Figure 5.9.a), which is converted to quasi-freestanding epitaxial graphene

![Diagram](image)

**Figure 5.9** (a-c), a schematic of the MEEG process that leads to the formation of 2D GaN (d). (a), the process of silicon sublimation from SiC(0001) to grow epitaxial graphene that consists of an initial partially bounded graphene-buffer layer (bottom) followed by a monolayer of graphene (top). The green halos at the SiC/graphene interface represents Si dangling bonds. (b), exposing epitaxial graphene in (a) to ultrahigh purity hydrogen at elevated temperatures decouples the initial (bottom) graphene-buffer layer to form bilayer QFEG. (c), the proposed MEEG process for the formation of 2D GaN: first, trimethylgallium precursor decomposition and gallium adatom surface diffusion; second, intercalation and lateral interface diffusion; finally, transformation of gallium to 2D GaN *via* ammonolysis.
Figure 5.10 | (a), SEM showing the formation of 3D doughnut-shaped islands of GaN on SiC(0001) via MEEG when graphene capping is not utilized. (b), SEM showing the formation 2D GaN on SiC via MEEG when graphene capping (QFEG) is utilized. Patchwork of regions of bright contrast (b) consist of 2D GaN. (c-f), regions of bright contrast in SEM (d) identified as area of nitrogen (c) and gallium (e) from surface sensitive elemental maps collected in high resolution scanning Auger electron spectroscopy (AES). (f), AES survey spectra of kinetic energy versus counts of three selected areas in SEM (d) labeled areas 1, 2 and 3. From the SEM contrast, Area 1 is a region of bare QFEG on SiC outside the regions of 2D GaN, as clearly reflected in the AES survey spectrum by the presence of negligible gallium and nitrogen signal when compared to Areas 2 and 3. In the case of Areas 2 (3D GaN island on the surface of graphene) and Area 3 (region of 2D GaN) in SEM (d), their corresponding AES spectra are clearly representative of the relative changes of gallium and nitrogen counts collected from those regions. (g-f), AFM of the surface of epitaxial graphene, illustrating the dense network of graphene wrinkles.
(QFEG) via hydrogenation\textsuperscript{79}. Hydrogenation passivates dangling bonds between graphene-buffer/SiC(0001), converting the graphene-buffer to an additional layer of graphene (Figure 5.9.b)\textsuperscript{80}, thus creating a pristine interface of reduced energy for the realization of 2D nitrides via MEEG. QFEG/Si(0001) is then exposed to cycles of trimethylgallium at 550 °C (Figure 5.9.c), which decomposes to gallium adatoms that diffuse readily on the surface of graphene, subsequently intercalating between QFEG/SiC(0001). Finally, transformation of the intercalated gallium to 2D GaN is performed via ammonolysis at 675 °C. During this process, atomic nitrogen resulting from the decomposition of ammonia, intercalates graphene and reacts with gallium to form 2D GaN\textsuperscript{81}. Samples were then cooled naturally to room temperature in ultrahigh purity nitrogen and then investigated using a Carl Zeiss Merlin field emission scanning electron microscope (SEM) operated at 1.0 kV.

Ammonolysis of gallium on SiC(0001) \textit{without} a graphene capping layer results in the formation of 3D doughnut-shaped structures of GaN due to enhanced desorption of gallium from the apex of liquid gallium droplets prior to ammonolysis (Figure 5.10.a). In contrast, when QFEG is utilized, GaN wets the surface in a patchwork of regions in addition to forming 3D structures on the surface of graphene (Figure 5.10.b). In SEM, the regions of bright contrast are found to consist of gallium and nitrogen when evaluated by AES (Figure 5.10.c-f). Here the AES instrument detection limit is between 0.1 to 0.01 atomic%. The structure of 2D GaN was also analyzed using high resolution electron microscopy. Aberration-corrected scanning transmission electron microscopy (STEM, Figure 5.11.a) subsequently reveals that these regions are 2D GaN, consisting of two sub-layers of gallium, located at the graphene/SiC(0001) interface. Moreover, inspection of
Figure 5.11 | (a) HAADF-STEM cross-section of 2D GaN, consisting of two sub-layers of gallium, between bilayer graphene and SiC(0001). (b-d), elemental EDX mapping of silicon (b), gallium (c) and nitrogen (d) in 2D GaN.
specimens with elemental mapping via energy dispersive x-ray spectroscopy of silicon (Figure 5.11.b), gallium (Figure 5.11.c), and nitrogen (Figure 5.11.d) in the STEM cross-section specimens confirms that these layers are GaN, and provides direct evidence that MEEG is a viable route for 2D nitride synthesis.

5.4.3 The role of defects in epitaxial graphene on the MEEG process of 2D GaN

Defects in graphene facilitate intercalation. Similar to intercalation of elements with small atomic radii such as H, N and F and elements with relatively large atomic radii such as Ge, Si, Au, Ni, In, Hf, Li, Cs, Eu, Pt, Pd, Co and Ce in epitaxial graphene\textsuperscript{55,60,80-90}, pre-existing point defects, wrinkles, and metal-graphene interactions serve as penetration

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.12.png}
\caption{(a-b), SEM of 2D GaN (patchwork regions of bright contrast) concentrated near 3D GaN islands (a) and networks of graphene wrinkles (b). (c-d,) schematic of proposed pathways for intercalation through the accumulation and penetration of gallium through point defects in the graphene lattice (c) and through nanoscale tears at the apex of graphene wrinkles (d).}
\end{figure}
sites during MEEG for gallium intercalation. As evidence of this, we find that the regions of 2D GaN are concentrated near 3D islands of GaN formed via ammonolysis of accumulated gallium (Figure 5.12.a) and networks of graphene wrinkles (Figure 5.12.b). The accumulation of gallium at defects in graphene, where nucleation of gallium nitride is preferential\textsuperscript{91}, likely provides the necessary energy to overcome the vdW interfacial binding and drive intercalation (Figure 5.12.c)\textsuperscript{91,92}. Additionally, the pronounced distribution of 2D GaN preferentially near dense networks of graphene wrinkles (Figure 5.10.g-h) provides evidence that gallium intercalates through nanoscale tears (Figure 5.12.d) that result from the large deformation at the apex\textsuperscript{93}. Once intercalation is initiated, the passivated surface of SiC(0001) and the low migration energy of gallium on the surface of graphene (0.05 eV)\textsuperscript{94}, provide a mechanism for large diffusion across the QFEG/SiC(0001) interface.

