The present research was undertaken with the goals of understanding the evolution of defects and strain in heteroepitaxial AlN and GaN films deposited via metalorganic vapor phase epitaxy and minimizing those defects through manipulation of the substrate. As observed with atomic force microscopy (AFM), AlN initially grew in the form of flat-topped islands on as-received SiC substrates. Threading dislocations (TDs) observed in transmission electron microscopy (TEM) images initiated at the AlN/SiC interface as the result of defects at the surface of the mechanically polished substrate and/or condensation of point defects. GaN initially grew in the Stranski-Krastanov mode on AlN/SiC before transitioning to the dislocation-mediated step flow mode. The TDs in GaN resulted from the propagation of the TDs present in the AlN layer. The biaxial strain in the GaN layers varied with buffer layer material and layer thickness yet all samples investigated remained in residual compression due to incomplete relaxation of the coherent strain. The presence of strain during the initial growth of Al\textsubscript{x}Ga\textsubscript{1-x}N layers directly on as-received SiC also resulted in phase-separated regions of Al-rich and Al-poor film. A high temperature hydrogen etch was then used to remove mechanical polishing scratches from the SiC substrates. Subsequently deposited AlN layers featured reduced pit density and the elimination of scratch-induced undulations. GaN layers deposited with AlN buffer layers on these substrates resulted in slightly reduced TD densities as observed by AFM, TEM, and high resolution X-ray diffraction (HRXRD). Regions of dramatically reduced dislocation densities were observed by HRXRD, TEM, and
cathodoluminescence for GaN layers on stripe-patterned Si substrates. However, long growth times resulted in outdiffusion of Si from the substrate and subsequent film roughening. Finally, it was demonstrated that the presence of ammonia during heating of GaN templates to the growth temperature for homoepitaxy resulted in removal of carbon- and oxygen-based contaminants from the template surface.
THE CHEMISTRY AND SURFACE MICROSTRUCTURE OF Si-BASED SUBSTRATES
AND THEIR EFFECT ON THE EVOLUTION OF THE MICROSTRUCTURES OF III-
NITRIDE FILMS GROWN VIA METALORGANIC VAPOR PHASE EPITAXY

by
Zachary J. Reitmeier

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North Carolina State University
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In
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2005

Approved by:

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Dr. Robert F. Davis                          Dr. Zlatko Sitar
Chair of Advisory Committee

__________________________________________  __________________________________________
Dr. Mark Johnson                            Dr. John Muth
DEDICATION

For Lisa

At times our own light goes out and is rekindled by a spark
from another person. Each of us has cause to think with deep
gratitude of those who have lighted the flame within us.

--Albert Schweitzer
BIOGRAPHY

Zachary Justin Reitmeier was born November 4, 1978 in Buffalo, NY to Skip and Ellin Reitmeier. Along with his sister Kati and brother Kyle, he grew up in East Aurora and Wales, NY. He graduated valedictorian from Iroquois Central High School in Elma, NY in 1996 and enrolled at Clemson University in Clemson, SC. It was there that he met his future wife Lisa Jacobson. Zach graduated from Clemson in May 2000 with a B.S. in Ceramic Engineering and married Lisa on July 29, 2000. After returning from their honeymoon, Zach and Lisa settled in Raleigh, NC where Zach began his graduate career in the Department of Materials Science and Engineering under the direction of Dr. Robert Davis. On July 24, 2004, Zach and Lisa were blessed with the birth of their first child Ella Caroline.
ACKNOWLEDGMENTS

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On the personal side, I would first like to thank my parents, Skip and Ellin, for their constant support and encouragement throughout my life and for instilling in me a sense of hard work and a belief in the importance of education. If I am half the parent that they are, I will consider myself a success.

Finally, and most importantly, I would like to thank my wife Lisa for everything that she has done and continues to do for me. From dealing with a husband that was frequently
absent, either physically or mentally, to hearing yet another story about a broken vacuum system, she never wavered in her support, encouragement, and understanding. To say that this work would not have been possible without her is an understatement. Thanks Lisa for providing me with the motivation to get through and the assistance to make it happen.
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Figure 16  (a) Cross sectional bright field transmission electron microscopy image of GaN grown by cantilever epitaxy on Si substrates and aligned to the [\bar{1}12] zone axis of Si. The black arrows indicate a carbon-based filler material employed during sample preparation. (b) A magnified TEM image of a GaN wing, where the black arrows indicate dislocations on the GaN basal plane and the white arrow indicates the edge of the AlN buffer layer from which the GaN has grown laterally. (c) Selected area diffraction pattern from the GaN/AlN/Si interface.
Figure 17  Deposition of GaN/AlN on the sidewall of an etched Si substrate.  (a) A cross sectional bright field TEM image along the Si [112] zone axis with arrows indicating planar defects believed to correspond to stacking faults.  (b) Selected area diffraction pattern from the GaN on the sidewall superimposed over the Si pattern.  (c) SEM image of the sidewall shown in cross section in (a).  (d and e) SEM images of the sidewall 100 nm of AlN and 200 nm of GaN deposition respectively.  (f) Schematic of the growth process occurring on the sidewall.

Figure 18  (a) Plan-view SEM image of two Si stripes, one of which features a roughened surface.  (b) Profile view SEM image showing the presence of a void in the Si substrate beneath an area featuring the rough surface.  (c) EDS spectrum acquired from the region in (a).  (d and e) EDS maps of the Ga Lα1 and Si Kα signals as acquired from the region shown in (a).

Figure 19  (a and b) STEM images of GaN layers featuring smooth and rough surfaces respectively.  The inset of (b) is a selected area diffraction pattern observed from the deposit on top of the Si stripe.  (c and d) EDS spectra acquired from the GaN layer in (a) and regions “A” and “B” in (b) respectively.  (f-h) EDS maps of the Ga Lα, Si Kα, and N Kα signals acquired from the region shown in the STEM image (e).

Figure 20  (a-c) SEM images of a cracked GaN film on a planar Si substrate, a subsequently annealed cracked GaN film, and a GaN layer re-grown on a cracked GaN template respectively.  The arrows in (a) indicate the ends of cracks traversing the GaN surface.  (d) Profile view SEM image of the sample in (c) showing voids in the Si substrate beneath the cracks.  (e) XPS spectra acquired from the layers shown in (a-c).

Figure 21  (a-d) Schematic showing the process by which Si diffuses from the substrate to the GaN surface resulting in the formation of Si,N_y and subsequent GaN overgrowth.  (e) 1x1 µm AFM height image of GaN deposited over a Si stripe.  The white islands occur at the termination of heterogeneous steps and are believed to correspond to the early stages of Si,N_y formation on the surface.  (f) SEM image showing GaN overgrowing the Si,N_y on the surface.

Figure 22  The percentage of the cantilever GaN surface degraded due to Si,N_y formation as a function of GaN growth time for three different AlN buffer layer thicknesses.  The lines are guides to the eye.

Figure 23  Plan view SEM images of two cantilever GaN samples near coalescence.  The “s” denotes the regions of deposition over the Si stripe and the broken lines indicate the boundary between the GaN over the stripe and the laterally grown GaN wings.
Figure 24  a) Plan-view SEM micrograph of CE-GaN template.  b) SEM micrograph showing the surface and cross-section of a GaN layer grown by IVPG which spontaneously separated from the Si substrate during cooling. The original substrate was located toward the bottom of the layer as it is oriented in (b).  c) Magnified view of the former interface between GaN/AlN and Si showing that the Si stripes have completely diffused into the growing film, leaving surface voids in their former location.

Chapter 7

Figure 1  SIMS depth profiles of H, C, and O acquired from [0001]-oriented GaN-film/GaN-template heterostructures in which the template was heated to 1020°C in a mixture of either (a) nitrogen and hydrogen or (b) ammonia and hydrogen prior to the homoepitaxial growth of the films having a nominal thickness of 0.22 µm.

Figure 2  AFM images acquired using 5 x 5 µm scans of the (0001) surface of a GaN template (a) before and (b) after being heated, annealed for 5 minutes and cooled in an ammonia/hydrogen atmosphere. The Z range is 4 nm in each case.

Figure 3  AFM images acquired using 5 x 5 µm scans of the (0001) surfaces of homoepitaxial GaN films deposited on GaN templates previously heated to 1020°C in (a) nitrogen and hydrogen and (b) ammonia and hydrogen. The Z range is 5 nm in each case.

Figure 4  SEM images showing both the surface and cross section of GaN templates subjected to the following heat treatments: (a) heating in nitrogen/hydrogen to 1020°C and cooling in ammonia/hydrogen, (b) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, (c) heating in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen, (d) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in nitrogen/hydrogen. The hexagonal pits are the result of GaN decomposition. Note the Ga droplets within pits shown in (d).

Figure 5  5x5 µm AFM scans of GaN templates after (a) heating in nitrogen/hydrogen to 1020°C and cooling in ammonia/hydrogen, (b) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, (c) heating in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen, (d) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in nitrogen/hydrogen. The Z ranges are 15, 15, 30, and 100 nm for the respective images. (a) and (b) show a thin GaN-containing layer formed via reaction of liquid Ga with ammonia. (c) and (d) show a decomposed roughened GaN surface.
Figure 6 5x5 μm AFM scans of GaN templates exposed to 30% HNO$_3$ for 10 minutes following (a) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, and (b) in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen. The Z ranges are 15 and 30 nm respectively. (a) reveals the roughened GaN surface after removal of the thin GaN-containing layer observed in figure 5 (b). (b) shows that the roughened surface formed upon heating in the absence of ammonia is unaffected by exposure to HNO$_3$.

Appendix 1

Figure 1 2x2 μm AFM height images of 100 nm AlN films deposited on Si(111) previously exposed to Al pre-flows of 0 (a), 10 (b), 20 (c) and 30 seconds (d). Respective RMS roughness values are 3.6, 1.0, 4.9 and 3.4 nm.

Figure 2 500x500 nm AFM surface plots of 30 seconds AlN deposition on Si(111) previously exposed to Al pre-flows of 0 (a) and 10 seconds (b).

Figure 3 5x5 μm AFM height images of 0.5 μm GaN films deposited on 100 nm AlN buffer layers previously initiated with 0 (a), 10 (b), 20 (c) and 30 second (d) Al pre-flows.

Figure 4 RMS roughness of GaN films from Figure 3 vs. Al pre-flow time. Dashed line is a guide to the eye.

Figure 5 XRD rocking curve FWHM for three GaN reflections vs. Al pre-flow time. Dashed lines are a guide to the eye. Error bars represent plus and minus one standard deviation from the mean.

Figure 6 FWHM of GaN HRXRD rocking curves for three inclination angles for the cases of no Al pre-flow and 10 second Al pre-flow. Dashed lines are a guide to the eye.
1. Introduction
Gallium nitride (GaN), in conjunction with the alloys it forms with aluminum nitride (AlN) and indium nitride (InN), is a semiconductor of considerable interest for optoelectronic and electronic devices. The theoretical ability to tailor the direct bandgaps of this alloy system from 0.8-6.2 eV makes it suitable for light emission and detection applications ranging from the red to the deep ultra-violet (UV) regions of the electromagnetic spectrum. Light emitting diodes (LEDs) based on III-Nitride materials emitting from green to UV have been commercialized over the last decade [1]. The visible LEDs are well suited to indicator applications such as automotive lights and traffic signals as well as in the development of full color displays. UV LEDs are finding commercial and theoretical applications in bio-agent detection, air and water purification, and medical treatment and diagnosis. The excitation of phosphors to produce white light represents a potentially lucrative market for UV LEDs since illumination accounts for approximately twenty percent of the world’s electricity consumption [1]. Current white LEDs are twice as efficient as incandescent bulbs yet emitters in laboratories have demonstrated a tenfold increase in efficiency [1]. The wide bandgap energies of the III-Nitrides also make them suitable for laser diodes and optical detectors operating at short wavelengths. The former will enable increased optical data storage compared to the current Al$_x$In$_y$Ga$_{1-x-y}$P devices and also serve in medical applications while the latter can function as solar blind detectors for combustion monitoring, fire and missile launch detection.
In addition to optical applications, the large dielectric breakdown field, high electron saturation velocity, and good thermal conductivity of GaN, as well as its alloys, make it an attractive materials system for high-power, high-temperature, and high-frequency electronic devices. These devices are expected to serve as amplifiers in radar, missile and satellite systems as well as in wireless base stations, automotive and avionic applications.

Despite the realized and potential applications for GaN, full exploitation of this material has been hindered by the lack of mono-crystalline GaN wafers to serve as homoepitaxial substrates for the growth of films and device structures. Instead, researchers have been forced to deposit GaN heteroepitaxially on substrates such as sapphire ($\alpha$-Al$_2$O$_3$), silicon carbide (SiC) and silicon (Si). Although devices have been commercialized on Al$_2$O$_3$ and SiC and are nearing commercialization on Si, the mismatches in lattice parameter and coefficient of thermal expansion between the film and substrate generate threading dislocations (TDs) with densities approaching $10^{10}$ cm$^{-2}$. Combined cathodoluminescence (CL) and atomic force microscopy (AFM) studies [2,3] have shown that TDs act as non-radiative recombination centers in GaN. Sugahara et al. [4] provided further evidence of the non-radiative nature of TDs by observing a one-to-one correspondence between TDs in transmission electron microscopy (TEM) and dark spots in CL.

Electronic structure calculations of TDs in GaN have shown that they are also likely to cause deep levels and shallow states in the forbidden bandgap [5,6,7]. Leung et al. [8] showed that the semi-insulating behavior of high-TD density GaN can be attributed to the absence of free carriers due to trapping by these levels but for high dopant densities and/or low TD densities, the TDs are fully charged and excess free carriers remain. Look and Sizelove [9] and Hansen et al. [10] provided experimental evidence that TDs act as charged
scattering centers in doped material through the use of transverse mobility measurements and scanning capacitance microscopy respectively. The concept of carrier scattering by charged dislocation lines is a well known phenomenon in semiconductor physics and results in degraded performance of electronic devices.

A growing body of evidence also shows that TDs provide a leakage current pathway and shorten the lifetime of laser diodes. Heterojunction bipolar transistors [11], p-n junctions [12], and LEDs [13] demonstrate leakage current reductions of ~3-4 orders of magnitude when the TD density in the III-Nitride layers is reduced. However, high TD densities are especially detrimental to the performance of more complex and demanding structures such as laser diodes operating at high power densities [14], as evidenced by the dramatically increased lifetime for these devices when deposited on low dislocation density templates [15].

In light of the multitude of deleterious effects of TDs, the current research was undertaken with the goals of:

1) understanding the evolution of the surface and defect microstructures and strain in GaN during metalorganic vapor phase epitaxy (MOVPE) growth with various buffer layers on various substrates

2) exploring a simplified technique of lateral overgrowth for reducing the dislocation density of GaN on Si substrates

3) employing lateral overgrowth in conjunction with the deposition of thick layers by hydride vapor phase epitaxy (HVPE) to achieve freestanding pseudo-bulk GaN substrates

4) developing a in-situ cleaning procedure for GaN surfaces in an MOVPE environment.
In chapter 2, the growth modes and the microstructures of the surfaces and the defects generated during the initial and subsequent stages of MOVPE growth of AlN(0001) films on 6H-SiC(0001) substrates and GaN(0001) films on AlN/SiC(0001) substrates are investigated using atomic force microscopy and cross-sectional and plan-view transmission electron microscopy. SiC represents an attractive alternative substrate to sapphire due to its easier cleavage along [1̅1̅2̅0] and higher thermal conductivity (4.9 W/cm K [16] vs. 0.23 W/cm K [17] for sapphire). The greater value of the latter property is believed to contribute to the improved performance of ultraviolet light emitting diodes [18] and heterojunction field effect transistors [19,20] fabricated in III-Nitride material structures grown on SiC substrates compared to that of similar devices fabricated on sapphire substrates.

Chapter three builds upon the above research by also examining the surface microstructure of Al$_{15}$Ga$_{85}$N buffer layers and subsequently deposited GaN films on 6H-SiC substrates. In addition, the evolution of the strain in the GaN as a function of layer thickness and buffer layer type (i.e. AlN vs. Al$_{15}$Ga$_{85}$N) is investigated via high resolution X-ray diffraction. Although the mismatch in the coefficients of thermal expansion between GaN and SiC would predict the residual strain to be tensile in nature, the results show that films can be compressively strained due to a long-range relaxation of the coherent stain between GaN and the buffer layer. The microstructure and phase separation of Al$_{15}$Ga$_{85}$N layers on 6H-SiC substrates is explored in greater detail via TEM, AFM, energy dispersive X-ray spectroscopy (EDS), and finite element analysis in chapter 4.

Despite the apparent benefits of SiC substrates, namely reduced lattice parameter and thermal expansion mismatches, GaN films deposited thereon have yet to demonstrate less defective microstructures than films of comparable thickness on sapphire. One reason
proposed for this discrepancy is the damaged surface of as-received SiC wafers as a result of slicing from the boule, lapping and polishing. Therefore, in chapter 5, AlN films and GaN films with AlN buffer layers were deposited on 6H-SiC substrates previously etched in flowing hydrogen at high temperature. This process results in the complete removal of mechanical polishing scratches and leaves unit-cell-height steps on the SiC surface. The surface and defect microstructures of the subsequently deposited layers were investigated using AFM, HRXRD, and plan-view and cross-sectional TEM.

In an effort to reduce the TD density in GaN films, various techniques of lateral overgrowth have been developed which make use of the anisotropy in growth rates of GaN along different crystallographic directions. These techniques include epitaxial lateral overgrowth [21], pendeo-epitaxy [22], and cantilever epitaxy [23]. The research described in chapter 6 investigates cantilever epitaxy on Si substrates due to the ease of processing the latter material and the ease with which it can be removed from the backside of a thick layer by wet etching. The primary goal of the research was to use GaN layers deposited via the cantilever epitaxy technique as templates for thick GaN layers grown by HVPE. In that aim, an analytical mechanics model was developed to predict the stress and strain which developed in the Si stripes as the structures were cooled from the growth temperature. This model was supported by a finite element simulation. The GaN template layers were extensively characterized by scanning electron microscopy, AFM, HRXRD, TEM, EDS, scanning transmission electron microscopy and X-ray photoelectron spectroscopy.