5.4.3.1 Raman analysis of the structure of graphene and 2D GaN after MEEG

Furthermore, Raman spectra and mapping was performed on the graphene/2D GaN/6H-SiC heterostructures which were collected with a Horiba LabRAM HR Evolution confocal Raman system operated at room-temperature using (633 nm “max at 16 mW”, 532 nm “max at 48 mW”, 364 nm “max at 50 mW”) excitation sources (Figure 5.13.a-d). Raman showed that the layer’s exhibit unique longitudinal optical phonon mode $A_1$(LO) for 2D GaN at 731.87 cm\textsuperscript{-1}. This mode is blue-shifted from the $A_1$(LO) mode at 738.68 cm\textsuperscript{-1} for wurtzite bulk GaN that is observed with a 364 nm laser excitation energy (Figure 5.13.a). Furthermore, the $E_2$(high) mode in bulk GaN using 364 nm laser excitation does not appear in 2D GaN, regardless of the laser excitation. This gives clear evidence of structural differences of 2D GaN from that of bulk GaN. In addition, with no clear defects
Figure 5.13 | (a), comparison of Raman spectra (from top to bottom): QFEG/6H-SiC, β-Ga2O3 substrate and bulk GaN/6H-SiC (black curves collected at 364 nm laser excitation), to the heterostructure consisting of graphene/2D GaN/6H-SiC collected at varied laser excitation (blue, green and red curves at 364 nm, 532 nm and 633 nm, respectively). In 2D GaN, a longitudinal optical phonon mode A1 (LO) appears at 731.87 cm⁻¹, blue-shifted from the A₁(LO) mode (738.68 cm⁻¹) for bulk GaN at the same laser excitation energy and power. The E₂(high) mode in bulk GaN with 364 nm laser excitation does not appear in 2D GaN, regardless of the laser excitation. In addition, no active Raman modes related to gallium oxide or oxynitrides are observed in our 2D GaN patchworks. (b), optical micrograph of the sample region containing 2D GaN within the heterostructure and (c), Raman map (c) of the position of the graphene defect (D)-peak (at 532 nm laser excitation energy), illustrating (e), a large blue-shift in the Raman D-peak position relative to non-intercalated regions of graphene (~1351.9 cm⁻¹ to ~1331.2 cm⁻¹).
observed in the 2D GaN layer from STEM and the appearance of a clear phonon mode associated to 2D GaN in UV Raman, suggests good crystallinity of the quintuple layer. Moreover, as evident in Figure 5.11.d, graphene remains after MEEG; however, it is defective as identified by Raman.

As illustrated in Figure 5.13.b-d, we find a large Raman blue-shift in graphene’s defect (D)-peak position relative to non-intercalated regions of graphene (~1351.9 cm\(^{-1}\) to ~1331.2 cm\(^{-1}\)). This indicates strain and/or structural changes to graphene and possible interactions at the interface.

5.4.3.2 Engineering defects into the graphene lattice to improve coverage of 2D GaN

From Raman spectroscopy, we can also conclude that defects play a critical role in the intercalation process. Though the domains within the patchwork regions that we observe in SEM are on the order of ~300-700 nm, we find that we can form larger patchwork regions of 2D GaN by intentionally introducing defects into the graphene lattice via oxygen plasma exposure prior to hydrogenation and MEEG. A TePla M4L Barrel plasma etch system operated at 100 W, 30% O\(_2\)/He mixture and 500 mTorr total pressure was used to increase the point defect density in the graphene lattice. Short exposures showed to significantly increases the domain size and coalescence of the patchwork of 2D GaN without changing the growth conditions. As evidence of this, we find domains of 2D GaN > 1 \(\mu\)m (Figure 5.14.a-b), which we confirmed the compositions of these domains using AES (Figure 5.14.c). Further optimization and engineering specific defects into graphene may lead to even larger-areas of 2D GaN.
5.4.4 Resolving the structure of 2D GaN in aberration corrected S/TEM

Two-dimensional GaN grown via MEEG is isostructural to layered alpha-phase In$_2$Se$_3$, gamma-phase InSe, and 3R-MoS$_2$ (space group: R3m)$^{95}$, and exhibits covalent bonding to the SiC(0001) substrate while preserving a vdW gap with graphene. This is evident in annular bright field (ABF) STEM (Figure 5.15.a-b), which directly resolves the atomic columns$^{96}$. The use of annular bright field (ABF)-STEM mode to characterize the
structure of crystalline materials has been well established in the literature as a go-to method to directly resolve the positions of light and heavy atomic displacements without ambiguity and a direct measurement of polarity in many non-centrosymmetric solids, particularly in GaN. Resolving the atomic positions in 2D GaN gives deep understanding of the resulting symmetry and unit cell when interfaced with graphene and SiC. To achieve this, we captured simultaneous high angle annular dark field (HAADF) and ABF images at 200kV.

Figure 5.15 | (a-b), annular bright field (ABF) images collected with aberration corrected STEM near the [11\(\bar{2}\)0] zone axis, resolving the atomic columns of gallium, nitrogen, silicon and carbon in graphene/2D GaN/6H-SiC(0001) heterostructure. (b), is an inverted image of (a) for enhanced visualization. The R3m structure of 2D GaN is highlighted from the position of the nitrogen and gallium atomics columns.
Traditionally, the structures of GaN exist in the hexagonal wurtzite and cubic zinc-blend forms, with the addition of the rock-salt structure that can be accessed at high pressures. In the wurtzite structure of bulk GaN, the displacement of projected atomic pairs, referred to as dumbbells, can be resolved along the [11\bar{2}0] zone axis. Heavy atoms (gallium and silicon) in ABF-STEM appear more intensely black than light (nitrogen and carbon) atoms. The local polarity of the dumbbells indicates the structural nature of 2D GaN (planar or buckled). If the 2D structure is buckled, the polarity of the dumbbell, given by the terminating (gallium or nitrogen) atom facing SiC(0001) can be directly imaged. We do not observe the wurtzite, cubic zinc-blend nor rock-salt structures in 2D GaN from ABF-STEM. The spatial resolution of aberration corrected STEM in annular bright field (ABF) mode makes it possible to directly image the position of nitrogen and gallium in the 2D GaN structure which shows the R3m space group symmetry.

Since the quintuple structure of 2D GaN has an R3m space group symmetry, we would like to note that the nomenclature (GaN) reported here refers to the binary compound semiconductor “gallium nitride” and not the 1:1 stoichiometry. The driving force for forming short periods of the R3m polytype in many semiconductor systems is, however, still unclear\textsuperscript{97}, but in our case, we believe it may be stable for thermodynamic reasons: to accommodate the energetics of the hexagonal wurtzite substrate on one side and the van der Waal interaction with graphene that exhibits a different space group symmetry from that of the supporting substrate. As a result we hypothesize that the passivated QFEG/(0001)SiC interface and the pronounced spontaneous polarization of 6H-SiC, leads to an initial stabilization of bilayer gallium at this interface prior to ammonolysis. The stability of bilayer gallium on polar surfaces has been well documented in literature,
particularly the pioneering work of Randall M. Feenstra, J. Neugebauer and J. E. Northrup (and others)\textsuperscript{98-101} that combines scanning tunneling microscopy (STM) during MBE growth of GaN films (under gallium rich conditions) in ultra-high vacuum with energy calculations on many polar surfaces, including SiC. During MBE growth, the pseudo-1×1 reconstructed GaN(0001) surface stabilizes a dynamic bilayer of gallium, known as the laterally contracted bilayer model\textsuperscript{101}. This bilayer of gallium has been shown to theoretically be even more energetically stable when interfaced with graphene\textsuperscript{102}. These prior established literatures corroborate well with our experimental observations and thus supporting the observed R3m 2D GaN structure that interfaced graphene. Moreover, this R3m polytype has been reported in bulk GaN films and other semiconductor systems, interfacing hexagonal crystal structures\textsuperscript{103-108}.

5.4.5 Role of graphene in the atomic stabilization of 2D GaN

In addition to 2D GaN, MEEG with QFEG/SiC(0001) enables the formation of thicker (>5 nm) layers of GaN at the interface. Interestingly, even this “thick” GaN (Figure 5.16.a) exhibits the same surface termination as 2D GaN observed in Figure 5.9.e-f (Figure 5.16.b), thus confirming graphene’s significant role in stabilizing the 2D buckled quintuple R3m structure regardless of the underlying passivated surface. The role of graphene in the formation of 2D GaN is further accentuated upon comparing ABF-STEM cross-section images of 2D GaN (Figure 5.16.b) to the surface of bulk GaN (Figure 5.16.c) grown directly on SiC(0001), where only native oxide reconstruction is observed on the surface of bulk GaN. The conditions for the growth of bulk GaN directly on 6H-SiC is outlined in chapter 4\textsuperscript{73}. Moreover, ABF-STEM images were simulated using the multislice method implemented in a MATLAB code, following the methods given by Kirkland et al.\textsuperscript{74} In the
Figure 5.16 | (a), TEM revealing the formation of thick GaN beneath graphene. (b-c), inverted ABF-STEM images near the [11$ar{2}$0] zone axis with overlaid insets of non-inverted simulated ABF-STEM images, comparing the interface of graphene and GaN (b) seen in (a) and the surface of bulk GaN grown directly on 6H-SiC(0001) without graphene capping (c, see Methods). (b), the atomic columns of 2D GaN on thick GaN clearly shows the polarity inversion of the nitrogen-gallium termination in 2D GaN interfacing graphene (arrow labeled nitrogen-polar) from that of the polarity of thick GaN (arrow labeled gallium-polar). The role of graphene here in stabilizing the buckled R3m 2D structure and inverting polarity is undoubtedly evident from the displacement of (gallium and nitrogen) dumbells in the magnified insets. (c), only reconstructed surface oxide is observed in bulk GaN grown directly on 6H-SiC(0001) without graphene capping and with no inherent changes in polarity (arrow labeled gallium-polar). In each inset (c,d), gallium-nitrogen positions and bonding (obtained from our DFT models) are overlaid on the micrographs.
magnified insets of Figure 5.16.b and 5.16.c, we have overlayed the DFT optimized structure of R3m 2D GaN and P63mc wurtzite bulk GaN to clearly illustrate structural difference. It becomes evident the existence of the quintuple R3m 2D GaN structure, consisting of N-Ga-N-Ga-N buckled sub-layers, where structural buckling, as we suggest from our binding energy calculations in Figure 5.7.a, alludes to the direct bandgap nature of 2D nitrides. Furthermore, from experimental and simulated ABF-STEM images, we find that the polarity of the nitrogen-gallium termination in 2D GaN is inverted at the top interface compared to thick GaN (Figure 5.16.b). We hypothesize that during ammonolysis, nitrogen replaces hydrogen on the SiC surface, effectively passivating sites of high surface energy\(^{109}\), which leads to charge neutrality and stability of 2D GaN. Consequently, this leads to the observed covalent bonding of 2D GaN with SiC, which is further evident in x-ray photoelectron spectroscopy (XPS) measurements of the samples.

5.4.6 Role of graphene encapsulation on preventing oxidation in 2D GaN

The combined use of EDX, ABF-STEM, XPS and UV-Raman spectroscopy of our 2D GaN domains provides strong evidence that the composition of the layers consisted of gallium and nitrogen and were not an oxide or oxynitride.

5.4.6.1 Understanding oxygen incorporation in 2D GaN from cross-section EDX measurements

We show clearly in Figure 5.17.a and 5.17.b strong localization of the gallium and nitrogen signal in the 2D GaN layer. The thickness of the sample taken here is < 30 nm. For much thicker prepared TEM specimens (Figure 5.17.c), the nitrogen and gallium signals are even more pronounced (improved signal-to-noise ratio) and confined to the 2D
From the EDX spectrum, distinct gallium and nitrogen peaks are evident. The sensitivity of EDX increases with atomic (Z) number, however, the nitrogen signal is distinctly higher than the noise level and hence can be accurately spatially resolved within the 2D GaN. Our results from the EDX cross-sections are in good agreement with the plan-

**Figure 5.17** | (a-b), HAADF images with corresponding EDX maps. An initial protective amorphous carbon layer was deposited during FIB on these samples. (c), HAADF images with corresponding EDX maps of gallium, nitrogen and oxygen with improved signal-to-noise. An initial protective SiO$_2$ layer was deposited during FIB in this case. (d), EDX spectra of the entire 2D GaN area from the STEM in Figure 5.11.a. GaN region. From the EDX spectrum, distinct gallium and nitrogen peaks are evident. The sensitivity of EDX increases with atomic (Z) number, however, the nitrogen signal is distinctly higher than the noise level and hence can be accurately spatially resolved within the 2D GaN. Our results from the EDX cross-sections are in good agreement with the plan-
view analysis of 2D GaN using high-resolution Auger electron spectroscopy (AES) maps (Figure 5.10.c-d) and surveys (Figure 5.10.f) of nitrogen and gallium. The presence of oxygen in an electron microscope is common and dangling bonds on the surface of the FIB prepared TEM specimens are susceptible to oxygen-containing adsorbates from the environment, particularly since these samples are examined over periods of time. Therefore, we believe to accurately assess oxidation, specifically oxygen bonded to gallium, high resolution XPS analysis was necessary.