Finally, in chapter 7, a process route previously developed by Tracy et al. [24] for the cleaning of GaN surfaces in a molecular beam epitaxy chamber in flowing ammonia is extended to the higher pressure regime of MOVPE. The surfaces of GaN films and GaN
wafers, the latter derived via laser lift-off [25] or the cantilever epitaxy technique developed in chapter 6, exposed to the ambient acquire a contamination layer containing carbon and oxygen [26,27]. These impurities have a deleterious effect on the properties of films [28] and of metal contacts [29,30] subsequently deposited on the contaminated surface. Secondary ion mass spectroscopy is used to quantitatively analyze the contamination present at a buried interface and SEM and AFM are used to verify the preservation of the GaN surface during the cleaning procedure and assess the effect of different heating ambients on the microstructure of the homoepitaxial film.
1.1 REFERENCES


2. **Surface and defect microstructure of GaN and AlN on 6H-SiC(0001) substrates**

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2.1 ABSTRACT

The growth modes and the microstructures of the surfaces and the defects generated during the initial and subsequent stages of growth via metalorganic vapor phase epitaxy of AlN(0001) films on 6H-SiC(0001) substrates and GaN(0001) films on AlN/SiC(0001) substrates were investigated using atomic force microscopy and cross-sectional and plan-view transmission electron microscopy. Partially coalesced islands of AlN were present after nominally ~15 nm of growth. Increasing the thickness to 100 nm resulted in complete island coalescence and the formation of undulating films as a result of the polishing scratches in the SiC substrate and a surface microstructure containing steps, terraces and small pits. The AlN/SiC interfaces showed steps delineated by misfit dislocations and a complex misfit dislocations network. The 100 nm AlN layers exhibited reduced dislocation density as compared to the 15 nm layers. GaN initially grew in the Stranksi-Krastanov growth mode on 100 nm thick AlN buffer layers with islands forming preferentially within the undulations of the AlN. Complete coalescence of these islands occurred at thicknesses less than 100 nm, and the subsequently deposited film grew via dislocation-mediated step-flow. Threading dislocations TDs in AlN were replicated into GaN overgrowths. The density of TDs in GaN is reduced by increasing the thickness of either the AlN buffer layer or the GaN layer itself.
2.2 INTRODUCTION

The lack of readily available monocrystalline GaN boules from which wafers can be obtained has necessitated the growth of GaN films and device material structures on substrates such as sapphire (α-Al2O3) and silicon carbide (SiC). The mismatches in lattice parameters and coefficients of thermal expansion between a GaN film and either of these substrates result in high densities (~10⁸-10¹⁰ cm⁻²) of misfit and threading dislocations (MDs and TDs). The latter introduce intergap states that serve as non-radiative recombination centers, act as charged scattering centers, and provide leakage current pathways [1]. It is therefore important to determine the origins and the evolution of these defects to more effectively control their type, density and distribution within the heteroepitaxial III-Nitride films. A large body of literature exists that addresses these topics for dislocations in III-nitride thin films deposited on the (0001) surface of sapphire substrates (see, e.g. refs. 2, 3 and the references therein). Three types of TDs have been reported: pure edge (a type: \( \mathbf{b} = 1/3 \langle 11\bar{2}0 \rangle \)), pure screw (c type: \( \mathbf{b} = [0001] \)) and mixed (c+a type: \( \mathbf{b} = 1/3 \langle 11\bar{2}3 \rangle \)). Two mechanisms have been proposed to explain the generation of these TDs. Ning, et al. [4] and Wu, et al. [5] have claimed that the TDs formed as a result of local tilt and twist at the boundaries between coalescing GaN islands. However, these investigators were unable to demonstrate visual evidence of this phenomenon. More recently, Narayanan and coworkers [6,7] have demonstrated two alternative sources of TD generation: planar defects in the low-temperature GaN nucleation layer and point defects incorporated during growth. The stacking faults in the nucleation layers were shown to be the major source of defects. These faults developed into TDs via self-glide and climb.
SiC represents an attractive alternative substrate to sapphire due to its easier cleavage along [11̅20] and higher thermal conductivity (4.9 W/cm K [8] vs. 0.23 W/cm K [9] for sapphire). The greater value of the latter property is believed to contribute to the improved performance of ultraviolet light emitting diodes [10] and heterojunction field effect transistors [11,12] fabricated in III-Nitride material structures grown on SiC substrates compared to that of the same devices fabricated on sapphire substrates. Deposition of GaN directly on SiC(0001) substrates has been accomplished via plasma-assisted molecular beam epitaxy (MBE) [13,14] and metalorganic vapor phase epitaxy (MOVPE) [15,16]. However, these films typically suffer from rough surfaces, higher TD density and/or biaxial tensile strain, which may result in cracking of the films even for relatively small thicknesses. This tensile strain has been attributed to the mismatch in thermal expansion coefficients between GaN and SiC [17] and has a magnitude of -0.1% in GaN films grown at 1000°C [18].

Alternatively, the microstructural and electronic properties of GaN films deposited on SiC have been improved by inserting a high-temperature (≈1100°C) AlN buffer layer prior to GaN deposition [19,20]. This practice facilitates the nucleation of the subsequently deposited GaN film, allowing fully coalesced films at smaller thicknesses. The lattice mismatch between AlN and GaN (+2.5%) results in films of the latter material whose volume is compressively strained when deposited on SiC substrates, despite the counteracting volume tensile strain generated by the differences in the coefficients of thermal expansion [17]. Thus, the tendency for crack formation within the heterostructures is reduced. This residual compression results from a long-range two-step relaxation of the coherent strain as the film thickness increases [21]. AlN buffer layers have also been shown to improve the
performance of high electron mobility transistors by inhibiting parasitic substrate conduction [22].

The transmission electron microscopy (TEM) investigations of Tanaka [23] and Torres [24] of AlN(0001) thin film/SiC(0001) substrate heterostructures revealed TDs having densities of $10^{11}$-$10^{12}$ cm$^{-2}$ and composed predominantly of a type dislocations. Numerous investigators (see, e.g., refs. 25 and 26) have also reported high TD densities in GaN/AlN/SiC assemblies. However, these studies have usually presented results for one thickness of GaN film deposited on one thickness of the AlN buffer layer. In contrast to the GaN/sapphire heterostructures, those composed of GaN/AlN/SiC and AlN/SiC have not been extensively studied in terms of growth modes and evolving defect microstructures. In the present research the surface and defect microstructures of the initial and subsequent stages of growth of AlN on 6H-SiC(0001) and GaN on AlN/SiC heterostructures have been determined and correlated.

2.3 EXPERIMENTAL PROCEDURE

The AlN was grown via MOVPE at 1100°C and 20 Torr total pressure on the Si-face of conventionally-polished, on-axis 6H-SiC(0001) wafers, which had been etched in a HF:H$_2$O (1:10) solution for ten minutes at room temperature to remove the native oxide and blown dry with nitrogen. The GaN was grown at the same total pressure on 100 nm thick AlN buffer layers after cooling to 1020°C over a period of five minutes. The MOVPE reactor was a cold-walled vertical pancake-style system, which was evacuated to $10^{-6}$ Torr prior to growth. The temperature of the SiC-coated graphite susceptor was measured using a single wavelength optical pyrometer. Trimethylaluminum (TMA), triethylgallium, (TEG) and ammonia were used as the precursors; hydrogen was used as both the carrier and the
diluent. The V/III ratios of 24,400 and 1,300 were employed for the growth of the AlN layers and for GaN layers thicker than 2 nm; the corresponding growth rates were 0.3 µm/hr and 1.8 µm/hr, respectively. The TEG/ammonia ratio was increased to 10,600 by decreasing the flow of the TEG to investigate the initial nucleation and growth of GaN on the AlN to a maximum thickness of 2 nm. This change reduced the growth rate of the GaN to 0.22 µm/hr. Atomic force microscopy (AFM) and high resolution X-ray diffraction (HRXRD) investigations of GaN layers of the same thickness but deposited using two different growth conditions did not reveal significant differences. All film thicknesses quoted are nominal values based on these established growth rates.

The surface microstructure of the heteroepitaxial films were determined using a Digital Instruments D3000 AFM equipped with a Si cantilever and tip operating in the tapping mode. Cross-sectional samples for transmission electron microscopy (TEM) were prepared using the standard ‘sandwich’ technique followed by dimpling and ion milling until electron transparency. Plan-view samples were prepared by cutting 3 mm discs from SiC substrates. These discs were then ground, dimpled and ion milled from the SiC side to obtain electron transparency. Structural analyses of the epitaxial layers were performed in cross-section and in plan view using a JEM-4000EX microscope operating at 400 kV that has an interpretable resolution of 0.16 nm.
2.4 RESULTS AND DISCUSSION

2.4.1 SURFACE MICROSTRUCTURES AND GROWTH MODES OF AlN ON SiC SUBSTRATES

Representative micrographs of the surfaces of the polished 6H-SiC(0001) substrates and the AlN(0001) films with thicknesses of 15 and 100 nm grown in this research are shown in the AFM images in Fig. 1. The 10x10 µm images reveal the influence of the roughness of the substrate shown in Fig. 1 (a) on that of the AlN films shown in Figs. 1 (b) and (c). The 2x2 µm images reveal the details of the microstructures of the substrate surface (Fig. 1 (d)) and the AlN layers (Figs. 1 (e) and (f)). Standard mechanical polishing of the surfaces of this hard, inert and difficult to polish material [27] normally produces numerous randomly oriented scratches with widths from 100-800 nm and depths to 12 nm, as shown in Figures 1(a) and (d). Our AFM studies did not reveal steps on the surfaces of the as-received SiC substrates; however, scanning tunneling microscopy studies by Owman et al. [28] have revealed steps with random heights and orientations.

The 15 nm thick AlN layer nucleated both within and between the scratches of the SiC substrate, as shown in Figs. 1 (b) and (e). The scratches remain evident in both images. The depression running from the upper left to the lower right in Fig. 1(e) is a polishing scratch into which AlN islands have grown. The islands appear homogeneously distributed across the surface, indicating that preferential nucleation within the scratches or between the scratches did not occur. At this nominal thickness, the AlN film is partially coalesced and composed of islands with random shape and orientation, i.e. the sides of the islands do not appear to coincide with any specific crystallographic facet. Observations of single scan lines suggested that the islands have flat tops. However, these islands are somewhat difficult to
image, since the 10 nm radius of the AFM tips is comparable to the lateral size of the islands. AlN(0001) deposited on 6H-SiC(0001) by MBE grows in the Stranski-Krastanov (S-K) mode [29] in which a pseudomorphic wetting layer having a thickness of several monolayers is followed by strain-induced island growth. This growth mode was not observed in our AFM studies, since the roughness of the SiC substrate made the observation of AlN layers difficult when growth times shorter than that used to grow the 15 nm samples were investigated. The polishing scratches in the substrate remained manifest in the film even after 100 nm of AlN growth, as clearly shown in Fig. 1(c). Straight undulations in AlN have also been observed by Smart [30], Nishida [31], and Einfeldt [21] and attributed to scratches in the substrate. One of these scratch-induced undulations in the AlN film is clearly observed running from lower left to upper right in Fig. 1(f). In contrast to the islands observed for the 15 nm layer and in addition to the undulations, the 100 nm film also exhibits terraces separated by bi-layer high steps and pits, the latter as a result of incomplete coalescence at this stage of growth.

2.4.2 DEFECT MICROSTRUCTURE OF AlN ON SiC SUBSTRATES

A (1̅1̅00) cross-sectional TEM image of a 15 nm AlN film deposited on a mechanically polished SiC substrate is shown in Fig. 2; the operating reflection is (0002). The AlN islands have coalesced to form a flat surface, a result consistent with our AFM studies. The dark bands in the layer and the substrate imply that the composite structure may not be fully relaxed while the dark regions at the AlN/SiC interface suggest the presence of a defective structure in this region. Imaging the layer using other reflections proved difficult since the defect density was so high that individual dislocations were difficult to discern.
Combining these results with those of Fig. 2, we can infer that the most likely Burgers vectors of dislocations in the AlN layer are $1/3 <11\bar{2}0>$ and may be $1/3 <11\bar{2}3>$.  

Figure 3 shows a plan-view, weak-beam, dark-field (WBDF) image of a 15 nm AlN/SiC composite. Steps separated by 250-300 nm and delineated by dislocations are observed. The majority of the steps are aligned close to a $<\bar{1}100>$ direction. The terraces between steps are defined by a very dense network of jagged dislocations whose orientations are not well defined. Results on 100 nm AlN layers deposited on SiC were qualitatively similar to the preceding results. The major difference was a lower density of dislocations in the thicker layer.

Results on dislocation-delineated steps and jagged misfit dislocation networks in Fig. 3 are very interesting. They can be rationalized by referring to the schematic shown in Fig. 4. Ideally, a relaxed (0001) AlN/SiC interface should consist of a hexagonal network of three perfect edge $a$ type dislocations because the misfit is accommodated most efficiently in this manner. This situation is shown schematically in Fig. 4(a), where we depict a portion of the hexagonal misfit dislocation network on a terrace that is bounded by two steps. When we extend this situation to two terraces, as shown in Fig. 4 (b), it is easy to see the alignment of misfit dislocations along the step edges.

The jagged structure of misfit dislocations in Fig. 3 could be due to the fact that the AlN/SiC interface is rough. This could be caused by the non-planarity of as-polished SiC surfaces. An additional complication could arise from the projection of the defective structure in the AlN layer on the plane of the observation.
2.4.3 SURFACE MICROSTRUCTURES AND GROWTH MODES OF GaN ON AlN/SiC SUBSTRATES

The surfaces of the GaN(0001) films having thickness values from 1-4000 nm and grown on the 100 nm AlN(0001) buffer layers are shown in the AFM height images of Fig. 5. A comparison of the surface of the nominally 1 nm thick GaN film shown in Fig. 5 (a) with that of the bare AlN buffer layer shown in Fig. 1 (f) reveals steps and terraces on an undulating surface in both cases. Three dimensional nucleation of GaN was not observed. There are two possible explanations for this observation. First, there could be a reduced growth rate during the initial nucleation compared to the steady-state growth rate, as has been observed in similar MBE studies [32]. Therefore, the surface shown in Fig. 5 (a) would be that of the AlN buffer layer. The microstructure of this surface may also be explained by the pseudomorphic growth of a very thin GaN layer. Close inspection of the two figures reveals that the step edges in Fig. 5 (a) are smoother and more regular than those of the AlN buffer layer. It has been determined [33,34,35] that GaN deposited via MBE at sufficiently elevated temperatures grows in the S-K mode in a manner similar to that of the growth of AlN on SiC (see above). The thickness of the pseudomorphic wetting layer in the GaN film is reported to be between 1-5 bilayers [33,34,35]. It is therefore reasonable to assume that the S-K mode will also pertain for the initial growth of GaN via MOVPE. We therefore believe the surface shown in Fig. 5 (a) is that of the initial two-dimensional layer of GaN growing in the S-K mode; hence the observed change in the step and terrace structure of the surface as compared to that of the bare AlN buffer layer.

The strain induced two dimensional-to-three dimensional transition in the S-K growth mode is observed to occur between 1.0 and 1.5 nm, as evidenced by the appearance of the
GaN islands denoted by arrows in Fig. 5 (b). The majority of the islands observed occurred in a straight line corresponding to one of the scratch-induced undulations in the AlN surface. Fig. 4(c) shows a line of GaN islands which have formed on the lower left as well as a few small islands which appear to have formed at step edges (see arrows). The larger scale image of the 2 nm GaN layer shown in Fig. 6(a) supports the postulate drawn from the observations in the smaller scale image that the most prevalent GaN nucleation occurs within the undulations in the AlN which mimic the linear morphologies of the scratches in the SiC. Nishida [31] and Koleske [36] have also observed GaN nucleation in the form of aligned islands when deposited on AlN/SiC substrates. Even with a carefully optimized process, mechanically polished 6H-SiC(0001) wafers possess a damaged region extending 8 nm beneath the surface [37]. Studies of the homoepitaxial growth of SiC on mechanically polished SiC(0001) substrates have shown locally higher densities of edge and screw TDs in the areas of the film directly over a polishing scratch [38,39]. Therefore, it is reasonable to assume that AlN films deposited on SiC substrates will also contain locally higher TD densities in these highly damaged regions of the substrate. GaN preferentially nucleates in these areas, since clusters of extended defects in the AlN buffer layer have been shown to serve as sites for the initial nucleation of GaN [40,41].

The GaN islands of the 5 nm deposit are irregular in shape in a manner similar to that of the AlN islands grown on SiC, and the sides of the former do not appear to correspond to any particular crystallographic facets. Observations of single scan lines such as that shown in the inset of Fig. 5 (d) reveal that the tops of the GaN islands are essentially atomically smooth. The flat-topped islands grow laterally, as shown by the progression from Figs. 5 (c)-(f) and from Figs. 6 (a) and (b), and coalesce. Between the thickness of 50 nm and 100 nm,
the growth mode of the GaN changes from the thermodynamically-controlled S-K mode to the kinetically controlled and commonly observed dislocation-mediated step-flow growth mode [42], as evidenced by the roughly parallel array of terraces and steps observed in Fig. 5 (g). The surface microstructure of the 1 µm GaN film shown in Figs. 5 (h) and 6 (c) and the 4 µm GaN film in Fig. 5 (i) contain terraces and bilayer high steps. The arrows in Fig. 5(h) and (i) denote step terminations that are the ends of TDs having screw or mixed character [42]. From averaging over several AFM images, the density of step terminations for the respective films is $1 \times 10^9$ cm$^{-2}$ and $5 \times 10^7$ cm$^{-2}$, respectively, indicative of the previously reported reduction in TD density via dislocation annihilation mechanisms as the film thickness increases [43].

2.4.4 DEFECT MICROSTRUCTURE OF GaN ON AlN/SiC SUBSTRATES

Figure 7 (a) depicts a WBDF image of a cross-section obtained from a 1000 nm GaN/15 nm AlN/SiC composite. A highly defective region is observed at the AlN/SiC interface. The thickness of this region is 100 nm; thus it extends well beyond the AlN layer. However, individual dislocations are not easily discernible in the defective area. A large number of dislocations come together to form closed loops in the GaN layer near the GaN/AlN interface. The TDs appear uniformly distributed across the GaN layer but decrease in density in the direction of film growth. From plan-view TEM the TD density was determined to be $4.5 \times 10^9$ cm$^{-2}$.

Figure 7(b) shows an enlargement of a region delineated by an arrow in Fig. 7(a). It is clear that the highly dislocated area contains a high density of very small dislocation loops and dislocation clusters that are difficult to resolve even at a high magnification.
Furthermore, almost all TDs in the GaN layer appear to originate from the defective region described above.

Figure 7(c) shows an area close to the one shown in Fig. 7 (a), but the operating reflection is (0002) instead of (1120). Comparing dislocation distributions in Figs. 7 (a) and (c), it is clear that the majority of TDs are a type and that only a few c and c+a dislocations are present. In addition, the observed contrast within the AlN layer indicates that it may also contain some c and c+a dislocations.

The increase in thicknesses of AlN and GaN to 100 and 2000 nm respectively reduced the density of TDs in the GaN layer. Figures 8 (a) and (b) show cross-sectional images of a 2000nm GaN/100 nm AlN/SiC sample for two different operating reflections, (11-20) and (0002) respectively. Again there is almost one-to-one correlation between the TDs in GaN and AlN layers and from comparison of Figs. 8(a) and (b) it is clear that the majority of the dislocations are a type, but a few c and c+a dislocations are also present. A typical plan-view TEM image of this GaN layer is shown in Fig. 9. Only a and c+a dislocations are visible in this micrograph. Furthermore, the TDs appear to form a cellular structure, and their density is estimated to be 1.5x10^9 cm^-2.

Cross-sectional and plan-view TEM images (not shown) were also obtained for 4000 nm GaN/100nm AlN/SiC heterostructures. As in the case of two previous samples, the majority of TDs were a type and few c and c+a dislocations were observed. The TD density was 5.5x10^8 cm^-2, and they were randomly distributed and did not form a cellular pattern.

The highly defective regions, observed at, within, and beyond the AlN/SiC and GaN/AlN interfaces could stem from defects in mechanically polished SiC substrates or condensation of point defects. Consider a situation where an AlN layer is grown on a highly
dislocated SiC substrate; mechanical polishing and scratches increase the density of
dislocations terminating on the SiC surface. Since the lattice parameters of AlN and SiC are
different, misfit-dislocations must be introduced at the AlN/SiC interface when the thickness
of AlN exceeds a critical value. In addition, dislocations terminating at a SiC surface
replicate into the AlN overgrowth. As argued by Beam et al. [44], two distinct situations
could arise for homoepitaxial growth: a Burgers vector inclined to the growth surface or a
Burgers vector parallel to the growth surface. They showed that in both cases dislocations are
replicated into the overgrowth; however the situation for the growth of AlN on SiC is more
complicated since the two materials have different lattice parameters. Mahajan and Sree
Harasha [45] suggested that a dislocation with a Burgers vector $b_1$ in SiC will be replicated
into AlN as a threading dislocation with a Burgers vector $b_2$ and a residual dislocation with
Burgers vector $b_3$ that is left at the AlN/SiC interface, i.e.,

$$b_1 \text{(SiC)} \rightarrow b_2 \text{(AlN)} + b_3 \text{(Interface)} \quad (1)$$

Eq. (1) is generic in nature and should apply to the replication of threading dislocations in
any heteroepitaxial structure. Therefore, this argument can also be used to rationalize the
association of TDs in GaN with those in AlN, Figs. 7 and 8. The distribution of dislocations
observed in Fig. 7 can also be understood. Our assessment is in contrast to that of Moran et
al. [46] who postulated that TDs result from the coalescence of GaN islands when deposited
on AlN/SiC substrates. These authors did not discuss the role that TDs in AlN may have on
the formation of TDs in GaN.

Comparing Figs. 7 and 8, it is apparent that the density of TDs or dislocations in a
100 nm thick AlN layer is much lower than that in a 15 nm layer. This could occur if closely
spaced edge dislocations of opposite signs annihilate each other. This process is facilitated by
glide and climb. The glide is driven by elastic interactions, whereas growth-induced point
defects may drive climb. The preceding arguments can also be used to understand the
observed decrease in TD density with the increasing thickness of GaN.