5.4.6.2 Stability of 2D GaN monitored by x-ray photoelectron spectroscopy (XPS)

To evaluate the stability of 2D GaN after removal of graphene, a time dependent air exposure study of the GaN chemical states was performed using XPS. XPS probes areas ~300 µm in diameter. Though mechanical exfoliation of graphene, via scotch tape, can remove regions of graphene for spectroscopic measurements, in situ complete removal of graphene is necessary for the accurate assessment of the stability of 2D GaN by XPS, before and after removal of graphene and after exposure to air. Therefore, we have developed a process to remove graphene using a remote forming gas (FG) plasma in a multi-chamber UHV system as outlined in our experimental section. The successful removal of graphene can be observed from the C 1s core-level spectrum post MEEG and after exposure to a forming gas plasma (Figure 5.18.a). The sp² C-C bonding of graphene at 284.3 eV was near the XPS detection limit after the FG exposure, indicating a complete removal of the graphene capping layer. From prior surface treatment studies of AlGaN and GaN with remote FG plasma, removal of carbon from the surface can be achieved without any detectable chemical changes or destruction of the AlGaN and GaN surfaces. Before removal of graphene, however, two distinct chemical states of gallium were
detected from collected high resolution XPS spectra (labeled: Post MEEG in Figure 5.18). The higher binding energy (BE) peak corresponds to Ga$_2$O$_3$ (from the oxidized 3D GaN islands on the surface of graphene, Figure 5.12.a and 5.12.b) and the lower BE peak is attributed to the underlying 2D GaN (Figure 5.11.a), respectively shown in Figure 5.18.f and 5.18.g. Oxidation of such 3D islands that form on graphene was also observed in our previous report on the growth of GaN directly on epitaxial graphene$^{91}$. These 3D islands, however, are easily detached from the surface by exfoliation with scotch tape and completely removed after in situ FG plasma selective etching of graphene, as verified in the “Post FG plasma” of the C 1s core level spectrum (Figure 5.18.a) as well as in the associated Ga 2p$^{3/2}$ and Ga 3d core level spectra (Figure 5.18.f and 5.18.g). After exposure to the remote FG plasma, 2D GaN is detected with the concomitant increase of the associated Ga 2p$^{3/2}$ and Ga 3d peak intensities due to the removal of graphene, while the Ga$_2$O$_3$ concentration is near the limit of detection. Due to the removal of the graphene layer, the intensity of Si-O bonding that originates from the native oxide on SiC also increases (Figure 5.18.b)

Furthermore, we find exposed areas of the 6H-SiC substrate, which are not encapsulated with QFEG or graphene/2D GaN, to be comprised of Si-N bonding in the Si 2p core level spectrum after the remote FG plasma exposure (Figure 5.18.b). Moreover, no changes in the shape or shifts in binding energy of the O 1s core level peak are observed for the case of graphene/2D GaN/SiC and QFEG/SiC samples after exposure to the remote FG plasma (Figure 5.18.c-d), supporting Si-O and Si-ON bond formation on the surface of 6H-SiC, without Ga-oxide formation. Successive XPS measurements after graphene
Figure 5.18 | High-resolution XPS spectra collected after the growth of 2D GaN (Post MEEG, black); after removal of graphene with forming gas plasma (Post FG plasma, red); after exposure to air for 1 hour (blue) and 24 hours (green) for the core-levels of a, C 1s. b, Si 2p. c-d, O 1s, also comparing the intensity and shape (normalized inset) of the QFEG/6H-SiC (red) and graphene/2D GaN/6H-SiC (black) after exposure to FG plasma (d). e, N 1s. f-g, Ga 2p$_{3/2}$, where (g) shows no changes in the Ga-N bonding after exposure to air. h, shows the Ga 3d core-level spectra. From deconvolution of the Ga 2p$_{3/2}$ (f) and Ga 3d (h) core-level spectra, no detectible changes in the chemical state are observed. Therefore, 2D GaN is stable in air after removal of graphene from the surface of the graphene/2D GaN/6H-SiC heterostructure in FG plasma.
removal reveals no detectable chemical state change of the N 1s, Ga 2p$_{3/2}$, and Ga 3d core level spectra after 1 or 24 hour exposure to air (Figure 5.18.e-h), while the overall peak intensities decrease due adsorption of adventitious carbon and contaminates from air exposure. The N 1s core level spectra indicate predominant Ga-N bonding from 2D GaN, with slight asymmetry on the high side of the binding energy due to Si-ON formation on the SiC substrate (Figure 5.18.b). More importantly, no changes in the shape and energy position of the Ga 2p$_{3/2}$ and Ga 3d core level spectra are observed with exposure to air (Figure 5.18.f-h), supporting the chemical state stability of the 2D GaN in air, even without the overlying graphene capping layer.

### 5.4.6.3 Understanding oxidation of 2D GaN from UV-Raman measurements

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<th>Space group</th>
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**Table 5.1** | Raman Modes of gallium-nitride, -oxynitrides and -oxyhydrides from literature.
Our ABF-STEM images clearly compare the structure of 2D GaN (Figure 5.16.b) to the structure of the reconstructed gallium surface oxide on bulk GaN (Figure 5.16.c). The structures of gallium oxide or oxynitride containing compounds are significantly different from 2D GaN. We support this claim with UV-Raman measurements of 2D GaN and compare the modes of this structure to SiC, graphene on SiC and β- Ga₂O₃ (Figure 5.13.a). We also have compiled all active Raman modes for the most thermodynamically stable phases of gallium oxide and oxynitrides are listed in Table 5.1. The shallow penetration depth of UV Raman (364 nm laser excitation) enhances surface sensitivity and improves Raman scattering efficiency. We do not observe any active Raman modes associated with a gallium oxide or gallium oxynitride in our UV-Raman spectra of 2D GaN. What we do see is a unique longitudinal optical phonon mode for 2D GaN that is distinct from that of bulk GaN (Fig. 6.7.a). We believe our results provide compelling evidence that the 2D GaN layers are not an oxide or oxygen containing compound.

5.4.7 Verifying the experimental bandgap of 2D GaN

The atomic arrangement of 2D GaN considerably impacts the electronic structure. To determine the nature of the bandgap in 2D GaN, we first simulated the R3m structure that was resolved in ABF-STEM. After structure optimization in DFT, all surface states are passivated between the 2D GaN and SiC as a result of the covalent bonding suggested experimentally from ABF-STEM. The bandstructure was then determined from DOS calculations of the graphene/2D GaN/SiC(0001) heterostructure (Figure 5.19.a), using DFT functional meta- generalized gradient approximation (meta-GGA) and Heyd-Scuseria-Ernzerhof density functionals. The DOS calculations showed p-type semiconducting behavior for 2D GaN with theoretical $E_g$ values of 4.79 eV and 4.89 eV,
for the respective *meta*-GGA and Heyd-Scuseria-Ernzerhof density functional approaches (Figure 5.19.b).

**Figure 5.19** | (a), structure simulation with DFT of the graphene/2D GaN/6H-SiC heterostructure as observed in ABF-STEM (Figure 5.15a-b). 2D GaN was modeled as a rhombohedral cell having R3m symmetry and optimized between bilayer graphene and 6H-SiC. (b), DOS calculation *via* *meta*-GGA and HSE06 functionals, revealing the $E_g$ of 4.79 eV and 4.89 eV for 2D GaN from each approach, respectively. From the DOS in (b), the valance band shifts up towards the Fermi level ($E_f$), indicating p-type semiconducting behavior in 2D GaN.

**5.4.7.1 Determining the bandgap from UV-reflectance and UV-ellipsometry measurements**

We first determined the experimental bandgap of 2D GaN using UV-vis measurements. Spectra of the samples were collected in reflection mode using a 60 mm
integrating sphere on a *PerkinElmer LAMBDA 1050 UV/Vis/NIR* spectrophotometer (resolution of spectral bandwidth ≤ 0.05 nm) operated at room temperature. From ultraviolet-visible reflectance measurements of 2D GaN (UV-Vis), an inflection point in the spectra of 2D GaN at 4.90 eV is clearly evident (Figure 5.20). This specular feature is not observed in the QFEG/SiC reflectance and therefore indicates experimental observation of the $E_g$ of 2D GaN, well within the range predicted by DFT. The FWHM of the derivative of the spectral inflection point associated with the bandgap of 2D GaN was ~16 nm, which is well within the specular resolution detection capabilities of the UV-Vis spectrometer.

![Graph of UV-Vis reflectance](image)

**Figure 5.20** | UV-Vis reflectance collected with an integrating sphere. Spectra from top to bottom: QFEG/SiC; graphene/2D GaN/SiC; 2D GaN after QFEG/SiC background subtraction and the derivative of the 2D GaN extracted reflectance plotted in Log$_{10}$ scale, revealing the $E_g$ of 2D GaN is 4.90 eV.

250
In general, bandgap measurements of the 2D GaN is a challenging. This is largely due to limited characterization techniques with capabilities of probing far into the deep UV that are readily available, particularly with the overlayer of graphene. It is well reported that graphene and other analogous 2D materials exhibit excellent quenching of fluoresces of other materials within their vicinity\textsuperscript{119-122}. The UV-Vis measurements of 2D GaN is taken in reflection mode, therefore, one can expect sever quenching from graphene/2D GaN heterostructure, inhibiting signal from the regions of thick GaN. In fact, room-temperature photoluminescence (PL) and cathodoluminescence (CL) of the graphene/2D GaN/thick GaN/6H-SiC heterostructure showed no band-edge emission from the thick GaN. However, CL measurements at 13 Kevin provided sufficient signal enhancement from the thick GaN layers. We observed predominate band-edge emission near 3.31 eV for thick GaN. The blue-shift observed in the band-edge emission may arise from the strain state of thick GaN, as the thickness is below the critical thickness for stress relaxation, and therefore is pseudomorphically strained to the SiC substrate. We could not obtain signal from the 2D GaN via PL and CL measurements, due to the unviability of a deep UV excitation source and spectrometer being out of the collection range, respectively.

Furthermore, we extract the absorption coefficient ($\alpha$) of 2D GaN (Figure 5.21.b), by fitting the dielectric function of the heterostructure (Figure 5.21.a) collected with UV-Vis spectroscopic ellipsometry. UV-Vis ellipsometric measurements were performed using a \textit{J.A. Woolam Co., Inc. V-VASE} spectroscopic ellipsometer. Data was collected over the spectral range from 1.55 eV to 6.42 eV at 40, 50, 60 and 70 degrees. The dielectric function was defined by first taking the measured ellipsometric data from the control sample consisting of epitaxial graphene on a 6H-SiC substrate. The model consisted of
Lorentz oscillators to define the optical response of the SiC and a 5.5 Å thick layer using the dielectric function reported by Boosalis et al. for graphene. Following the establishment of a high-quality fit, this dielectric function was used as the base model for the measured sample featuring the graphene/2D GaN/6H-SiC heterostructure. This was modeled as a single Gaussian oscillator, with the amplitude, center frequency and line width provided as variable parameters. The thickness was initially defined as 6 Å, then after initial fitting and with the Gaussian parameters also treated as a variable, a final thickness of 5.6 Å was determined. This thickness is in good agreement with STEM measurements of 2D GaN. Using a Gaussian fit of the center frequency, we find a direct transition consistent with the predicted direct $E_g$ of 2D GaN centered at 4.98 eV $\pm$ 0.13 eV.

Due to the discontinuous nature of the 2D GaN, an exact dielectric function for the 2D GaN layer could not be established. However, in the context of this work, these measurements served to provide additional spectroscopic evidence of the ~4.9 eV direct bandgap transition associated with the 2D GaN as predicted by DFT.