2.5 SUMMARY

Varying thicknesses of AlN layers on 6H-SiC(0001) substrates and GaN layers on
AlN/SiC substrates were investigated in regard to their growth mode, surface microstructure
and defect microstructure. AFM analysis revealed that AlN initially grew on the SiC in the
form of flat-topped islands, which coalesced to form a continuous film; subsequent growth
occurred via the dislocation-mediated step-flow mode. The presence of polishing scratches
in the surface of the SiC substrates resulted in undulations in the surface of the 100 nm AlN
films. The structural quality of AlN layers can be improved substantially by increasing their
thickness. Furthermore, the AlN/SiC interfaces show steps defined by misfit dislocations
and terraces consisting of complex misfit dislocations networks.

GaN layers less than 1 nm thick mimicked the step and terrace structure of the AlN
buffer layer, indicating a pseudomorphic two-dimensional wetting layer. Further deposition
resulted in the nucleation of GaN islands indicative of the Stranski-Krastanov growth mode.
The GaN islands formed preferentially in the scratch-induced undulations in the AlN surface,
which are believed to serve as low energy nucleation sites due to the presence of clusters of
extended defects. TDs from AlN layers are replicated into GaN overgrowths. The flat-
topped GaN islands grew laterally and coalesced, and the growth mode changed to
dislocation-mediated step-flow at a thickness between 50-100 nm. Increasing the GaN
thickness from 1 µm to 4 µm resulted in a reduction of the step terminations from $1 \times 10^9$ cm$^{-2}$
to $5 \times 10^7$ cm$^{-2}$, indicative of a reduction in the density of TDs having a screw component (e and c+a). This conclusion was supported by plan-view TEM images showing that the density of TDs in GaN can be reduced from $1.5 \times 10^9$ cm$^{-2}$ to $5.5 \times 10^8$ cm$^{-2}$ by increasing the thickness of GaN from 1000 to 4000 nm in a GaN/100 nm AlN/SiC heterostructure.
2.6 REFERENCES


1999;85:6470.

[43] Mathis SK, Romanov AE, Chen LF, Beltz GE, Pompe W, Speck JS, Phys Stat Sol (a)
2000;179:125.


[45] Mahajan S, and Sree Harasha KS, Principles of Growth and Processing of

2004;273:38.
2.7 FIGURES

**Figure 1** 10x10 μm and 2x2 μm AFM height images of mechanically polished 6H-SiC(0001) substrates ((a) and (d), respectively) and AlN(0001) layers ((b) and (c) and (e) and (f), respectively) grown on the 6H-SiC. The layer thickness is noted in the upper left corner of each image, and the vertical height scale is given on the upper right. A polishing scratch into which AlN islands have grown is indicated by the arrows in Fig. (f).
**Figure 2** Cross-sectional TEM image of a 15 nm AlN/as-polished SiC substrate composite.

The operating reflection is (0002) for which all a type dislocations should be out of contrast. Note the presence of strains in both the layer and the substrate.
Figure 3  Plan-view TEM micrograph obtained from a 15 nm AlN/as-received SiC substrate composite. Steps delineated by misfit dislocations are visible and networks of misfit dislocations on terraces are complex.
Figure 4  (a) Schematic showing a hexagonal network of misfit dislocations on a terrace; one segment is aligned along a step; (b) Schematic showing hexagonal dislocation networks on two terraces; segments of misfit dislocations tend to align with step edges.
Figure 5 (a) – (i) 2x2 µm AFM height images of GaN layers grown on 100 nm AlN buffer layers. The layer thickness is based on established growth conditions and is listed in the upper left corner of each image. The vertical height scale is given in the upper right corner of each image. Note the GaN islands observed in (b) and (c) and the step terminations indicated by arrows in (h) and (i). The lower right inset in (d) shows a single 2 µm long scan line which allows the observation of the flat-topped nature of the GaN islands. The vertical height range of this inset is 8 nm.
Figure 6 (a) – (c) 10x10 µm AFM height images of GaN layers grown on 100 nm AlN buffer layers. The layer thickness is based on established growth conditions and is listed in the upper left corner of each image. The vertical height scale of each image is given in the upper right corner of each image. The layers are the same samples as those labeled with the same nominal thicknesses in figure 2. Note the influence of the undulations in the AlN buffer layer on the nucleation of the GaN islands.
Figure 7 Cross-sectional TEM WBDF images from a 1000 nm GaN/15 nm AlN/as-polished SiC substrate composite: (a) operating reflection is \((\text{1100})\), (b) enlargement of a region marked by an arrow in (a), and (c) operating reflection is \((0002)\).
Figure 8 Cross-sectional TEM WBDF images from a 2000nm GaN/100 nm A1N/as-deposited SiC substrate composite: (a) operating reflection is $\bar{2}110$, and (b) operating reflection is (0002).
Figure 9  Plan-view image from a 2000 nm GaN/100 A1N/as-polished SiC substrate composite. Note that TDs appear to form a mosaic structure.
3. **Surface morphology and strain of GaN layers grown using 6H-SiC(0001) substrates with different buffer layers**

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Abstract

The evolution of both the surface morphology and the strain in GaN layers grown by metalorganic vapor phase epitaxy on either AlN or Al₁₋ₓGaₓN (x ≃ 0.15) buffer layers previously deposited on 6H-SiC(0001) substrates has been investigated by varying the layer thickness from one GaN bilayer to 4 μm. The GaN surfaces initially contained pits and undulations; the latter became smoother with continued growth. The growth of a 1−1.5 nm thick and continuous wetting layer and the subsequent formation of islands within the undulations are characteristic of the Stranski-Krastanov growth mode observed for the growth of GaN on AlN. The islands coalesced within the first 10 nm. Instead, a step-flow growth mode was observed for the growth of GaN on AlGaN. Increasing the thickness of the GaN grown on either AlN or AlGaN caused these biaxially stressed layers to gradually change their state of stress from compression to tension with regard to both their average strain and their local strain along the growth direction. The compressive and tensile stress components are attributed to the mismatch in lattice parameters between the GaN and the buffer layer and the mismatch in the coefficients of thermal expansion between GaN and SiC, respectively. A portion of the compressive stress is relieved within the first 20 nm of GaN grown on AlN buffer layer. The relief of the remaining stress follows an exponential dependence on the thickness of the GaN layer with values for the characteristic decay length of 0.24 and 0.64 μm for the AlN and AlGaN buffer layer, respectively. The relaxation mechanism is discussed in terms of the formation of misfit dislocations via surface undulations.

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1. Introduction

Sapphire and 6H-SiC are the most commonly used substrates for the heteroepitaxy of GaN. A comparison of the two with regard to device fabrication shows that 6H-SiC has several advantages including superior lattice matching to GaN, higher thermal conductivity and easier cleavage

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along [1120]. From the very beginning AlN has been the buffer layer of choice for all growth of GaN on 6H-SiC(0001) due to the close lattice matching of about 1% of the a-axis lattice parameters [1]. An AlN buffer layer has been repeatedly found to be necessary to achieve GaN layers via metalorganic vapor phase epitaxy (MOVPE) with a smooth surface and a reasonably low density of threading dislocations. It was further shown that the AlN deposition temperature should be beyond 1100 °C to minimize the concentration of growth pits that intersect the surface [2,3]. Conductive AlGaN buffer layers on SiC have been increasingly investigated [4,5], as they are needed to fabricate light emitting diodes and laser diodes on SiC with a completely vertical design [6,7]. A minimum Al content of 6% was found to be necessary for the AlGaN to wet the SiC surface [8]. However, recent reports claim the growth of GaN of reasonable quality on SiC by molecular beam epitaxy (MBE) [9], by MOVPE [10] and hydride vapor phase epitaxy (HVPE) [11] without using any buffer.

GaN layers grown directly on SiC(0001) are usually under tension at room temperature which is attributed to the difference in the coefficients of thermal expansion between the two materials. The latter causes a strain of ~0.1% for a growth temperature of 1000 °C [12]. The use of an AlN buffer layer reduces this tensile stress and even compressively strained GaN layers on SiC have been reported [11,13–17]. The compensating compressive stress component is believed to result from the lattice mismatch of +2.5% between GaN and AlN. Although the critical thickness, to which GaN layers can be coherently grown on AlN, is only a few nanometers for such a large mismatch [18–21], part of the compressive stress remains beyond this thickness. High-resolution transmission electron microscopy (HRTEM) images have revealed a residual compressive strain of 0.9% in GaN at the AlN/GaN interface [16]. Moreover, it was found that the average strain in GaN on AlN depends on the GaN layer thickness and usually changes from compression to tension with increasing thickness [22–24]. However, the opposite trend has been reported as well [22,25]. Finally, the stress in GaN grown on AlGaN buffer layers can be engineered by altering the composition and/or the thickness of this buffer layer [8,11,26].

In the present research GaN layers of different thickness, grown on 6H-SiC(0001) substrates using AlN and AlGaN buffer layers, have been investigated with two objectives: the determination of (1) the onset of GaN nucleation on the different buffer layers and the evolution of the surface morphology via atomic force microscopy (AFM) and (2) the evolution of the average strain in GaN and the change in strain within a sample along the growth direction via high-resolution X-ray diffraction (HRXRD) measurements.

2. Experimental procedures

The growths were performed on the Si-face of on-axis 6H-SiC(0001) wafers provided by Cree, Inc. Prior to loading into the MOVPE reactor, the substrates were etched in a HF:H2O (1:10) solution for 10 min at room temperature, rinsed in de-ionized water and blown dry with nitrogen. The MOVPE reactor was a cold-walled vertical pancake-style system which was evacuated to ~10⁻⁶ Torr prior to growth. Trimethylaluminum (TMA), triethylgallium (TEG) and ammonia were used as the precursors, with hydrogen as both the carrier and the diluent gas. The reactor pressure was fixed at 20 Torr throughout each growth run. The temperature of the SiC-coated graphite susceptor was measured by a single wavelength optical pyrometer. The main growth conditions are listed in Table 1.

The thickness of both the AlN and the AlGaN buffer layers was 100 nm. The Al mole fraction of the AlGaN buffer layer was about 0.15 as estimated from HRXRD measurements. The surface morphology of thick GaN layers grown on AlGaN buffer layers was found to be very sensitive to the growth temperature and the growth rate of the latter. Growth temperatures and V/III ratios for the AlGaN buffer layer higher than those listed in Table 1 resulted in spiral hillocks on the GaN surface, as we recently described in detail [27]. No growth interruption was performed for the deposition of GaN on the AlGaN buffer layer; whereas, the growth was suspended for 5 min after the
deposition of the AlN buffer layer to readjust the growth temperature. The thickness of the GaN layer was varied between 0.25 nm and 4 μm without any problem of layer cracking. For the GaN layers with thicknesses below 2 nm, the standard growth conditions used for thicker layers had to be changed to achieve a reasonably small growth rate, as shown in Table 1. However, AFM images of 2 nm thick layers grown with the two sets of GaN growth conditions did not reveal significant differences. The intended thicknesses of the thicker GaN layers were confirmed by the interference effects observed in HRXRD scans; the numbers given for the thinner layers are nominal values based on the deposition time.

The HRXRD studies were conducted using a Philips XPert MRD diffractometer equipped with a fourfold Ge(220) monochromator, a threefold Ge(220) analyzer and an Eulerian cradle. The c- and ω-axis lattice parameters were determined using triple-axis ω-2θ scans on the (00 2) and the (2 0 5) reflections, respectively, in tandem with correction of the Bragg angles for the refraction of the X-rays. AFM was performed using a Digital Nanoscope 3000 in the tapping mode.

3. Results and discussion

3.1. Surface morphology

3.1.1. Results

The surface image of the bare AlN buffer layer is shown in Fig. 1(a). It exhibits narrow terraces separated by bilayer high steps (1/2 c) that are difficult to resolve. Moreover, undulations and deep pits, which appear to be arranged along lines, can be found throughout the surface. GaN layers with thicknesses to 1 nm exhibit similar surface features as the AlN buffer layer on which they were grown, as shown in Fig. 1(b). However, their bilayer terraces are more regular and better resolved. New features were only observed for layer thicknesses of 1.5 nm and larger. Fig. 1(c) corresponds to a 1.5 nm thick GaN film which reveals isolated GaN islands that formed in the undulations of the surface. During further growth, the density of the islands in the undulations increases such that they form strings, as illustrated in Fig. 1(d). The sidewalls of the islands do not correspond to any clear crystal facets, i.e., the islands seem to possess rather arbitrary shapes. In contrast, the islands are believed to have atomically smooth (0 0 0 1) surfaces, as terraces were not observed on their flat tops. The islands have different heights with larger islands usually higher than smaller ones, as illustrated by the data in Fig. 2. The aspect ratio of the islands, which is the ratio of the height to the diameter, is not homogeneous but scatters within the range of about 1 to 8.

The GaN islands grow laterally over the AlN buffer layer and coalesce, as shown in Figs. 1(e) and (f) for a 5 and a 10 nm thick GaN layer, respectively. Although island coalescence is essentially completed at about 10 nm, the undulations remain beyond this thickness, as shown in Figs. 1(g) and (h) for the 50 and 100 nm thick films, respectively. However, the density and amplitude of the undulations is reduced with increasing GaN thickness, finally resulting in a smooth and regularly stepped surface such as that for a 1 μm thick film presented in Fig. 1(i).

A representative surface of the AlGaN buffer layer is shown in Fig. 3(a). It also exhibits pits and undulations in the manner of the AlN buffer layer discussed above. Irregularly curved narrow trenches without any preferred crystallographic
orientation were also observed throughout the surface. Their width was estimated to be within the range of 15–40 nm; however, their depth could not be resolved with the AFM tip used in this study. The surface of the AlGaN also contained terraces separated by bilayer high steps that formed spiral hillocks around small pits. However, these hillocks disappeared at the outset of GaN growth on this buffer layer and were replaced by more randomly shaped atomic terraces such as those shown on the 2–10 nm thick films in Figs. 3(b)–(d). The formation of distinct GaN islands such as grew on the AlN buffer layer was not observed on the AlGaN buffer layer (compare Fig. 1(c) to (e)). The wide undulations and the narrow trenches remained but decreased in density when the GaN layer thickness was increased, as the image of the 100 nm thick layer shown in Fig. 3(e) illustrates. For thicker layers, the surface became smooth and appeared similar to the thick layers grown on the AlN buffer layer (compare Figs. 1(f) and 3(f)).

The evolution of the surface roughness of the GaN layer as a function of thickness is shown in Fig. 4. The values of the peak-to-valley roughness for the AlN and the AlGaN buffer layers show the same trend. The roughness of the GaN layers initially increases when grown on either buffer layer and is largest for a GaN layer thickness of about 5 nm. For thicker layers, the roughness decreases steadily. Growth on the AlGaN buffer layer resulted in a rougher GaN surface than growth on the AlN buffer layer. This is partially due to the narrow trenches shown in Fig. 3. It should be noted that the values of the root mean square (RMS) roughness exhibited a similar maximum as those of the peak-to-valley roughness plotted in Fig. 4. However, these values did not show any pronounced differences between the two
buffer layers, because the deep, narrow trenches, which were observed only on the samples employing an AlGaN buffer, did not significantly contribute to the averaged roughness represented by the RMS value.

3.1.2. Discussion

Smart et al. [8] and Koleske et al. [28] have reported that pits and undulations on the surface of an AlN buffer layer can result from polishing.

Fig. 2. Height versus diameter of GaN islands grown on an AlN buffer layer (circles). The data was extracted from AFM images of GaN layers with nominal thicknesses of 1.5 and 2 nm, respectively. The aspect ratios of $\frac{h}{t}$ and $\frac{d}{h}$ are marked by dotted and dashed lines, respectively.

Fig. 4. Peak-to-valley surface roughness of GaN layers of different thickness grown on AlN buffer layers (filled circles) and AlGaN buffer layers (open circles), respectively, as determined from $2\mu m \times 2\mu m$ size AFM images. The broken lines are guides to the eye.

Fig. 3. $2\mu m \times 2\mu m$ AFM surface images of GaN layers grown on AlGaN buffer layers. The GaN layer thickness is indicated for each image. Note the spiral hillock in (a) and the very narrow, irregularly curved trenches marked by arrows in micrograph (b).
scratches in the SiC substrate. This would be in accordance with the fact that the features observed on our AlN surfaces are roughly straight lines. The surfaces of the GaN layers also mimicked the AlN for GaN thicknesses to 1 nm. On the one hand, there could be a delay in the sticking of GaN to the AlN surface such that the real GaN layer thicknesses are less than the expected values. Therefore, the surface corresponding to nominally 1 nm thick GaN on AlN could be bare AlN instead. On the other hand, GaN is known to grow on AlN in a Stranski–Krastanov mode where a pseudomorphic wetting layer is first formed before the increasing strain drives the transition into an island growth mode. The latter was found by Daudin et al. [29] for the MBE growth of GaN quantum dots on AlN at sufficiently high temperatures. The corresponding wetting layer thickness was reported to be about 1-5 bilayers depending on the dynamics of the growth process [20,21,29-31]. Thus, it is reasonable to assume that the Stranski–Krastanov growth mode of GaN on AlN also occurs under the MOVPE growth conditions used in this study. The formation of a GaN wetting layer also is in agreement with the improved resolution of the bilayer terrace structure on the nominally 1 nm thick GaN layer, since a significant oxide layer, which usually interferes with high resolution in AFM measurements, is expected to form more easily on the AlN compared to the GaN surface.

Similar to our observations, Kolesske et al. [28] and Nishida et al. [32] have observed that the preferential nucleation sites of GaN islands are the undulations of the AlN surface. Assuming that the undulations correspond to defect features in the SiC such as polishing scratches, the former are very likely accompanied by a locally higher density of threading dislocations in the AlN. Moreover, the results of studies [33-35] have revealed the preferential nucleation of GaN islands at dislocations in the AlN; thus, reason for observed GaN island formation in the surface undulations is provided.

The surface of the GaN islands on AlN appears atomically smooth. This was also found by Lorenz et al. [36] who studied the evolution of GaN grown on AlN buffer layers deposited on sapphire. They attributed this effect to the localized growth enhancement at the nucleated GaN islands due to the difference in surface energy between GaN and AlN. Widmann et al. [31,34] extracted a constant aspect ratio of 1/5.2 for their MBE-grown GaN quantum dots on thick AlN layers. While their islands had the shape of a truncated pyramid with a hexagonal base, a similar defined shape and a homogeneous aspect ratio were not observed for our samples. This can be attributed to the nucleation of GaN at clusters of dislocations in our highly defective AlN buffer layer instead of the free strain-driven formation on a rather perfect surface of a thick AlN layer. However, it should be noticed that the aspect ratios of 1/5 to 1/1 measured in this study are significantly smaller than those reported by Widmann et al. [31,34] for MBE growth. Besides the different AlN layers used in both studies, this can be attributed to the larger ratio of lateral-to-vertical growth rate during MOVPE compared to MBE, which is largely due to the higher growth temperature usually employed with the former technique. In fact, the density and aspect ratio of the GaN dots grown on AlGaN depended sensitively on both the growth temperature and the growth time [37,38].

The formation of GaN islands was not observed on the AlGaN buffer layer. Instead, the step-flow growth mode was maintained with only a change in the step pattern. This agrees with the results of MOVPE and MBE investigations of Tanaka et al. [17] and Shen et al. [38], respectively, who had to use Si as an antisolvent to form GaN quantum dots on Al$_{x}$Ga$_{1-x}$N ($x\lt0.2$). As the lattice mismatch between GaN and the AlGaN buffer layer, the latter having an Al mole fraction of about 0.15 in our case, is smaller than that between GaN and AlN, the observed formation of GaN islands on AlN is likely driven by strain.

The surface of the AlGaN buffer layer exhibited spiral hillocks around pits which changed to a pattern of less curved steps as soon as the GaN was deposited. Tarsa et al. [39] and Heying et al. [40] attributed the occurrence of those pits on GaN that terminate two pinned steps to the intersection of the surface by threading dislocations with a
screw component. They also proposed that spiral hillocks occurred with regard to the deviation of the growth conditions from thermodynamic equilibrium on the one hand and the interaction of spiral growth and the flow of steps due to the miscut of the substrate on the other hand [40]. The changes we observed in the step pattern suggest that the transition from AlGaN to GaN shifts the thermodynamic system closer to equilibrium. This is understandable as the equilibrium constant for the formation reaction of AlN from Al and ammonia is significantly larger than that for the formation of GaN from Ga and ammonia [41]. Therefore, the decomposition rate during the growth of AlGaN is smaller compared to GaN which corresponds to a more non-equilibrium process in the case of AlGaN.