**Figure 5.21** | (a), the real (right) and imaginary (left) parts of the dielectric function of 2D GaN measured from UV-ellipsometry. (b), absorption coefficient ($\alpha$) of 2D GaN, revealing a direct $E_g$ of 4.98 eV. The connecting line is to guide the eye.
5.4.7.2 Determining the bandgap from electron-energy loss spectroscopy (EELS)

In addition, dual low-loss electron energy-loss spectroscopy (dual-EELS) measurements were performed to measure the bandgap energy of 2D GaN using a source electron monochromator to improve the signal-to-noise and reduce spectral delocalization at 80 kV. The energy spread full width at half maximum (FWHM) of the monochromator was setup to be < 0.2 eV. For these measurements, TEM cross-section specimen with thicknesses < 30 nm with minimal sidewall damage were necessary in order to eliminate plural scattering in our EELS spectra. We have taken percussions in these measurements and only compare the bandgap to a well-known material that can be easily deposited and measured under identical conditions on the same sample. In this case, we use SiO₂, deposited by e-beam evaporation. Therefore, prior to milling of specimens for \( E_g \) measurements of 2D GaN via low loss EELS, samples were first prepared for TEM after MEEG by mechanical exfoliation of graphene layers from the surface, followed by the deposition of 30 nm of SiO₂ using thermal evaporation in a Kurt J. Lesker Lab 18 evaporator. Exfoliation of graphene from the surface of the samples containing 2D GaN was performed in order to minimize the potential influence of the graphene plasmon peaks on the EELS spectra. Dual EELS measurements in STEM mode allows collection of both high intensity low energy loss spectra (shifted from the zero loss peak) and weak intensity high energy loss spectra (containing the zero loss peak), simultaneously from the same sample position and under identical microscope conditions\(^{124}\). This allows for the correction for any drift in the spectra by calibrating the zero loss peak energy at 0.0 eV. To extract the \( E_g \) from low loss EELS, the zero loss peak and background were subtracted from the spectrum by stitching both the high energy loss and low energy loss spectrum and
using a power-law fit. No plural scattering deconvolution of our spectra was needed due the thickness of the FIB cross-section prepared sample being < 30 nm, as measured by EELS. Following careful background subtraction, a Savitzky-Golay smoothing function (second-order polynomial) was applied to the spectra. The low loss EELS spectrum relates to the joint density of states in the material. Therefore, the $E_g$ transition can be extracted from the first prominent rise in the spectrum. We used the parabolic fitting method of the first rise to extract the $E_g$ of 2D GaN, where the parabola intersects the energy axis$^{125}$. From

**Figure 5.22** | Point spectrum of low-loss EELS collected from regions of interest in the STEM image shown in the inset. The $E_g$ is extracted from the low-loss EELS spectrum after background subtraction using the parabolic fitting method (red curves) of the first prominent rise. The blue curve is the spectrum collected in the bulk of the SiO$_2$ protective layer and the green curve is the spectrum collected in the region of 2D GaN, which show an extracted $E_g$ of 9.56 eV and 5.53 eV, respectively.
low-loss EELS (Figure 5.22), the extracted $E_g$ of 2D GaN is ~5.5 eV, while the $E_g$ of SiO$_2$ is ~9.6 eV, providing further evidence of the increased $E_g$ in 2D GaN. The ~0.6 eV deviation in the $E_g$ obtained via low-loss EELS from that collected experimentally (UV-vis reflectance and spectroscopic ellipsometry) and/or calculated theoretically (meta-GGA and HSE06) arises from Cerenkov loss that are observed in EELS measurements of high dielectric materials$^{124}$. We mitigate these effects on the spectra by acquiring the low-loss EELS spectra at 80 kV and using a monochromator with an energy resolution of < 0.2 eV.

Finally, our samples were checked for the presence of aluminum in order to eliminate the possibility of alloying with gallium and contribute to the increase in the observed band gap energy. In Figure 5.10.f, we show high resolution AES surveys of the kinetic energy versus counts of three selected areas in SEM (Figure 5.10.d). No Auger electron peaks associated with aluminum are observed in the collected spectra, where major Auger peaks for aluminum span between 1345 eV to 1487 eV in kinetic energy. Our results, therefore, provide direct evidence that the $E_g$ is much larger than that found in bulk GaN, with theoretical and experimental values being in good agreement.

5.4.8 Preliminary vertical transport measurement of 2D GaN using conductive AFM

We also carried out vertical transport measurements of the heterostructure with conductive atomic force microscopy (C-AFM). For electrical measurements, 2D GaN was grown via MEEG using epitaxial graphene grown on n-type 6H-SiC. Site specific regions of the graphene/2D GaN/6H-SiC heterostructure were isolated using focus ion beam (FIB), in order to probe consistent vertical transport measurements without shorting via graphene. Measurements were performed under PeakForce TUNA mode in a BRUKER Dimension
conductive AFM (C-AFM) using a platinum AFM tip. Current-voltage (I-V) characteristics of the heterostructure were investigated by sweeping the voltage from the conductive tip between -2.5 V to 2.5 V, under a loading force and sensitivity of 5 nN and 1 nA/V, respectively. As shown in the current-voltage (I-V) curve in Figure 5.23, under forward bias, conduction is likely from electrons being pulled from the accumulated n-type 6H-SiC over the conduction band offset between SiC and 2D GaN. From the DOS, the conduction band offset is ~1.7 V. Therefore, the turn-on voltage is within that range. Under reverse bias, conduction is likely due to electron injection from graphene over the Schottky barrier provided by 2D GaN, and into the depleted n-type 6H-SiC. In all other cases, where the 2D GaN is absent, the I-V curves exhibit an ohmic behavior (Figure 5.23, inset), confirming that ambipolar graphene makes a low Schottky barrier contact with n-type 6H-SiC.
SiC. Therefore, one may be able to design novel device architectures based on the current heterostructure. For applications where the removal graphene is beneficial, the high stability of GaN after removal of graphene allows for practical device fabrication.
5.5 Conclusions

The experimental observation of buckling in 2D GaN from ABF-STEM validates our theoretical predictions that structural buckling leads to the most thermodynamically stable structure for 2D nitrides, which retains a direct E_g, unlike reported theory^8,9,11. Graphene has proven to be a remarkable material over the last decade; and with the discovery that it can stabilize 2D forms of traditionally “3D” binary compounds, we have provided the foundation to realize many other classes of materials that are not traditionally 2D. Furthermore, the MEEG process could enable vertically stacked 2D layered heterostructures with yet to be predicted properties. Moreover, modifications to the phonon DOS of 2D GaN with respect to bulk GaN are anticipated to modify polaritonic behavior for additional nanophotonic functionality in the mid-infrared^{126}. Finally, recognizing the impact of 2D nitrides, it can be expected that the addition of 2D GaN and other 2D nitrides (and alloys) will open up new avenues of research in electronic and optoelectronic devices, composed of 2D atomic layers of group-III nitride semiconductors.
5.6 References

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CHAPTER 6

FUTURE WORK

6.1 Motivation

I would like to focus the discussions of future work of this dissertation on the final part of my thesis that concerns the development of new synthesis routes to experimentally realize two-dimensional forms of conventional compound semiconductors, such as 2D gallium nitride (GaN), via a mechanism of adatom intercalation from the vapor phase through the lattice of graphene. This synthesis process that was developed is referred to as “Migration Enhanced Encapsulated Growth” (MEEG). Unlike material synthesis by molecular beam epitaxy (MBE), MEEG is a low-pressure synthesis process. Here, graphene not only stabilizes new two-dimensional monolayers on technological relevant substrates like SiC, but also establishes a platform to address challenges associated with creating clean, atomically abrupt vertical heterostructures, protected from air and thus stable for conventional ex situ characterization. Therefore, this process could potentially be extended to other materials systems, as an approach to tackle some of the growth and stability challenges associated with conventional 2D and layered materials. Future research interests here are to use MEEG as a platform for the synthesis of 2D superconductors and to modulate the properties of graphene by changing its dielectric environment by the intercalation of various elements that can chemically react to from new crystals, specifically those that inherit large spontaneous polarizations. Both of these examples will be discussed in the following sections.
6.1.1 Graphene as a key platform to realize two-dimensional superconductors

One may argue that the grand challenge in current electronic devices is the generation and management of power in a sustainable way. Power management is a pressing problem in complementary-metal-oxide-semiconductor (CMOS) based supercomputers that handle everything from our daily internet traffic to cloud computing. With no clear economic path to increase energy efficiency in time to meet the expanding depends for computation speed, the design of the circuitry in these supercomputers must be reconsidered. The problem is quite fundamental: the more densely packed CMOS circuitry becomes, the more energy is lost in the form of heat due to electrical resistance, and therefore, the more extensive cooling of these supercomputers is required. One approach to eliminate resistance, improve efficiency and transistor switching speeds while tackling the issue of scalability is through the use of superconductors.

Superconductivity (zero-resistance) arises from Cooper pair formation of conduction electrons at sufficiently low temperatures. Supercurrent flowing indefinitely nearly without a power source and without heat generation is an idea that is not far from reality. The renewed interest in superconductors for supercomputers may, in fact, be at an important pivot point in history, specifically with the discovery of high-temperature superconductivity. The combined properties of superconductors are key enablers for disruptive technologies that now have become truly ubiquitous. Superconducting materials are used today in sensitive magnetometers, magnetic resonance imaging and single photon detectors. Superconducting based supercomputers process information as quantum bits (qubits) in reciprocal quantum logic (RQL)\(^1\), with the Josephson tunnel junction being at the core of these superconducting qubits. An attractive alternative to CMOS, these non-
linear switching devices can well outperform even the most advanced steep switching semiconductor devices available today. Josephson junctions consist of two superconducting materials coupled with a metal or ultra-thin insulator that can permit the tunneling of Cooper pairs. In RQL, these Josephson junctions take up only a fraction (1/300th) of the power that would be used in most advanced CMOS circuitry, and therefore, are overall more efficient even with the cryogenic cooling required for superconductors. In addition, the emergence of simple binary two-dimensional and layered superconductors, such as magnesium diboride (MgB$_2$) with two superconducting bandgaps and iron selenide (FeSe) with a superconductivity bandgap above 100 Kelvin at the atomic layer limit, all proves the viability of achieving scalability in supercomputer logic. One advantage of using two-dimensional and layered superconductors is that these atomically thin layers can be entirely modulated by an applied electric field. This could give rise to a new degree of freedom in controlling the superconductor coupling and thus qubit frequency, leading to new gate-tunable Josephson qubits that will help simplify the design complexity of quantum circuits. Superconductivity could provide an answer to the power and thermal management problem in supercomputers — however the technology used for the synthesis of these materials must significantly mature.

The major impetus behind the immense research activity surrounding superconductivity today has, of course, spawned from the discovery of materials that superconduct at temperatures accessible with modern cryogenic coolers. Commercial implementation of two-dimensional and layered high-temperature superconducting materials in supercomputers has been slow and this is largely due to the challenges associated with materials synthesis. Take the classical example of MgB$_2$: The high vapor
pressure of magnesium results in layers with a range of structural defects that ultimately can affect the critical current density, the critical field and hence the critical temperature of superconductivity. Some success has been demonstrated in epitaxially grown MgB$_2$ films by hybrid physical-chemical vapor deposition (HPCVD) on nearly lattice matched substrates such as SiC$^4$. *In situ* fabrication of heterostructures for Josephson junctions on a wafer scale has, however, not come to fruition. This is due in part to difficulties in controlling stoichiometry and phase transformation as a function of layer thickness. MgB$_2$ is also prone to oxidation, making *ex situ* fabrication of atomically clean heterostructures of Josephson junctions even more difficult. All of these discussed factors relate to the synthesis of MgB$_2$ and all these factors can tremendously impair superconductivity in the material.

Moreover, superconductors have resisted miniaturization for some time. This is because as the material thickness approaches a few atomic layers, it essentially becomes a surface/interface, but these surfaces and interfaces are easily vulnerable to the structural and chemical influences of the surroundings. Moreover, as we decrease the dimensions of superconductors beyond the coherence length of the Cooper pairs, superconductivity is suppressed. However, unlike MgB$_2$, superconductivity in FeSe is rather unique. In FeSe, the superconducting bandgap was found to increase from ~8 Kelvin in the bulk to ~100 Kelvin in the atomic-limit$^{3,5}$. Conventionally, superconductivity should go down as we decrease the number of layers. The superconducting bandgap in FeSe is, however, influenced by pressure, strain, intercalation, isovalent and/or electrostatic doping$^6$. Indeed, the highest superconducting critical temperature reported in an atomic layer of FeSe was demonstrated on SrTiO$_3$,$^3$ where the work function mismatch at the interface drives charge
transfer and thus doping in FeSe. It is difficult to investigate the effect doping in an atomic layer of FeSe. For this purpose, to truly understand the effect of doping and pressure on the critical temperature of superconductivity in monolayer FeSe, a novel synthesis platform must be developed. Epitaxial graphene is an excellent synthesis platform to investigate these effects in monolayer FeSe and therefore a complete phase diagram for superconductivity may finally be established.