The evolution of the surface roughness, as shown in Fig. 4, can be explained by two superimposing processes. The first process is the formation of GaN islands on the buffer layers which results in a peak roughness at a layer thickness of about 5 nm. Beyond this thickness, the islands coalesce and the roughness decreases. As discussed before, however, islands were only observed for the growth on the AlN buffer layer. The surface roughening for the growth on AlGaN suggests that in this case the GaN is also not homogeneously deposited. The GaN is believed to reproduce the undulated AlGaN surface but enhance its amplitude. In this way, the compressive stress in the GaN can be more effectively relieved elastically without the need to build up significant surface energy associated with the formation of numerous small islands. For very large layer thicknesses, the surface roughness steadily decreases as the undulations and pits are slowly filled with GaN. This process might be accompanied by a reduction of dislocations associated with these surface features.

Finally, the nature of the narrow trenches observed on the AlGaN buffer layer as well as on the GaN layers grown thereon remains unclear in this study. We speculate that these features are somehow related to a phase separation in AlGaN that was found for the growth on SiC [15,42]. Transmission electron microscopy investigations are underway to clarify this issue.

3.2. Strain

3.2.1. Results

Fig. 3(a) shows triple-axis ω-2θ scans of the GaN(002) reflection for GaN layers with thicknesses between 20 nm and 4 μm which were grown on AlN buffer layers. All curves show a single dominant peak which shifts to larger Bragg angles when the layer thickness increases. That is, the average lattice parameter, c, decreases with increasing layer thickness. Moreover, all peaks are asymmetric which is particularly obvious for the thicker GaN layers by the shoulder at the low-angle side of the peak. The fact that the peaks become narrower with increasing layer thickness is simply a consequence of the diffraction within crystals of different spatial extension along the c-axis. The scans of the thinner GaN layers in Fig. 5(a) exhibit distinct thickness interference fringes which indicate a relatively smooth GaN surface and a smooth GaN/AlN interface. The thicknesses extracted from the fringe periods fit accurately to the intended GaN layer thicknesses.

The corresponding results for GaN layers grown on AlGaN buffer layers are shown in Fig. 3(b). They exhibit features similar to those discussed before. However, for GaN layer thicknesses ≤ 0.1 μm, a broad background from the AlGaN buffer layer is superimposed on the GaN peak making it difficult to extract the GaN peak position. The broad AlGaN peak points to large strain or compositional variations in the AlGaN buffer layer, the latter of which agrees with the phase separation observed in AlGaN buffer layers by Brenner et al. [15] and Vennéquès et al. [42]. In the following, only the HRXRD data for the GaN samples having a thickness > 0.1 μm and grown on the AlGaN buffer layers were evaluated.

Fig. 6 shows the linear relationship between the average values of the c and a lattice parameters determined for all GaN samples. Fig. 7 shows the evolution of the average lattice parameters with the GaN layer thickness. The plotted strain values were obtained by relating the lattice parameters to the values of c₀ and a₀ determined for the 4 μm thick GaN layers, as listed in Table 2. It should be emphasized that the 4 μm thick layers are not believed to be completely strain-free. Nevertheless,
Fig. 5. HRXRD triple-axis ω-2θ scans of the GaN (602) reflection for GaN layers of different thickness grown on AlN (a) and AlGaN (b) buffer layers, respectively. The GaN layer thicknesses are 4 μm (A), 1 μm (B), 1 μm (C), 0.5 μm (D), 0.2 μm (E), 0.1 μm (F), 0.05 μm (G) and 0.02 μm (H), respectively. The curves are vertically shifted against each other for clarity.

their lattice parameters, rather than published values for nominally unstrained GaN, were used as references to avoid confusion due to possible hydrostatic stresses in our samples. However, among all the samples investigated in this research, the 4 μm thick GaN layers exhibited a c/a ratio closest to the value 1.626 which is believed to correspond to strain-free GaN [43]. The slope of the data in Fig. 7 can be fitted assuming that (1) the local strain ε(z) follows an exponential law and (2) the measured strain ε(τ), with τ as the GaN layer thickness, corresponds to the average local strain, i.e.

\[
\varepsilon(z) = \varepsilon_0 + \Delta \varepsilon \times \exp \left( -\frac{z}{\lambda} \right),
\]

(1)

\[
\overline{\varepsilon}(\tau) = \frac{1}{t} \int_0^t \varepsilon(\tau) \, d\tau = \varepsilon_0 + \Delta \varepsilon \left[ 1 - \exp \left( -\frac{t}{\lambda} \right) \right] \frac{\varepsilon_0}{\tau},
\]

(2)

where \( \Delta \varepsilon \) is the total change in strain within an infinitely thick GaN layer and \( \varepsilon_0 \) is a characteristic decay length. For a purely biaxial strain, the in-plane strain \( \varepsilon_{xx} \) and the out-of-plane strain \( \varepsilon_{zz} \) should not be independent of each other but satisfy the boundary condition

\[
\frac{c - c_0}{\varepsilon_0} = \frac{a - a_0}{\varepsilon_{xx}},
\]

(3)
where \( c_{13} \) and \( c_{33} \) are elastic stiffness constants. Using Eq. (3) and assuming the strain in very thick GaN layers to be independent of the buffer layer used, the fitting of Eq. (2) to our data results in the solid curves shown in Fig. 7. The corresponding fit parameters are listed in Table 2.

3.2.2. Discussion

The stress in the GaN layers can be thought as a superposition of a hydrostatic stress and a biaxial stress in the growth plane. The observed linear dependence in Fig. 6 indicates that the samples under investigation only differ in their biaxial stress, whereas the hydrostatic stress component can be assumed as constant. For this case, the biaxial strain is given by Eq. (3) with \( c_0 \) and \( \Delta c_{13} \) as the lattice parameters of GaN under zero biaxial stress. Fitting Eq. (3) to the X-ray data and employing \( c_0/c_0 = 1.626 \) resulted in \( -2c_{13}/c_3 = -0.468 \pm 0.004 \) which is shown as a solid line in Fig. 6. Similar procedures were employed by Perry et al. [16] and Lahréche et al. [19] who deduced the values \(-0.446 \pm 0.03\) and \(-0.53\), respectively. All these numbers are in reasonable agreement with published values on stiffness constants of GaN for which \( -2c_{13}/c_3 \) is in the range from \(-0.509\) to \(-0.598\) [44-48]. With regard to Fig. 7, thin GaN layers are under high in-plane biaxial compression. This results from the fact that GaN first grows coherently on both AlN and AlGaN buffer layers as described above. Beyond a critical layer thickness, this compression is relieved. As Fig. 7 shows, the stress relief is not abrupt but the strain decreases steadily over a large thickness range. For very thick layers, the compressive stress due to the buffer layer is fully relieved and the remaining strain only results from defects and the mismatch in the coefficients of thermal expansion between the GaN and the SiC. The asymmetry of the scans shown in Fig. 5 further indicates that not only does the average strain change with the thickness, but that there is a strain gradient along the growth direction within

Fig. 7. Average in-plane strain (open circles) and out-of-plane strain (filled circles) of GaN layers of different thicknesses grown on AlN buffer layers (a) and AlGaN buffer layers (b), respectively. The strain was set to zero at a thickness of 4 μm. The solid lines were fitted using Eq. (2). The dotted lines correspond to fits of hyperbolic functions similar to those given in Ref. [19].

Table 2

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>AlN</th>
<th>AlGaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 ) (Å) for ( t = 4 ) μm</td>
<td>3.1909 ± 0.0008</td>
<td>3.1922 ± 0.0008</td>
</tr>
<tr>
<td>( c_0 ) (Å) for ( t = 4 ) μm</td>
<td>5.1898 ± 0.0002</td>
<td>5.1890 ± 0.0002</td>
</tr>
<tr>
<td>( -2c_{13}/c_3 )</td>
<td>(-0.470 \pm 0.010)</td>
<td>(0.64 \pm 0.10)</td>
</tr>
<tr>
<td>( \bar{t}_D ) (μm)</td>
<td>0.24 ± 0.02</td>
<td>0.64 ± 0.10</td>
</tr>
<tr>
<td>( \Delta c_{13} ) (%)</td>
<td>(-0.75 \pm 0.05)</td>
<td>(-0.34 \pm 0.03)</td>
</tr>
</tbody>
</table>
each sample. The GaN close to the buffer layer is under stronger compression compared to the GaN close to the surface.

The in-plane lattice mismatches between relaxed GaN and the AlN and AlGaN buffer layers are about 2.5% and 0.37%, respectively. In contrast, the fit parameters \( \Delta \sigma_{\text{eff}} \) in Table 2 show that the strain, which relaxed within the thickness range accessible to HRXRD, is only about 0.75% and 0.34%, respectively. Therefore, if it is assumed that the GaN initially grows coherently on both AlN and AlGaN, only the data in Fig. 7 corresponding to the growth on AlGaN cover the total relaxation process. It is suggested that the stress relief of GaN grown on AlN and AlGaN is a single and two-step process, respectively.

(i) The coherent stress of GaN on the AlN buffer layer is partially relieved within the first 20 nm of GaN growth. This thickness range includes the reported critical thickness values for the coherent growth of GaN on AlN, namely 3.0 nm from theoretical calculations [18], 2.9 ± 0.4 nm from the extrapolation of XRD data [19], and both the 0.5 nm and the 3.1 ± 0.2 nm determined from in situ lattice parameter measurements at different growth temperatures [20,21]. The former numbers correspond to the plastic stress relief by misfit dislocations which, however, can be superimposed by an elastic relaxation of GaN islands via their sidewalls before coalescence occurs [29]. About 70% of the coherent strain of GaN on AlN is relieved in the first step, this agrees well with the value of 64% deduced by Perry et al. [16] from HRTEM images.

(ii) The stress remaining in GaN on AlN after the first step is relieved in a second step, as illustrated by Fig. 7. This stress relief extends over a large depth range in the GaN layer, as the decay length, \( \delta_0 \), in Table 2 of about 0.24 \( \mu \text{m} \) indicates. The same effect was determined to be true for the total strain of GaN on AlGaN where the value of the decay length is even 0.64 \( \mu \text{m} \). The long-range relaxation may result from the difficulty of threading dislocations in the group III-nitrides, most of which run along the c-axis, to bend over and glide in the c-plane [49]. A qualitative model for the long-range strain relaxation can be developed using the evolution of the film microstructure discussed in Section 3.1. The film becomes increasingly smoother, i.e. the undulations and pits become filled with material with increasing layer thickness. Therefore, the elastic relaxation of the film via the lateral deformation of the undulated structure is suppressed and plastic relaxation by dislocations begins to occur. It is assumed that the generation of misfit dislocations is promoted at the deepest regions of the pits and the undulations. A similar phenomenon has been shown for coherent AlGaN and InGaN layers in which the tips of cracks and V-shaped defects act as nucleation sites for dislocations [49,50]. As the deepest regions of the pits and undulations rise, the generated misfit dislocations are distributed over different depths in the layer, and the strain becomes non-homogeneous along the growth direction. The latter effect is responsible for the asymmetry of the HRXRD scans shown in Fig. 5.

The use of the exponential function given in Eq. (2) to fit the data in Fig. 7 represents an empirical approach, as it was not motivated by a certain model for the relaxation process. Interestingly, Hiramatsu et al. [51] used a similar dependence to describe the strain relaxation of thick GaN layers grown on AlN/sapphire. These investigators proposed the formation of micro-cracks at the sapphire interface to hold the thermally induced stress in the bent heterostructure below a critical value. The layers investigated in the present study, however, are assumed to be too thin to cause cracking. Kim et al. [19] fitted a hyperbolic thickness dependence, \( \sigma_{\text{eff}} \propto 1/t \), to strain values obtained for GaN layers on AlN/sapphire beyond the critical thickness which was motivated by a model that balanced the energies for strain and dislocations. The same approach was used by Dunstan [52] who recently reviewed the strain relaxation in semiconductors with the focus on InGaAs layers on GaAs where the relaxation is assumed to result from dislocation multiplication. The fits of hyperbolic functions to our data are shown as dotted lines in Fig. 7. The experimental results are better described by the exponential functions than by the hyperbolic functions.

It is generally known that thick GaN layers grown on SiC(0001) tend to crack beyond a
critical layer thickness due to the build-up of a high tensile stress [53–55]. However, the strain data of this study has shown that GaN layers grown on SiC(0001) are in average under compression in the growth plane when either an AlN or an AlGaN buffer layer is employed. The compression is a consequence of the large lattice mismatch between GaN and the buffer layer which amounts to 2.5% and 0.37% for the AlN and AlGaN buffer layer, respectively. In comparison, the tensile strain at room temperature resulting from the mismatch in the coefficients of thermal expansion between the GaN and the SiC is only −0.1% for typical MOVPE growth temperatures [12]. Although the average strain in the GaN layers is compressive, the strain at the GaN surface can be tensile which gives rise to the formation of cracks. The evaluation of Eq. (1) using the fit parameters in Table 2 reveals that the GaN surface tends from compression into tension at a layer thickness of 0.7 μm and 1.4 μm for the AlN and the AlGaN buffer layer, respectively. Moreover, from growth experiments on AlGaN buffer layers it was found that the stress in GaN can, e.g., depend on the buffer layer thickness [8,11]. Therefore, the problem of cracking in thick GaN layers on SiC can be minimized by optimizing the composition and the thickness of the buffer layer of choice towards a maximum compressive stress remaining at a certain GaN layer thickness.

4. Summary

GaN layers grown by MOVPE on either AlN or AlGaN buffer layers previously deposited on 6H-SiC(0001) substrates were investigated with regard to their surface morphology and strain by varying the layer thickness from a few bilayers to 4 μm. The thickness of all buffer layers was 100 nm. Undulations and pits, characteristic of the surface microstructure of the buffer layer, are assumed to result from scratches in the SiC substrate and to be associated with threading dislocations. They continue into the growing GaN film. GaN grows in a Strasinski-Kranstanov mode on AlN, i.e., a homogeneous GaN wetting layer is formed initially. GaN islands are preferentially formed in the surface undulations beyond a critical thickness of 1–1.5 nm. The surface is roughest for a GaN layer thickness of ~5 nm; it becomes progressively smoother during the island coalescence process, which is largely finished after ~10 nm of GaN. In contrast, it takes several hundred nanometers to smooth out the undulations and significantly reduce the pit density. Island formation of GaN is suppressed during growth on the AlGaN buffer layer because the driving force for this phenomenon, i.e., the coherent stress in the GaN is considerably smaller compared to the growth on AlN. Nevertheless, the roughness of the GaN on the AlGaN buffer increases during the initial stage of growth which is attributed to the enhancement of the preexisting surface undulations. Additionally, narrow deep trenches were generated within the AlGaN buffer layer which might be related to a phase separation in the buffer.

The thickness of the GaN layer influences the biaxial strain in the layers. GaN layers grown on either AlN or AlGaN buffer layers were determined to be under compression in the growth plane due to incomplete relaxation of the coherent strain. With increasing thickness, this stress is progressively relieved. Approximately 70% of the coherent strain remained after a first relaxation step in a 20 nm thick GaN layer on AlN. Relief of the remaining stress followed an exponential dependence over a large range of GaN layer thickness. Values of 0.24 and 0.64 μm were determined for the characteristic lengths of this relief for the growth on AlN and AlGaN, respectively. The misfit dislocations associated with the relaxation are assumed to be formed at the bottom of the surface undulations. As the latter fill with material during growth, the misfit dislocations are distributed throughout the GaN layer such that the strain within each layer becomes inhomogeneous, i.e., the GaN closer to the buffer layer is under higher compression than the GaN at the surface.

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References

4. On the microstructure of Al\textsubscript{x}Ga\textsubscript{1-x}N layers grown on 6H-SiC(0001) substrates

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4.1 ABSTRACT

The microstructural as well as the compositional evolution of Al$_x$Ga$_{1-x}$N ($x \sim 0.15$) layers grown on 6H-SiC(0001) substrates by metalorganic vapor phase epitaxy were analyzed by atomic force microscopy, X-ray diffraction and transmission electron microscopy in conjunction with energy dispersive X-ray spectroscopy. The epitaxial growth was followed from the early nucleation stage on the substrate to the development of a thick bulk-like film. Phase separation was observed during the early stage of growth, i.e. islands of two different shapes formed whose Al mole fractions were about 0.035 and 0.18, respectively. The Al$_x$Ga$_{1-x}$N coalesced at a film thickness of about 100 nm with the domains of varying Al content being fully coherent. Such domains were not only found at the film/substrate interface but also further away from the interface. They were arranged in layers, which were shifted laterally against each other, i.e., Al-deficient domains formed on top of Al-rich domains and vice versa. Increasing the film thickness to more than 100 nm finally led to a homogeneous Al distribution. Finite element simulations were performed to calculate the strain distribution in these inhomogeneous systems. They allowed the experimental results to be explained by an interplay of strain minimization in the epitaxial film and growth kinetics.

4.2 INTRODUCTION

The use of conductive SiC rather than insulating sapphire as a substrate for the epitaxy of group-III nitrides facilitates the fabrication of fully vertical devices that are significantly smaller in their chip size as compared to devices with lateral current paths. AlN, which has a lattice mismatch in the $a$ lattice parameter of only 1.1 % to SiC, was shown to be a suitable
buffer layer for the growth of GaN on 6H-SiC(0001) [1]. However, it suffers from its doping limits. Therefore, Al$_x$Ga$_{1-x}$N with an Al mole fraction of about 0.15, which can be made reasonably conductive, is now preferred as a buffer layer [2,3]. During the initial stage of film growth, phase separation was found to occur leading to areas with varying Al content close to the interface between the Al$_x$Ga$_{1-x}$N and the 6H-SiC(0001) [4-7]. The exact reasons for this behavior have not been identified yet. Vennegués et al. [4] report that first a thin and smooth AlN wetting layer forms on the SiC due to its lower lattice mismatch as compared to GaN, followed by the formation of Ga-rich islands. In contrast, Petterson et al. [5] believe that pre-existing scratches on the SiC substrate surface cause the phase separation. As far as strain is involved in the phase separation, it is interesting to note that Waltereit et al. [8] found a 0.3 % residual strain in thick AlN layers on SiC; whereas, pure GaN grew completely relaxed on SiC. Heikman et al. [7] observed a significant difference in diffusivity of Al and Ga during lateral epitaxial growth indicating that Al diffuses much slower compared to Ga on the Al$_x$Ga$_{1-x}$N(0001) surface. This work presents the results of a detailed investigation of the development of microstructure, chemical composition, surface topography and strain state of Al$_x$Ga$_{1-x}$N layers with a nominal Al mole fraction of $x = 0.15$ grown on SiC substrates. The principal objective has been to obtain a comprehensive understanding of the transition from the nucleation state to the bulk-like layer.

4.3 EXPERIMENTAL DETAILS

The Al$_x$Ga$_{1-x}$N films were grown via metalorganic vapor phase epitaxy (MOVPE) using a cold-walled, pancake style vertical reactor in which the gases were mixed in a column located five cm above the SiC-coated graphite substrate holder. The temperature of
the latter was measured using a single wavelength optical pyrometer. Si-face on-axis 6H-SiC(0001) wafers provided by Cree, Inc. were used as substrates. Prior to loading into the MOVPE reactor, the substrates were etched in a HF:H2O (1:10) solution for 10 min at room temperature, rinsed in de-ionized water and blown dry with nitrogen. The reactor was evacuated to 10^-6 Torr prior to growth. Trimethylaluminum, triethylgallium and ammonia were used as precursors with typical flow rates of 2.3 µmol/min, 26.9 µmol/min and 3.0 slm, respectively. This resulted in a growth rate of 0.60 µm/h for AlxGa1-xN with a nominal aluminum mole fraction of 0.15. Hydrogen was used as both the carrier and the diluent gas; nitrogen served as a curtain gas separating the reactants from the reactor walls. The total hydrogen and nitrogen flow rates were 3.0 slm and 4.5 slm, respectively. The reactor pressure was fixed at 20 Torr throughout each growth run. Before growth, the substrates were thermally cleaned at approximately 1100°C in a hydrogen ambient in the reactor. The temperature was then reduced to 1010°C, the metalorganics and ammonia were introduced into the chamber and the growth of nominally undoped AlxGa1-xN initiated. In order to avoid a rapid increase in the total gas flow into the reactor at the initiation of growth, the ammonia flow was ramped over a period of 30 seconds from an initial flow rate of 0.50 slm to the final flow rate of 3.0 slm. The nominal thickness of each of the AlxGa1-xN films was estimated from the measured thickness of the 1 µm thick film by linear downscaling according to the growth time; the values were 20 nm, 60 nm, 100 nm, and 1 µm. It is noted that the growth conditions for AlxGa1-xN were optimized regarding their use as buffer layers for the subsequent growth of GaN. The 1 µm thick GaN layers deposited on 100 nm AlxGa1-xN buffer layers possessed state-of-the-art surface microstructure, dislocation density, and luminescence characteristics [9].
Atomic force microscopy (AFM) was performed using a Digital Instruments Dimension 3000 in the tapping mode. High resolution X-ray diffraction (HRXRD) measurements were conducted with a Philips X'Pert diffractometer equipped with a fourfold Ge(220) monochromator, a threefold Ge(220) analyzer and a Eulerian cradle. Reciprocal space maps (RSMs) of the AlGaN(10\overline{1}5) and the SiC(10\overline{1}15) reflections were recorded to determine the composition and the strain state of the layers. Conventional and high-resolution transmission electron microscopy (TEM) was used to study the microstructural evolution of the films in plan-view and in cross-section. TEM specimens were prepared by the usual mechanical grinding and polishing followed by Ar\(^+\) ion milling to obtain electron transparency. The TEM analysis was performed using both a Philips CM20 equipped with an Ultra-Twin lens for high-resolution imaging and a Philips CM30 in conjunction with an energy dispersive X-ray spectrometer (EDS), an annular dark field detector and a scan generator which allowed simultaneous element sensitive mapping and imaging in the scanning TEM (STEM) mode.

4.4 EXPERIMENTAL RESULTS

AFM images of the Al\(_x\)Ga\(_{1-x}\)N surface are shown in Fig. 1. The initiation of growth of Al\(_x\)Ga\(_{1-x}\)N on SiC is marked by the formation of islands, as shown in Fig.1(a) for the layer with a nominal thickness of 20 nm. The islands have flat tops, and the shape of their base loosely mirrors the hexagonal crystal symmetry in the c-plane. The average island height is 68 nm. The island density is \(\sim10^9\) cm\(^{-2}\). Estimation of the total volume of the islands indicate that, within experimental accuracy, the growth rate is constant from the very beginning of growth, i.e. it is not modified by the nucleation process. Although the area between the
islands appears featureless in the height images, a weak grainy contrast is observed in AFM phase images. The TEM images presented below also reveal the SiC between the islands covered by a thin Al\(_x\)Ga\(_{1-x}\)N layer. Additional deposition to a nominal layer thickness of 60 nm results in both the coalescence of some of the islands, as shown in Fig. 1(b) and secondary nucleation, as indicated by arrows in the insert of this figure. The coalescence is nearly completed at a nominal layer thickness of 100 nm. Trenches and holes can still be observed, as shown in Fig. 1(c). Figure 1(d) reveals that at a layer thickness of \(\sim\) 1 \(\mu\)m, the epitaxial surface exhibits mainly terraces separated by steps of monolayer height. Narrow trenches like those observed in Fig. 1(c) are separated by several microns in these thicker layers and are only occasionally observed.

The strain and the composition of the Al\(_x\)Ga\(_{1-x}\)N layers were determined using HRXRD. Figure 2 shows an RSM of the Al\(_x\)Ga\(_{1-x}\)N (10 1 5) reflection. Two peaks originating from the Al\(_x\)Ga\(_{1-x}\)N are clearly resolved. Filled circles indicate their maxima. These results show that the aluminum is sufficiently inhomogeneously distributed in the layer such that phases with different aluminum mole fractions have been formed. The two peaks in the RSM of Fig. 2 have approximately the same in-plane scattering vector, \(q_x\), thus, the phases are assumed to be fully coherent with respect to each other in the growth plane. The theoretical position of the (10 1 5) reflection of strain-free Al\(_x\)Ga\(_{1-x}\)N, shown by the solid line in Fig. 2, was derived using the lattice parameters of nominally strain-free 6H-SiC, GaN and AlN [10], and correcting the scaling of the RSM regarding the measured position from the SiC(10 1 15) reflection. The measured peaks are close to this line, and their \(q_x\) value is far from that of the SiC(10 1 15) reflection. Thus, the Al\(_x\)Ga\(_{1-x}\)N layer as a whole is not significantly strained by the SiC substrate. The aluminum mole fraction, \(x\), and the strain parameter, \(\gamma\), relative to the
substrate can be determined for both phases assuming the stress of Al$_x$Ga$_{1-x}$N to be purely biaxial in the c-plane without any hydrostatic contribution. The peaks have to lie on the “relaxation lines”, which are shown as dotted lines in Fig. 2. These lines were determined in the manner employed in Ref. [11] using a ratio of stiffness constants of $2c_{13}/c_{33} = -0.51$ [12]. The calculated aluminum mole fractions for the two phases are 0.10 and 0.18, respectively. For both phases $|\gamma| < 0.05$.

TEM was used in both conventional and high-resolution mode in conjunction with energy dispersive X-ray analysis to determine the microstructural as well as the compositional evolution of the Al$_x$Ga$_{1-x}$N layers. Figure 3 shows a HRTEM cross-section image of the nominally 20 nm thick Al$_x$Ga$_{1-x}$N film. The image was taken along the [01$ar{1}$0] zone axis and shows the {0002} lattice fringes. The (01$ar{1}$0) lattice spacing of 0.16 nm could not be resolved due to the spatial resolution limit of 0.19 nm of the microscope. In accordance with the AFM images discussed above, distinct islands were found showing a height of about 50 nm with flat surfaces and diameters of about 100 nm. In addition, islands with diameters of several hundred nanometers and a thickness of only 10 nm were observed between the tall islands. This suggests that the area between the islands, which was observed by AFM, is not bare SiC but Al$_x$Ga$_{1-x}$N. Moreover, it can be seen that the edges of both types of islands are step-shaped and consist of a combination of {11$ar{2}$2} and {01$ar{1}$0} facets. At first glance the thicker islands appear to have been formed on top of the thinner ones. However, trenches separating the thicker and the thinner islands, which were occasionally found, suggest that both were formed simultaneously upon nucleation. This is in contrast to the interpretation given by Vennegués et al. [4], namely that islands consisting of almost pure
AlN play the role of a wetting layer on the SiC, and that Al-deficient islands form subsequently on top of this layer.

EDS mappings of the nominally 20 nm thick layer were taken in cross-section using the intensity of the GaK$_\alpha$ and AlK$_\alpha$ signals from an area covering the edge of a thick island and a part of a thin island. The results are shown in Fig. 4. The GaK$_\alpha$ signal is significantly stronger in the thick island whereas, the AlK$_\alpha$ signal (which is not shown in Fig. 4) is stronger in the thin island. Quantitative EDS point analyses reveal Al mole fractions in the thin islands to be 0.15 to 0.18 ± 0.01, compared to a value of about 0.035 ± 0.010 in the thick ones. These results also suggest the formation of at least two different Al$_x$Ga$_{1-x}$N phases upon nucleation and confirm the results obtained by XRD. The EDS measurements may not be representative of the entire film; thus, the value of $x = 0.1$ determined by XRD could still be the average Al mole fraction of the Al-deficient phase. It is assumed that the trench formation, as observed by AFM, is related to the phase separation occurring during the early stage of film growth. Further evolution of the growing film with time was evaluated from the TEM cross-section images shown in Fig. 5 of the nominally 100 nm thick Al$_x$Ga$_{1-x}$N film. The bright field image in Fig. 5(a) confirms that the nominal and the actual layer thickness are almost the same. The film surface is mostly smooth; however, occasionally trenches can be observed. An EDS elemental mapping of the AlK$_\alpha$ intensity shown in Fig. 5(b), reveals strong fluctuations of the Al content at the interface between the layer and the substrate, which is consistent with the afore mentioned thinner Al$_x$Ga$_{1-x}$N layer. Interestingly, a second layer of Al-rich domains is found close to the surface. It is laterally shifted with respect to the first layer of Al-rich regions at the interface, i.e. the Al-rich domains in the second layer are on top of the Al-deficient domains in the first layer and vice versa. From this it is concluded
that there is a driving force for phase separation in the Al\textsubscript{x}Ga\textsubscript{1-x}N film even after the SiC substrate is already completely wetted. Since the trench density, as observed by AFM, was by an order of magnitude lower in this film compared to the thinner ones, few of them were observable in the TEM specimen. From the TEM results it is difficult to clarify how their formation is related to the phase separation.

Figure 6(a) shows a TEM cross-section dark field image of the 1 µm thick Al\textsubscript{x}Ga\textsubscript{1-x}N layer recorded with an annular dark field detector, which provides a Z-contrast image. A bright region of about 100 nm thickness can be observed at the interface between the film and the substrate which corresponds to the Al-rich regions found already in the thinner samples. An EDS-mapping using the intensity of the AlK\textsubscript{α} line is presented in Fig. 6(b). Two layers of Al-rich domains that are laterally shifted with respect to each other can be observed near the substrate. Beyond these layers the Al mole fraction approaches a constant value equal to the nominal value of 0.15 ± 0.01, as confirmed by quantitative EDS point measurements. The microstructure of the films was further studied using TEM plan view images taken from the nominally 20 nm and the 60 nm thick Al\textsubscript{x}Ga\textsubscript{1-x}N films. Corresponding bright field images are shown in Figs. 7(a) and 7(b), respectively. The overlap of the corresponding lattice images leads to the formation of a Moiré pattern due to the mismatch of the in-plane lattice parameters between the SiC substrate and the Al\textsubscript{x}Ga\textsubscript{1-x}N film. Areas of different Moiré lattice parameters can be distinguished indicating a spatial variation of the Al\textsubscript{x}Ga\textsubscript{1-x}N lattice parameter and thus its compositional inhomogeneity. The spatial variation of the Moiré lattice parameter is also observable in the Fast Fourier Transformed (FFT) of the two images shown as inserts in the respective images. An evaluation of the FFT was performed by taking a line-scan through two opposing first order reflections for both the
nominally 20 nm and the 60 nm film the results of which are displayed in Fig. 8. Clearly observable are the narrow -1st and 1st order peaks of the FFT for the nominally 20 nm thick film which suggests a reasonable spatial homogeneity of the Al$_x$Ga$_{1-x}$N in-plane lattice parameter. However, this is only due to the fact that the thin Al-rich islands contribute weakly to the Moiré fringe formation in comparison to the thicker Al-deficient islands. For the nominally 60 nm thick film, the corresponding peaks of the FFT are broadened towards lower reciprocal distances, which can be attributed to an increasing contribution of a phase of higher Al content. Considering a small twist angle $\alpha$ around the $c$-axes of Al$_x$Ga$_{1-x}$N and SiC the Moiré lattice parameter, $\Lambda$ is given by [13]

$$\Lambda = \frac{\sqrt{3}}{2} \frac{a_{Al_{x}Ga_{1-x}N}a_{SiC}}{\sqrt{a_{Al_{x}Ga_{1-x}N}^2 + a_{SiC}^2 - 2a_{Al_{x}Ga_{1-x}N}a_{SiC} \cos(\alpha)}}$$

(1)

with $a_{SiC}$ and $a_{Al_{x}Ga_{1-x}N}$ being the basal plane lattice parameters of the SiC and the Al$_x$Ga$_{1-x}$N, respectively. The relation $d_{01\overline{1}0} = \sqrt{3}/2 \times a$ between the (01 $\overline{1}$ 0) lattice plane distance and the respective lattice parameter was used. For the nominally 20 nm thick film, with the two phases of different Al mole fraction being still laterally separated from each other, it can be assumed that all the Al$_x$Ga$_{1-x}$N is fully relaxed such that its $a$-lattice parameter follows Vegard's law:

$$a_{Al_{x}Ga_{1-x}N} = xa_{AlN} + (1-x)a_{GaN}.$$  (2)
Here, $a_{\text{AlN}}$ and $a_{\text{GaN}}$ are the lattice parameters of unstrained AlN and GaN, respectively.

Inserting Eq. (2) into Eq. (1) enables the determination of the dependence of $\Lambda$ on $x$ as shown in Fig. 9 using $a_{\text{SiC}} = 0.3081$ nm, $a_{\text{GaN}} = 0.3188$ nm and $a_{\text{AlN}} = 0.3112$ nm [10] and varying $\alpha$ between 1.5° and 2.5°. If a zero twist angle was assumed between layer and substrate the resulting Moiré-lattice parameters would be larger than 7.3 nm, which is far above the experimentally observed values of 5.0 to 6.0 nm. Indeed, the angular variation of Moiré fringes in Fig. 7 indicates a rotational variation of the fringes. The twist appears to be a function of the Al mole fraction since a constant twist angle value does not reproduce the experimentally observed Al mole fractions of 0.035 to 0.25. It is suggested that the twist angle increases with decreasing Al mole fraction of the islands, i.e. with increasing mismatch between the layer and the substrate. A twist of 1.89° results in a Moiré lattice parameter value $\Lambda = 6.0$ nm for the maximum observed Al mole fraction of 0.25. Similarly, a twist angle of 2.33° fits to $\Lambda = 5.0$ nm and $x = 0.035$. From this it can be deduces that the Al$_x$Ga$_{1-x}$N layer does not only nucleate in at least two different phases of high and low Al mole fraction but shows furthermore a rotational misorientation of 1.89° to 2.33° to the substrate depending on the Al mole fraction.

4.5 DISCUSSION

As was shown in the previous section, the inhomogeneous distribution of Al in the Al$_x$Ga$_{1-x}$N layer close to the SiC substrate consists of Al-rich domains embedded in an Al-deficient matrix. The Al-rich domains are vertically anticorrelated, i.e., Al-rich domains are located on top of Al-deficient domains and vice versa. These observations raise the question whether the formation of this structure is due to elastic strain. From the epitaxial growth of
stacked layers of self-assembled quantum dots or quantum wires it is known that either vertical correlation or anticorrelation of the strained quantum structures can result in a minimization of the total strain energy depending on the elastic anisotropy of the material, the growth direction and the thickness of the spacer layer [14-19]. Although there is only limited data available on correlation effects in (0001)-oriented group-III nitride heterostructures, preliminary theoretical investigations predict vertical correlation rather than anticorrelation [20-22].

To investigate correlation effects in more detail, FE simulations were performed for an Al$_x$Ga$_{1-x}$N layer exhibiting phases of different Al mole fractions. The assumed simplified model structure consists of two layers of Al-rich cylinders embedded in an Al-deficient matrix, as shown in Fig. 10. The cylinder had a hexagonal base with an edge length $a = 125$ nm, and a height $h = 35$ nm. They were laterally arranged in a hexagonal pattern. The two layers of Al-rich cylinders were separated by an Al-deficient spacer layer. When the Al-rich cylinders of the top layer were directly above those in the lower layer, we had a correlated arrangement (see Fig. 10b). In contrast, when the Al-rich cylinders in the upper layer were displaced laterally, so that, when viewed from the top, they were directly above one of the six hexagonal Al-deficient spaces surrounding the Al-rich cylinder in the lower layer, we had an anticorrelated arrangement. From symmetry arguments, the resultant strain energy is independent of which of the possible six overlaps we construct for the anticorrelation arrangement. For the strain energy calculation of the systems only a small unit FE, indicated in Fig. 10(a) and 10(b) was considered since a sample of any arbitrary size can be iterated from the unit FE by reflection symmetry. The reflection symmetry directly leads to the fixed boundary condition for the lateral edges of the unit FE in the actual simulation. Similar FE
simulations have been performed and produced reasonable results for other heterostructures [23, 24]. In the present investigation, without loss of accuracy, it is assumed that Al\textsubscript{x}Ga\textsubscript{1-x}N has the elasticity moduli of GaN [25]. The strain and strain energy arise due to the lattice constants mismatch between the Al-rich phase and the Al-deficient matrix. For the intended comparison of the strain energies of the correlated and anticorrelated arrangement, it seems reasonable to neglect the added complication of the presence of the SiC substrate. One could also consider a different anticorrelation arrangement. That is, the Al-rich cylinder in the upper layer in Fig. 10(b) can take a centered position between the Al-rich cylinders of the lower layer, i.e., the upper Al-rich cylinder partially overlaps the lower Al-rich cylinders. This would make the unit FE somewhat more complicated. Again for the purpose of comparing qualitatively strain energies from the correlated and anticorrelated arrangements, such added complexities seem unwarranted. For a spacer layer thickness between \( h/3 \) and \( 5h \) it was found that the strain energy of the correlated arrangement is smaller than the strain energy of the anticorrelated arrangement, as shown in Fig 11. Therefore, the arrangement of the phases in Al\textsubscript{x}Ga\textsubscript{1-x}N cannot be purely strain-driven, as the experimentally observed anticorrelation contradicts the minimization of the strain energy.

Based on the experimental and theoretical results presented above the following model is proposed for the process of nucleation, growth, and coalescence of Al\textsubscript{x}Ga\textsubscript{1-x}N films on 6H-SiC(0001). A schematic of this model is depicted in Fig. 12. The initial stage of the Al\textsubscript{x}Ga\textsubscript{1-x}N deposition on 6H-SiC(0001) is characterized by the simultaneous formation of Al-rich and Al-deficient islands (Fig. 12a). This process is probably driven by a combination of strain minimization in the Al\textsubscript{x}Ga\textsubscript{1-x}N layer on the SiC substrate and growth related kinetic effects due to the difference in surface diffusivity of Ga and Al. Thermodynamic
considerations favor the formation of a homogenous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer rather than phase separation. However, since the surface of the SiC substrate is not atomically flat but exhibits steps and kinks, it is likely that Al-deficient nuclei form at these energetically favored sites. The III/V precursor ratio was also fairly low at the initiation of growth of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ since it was ramped to its final value within the first 30 s of growth. This procedure may have also promoted the initial phase separation. The Al-rich islands grow much more rapidly in the lateral direction than in the normal direction, due to their better wetting with respect to the SiC substrate. The simultaneously formed Al-deficient islands have a smaller growth rate in the lateral direction compared to the Al-rich islands but grow much faster in the normal direction. As a result, thin Al-rich and thick Al-deficient islands form, as shown in Fig.12a. Trenches should evolve during this stage of growth when two islands of different Al mole fraction meet. They are slowly filled during further growth and gradually vanish after the coalescence of the film.

Upon coalescence (Fig. 12b) the growth mode changes and the Al-deficient islands begin to overgrow the Al-rich islands due to their larger lateral growth rate compared to the normal growth rate of the Al-rich islands. The Al-deficient islands cover most of the surface when they reach a film thickness of about 50 to 60 nm, as shown in Fig. 12(c). Due to strain minimization Al adatoms on the surface are most favorably incorporated at the Al-rich islands which surface, however decreases with further growth. Considering the smaller surface diffusion length of the Al adatoms compared to Ga [7] only the Al adatoms close to the remaining oben surface of the Al-rich islands are incorporated in these islands while the Al adatoms further away form the openings form a second layer of Al-rich nuclei on top of the Al-deficient islands. This process leads to the formation of a second layer of Al-rich
domains, which is laterally shifted against the first layer close to the film/substrate interface. The resulting Al-rich islands are subsequently overgrown laterally by the surrounding Al-deficient islands. The film composition becomes homogeneous as the film coalesces, and the driving force for inhomogeneous growth vanishes, as illustrated in Fig. 12(d).