The concept of MEEG discussed in chapter 5 to synthesize non-traditional two-dimensional materials may be extended to the van der Waals epitaxy of pristine two-dimensional layers of MgB$_2$ and FeSe. The interface between graphene and SiC can potentially host a variety of intercalants with endless combination possibilities and can circumvent processing limitations. For example, the need to have a high overpressure of magnesium in the vapor phase for MgB$_2$ synthesis is entirely eliminated, since the Mg intercalant is well encapsulated within the graphene/SiC interface. Once intercalation is initiated through graphene, the passivated surface of SiC and the low migration energy of the intercalant on the surface of graphene, provides a mechanism for long diffusion lengths across the graphene/SiC interface. This not only promotes Frank–van der Merwe growth, but also creates a new concept of realizing atomically abrupt vertical heterostructures. Therefore, it is possible to fabricate in situ within the graphene/SiC interface, multilayers of Josephson junctions consisting of thin insulators of 2D GaN sandwiched between two superconductoring materials, all encasulated between graphene and SiC. The graphene encapsulated sample protects the synthesized heterostructure from degradation in air and therefore samples can be removed from the reactor for ex situ low temperature transport measurements and other materials characterization approaches. Also because the sample is
encapsulated, graphene can exert high pressures (in the GPa range) on the two-dimensional sandwiched crystal\(^7\). Therefore, not only can we study the effects of systematic doping in monolayer FeSe as well on MgB\(_2\), but also the effects of pressure that is exerted by the graphene on the critical temperature for superconductivity.

6.1.2 Expanding the concept of MEEG for the realization of wafer scale *in situ* 2D heterostructures for Valleytronics

The execution of quantum computing is, however, a challenging task. Beyond the issues associated with scaling, quantum computing requires precise control of qubits over long coherence times. As a result, the tuning schemes used for qubits in quantum circuitry is rather complex. Therefore, developing new schemes to create flexibility and reliability in the design of qubits is of great interest.

Electrons are novel information carriers. At the quantum level, the nature of the electron is governed by its charge and spin state. In addition, it endows a degree of freedom that specifies the valley in which it occupies within electronic bandstructure, i.e. the local energy extrema. Electronic devices that harness this valley degree of freedom are referred to as ‘valleytronics’, analogous to the role of the electron spin in the blooming field of ‘spintronics’. For a material to be characterized as an ideal valleytronic system, it must possess at least two degenerate valleys located at inequivalent vertices of the 2D hexagonal Brillion zone, more specifically, useful electronic valleys that can be manipulated to store, process and transfer quantum information. This idea of manipulating valley polarization gleans from crystalline systems like AlAs, bismuth and low-dimensional structures of silicon. By taking advantage of the valley degree of freedom in addition to charge and spin,
a new realm of dissipation-free electronics could be created which may potentially offer an alternative path in reducing power consumption while improving the design of qubits. This will ultimately circumvent challenges with decoherence in processing quantum information.

Most recently, the phenomenon of manipulating valley polarization has occupied the imagination of researchers, particularly upon the isolation and probing of 2D monolayers with a hexagonal honeycomb lattice, such as graphene and chalcogen-based layered crystals. As discussed in the previous section, one advantage of 2D materials is that their atomic thinness can be entirely modulated by an applied field. Unlike graphene, the broken inversion symmetry, for example in transition-metal dichalcogenides (TMDs), gives rise to valleys with opposite Berry curvatures. The predominant research efforts surrounding the valley hall effect in TMDs have been performed mostly on exfoliated materials that are less prone to degradation in air, leaving a host of 2D materials (that are not as stable) unexplored for valleytronics. In the case of graphene, though the structure is centrosymmetric, it is an appealing candidate for valleytronics due to the small intervalley scattering rate and large mean free path of the Dirac fermions. As a result, breaking inversion symmetry in graphene still remains a topic of research interest. Inversion symmetry can be broken in graphene by inducing a bandgap through external perturbation, such as in electrically gated bilayer graphene. This gives rise to a non-zero Berry curvature of opposite signs. In addition to applying an electric field, chemical functionalization and structural changes to the graphene lattice, modifying the dielectric environment may be a viable way to open a gap in graphene. Experimentally, the effect of the dielectric environment on inducing a gap in graphene, however, has been a subject of controversy,
particularly with commensurate and incommensurate graphene/hexagonal boron nitride heterostructures. However, theoretical calculations have shown, polar layered crystals, like phase change GeTe, can modulate a gap in graphene (~80 meV)\(^1\) as it transforms between the amorphous to crystalline phases. Furthermore in epitaxial graphene (EG) grown on Ir(111), a sizable bandgap (~420 meV)\(^2\) was reported upon intercalation of bismuth at the graphene/Ir interface. In other words, inversion symmetry in graphene can be broken as a result of changes to the dialectic environment and thus of interest for valleytronics. For practical use of the valley degree of freedom in devices, the nature and magnitude of this bandgap should be considered.

To fully explore 2D materials for potential consideration in valleytronic qubits, a platform to systematically synthesize and investigate layered materials and graphene heterostructures of interest must be established. Again, I believe that the interface of EG grown on a host of substrates is an excellent synthesis platform for 2D materials using the concept of MEEG that was developed in chapter 5. Furthermore, MEEG may also provide a scheme to potentially realize wafer scale synthesis of 2D materials confined at the interface, as well as atomically abrupt heterostructures with graphene. This then becomes an ideal platform to investigate the effect of the dielectric environment on inducing a bandgap in graphene and inversion symmetry breaking for the purpose of valleytronics.

To achieve uniform wafer scale realization of 2D heterostructures using graphene encapsulation, significant improvements in the intercalation efficiency of the MEEG growth scheme must be realized. Therefore for future work, I propose investigating the MEEG growth process using monolayer graphene formed from the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) graphene buffer layer and on transition-metal substrates, like Ir(111), Pt(111), Rh(111), Ni(111) in
order to also understand the influence of graphene domain orientation on the MEEG process. Furthermore, it would be worth adapting the intercalation process in other systems beyond MOCVD. For example, the use of a UHV system will allow for better control over the MEEG processes, since the substrate and the temperature to drive intercalation would be the predominant variables in the process. In the case of intercalation of the graphene buffer on SiC, the appearance of the doublet in the C 1s core level peak in XPS after intercalation will be a direct measure if a metal/transition-metal can intercalate graphene and the shift in the Fermi level from valance band measurements gives insight into the amount and uniformity of the intercalated layers. Other methods, such as Angle-resolved photoemission spectroscopy and/or Momentum-Resolved EELS measurements, may need to be coupled in future experiments in order to investigate the effect of the dielectric environment on the bandstructure of graphene.
6.2 References

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