4.6 SUMMARY

The growth of Al$_x$Ga$_{1-x}$N on 6H-SiC(0001) substrates was investigated in detail using atomic force microscopy, X-ray diffraction and transmission electron microscopy in conjunction with finite element simulations. An inhomogeneous Al distribution was found in the film at the substrate interface. This phenomenon is attributed to the presence of strain at the initial growth stage at which Al-rich and Al-deficient islands of different morphology are formed. The phase separation leads to the formation of trenches during coalescence of the film. Further growth results in the formation of a layer of Al-rich and Al-deficient domains, which are laterally shifted with respect to the interfacial layer below. This effect is attributed to the growth kinetics before the film develops a smooth surface. Both the fluctuations in the Al mole fraction and the trenches disappear at a film thickness of more than 100 nm. In conclusion, the microstructural and compositional evolution during the early stage of film growth strongly depends on the presence of strain as well as on the growth kinetics.
4.7 REFERENCES


    82, 367 (2003).
4.8 FIGURES

**Figure 1** 2 x 2 μm AFM surface images of Al$_x$Ga$_{1-x}$N layers grown on 6H-SiC (0001) substrates. The nominal layer thicknesses were 20 nm (a), 60 nm (b), 100 nm (c) and 1000 nm (d), respectively. The grayscale from black to white corresponds to a variation in height of 150 nm (a), 50 nm (b), 10 nm (c) and 3 nm (d), respectively. The insert in (b) is a phase contrast image of the area indicated by the dashed square showing secondary nucleation.
Figure 2 Reciprocal space map of a nominally 100 nm thick AlGaN film on 6H-SiC (0001).

Two peaks are found for the (10\bar{1}5) reflection of the Al$_x$Ga$_{1-x}$N, which are marked by filled circles. They correspond to aluminum mole fractions of 0.10 and 0.18, respectively, as derived from the theoretical peak positions of strain-free Al$_x$Ga$_{1-x}$N (solid line) and the relaxation lines of Al$_x$Ga$_{1-x}$N under biaxial stress in the c-plane (dotted lines). The peak position of the SiC (10\bar{1}15) reflection, which is beyond the range of the figure, is marked by an arrow on the $q_x$ axis.
Figure 3 Cross section TEM image of the nominally 20 nm thick Al$_x$Ga$_{1-x}$N film. The image was taken along the [01\bar{1}0] zone axis and shows a trench between a thinner and a thicker island. The insert is a magnification of the area indicated by the black rectangle in the image.
Figure 4  EDS analysis of the nominally 20 nm thick Al$_x$Ga$_{1-x}$N film. (a) The STEM image of the mapped region. The grayish areas overlapping the image are caused by electron beam induced contamination. (b) GaK$\alpha$ mapping. (c) A line scan of the GaK$\alpha$ signal intensity taken along the line indicated by an arrow in (a).
**Figure 5** (a) Bright field TEM cross-section image of the nominally 100 nm thick $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film. (b) EDS mapping of the AlK$\alpha$ intensity of the region shown in (a).
Figure 6  (a) Dark field STEM image of a nominally 1 µm thick Al$_x$Ga$_{1-x}$N film. (b) EDS mapping of the AlKα intensity in the same region.
Figure 7  Plan-view TEM bright field images of nominally (a) 20 nm and (b) 60 nm thick Al$_x$Ga$_{1-x}$N films on 6H-SiC(0001) showing Moiré patterns formed due to the lattice mismatch between the film and the substrate. Inserts show the FFT of the respective images.
Figure 8  (a) Line scans crossing the first order reflections of the FFT patterns obtained from the plan view TEM images of the nominally 20 and 60 nm thick Al$_x$Ga$_{1-x}$N films.
Figure 9  Moiré lattice parameter calculated from Eqn. 1 as a function of Al mole fraction for varying twist angles. The plotted points represent the experimentally observed Al mole fractions of 0.035 and 0.25.
Figure 10 Geometrical arrangement of Al-rich domains assumed for finite element simulations. (a) In-plane arrangement in a single layer of the two domains. (b) Cross-section of two layers separated by a spacer layer for vertical correlation and anticorrelation of the Al-rich domains.
Figure 11  Total strain energy as determined from FE simulations for the vertically correlated (filled circles) and anticorrelated (open circles) arrangement of Al-rich domains in an Al-poor matrix as a function of the spacer layer thickness. The latter is given in units of the height, $h$, of the Al-rich domains.
Figure 12  Schematic of the proposed model for the film evolution during the early stage of growth of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on SiC as discussed in the text. The gray levels represent the Al content with darker areas corresponding to higher Al mole fractions. The solid and light arrows indicate the growth of Al-poor and Al-rich domains, respectively. Their length symbolizes the relative growth rates.
5. Surface and defect microstructure of GaN and AlN on hydrogen-etched 6H-SiC(0001) substrates

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5.1 ABSTRACT

Hydrogen etching of 6H-SiC(0001) substrates removed mechanical polishing damage and produced an array of parallel, unit cell high steps. The initial stage of AlN deposition on these etched substrates occurred via island nucleation both at the step edges and on the terraces. Coalesced AlN films on these substrates lacked the scratch-induced undulations present on the surface of the AlN films grown on as-received substrates and had a lower density of pits. The majority of the threading dislocations observed in the AlN were $a$ type and jagged networks of misfit dislocations were observed over terraces on the hydrogen-etched SiC surface for 15 nm thick AlN layers. GaN initially grew in the Stanski-Krastanov growth mode on 100 nm AlN layers for each substrate type. The GaN islands nucleated primarily in the undulations of the AlN and at hillocks on the AlN surface on the as-received and hydrogen-etched substrates, respectively. Complete coalescence of these islands occurred at thicknesses near 20 nm, and the subsequently deposited film grew via dislocation-mediated step-flow. Strain measurements indicated a more relaxed compressive strain in the GaN film on the hydrogen-etched substrate as a result of the smoother AlN buffer layer and more rapid plastic relaxation of the film. On- and off-axis X-ray rocking curves revealed statistically similar full width at half maximum values for both on- and off-axis reflections, indicative of similar densities of threading dislocations in the two films. This was supported by TEM analysis which indicated a reduction in dislocation density from 3.5- to 1.4x10$^9$ cm$^{-2}$ for 1000 nm thick GaN layers on AlN/hydrogen-etched-SiC substrates. The majority of the TDs in the GaN epi-layer resulted from a continuation of the TDs in the AlN layer.
5.2 INTRODUCTION

The Si-terminated basal plane of the 6H-polytype of silicon carbide (6H-SiC(0001)) has been investigated by several groups [1,2,3] as a substrate surface for heteroepitaxial growth of [0001]-oriented AlN and GaN due to the moderate mismatches in the atomic distances along the [11\bar{2}0] direction (-1.0% and -3.5%, respectively) and in the corresponding coefficients of thermal expansion. This substrate also has a thermal conductivity along [0001] of 4.9 W/cm K [4] at room temperature and can be cleaved along [11\bar{2}0]. The former property is believed to contribute to the improved performance of III-Nitride-based ultraviolet light emitting diodes [5] and heterojunction field effect transistors [6,7] deposited on SiC compared to similar devices on sapphire, as the films from which these devices are fabricated contain similar densities of threading dislocations after growth on both substrates. However, despite the apparent benefits of SiC substrates, GaN films deposited on AlN or related intermediate layers previously grown thereon have yet to demonstrate less defective microstructures than films of comparable thickness on sapphire. One reason proposed for this is the damaged surface of as-received SiC wafers as a result of slicing from the boule, lapping and polishing. As shown in the atomic force microscopy (AFM) image Fig. 1, the surfaces of SiC(0001) substrates feature numerous randomly oriented scratches due to mechanical polishing, with widths from 100-800 nm and depths to 12 nm. Scratches are commonly observed on as-received SiC wafers since the mechanical hardness and chemical inertness of this material makes polishing difficult [8]. The polishing process can result in damage extending to a micron beneath the surface [9], and even with a highly optimized polishing process, sub-surface damage extends up to 8 nm in the regions of the scratches [10]. Several researchers working on homoepitaxial growth of SiC have observed locally
higher densities of edge and screw threading dislocations (TDs) \([11,12]\), film surface defects \([13]\) and inclusions believed to correspond to the 3C polytype \([14]\) in the areas of the film directly over a polishing scratch or damaged surface region of the substrate. In an effort to improve the surface of SiC substrates, investigators have reported techniques for chemomechanical polishing \([15]\), oxidation and subsequent oxide removal \([16]\), sublimation etching \([17]\) and various gaseous etchants including \(\text{H}_2\), \(\text{H}_2+\text{hydrocarbon (C}_2\text{H}_4 \text{ or C}_3\text{H}_8\) and \(\text{H}_2+\text{HCl}\) \([18]\). Of these processes, etching in \(\text{H}_2\) is perhaps the most intriguing since it involves relatively simple equipment and could theoretically be incorporated into the growth system for homoepitaxial SiC or heteroepitaxial III-Nitrides.

Hydrogen etching of SiC was first reported by Chu and Campbell in 1965 \([19]\). Since that time other researchers have used thermodynamic calculations to predict that the reaction pathway for hydrogen etching proceeds by the dissociation of SiC into liquid silicon, which evaporates, and solid carbon, which reacts with atomic hydrogen to form hydrocarbons \([20,21]\). Owman et al. \([17]\) showed that hydrogen etching of on-axis 6H-SiC(0001) resulted in an array of regular straight terraces separated by steps with a height equal to the 6H unit cell (15.12Å). These steps were subsequently shown to occur in the \(<\overline{1}00>\) directions, with etching proceeding in an inverse step-flow mechanism \([22]\). Etching in \(\text{HCl}/\text{H}_2\) results in similar stepped surfaces \([23]\). The use of \(\text{H}_2\) \([13,24]\) or \(\text{HCl}/\text{H}_2\) \([13]\) etching prior to homoepitaxial SiC growth results in reduced defect density and smoother film surfaces.

In addition to the benefits of removing substrate surface damage, it has been predicted that the formation of unit cell height steps on 6H-SiC wafers will reduce the density of two dimensional threading defects in heteroepitaxial III-Nitrides. As-received SiC wafers feature surface steps with random heights and orientations, resulting in terraces terminated with
different bilayers of the …ABCA’C’B’… 6H(0001) stacking sequence [17]. In the
deposition of III-Nitrides with the 2H structure on this surface, the stacking sequence of
islands growing on adjoining substrate terraces is determined by the stacking of the
underlying SiC. Therefore, when two islands coalesce across a surface bilayer step, a two
dimensional threading defect known as a stacking mismatch boundary (SMB) can result
[25,26]. For example, for two SiC terraces terminated with …ABC and …BCA stacking and
separated by a bilayer step, the resulting III-Nitride islands would have the stacking
sequences of BCBC… and CACA… respectively, resulting in a SMB at their coalescence
front, since the “B” and “A” bilayers will not align. These SMBs have been predicted to be
bounded by stacking faults and/or dislocations parallel to the surface, and calculations
indicate that they may possess states in the bandgap corresponding to the commonly
observed yellow luminescence of GaN [27]. Hydrogen etching of 6H-SiC results in unit cell
height steps separated by terraces of the same stacking termination [28]. Therefore, since the
2H III-nitrides have a stacking sequence that is an integral multiple of the 6H-SiC substrate,
islands which coalesce across a unit cell height step will have the same stacking sequence
and SMBs will be eliminated.

The growth of AlN on H2- or HCl/H2-etched SiC has been studied by several groups.
Using high resolution transmission electron microscopy (TEM), Torres et al. [28] observed a
very disordered AlN/SiC interface with as-received SiC substrates and a smooth interface
devoid of SMBs when using H2-etched substrates. The latter films also demonstrated a
higher degree of crystalline order, as evidenced by Rutherford backscattering spectroscopy.
Cross sectional TEM has also demonstrated reduced contrast attributed to defects in AlN
films deposited on HCl/H2-etched SiC [29]. Other studies [30,31] have shown reduced X-ray
rocking curve full-width half-maximum (FWHM) values for AlN on H₂- or HCl/H₂-etched SiC.

GaN deposition on H₂- or HCl/H₂-etched SiC has not been examined as thoroughly as AlN deposition. Lantier et al. [32] reported lower X-ray rocking curve FWHM for GaN with an AlN buffer layer on H₂-etched SiC but cross sectional TEM showed approximately equal densities of edge and screw threading dislocations. Plan view TEM was not performed to confirm the dislocation densities. In addition, photoluminescence spectra at 10K showed similar features and linewidths, irrespective of substrate preparation. Xie et al. [33,34] deposited GaN films with high temperature AlN and low temperature GaN buffer layers on 6H-SiC substrates etched with H₂, H₂/C₂H₄, and H₂/HCl. They observed fewer pinholes, smoother surfaces, and decreased X-ray rocking curve FWHM values for films on gas-etched substrates. However, the gas-etched substrates lacked unit cell height steps due to the relatively low etching temperature employed in the studies (≤1500°C).

It has not been conclusively determined in any of the aforementioned studies whether H₂-etching of 6H-SiC substrates improves the microstructure of subsequently deposited III-Nitride films. Although X-ray rocking curves and cross sectional TEM can provide some indication, these techniques do not give absolute numbers for dislocation density in the film and their comparison has given conflicting conclusions regarding the growth of GaN on H₂-etched SiC substrates [32]. The current research focuses on the deposition of AlN films and GaN films, the latter on AlN buffer layers, on H₂-etched SiC substrates with the goals of ascertaining: 1) the surface microstructure and growth mode of AlN and GaN/AlN as observed with AFM, 2) the film strain and dislocation-induced rocking curve broadening of
GaN as determined by high resolution x-ray diffraction (HRXRD), and 3) the defect microstructure of AlN and GaN/AlN as observed by cross sectional and plan view TEM.

5.3 EXPERIMENTAL PROCEDURES

To minimize the effects of substrate variability, all films investigated in this research were deposited simultaneously on a hydrogen etched section and on an as-received, conventionally polished section acquired prior to etching from the same Si-terminated 6H-SiC(0001) wafer. Prior to etching, the on-axis, n-type 6H-SiC(0001) wafers were dipped in a HF:H₂O (1:10) solution for ten minutes at room temperature to remove the native oxide layer, rinsed in deionized water and blown dry with nitrogen. The hydrogen etching chamber was a vertical, cold-walled, resistively heated quartz system which was evacuated to <0.1 Torr prior to etching. The temperature of the tungsten sample platter was monitored using a single wavelength optical pyrometer. Samples were heated to the etching temperature of 1625°C in a dynamic 25% hydrogen/75% helium mixture having a flow rate of 1 slm. All samples were etched in 8 slm of the aforementioned mixture for 20 minutes at atmospheric pressure and rapidly cooled while maintaining the gas flow. The etching rate under these conditions was approximately 1 µm/hr. The substrates were then removed from the chamber and analyzed via AFM prior to film deposition.

Immediately prior to deposition, each substrate was etched in the aforementioned HF:H₂O solution for ten minutes at room temperature to remove native oxide and surface contaminants and dried in flowing nitrogen. AlN layers were subsequently grown on each substrate type via metalorganic vapor phase epitaxy (MOVPE) at 1100°C and 20 Torr total pressure. The GaN films were grown at the same total pressure on 100 nm thick AlN buffer
layers after cooling to 1020°C over a period of five minutes. The MOVPE reactor was a cold-walled vertical pancake-style system which was evacuated to 10⁻⁶ Torr prior to growth. The temperature of the SiC-coated graphite platter was measured using a single wavelength optical pyrometer. Trimethylaluminum (TMA), triethylgallium, (TEG) and ammonia were used as the precursors; hydrogen was used as both the carrier and the diluent. The V/III ratio employed in the growth of AlN was 24,400, with a corresponding growth rate of 0.3 µm/hr. GaN films were grown with a V/III ratio of 1,300, resulting in a growth rate of 1.8 µm/hr. All quoted film thicknesses are nominal values based on these established growth rates.

The surface microstructures of the heteroepitaxial films were determined using a Digital Instruments D3000 AFM equipped with a Si cantilever and tip operating in the tapping mode. HRXRD was conducted using a Philips X’Pert Materials Research Diffractometer equipped with a copper x-ray source, fourfold Ge(220) monochromater, threefold Ge(220) analyzer and an Eulerian cradle. On-axis and off-axis rocking curves (ω-scans) were acquired for the GaN and SiC. The latter scans were obtained using the skew geometry accomplished by tilting the sample to the relative inclination angle of the crystallographic plane of interest. The c- and a-axis lattice parameters of the 1 µm GaN films were determined using triple axis ω-2θ scans on the (0002) and (5220) reflections, respectively. The errors in the instrument zero angle and the refraction of the X-rays were corrected using the method of Fewster et al. [35]. Cross-sectional samples for TEM were prepared using the standard ‘sandwich’ technique followed by dimpling and ion milling until electron transparency. Plan-view samples were prepared by cutting 3 mm discs from SiC substrates. These discs were then ground, dimpled and ion milled from the SiC side to obtain electron transparency. Structural analysis of the epitaxial layers was preformed in cross-
section and plan view on a JEM-4000EX microscope operating at 400 kV that has an interpretable resolution of 0.16 nm.

5.4 RESULTS AND DISCUSSION

5.4.1 SURFACE MICROSTRUCTURE AND GROWTH MODE OF AlN ON HE-SiC

Representative micrographs of the surfaces of as-received and H₂-etched SiC substrates (hereafter referred to as AR-SiC and HE-SiC, respectively) and AlN films with nominal thicknesses of 15 and 100 nm deposited on each type of substrate are shown in the AFM images of Fig. 2. A polishing scratch is again evident in the AR-SiC substrate, as shown in Fig. 2(a). However, as shown in Fig. 2(d), the hydrogen-etching process has removed all visible traces of polishing damage on the surface, leaving an array of parallel steps and terraces. The steps, as measured by AFM, are ≈15Å high in the c-direction, corresponding to the height of the 6H-SiC unit cell. The terraces of the representative surface shown in Fig. 2(d) are approximately 380 nm wide. However, the terrace width varies from sample to sample based on the degree of unintentional miscut of the substrate [22]. The contrast visible on the terraces by AFM has been attributed to adsorbed oxide and hydrocarbon contaminants, as evidenced by scanning tunneling microscopy studies [36]. This contamination was subsequently removed by heating to 1100°C in flowing hydrogen prior to growth [37]. Other investigators [24,38] have observed silicon droplets on the surface of SiC heated in hydrogen above the melting point of silicon, reportedly due to the relatively large etch rate of SiC and the relatively low vapor pressure of silicon at these temperatures. Silicon droplet formation was suppressed [24,38] by the addition of a hydrocarbon to the gas stream while etching, thus providing a source of carbon and
decreasing the etching rate of SiC. Silicon droplets were not observed on the surface of any of our samples despite the lack of hydrocarbon flow. The use of an uncoated graphite heater likely resulted in sufficient hydrocarbon partial pressure to suppress the etch rate and thereby prevent the formation of silicon droplets.

Additional details and discussion of the growth and microstructure of our AlN films on AR-SiC can be found elsewhere [39] but selected micrographs are reproduced here for comparison purposes. In general, as shown in Fig. 2(b) and (c), AlN deposited on AR-SiC initially grows in the form of flat-topped islands which eventually coalesce resulting in dislocation-mediated step-flow growth. The surfaces of AlN on AR-SiC also contain small pits with a density of $7 \times 10^8$ cm$^{-2}$ and undulations as a result of the polishing scratches in the AR-SiC substrate. One of these undulations is denoted by the arrows in Fig. 2(b). The undulations are manifest in the 100 nm thick AlN film, and one is shown running from the lower left to the upper right corner of Fig. 2(c). For the latter film, the undulations are approximately 4 nm deep.

The nominally 15 nm thick AlN layer on the HE-SiC substrate shown in Fig. 2(e) shows some similarity to the layer on AR-SiC. Specifically, at this thickness, the layer is composed of partially coalesced islands with random shapes and orientations, i.e. the sides of the islands do not appear to coincide with any specific crystallographic facet. The islands are of comparable size and density to those on AR-SiC. Observations of single AFM scan lines suggested that the islands have flat tops. However, the exact cross sectional shape of the islands is difficult to determine since the 10 nm radius of the AFM tip is comparable in size to the lateral size of the islands. The step edges of the HE-SiC substrate remain clearly evident in the 15 nm AlN layer and are denoted by arrows in Fig. 2(e). As shown in the
image, the islands have formed a continuous string along the HE-SiC steps due to the large binding energy and hence decreased rate of adatom desorption at these sites. However, since the islands are not yet fully coalesced, it is clear that the relatively large terrace width and low surface mobility of the Al species at this temperature [40] has resulted in nucleation both at the step and on the terrace. The 100 nm thick AlN film shown in Fig. 2(f) is fully coalesced and growing in the dislocation-mediated step-flow mode commonly observed for III-Nitrides. However, there are relatively few step terminations in this film, indicative of a low density of threading dislocations with screw or mixed character [41]. The undulations observed in AlN on the AR-SiC substrate are absent in the 100 nm film on the HE-SiC substrate and the pit density has decreased to \(<1\times10^8\) cm\(^{-2}\).

The evolution of the root mean square (RMS) surface roughness of the AlN layers, as well as the GaN layers that will be discussed in section 3.3, on AR-SiC and HE-SiC substrates is shown in Fig. 3. The plotted points and error bars represent the average and range, respectively, which was observed from measurements at multiple locations on multiple samples. As shown in the figure, the hydrogen-etching process reduces the RMS roughness of the substrate by nearly a factor of three. However, the similar microstructure of the AlN islands in the 15 nm layers deposited on both substrates results in the same surface roughness independent of substrate preparation. Growth of the 100 nm thick AlN films on the AR- and the HE-SiC substrates resulted in both a smoother average roughness (0.16 vs. 0.59 nm) and a more uniform surface in the latter, as evidenced by the difference in the error bars. This uniformity is attributed to the absence of undulations and the reduced pit density of the AlN film on the HE-SiC substrates.
5.4.2 DEFECT MICROSTRUCTURE OF AlN ON HE-SiC

Figure 4 shows a cross-sectional TEM from a 15nm AlN/HE-SiC heterostructure. The islands are flat-topped and have grown laterally and vertically to form an almost continuous film. It appears that the lateral growth rate is considerably higher than the vertical rate, probably 4:1. The operating reflection in Fig. 4 is (0002). For this reflection, all $a$ type dislocations should be out of contrast, but $c$ and $c+a$ dislocations should be in contrast. Therefore, we infer that the majority of TDs are of $a$ type.

Figure 5 shows a weak-beam, dark-field plan-view (WBDF) TEM image of a 100nm AlN layer exhibiting steps along a $<\bar{1}00>$ direction defined by misfit dislocations and terraces containing networks of misfit dislocations. As argued in a companion paper [39], three sets of perfect $a$ type edge dislocations should best accommodate the mismatch between AlN and SiC. Since the operating reflection is $(\bar{1}2\bar{1}0)$, all the $a$ type dislocations should be in contrast. It is clear from fig. 5 that the alignment of misfit dislocations along the three $<\bar{1}00>$ directions is not perfect and the dislocations are highly jagged. This could stem from the projection of TDs in AlN on the plane of the micrograph and the inherent roughness of HE-SiC surface. In addition, some of the misfit dislocations go from one terrace to another across steps.

Figure 6(a) and (b) shows WBDF cross-sectional images of a 100nm AlN layer with operating reflections of $(1\bar{1}20)$ and (0002) respectively. Comparing Figs. 6(a) and 6(b), we can infer that the majority of TDs in AlN are of $a$ type. Furthermore, the density of defects and TDs is very high in Fig. 6(a). The density of TDs decreases as the layer thickens.
5.4.3 SURFACE MICROSTRUCTURE AND GROWTH MODE OF GaN ON AlN/HE-SiC

Representative micrographs of GaN of varying thickness deposited on 100 nm AlN buffer layers on both AR-SiC and HE-SiC substrates are shown in the AFM height images in Fig. 7. Additional details of the growth, microstructure, and strain of our GaN layers on AR-SiC substrates can be found in Refs. 39 and 42. As with the AlN layers, selected micrographs are reproduced here to make the comparison between films deposited on the two substrates. GaN layers grow in the Stransi-Krastanov (S-K) mode on 100 nm AlN buffer layers on AR-SiC substrates, with an initial 2-D wetting layer followed by the strain-induced formation of GaN islands between 1 nm and 1.5 nm of growth. The majority of the islands observed at these initial stages of growth occur in straight lines corresponding to the scratch-induced undulations in the AlN surface, as shown in the lower left of Fig. 7(a) for a nominal GaN thickness of 2 nm. Clusters of extended defects in the AlN buffer layers have been shown to serve as sites for the initial nucleation of GaN [43,44]. It is expected that the undulations in the AlN on the AR-SiC contain locally higher defect densities as a result of the damaged SiC surface in these regions. These defects, in turn, cause the preferential growth of the GaN islands in these undulations. Islands are also found along step edges, as shown by the arrows in Fig. 7(a), but in a lower density. The islands coalesce at thicknesses near 20 nm, as shown in Fig. 7(b). The growth mode changes in the range of GaN thickness between 50 nm and 100 nm from the thermodynamically-controlled S-K mode to the kinetically-controlled dislocation mediated step-flow growth mode observed in Fig. 7(c).

The lack of undulations in the 100 nm AlN film on HE-SiC, as shown in Fig. 2(f), necessitates the nucleation of GaN at other surface features. As shown in Fig. 7(d), three clusters of islands have formed in the nominally 2 nm thick GaN layer. Inspection of the
surface steps surrounding these islands reveals that the islands form in the area of spiral hillocks on the AlN surface. This is supported by Fig. 7(g)-(i) which show other areas of the nominally 2 nm thick GaN layer with 0, 1, and 2 spiral hillocks, respectively. In the last two images, GaN islands have formed at or near the top of the hillock and are not observed on the terraces surrounding the hillock. The hillocks are formed from the interaction between homogeneous steps, which result from the miscut of the surface, and heterogeneous steps, which remain pinned at TDs with a screw component (i.e. $c$ or $c+a$ type) [45].

Heterogeneous steps and their associated dislocation cores are believed to serve as the more probable sinks for adatom incorporation, resulting in preferred growth at heterogeneous steps as compared to homogeneous steps [46,47]. Therefore, the lowest energy, and hence preferred, sites for GaN island nucleation are the heterogeneous steps surrounding hillocks on the AlN buffer layer surface.

As discussed in section 3.2 and also suggested by the low density of step terminations in Fig. 2(f), the AlN buffer layer has a low density of screw-character TDs. In addition to the formation of 3D GaN islands on the spiral hillocks, it also appears that 2D GaN islands have formed at the step edges as a result of adatom diffusion and capture at homogeneous steps. This is most clearly seen by comparing Fig 7(g), a nominally 2 nm thick GaN layer, and Fig. 2(f), a 100 nm AlN layer. Careful examination of the step edges reveals that the steps in Fig. 7(g) are less smooth, and small 2D islands appear to be protruding from them. Assuming that GaN initially grows in the S-K mode on AlN/HE-SiC as occurs for MBE [48,49,50] and MOVPE [39,42] growth on AlN/AR-SiC, we propose that the surfaces in Fig. 7(d) and (g)-(i) are completely covered with a thin GaN wetting layer, and the increasing strain has induced the nucleation of 2D islands and 3D islands at step kink sites and spiral hillocks respectively.
As shown in Fig. 7(e), and similarly to GaN layers of the same thickness on AR-SiC, the islands have essentially coalesced for a nominal GaN thickness of 20 nm on AlN/HE-SiC and the surface is transitioning to the step-flow regime observed for the 1 µm thick layer shown in Fig. 7(f). From comparison of Fig. 7(f) and (c), it is apparent that the density of step terminations, examples of which are arrowed in each figure, is reduced in the GaN film on the HE-SiC substrate, indicating a reduction in the density of screw and/or mixed TDs [39]. Averaging over several AFM images revealed densities of 1x10⁹ cm⁻² and 5x10⁸ cm⁻² for the 1 µm GaN film on AR-SiC and HE-SiC substrates respectively.

The evolution of the root mean square (RMS) surface roughness of GaN layers grown on 100 nm AlN films previously deposited on AR-SiC and HE-SiC substrates is shown in Fig. 3. Due to island formation, the 2 nm GaN layer causes the RMS roughness of the GaN/AlN heterostructures on each substrate to increase relative to that of a bare 100 nm AlN buffer layer. However, the range of RMS roughness values observed for the GaN on HE-SiC is much larger due to the scattered spiral hillocks and corresponding 3D GaN islands. As the islands grow and coalesce, the RMS roughness is seen to increase before decreasing to the final average values of 0.20 and 0.13 nm for the AR-SiC and HE-SiC substrates respectively. The roughness of the latter is reduced due to the lower densities of step terminations and heterogeneous steps.

5.4.4 HIGH RESOLUTION X-RAY DIFFRACTION

The measured a- and c-axis lattice parameters of the 1 µm thick GaN films on AR-SiC and HE-SiC substrates are listed in Table I. The in-plane (εₓₓ) and out-of-plane (εẑẑ) strains were calculated using lattice parameters given by Porowski [51] for undoped
homoepitaxial GaN films (a = 3.1881Å, c = 5.1844Å). Both samples are under compression in the growth plane, as was previously observed and attributed to an incomplete relaxation of the coherent strain [42,52]. However, the GaN film deposited on HE-SiC has relaxed more than a film of the same thickness on AR-SiC (-0.130% and -0.157% average strain respectively). Photoluminescence measurements [53] of similar samples support the conclusion that GaN films on HE-SiC substrates relax more rapidly. Qualitatively, this can be understood from the observation of the growth mode of the respective heterostructures. As shown in section 3.3, the GaN initially grows in the undulations of the AlN buffer layer on the AR-SiC substrate. Therefore, the film is initially free to relax via the elastic deformation of the pits and undulations. Only when the pits and undulations become filled with material does the plastic relaxation by dislocations begin to occur. Conversely, the AlN layer on HE-SiC lacks undulations and has a reduced pit density. Therefore, the GaN is forced to begin the plastic relaxation process at smaller thicknesses due to the decreased ability for elastic relaxation via surface defects.

Typical 6H-SiC(0001) substrates contain numerous misaligned domains with an average diameter of 1 mm [54]. Preble et al. [55] showed that these domains are mimicked in GaN films deposited on AlN buffer layers and can mask the variations in X-ray rocking curve FWHM values. They separated the two components which broaden GaN rocking curves on SiC substrates, namely domain tilt and dislocation broadening, by plotting the GaN FWHM values versus those of the SiC substrate in the same location. In areas of the substrate which featured reduced domain misorientations, the rocking curve broadening could thus be attributed mainly to dislocations. Following this method, Fig. 8 shows a plot of the FWHM for 1 µm GaN films on AR-SiC and HE-SiC substrates as a function of lattice
The plotted points represent average values (from the dislocation broadening portion of the data only) of multiple spots on multiple samples. In the III-Nitrides, the FWHM of on-axis rocking curves ((0002)) are influenced by the density of screw TDs while off-axis rocking curves (such as (10.5) and 20.1)) are influenced by the densities of screw, edge and mixed TDs. If the inclination angle were increased to 90°, i.e. parallel to the film surface, the broadening would be due to pure edge dislocations.

However, the physical limitations of conventional X-ray diffractometers do not allow this measurement. Srikant et al. [56] have proposed a method of fitting the rocking curves to Pseudo-Voigt functions and extrapolating based on a mosaic crystal model to the 90° inclination angle for determination of the twist angle of the mosaic. Unfortunately, this method could not be employed in the current research due to the sometimes irregular and asymmetric rocking curves, which, in turn, were a result of the underlying SiC microstructure [55]. Instead, the FWHM of the (20.1) reflection was taken as a relative indicator of the edge dislocation density [57] since it is inclined ~75° to the film surface.

Rocking curves of the SiC substrates acquired before and after hydrogen-etching indicated that the surface damage did not affect the FWHM values [58]. This was to be expected since the rocking curve FWHM for 6H-SiC wafers is primarily determined by domain misalignment and these domains propagate through the SiC boule in the c direction [55]. Therefore, the removal of the relatively thin layer of polishing damage does not reduce the FWHM of the X-ray rocking curves for SiC and any changes observed between GaN on AR-SiC and HE-SiC can be attributed purely to changes in the film microstructure as a result of growth differences in the two cases. However, from the data in Fig. 8, it is apparent that hydrogen-etching of the SiC substrate has a minimal effect on the density of TDs in the
subsequently deposited GaN film, as evidenced by the statistically similar average FWHM for each of the five reflections. The largest difference between average FWHM for the two substrates was observed for the (00.2) reflection, with average FWHM values of 243±22 arcsec and 203±27 arcsec for the GaN films on AR-SiC and HE-SiC substrates respectively. As stated previously, this reflection is sensitive to the density of screw dislocations in the film, which was also concluded to be less for GaN films on HE-SiC based on the density of step terminations observed in the AFM images of Fig. 7. The FWHM values for the (20.1) reflection indicate that, within the sensitivity of X-ray diffraction, the density of edge TDs is statistically similar for the two GaN films. However, the scatter of the data prevents differentiating between densities close in magnitude. This scatter can be attributed to the large x-ray spot size for reflections with large inclination angles, resulting in a larger sampling volume and data acquired from several domains at once.

As stated in the introduction, previous investigators [32,33] reported a reduction in X-ray rocking curve FWHM for GaN films deposited on HE-SiC substrates. However, only on-axis (00.2) reflections were reported, and the FWHM values were typically larger than the values reported in the current study. Furthermore, only a single FWHM value was reported for each sample and it was not specified whether broadening due to SiC domain misalignment was taken into account. The values represented in Fig. 8 are the result of over five hundred data points taken from multiple spots on multiple 1 µm thick GaN films. Therefore, we believe the data obtained in this study is a true representation of the minimal effect of hydrogen-etching on the rocking curves FWHM of subsequently deposited GaN films.
5.4.5 DEFECT MICROSTRUCTURE OF GaN ON AlN/HE-SiC

Figure 9 shows a cross-sectional WBDF image from a 1000nm GaN/100nm AlN/HE-SiC heterostructure. Threading dislocations are resolvable in the AlN layer and a number of closed dislocation loops are observed within a distance of 400nm from the GaN/AlN interface. The density of TDs in the GaN layer progressively reduces as the thickness increases. The majority of these TDs in GaN are associated with TDs in the AlN buffer layer. Since the operating reflection is (1120), c type dislocations should be out of contrast. Combing results of Figs. 6 and 9, we can infer that the majority of TDs are of a type. From the plan-view image shown in Fig.10, the TD density is estimated to be ≈1.4x10⁹ cm⁻². This is slightly lower than the density of 3.5x10⁹ cm⁻² achieved in similar structures and similar to that of 2000 nm thick GaN layers on conventional as-polished substrates [39]. This result supports the conclusions of the AFM and HRXRD observations that hydrogen etching of the SiC substrate has only a minimal effect on the dislocation density of subsequently deposited GaN/AlN layers.

5.5 SUMMARY

Hydrogen-etching of 6H-SiC(0001) substrates at 1625°C removed the mechanical polishing damage on the surface and produced an array of steps with a height equal to the 6H-SiC unit cell in the c-direction. AlN nucleated both at the step edges and on the terraces of the HE-SiC due to the low surface mobility of the Al species at the growth temperature of 1100°C for AlN. The flat-topped islands subsequently coalesced and growth occurred via the mode of dislocation-mediated step-flow. AlN films 100 nm in thickness featured very smooth surfaces devoid of the undulations which appeared on the surface of AlN films.
deposited on AR-SiC substrates as a result of polishing scratches in the latter. The density of pits in the AlN decreased nearly an order of magnitude when the film was deposited on a HE substrate. Irregular networks of misfit dislocations were observed over the SiC terraces for 15 nm layers. Some of the misfit dislocations were shown to traverse a step from one terrace to another. The majority of the threading dislocations observed in the AlN layers were \textit{a} type.

GaN initially grew in the Stranski-Krastanov growth mode on 100 nm AlN buffer layers. For the AR-SiC substrate, the GaN islands nucleated in the undulations in the AlN surface as a result of clusters of extended defects in these regions. The lack of undulations in the AlN film deposited on HE-SiC substrates resulted instead in preferential GaN island nucleation on hillocks present on the AlN surface. The heterogeneous steps associated with these hillocks are believed to serve as lower energy nucleation sites than homogeneous steps. Features which are believed to correspond to two dimensional GaN islands were also observed at homogeneous step edges. The differences in surface microstructure of the two assemblies are believed to result in a greater relaxation of the compressive strain, as measured by HRXRD. Analysis of the x-ray rocking curves of on- and off-axis reflections revealed similar FWHM values for 1 \( \mu \text{m} \) thick GaN films deposited on AR and HE substrates, indicating that within the accuracy of x-ray diffraction measurements, the defect microstructures of the respective films are similar. TEM investigations of the GaN layers on AlN/HE-SiC substrates revealed the presence of high densities of closed dislocation loops near the GaN/AlN interface and a reduction of the TD density as the GaN thickness increased. The majority of the TDs observed in the GaN were seen to originate from TDs in the AlN and were \textit{a} type. Plan-view TEM measurements indicated a slight reduction from
3.5- to $1.4 \times 10^9$ cm$^2$ in TD density for GaN layers on hydrogen etched substrates as compared to conventional as-polished substrates.
5.6 REFERENCES


1993;132:504.

[55] Preble EA, Miraglia PQ, Roskowski AM, Vetter WM, Dudley M, Davis RF, J Cryst
Growth 2003;258:75.


[58] Reitmeier ZJ, Preble EA, unpublished.
5.7 TABLES AND FIGURES

Table I  Measured lattice parameters, $a_o$ and $c_o$, and in-plane and out-of-plane strain, $\varepsilon_{xx}$ and $\varepsilon_{zz}$ respectively, for 1 µm thick GaN films deposited on 100 nm AlN buffer layers on as-received and hydrogen-etched 6H-SiC(0001) substrates. Stains are calculated based on the lattice parameters for undoped homoepitaxial GaN given in [51]. Negative strain values indicate compression and positive values indicate tension.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$a_o$ (Å)</th>
<th>$\varepsilon_{xx}$</th>
<th>$c_o$ (Å)</th>
<th>$\varepsilon_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received SiC</td>
<td>3.1831±0.0001</td>
<td>-0.157%</td>
<td>5.1899±0.0001</td>
<td>0.106%</td>
</tr>
<tr>
<td>hydrogen-etched SiC</td>
<td>3.1840±0.0001</td>
<td>-0.130%</td>
<td>5.1891±0.0001</td>
<td>0.091%</td>
</tr>
</tbody>
</table>
Figure 1 10x10 µm AFM height image of as-received 6H-SiC(0001) wafer showing polishing scratches present on the surface. The vertical height scale is given in the upper right corner of the image.
Figure 2 2x2 µm AFM height images of a mechanically polished 6H-SiC(0001) substrate (a), AlN(0001) layers on mechanically polished SiC substrates ((b) and (c)), hydrogen-etched 6H-SiC(0001) substrate (d), and AlN(0001) layers on hydrogen-etched SiC substrates ((e) and (f)). The nominal AlN layer thickness, based on established growth rates, is given in the upper left corner of each image and the vertical height scale is given on the upper right. A polishing scratch into which AlN islands have grown is indicated by the arrows in (b). The arrows in (d) indicate the edges of unit cell height steps in the hydrogen-etched SiC substrate to which continuous strings of AlN islands have attached.
**Figure 3** Root mean square (RMS) surface roughness of AlN layers of different thickness and GaN layers of different thickness on 100 nm AlN buffer layers. Results for both as-received (denoted AR-SiC) and hydrogen-etched (denoted HE-SiC) SiC substrates are shown. The plotted points are the average of several measurement locations on multiple samples and the error bars represent the range of values typically observed. The broken lines are a guide to the eye.
Figure 4 Cross-sectional TEM image of a 15 nm AlN film on a hydrogen-etched SiC substrate.
Figure 5  Plan-view weak-beam dark-field TEM image of a 100 nm thick AlN layer on a hydrogen-etched SiC substrate.
Figure 6 Cross-sectional weak-beam dark-field TEM images of a 100 nm thick AlN layer on a hydrogen-etched SiC substrate. The images were acquired from the same region of the film but with varying g-vectors (given in the images).
Figure 7 (a)-(i) 2x2 μm AFM height images of GaN layers grown on 100 nm AlN buffer layers. (a)-(c) is for layers deposited on as-received mechanically polished 6H-SiC(0001) substrates. (d)-(i) is for layers deposited on hydrogen-etched SiC substrates. (d) and (g)-(i) are different areas of the same sample with 3, 0, 1 and 2 spiral hillocks observed respectively (arrowed in (g)-(i). The layer thickness is based on established growth conditions and is listed in the upper left corner of each image. The vertical height scale is given in the upper right corner of each image. Note the GaN islands observed in (a), (d), (h) and (i) and the step terminations indicated by arrows in (c) and (f).
Figure 8  Plots of the FWHM of X-ray rocking curves obtained at five inclination angles in GaN films deposited on as-received and hydrogen-etched SiC substrates. The plotted points were obtained in the manner of reference 55 to remove the effect of the misaligned SiC substrate domains. Line fits are a guide to the eye.
Figure 9  Cross-sectional weak-beam dark-field TEM image of a 1000 nm GaN/100 nm AlN/hydrogen-etched SiC heterostructure.
Figure 10  Plan-view TEM image of a 1000 nm GaN/100 nm AlN/hydrogen-etched SiC heterostructure showing a TD density of $\sim1.4\times10^9$ cm$^{-2}$.
6. Cantilever epitaxy of GaN on Si(111) substrates as a route towards freestanding pseudo-bulk GaN substrates

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6.1 ABSTRACT

Cantilever epitaxy of GaN on stripe-patterned Si(111) substrates is examined as a means of reducing the dislocation density in GaN layers and serving as a template for the growth of pseudo-bulk GaN substrates. Mechanics and finite element models indicate that significant tensile bending stress will be generated in the Si stripes during cooling from the growth temperature due to the mismatch in the coefficients of thermal expansion between GaN and Si. Examination of the lateral and vertical growth rates as a function of growth conditions reveal that the desired high lateral and low vertical growth rates are favored at high temperature and high NH₃ flow rates. The growth rates also depend on the geometry of the Si stripe array since near-conformal deposition occurs on the pattern. High growth rates are favored by stripes spaced closely together in order to minimize the deposition on the sidewalls of the Si stripes.

The laterally grown GaN “wings” contain a dramatically reduced dislocation density as evidenced by high resolution X-ray diffraction, cathodoluminescence and cross-sectional transmission electron microscopy. However, long growth times result in outdiffusion of Si from the substrate and subsequent formation of Si₃N₅ on the surface by reaction with NH₃, leading to rough layers. The Si₃N₅ phase was observed by energy dispersive X-ray spectroscopy in conjunction with scanning transmission electron microscopy and scanning electron microscopy and identified by X-ray photoelectron spectroscopy. The outdiffusion is limited by the defect enhanced diffusion through the AlN buffer layer. Thicker AlN buffer layers or AlN buffer layers with larger grain size result in a delay of the Si₃N₅ formation. Thick GaN layers deposited on the cantilever-GaN templates resulted in freestanding GaN
layers as a result of the complete outdiffusion of the Si stripes into the GaN and subsequent spontaneous separation during cooling.

6.2 INTRODUCTION

Optoelectronic devices based on alloys of aluminum-, gallium-, and indium-nitride (Al$_x$Ga$_y$In$_{1-x-y}$N) are one of the only commercialized semiconductor systems based entirely on heteroepitaxial growth. The threading dislocations (TDs) generated during this growth on a mismatched substrate occur in densities of 10$^8$-10$^{10}$ cm$^{-2}$ in conventional growth processes and introduce intergap states that serve as non-radiative recombination centers, act as charged scattering centers, and provide leakage current pathways [1]. Heterojunction bipolar transistors [2], p-n junctions [3], and LEDs [4] demonstrate leakage current reductions of ~3-4 orders of magnitude when the TD density in the III-Nitride layers is reduced. However, high TD densities are especially detrimental to the performance of more complex and demanding structures such as laser diodes operating at high power densities [5], as evidenced by the dramatically increased lifetime for these devices when deposited on low dislocation density templates accomplished by lateral overgrowth [6].

Various techniques for lateral overgrowth have been developed to minimize the densities of TDs in III-Nitride thin films. Three examples of this technique, namely epitaxial lateral overgrowth (ELO, also called LEO), pendeo-epitaxy (PE), and cantilever epitaxy (CE), are depicted schematically in Fig. 1. ELO is most commonly conducted on sapphire substrates [7]; however it has also been demonstrated on silicon carbide (6H-SiC(0001)) [8] and silicon (Si(111)) [9]. As shown in Fig. 1(a), ELO starts with a conventional GaN film grown by metalorganic vapor phase epitaxy (MOVPE), containing a high dislocation density,
upon which a dielectric mask (usually SiO$_2$ or Si$_x$N$_y$) has been patterned. During the overgrowth step (Fig. 1(d)) the GaN nucleates within the openings between the mask and grows vertically in these regions until reaching the top of the mask, at which point it grows laterally over the mask. Vertically-propagating TDs present in the original GaN template are blocked by the mask, resulting in areas with dislocation densities reduced by several orders of magnitude as compared to the GaN template and the GaN deposited within the mask openings. Despite the dislocation density reduction by ELO, the overgrown GaN “wings” typically contain high impurity concentrations due to decomposition of the mask material [10,11] and are crystallographically tilted on the order of 1° relative to the seed region. The tilt has been attributed to dislocations at the mask edges [12], thermal mismatch between the mask and GaN [13], or mask etching, densification and/or chemical instability [14,15].

Pendeo-epitaxy, as shown in Fig. 1(b,e,h,), is an alternative technique for lateral overgrowth which eliminates the problems associated with the dielectric mask by using the substrate itself as a pseudo-mask. PE is most often conducted on SiC substrates [16] but it has also been employed for growth on Si [17] and sapphire [18]. As depicted in Fig. 1(b), the template for PE consists of a conventional GaN film, which is subsequently patterned with parallel arrays of stripes and dry etched through the GaN film and AlN buffer layer to expose the SiC substrate. At the temperatures employed for GaN overgrowth, nucleation does not occur on the exposed SiC(0001) surface, but instead occurs both on the tops of the original GaN “stripes” as well as on the sides of the stripes. The laterally growing film contains several orders of magnitude fewer TDs than the seed stripes. As with ELO, further growth results in a coalesced film with areas of high and low dislocation density.
The obvious disadvantage of ELO and PE is that each technique requires two MOVPE growth steps, adding complexity and cost to the process. Alternatively, cantilever epitaxy is accomplished with only one growth step. CE was first reported by Ashby et al. [19] on sapphire, Detchprohm et al. on SiC(0001) [20] and Strittmatter et al. [21] on Si(111) substrates. As shown in cross section in Fig. 1(c), the template for CE consists of a substrate which has been patterned and etched into an array of parallel stripes without the need for an initial GaN layer. The III-Nitride film deposits both between the stripes and on top of the stripes, from which it grows laterally and coalesces. The substrate is etched sufficiently deep to prevent the film nucleating between the stripes from merging with the laterally growing wings. Initial attempts [19] revealed ~2x10^9 cm^{-2} dislocations over the substrate stripes and ~1x10^7 cm^{-2} dislocations in the wings, or cantilevers. However, recent results [22,23] using sapphire substrates have indicated a uniform density of ~2x10^7 cm^{-2} dislocations over the entire wafer as a result of growth optimization to minimize the TDs over the stripes as well.

Lateral overgrowth techniques represent one alternative for improving the performance of subsequently deposited III-Nitride devices. However, these devices would ideally be deposited on low dislocation density III-Nitride bulk substrates. Unfortunately, the high vapor pressure of nitrogen at the melting point of GaN makes the growth of low-defect bulk crystals an extremely challenging process. Single crystals of GaN with very low dislocation densities have been grown by sodium flux [24], ammonothermal [25], and high-temperature, high-pressure [26] methods. However, these crystals are typically limited to <1cm diameter and contain high concentrations of impurities due to the nature of the growth processes.
A further alternative for low dislocation density GaN substrates is so-called pseudo-bulk substrates. These substrates are grown heteroepitaxially on sapphire by hydride vapor phase epitaxy (HVPE) to thicknesses of several hundred microns, resulting in typical TD densities of \(~1 \times 10^7\) cm\(^{-2}\) at the surface [27] due to dislocation annihilation interactions. While this dislocation density is higher than that for bulk GaN crystals, the electrical and optical properties of thick HVPE layers are improved relative to the bulk crystals due to the drastically lower impurity content when employing this growth method [28]. The thick films are subsequently removed from the substrate by laser lift-off, resulting in a freestanding GaN substrate [29]. Homoepipatixial GaN films on HVPE grown pseudo-bulk substrates demonstrate very narrow luminescence peaks, smooth surfaces, and dislocation densities comparable to that of the substrate [30]. High power laser diodes have shown improved performance and lifetimes in excess of 15,000 hours when deposited on HVPE GaN substrates [31]. However, despite the advantages of pseudo bulk substrates, the heteroepitaxial HVPE growth on sapphire substrates results in bowing and subsequent polishing difficulties as well as cracking. The bowing can also result in further problems for the already complicated laser lift-off process [29].

The first goal of the current research is to further examine the process of cantilever epitaxy on Si(111) substrates to determine the optimum conditions for growth and characterize the layers grown by this technique. Silicon is a very promising substrate for CE due to the ease of patterning and dry etching this material. However, it has not been studied as thoroughly as CE on sapphire substrates. A second advantage of silicon is that it can easily be removed from the backside of the GaN layer with a HF:HNO\(_3\) solution. Therefore, the second goal of the current research is to combine lateral overgrowth via cantilever
epitaxy and HVPE-grown thick layers to produce low dislocation density GaN pseudo-bulk substrates with minimal bowing and to remove these thick layers via wet etching rather than relying on laser lift-off. A schematic of the process flow is shown in Fig. 2. The starting substrate is a Si(111) wafer patterned and dry-etched to form an array of parallel stripes as shown in Fig. 2(a). MOVPE is then used to grow a template layer according to the cantilever epitaxy technique, with the lateral growth stopped just prior to coalescence of the wings (Fig. 2(b)). HVPE is then used to deposit a thick GaN pseudo-bulk layer on the MOVPE-GaN template. During cooling from the growth temperature (Fig. 2(c) to (d)), it is expected that the Si stripes will bend as a result of the 57% larger coefficient of thermal expansion (CTE) for GaN as compared to Si. This deflection will act to absorb the thermal mismatch of the heterostructure and minimize bowing of the substrate and GaN. It is anticipated that the large CTE mismatch may even result in cracking and/or fracture of the Si stripes, as depicted in Fig. 2(d). The Si substrate can then be easily removed in a HF:HNO₃ wet etchant (Fig. 2(e)) and the freestanding GaN polished to result in an epi-ready surface (Fig. 2(f)).

6.3 MODELS OF STRESS AND STRAIN IN CANTILEVER EPITAXY ON SILICON

Two models were developed to predict the behavior of the cantilever epitaxy structure. The goals of the models were to determine the influence of the pattern geometry on the stress and deflection of the stripes and to predict whether the stripes would fracture or simply bend. A mechanics model based on the bending of a cantilever beam was developed to determine the deflection of the silicon stripes when a thick GaN layer is deposited and cooled to room temperature. To check the validity of the mechanics model, a finite element
(FE) model was constructed for a specific pattern geometry, and the results were compared to those derived via the mechanics model for the same pattern.

6.3.1 MECHANICS MODEL

The mechanics model is based on the simplified structure shown in Fig. 3. The following assumptions/simplifications were made in developing the model:

1) The 100 nm thick AlN buffer layer is ignored since it is at least two orders of magnitude thinner than the thick HVPE-grown GaN, and its mechanical and thermal properties are similar to those of GaN.

2) The strain in the structure is purely biaxial and the coherent strain due to the lattice mismatch between AlN and Si and between GaN and AlN has completely relaxed [32] during growth (i.e. the structure is strain-free at the growth temperature).

3) The radius of curvature of the cooled structure is very large (i.e. bending is minimal), since both the GaN and the Si substrate are assumed to be >100 µm thick, and the bending of the Si stripes is assumed to accommodate the entire CTE mismatch.

4) The silicon stripes behave linearly elastically until the point of fracture. This behavior has been observed in several studies of the bending of nano- and micro-sized single crystal silicon cantilever beams [33,34,35].

At the growth temperature, the length of the structure is denoted \( L_o \), as shown in Fig. 3(a). Upon cooling to room temperature, the GaN layer contracts by a larger amount than the Si substrate due to the larger CTE of the former material. The resulting strain in the GaN film, \( \varepsilon_f \), is given by:
\[ \varepsilon_f = \frac{L_o - L_f}{L_o} = \frac{\delta_f}{L_o} = \int_{T_o}^{T_g} \alpha_f dT \]  
(1)

where \(L_f\) is the length at room temperature, \(\delta_f\) is the change in length of the GaN film, \(\alpha_f\) is the temperature dependent coefficient of thermal expansion for GaN and \(T_g\) and \(T_o\) are the growth temperature and room temperature respectively. Similarly for the Si substrate:

\[ \varepsilon_s = \frac{L_o - L_s}{L_o} = \frac{\delta_s}{L_o} = \int_{T_o}^{T_g} \alpha_s dT \]  
(2)

Assuming that the Si stripes bend to accommodate the strain difference, the amount of deflection of a Si stripe, \(\Delta x\) as shown in Fig. 3(b), is given by:

\[ \Delta x = \frac{\delta_s - \delta_f}{2} \]  
(3)

Substituting equations (1) and (2) into equation (3) yields an expression for the deflection of a Si stripe in terms of the length of the unit structure shown in Fig. 3(a) and the thermal contraction of the two materials:

\[ \Delta x = \frac{L_o}{2} \int_{T_o}^{T_g} (\alpha_s - \alpha_f) dT \]  
(4)

This deflection is effectively the result of a load, \(P\), pushing the top half of the stripe out with respect to the GaN film, and the bottom half of the stripe in, with respect to the Si substrate, as shown in Fig. 3(b) and (c). Applying the equation for the deflection of the end of a cantilever beam under a load \(P\) [36] and considering only the top half of the structure, as shown in Fig. 3(c), due to symmetry:

\[ \frac{\Delta x}{2} = \frac{PH^3}{3YI} \]  
(5)
where H is one half the total height of the cantilever (h), Y is the Young’s modulus of Si and I is the moment of inertia of the cantilever beam defined by:

$$I = \frac{lw^3}{12}$$  \hspace{1cm} (6)

In equation (6) l is the length of the Si stripe in the z-direction (into the page). Combining equations (4), (5) and (6) and solving for P yields:

$$P = -\frac{Ylw^3L_o}{16H^3} \int_{T_o}^{T_g} (\alpha_s - \alpha_f) dT$$  \hspace{1cm} (7)

The load acting to bend the Si stripes is thus a function of growth temperature and stripe geometry. The load also allows for the shape of the deformed Si stripe to be determined. Again applying equations for the deflection of a cantilever beam [36]:

$$\frac{\Delta x}{2} = \frac{P}{6YL} (-y^3 + 3H^2y - 2H^3)$$  \hspace{1cm} (8)

where y is the coordinate as defined in Fig. 3(c). Substituting for I and P results in an equation for the deflection of the Si stripe as a function of position along the stripe, y, i.e. the shape of the stripe after cooling can be determined:

$$\Delta x = \frac{L_o}{4H^3} (-y^3 + 3H^2y - 2H^3) \int_{T_o}^{T_g} (\alpha_s - \alpha_f) dT$$  \hspace{1cm} (9)

Note that the maximum deflection will occur for y=0 and results in the expression used in equation (5). Equation (9) is plotted in Fig. 4 for the case $L_o=9 \, \mu m$, $H=5 \, \mu m$. This is the case for 10 \, \mu m high (h), 2 \, \mu m wide (w), Si stripes separated by 5 \, \mu m spaces (s). The growth temperature is taken as 1080°C [37] and the temperature dependent CTE values for Si and GaN are from Okada et al. [38] and Reeber and Wang [39]. Symmetry is applied to show the complete stripe, with the GaN at the top in the figure and the Si at the bottom. The figure
shows only the change in the shape of the stripe and not the net lateral movement in the -x-
direction due to the thermal contraction of the structure, as the size scales for these two
phenomena are very different (i.e. nanometers vs. microns respectively). For this geometry,
the total deflection of the silicon stripe is predicted to be 12.1 nm.

To determine whether the deflection would be sufficient to fracture the Si stripes, the
bending stress as a function of position, \( \sigma_b(x,y) \), was determined based on the load \( P \). The
load will result in a bending moment, \( M \), acting on the stripe:

\[
M = Py = -y\frac{Ylw^3L_o}{16H^3}\int_{T_o}^{T_g}(\alpha_s - \alpha_f) dT
\]  

(10)

and a subsequent bending stress:

\[
\sigma_b(x,y) = -\frac{Mx}{I}
\]

(11)

Accounting for the biaxial nature of the strain [40] and substituting equations (6) and (10) into equation (11) yields an expression for the bending stress as a function of position:

\[
\sigma_b(x,y) = \frac{Y}{1 - \nu} \frac{3L_o}{4H^3} x y \int_{T_o}^{T_g}(\alpha_s - \alpha_f) dT
\]

(12)

where \( \nu \) is Poisson’s ratio for the Si stripe. Using the same geometry as for Fig. 4 and taking material properties for Si from George [41], the bending stress as a function of position in the Si stripe is shown in the contour plot Fig. 5. The maximum tensile bending stress, that which could lead to fracture of the Si stripes, is predicted to occur at the top left and bottom right corners of the stripe, with a magnitude of 76.8 MPa for this geometry. The bending stress is symmetric about the center of the stripe and since the maximum tensile bending stress \( (\sigma_b^{\text{max}}) \) occurs at \( x = \frac{1}{2}w \) and \( y = H \), the following expression can be derived:
\[
\sigma_{b,\text{max}}^{\text{max}} = \frac{Y}{1 - \nu} \frac{3L_o w}{8H^2} \int_{T_o}^{T_g} (\alpha_s - \alpha_f) dT
\]  
(13)

Rewriting equation (13) in terms of the stripe parameters frequently cited in this research, namely the width (w), height (h) and space (s) of the Si stripes, yields the final expression for the maximum bending stress:

\[
\sigma_{b,\text{max}}^{\text{max}} = \frac{Y}{1 - \nu} \frac{6w^2 + 3sw}{2h^2} \int_{T_o}^{T_g} (\alpha_s - \alpha_f) dT
\]  
(14)

In Fig. 6, the maximum bending stress, as derived in equation (14), is plotted as a function of stripe width for three different stripe spacings (a) and three different stripe heights (b). The stripe height and stripe spacing are fixed at 10 µm in Fig. 6(a) and (b) respectively. It is difficult to predict whether the Si stripes will fracture under the calculated bending stresses since the fracture stress of the Si stripes is not known. The theoretical fracture stress of bulk single crystalline Si along \{111\} planes is 33 GPa [42]. However, it is well known that fracture of materials typically initiates at a surface flaw, resulting in measured fracture stresses much less than the theoretical value. Numerous researchers [33,34,35,42,43,44] have investigated the fracture strength of nano- and micro-sized Si cantilever beams under bending loads. Typical values measured for Si beams with sizes comparable to the stripes employed in the current research range from 1.0 to 7.7 GPa. Wilson and Beck [44] subjected Si microcantilevers to a side load rather than the more conventional top load and measured an average fracture stress of 1.3±0.3 GPa. This testing geometry is expected to more realistically duplicate the current research since it applies the load parallel to the polished surface of the cantilevers rather than perpendicular to it as for vertical loading. Wilson and Beck’s experimental value is plotted as the horizontal line in Fig. 6(b). From the mechanics-based model it appears unlikely that the Si stripes will fracture during cooling for the
majority of stripe geometries. However, it must be stressed that the fracture stress of the Si stripes is unknown. As will be shown later, the sidewalls of the stripes are significantly rough due to the dry etching process, resulting in flaws which may serve as sites for the initiation of fracture during cooling. Fracture of brittle materials can be described by a statistical relation known as a Weibull distribution [45] since they will tend to fracture at the site of the largest surface flaw. Therefore, a large range of fracture stresses can be expected for the current structure. The model simply shows that significant tensile stresses develop in the Si stripes during cooling and these stresses may be sufficient to result in fracture.

Assuming linear elastic bending of the stripes, the maximum bending stress should be generated for wide, short stripes spaced far apart. Furthermore, the model assumes that the GaN remains rigidly attached to the silicon stripes and does not account for delamination at the defective GaN/Si interface, which may function as a secondary mechanism of self-separation. Interestingly, since the initiation of the current research, Tomita et al. [46] and Gogova et al. [47] have demonstrated self-separation during cooling of thick HVPE-grown GaN layers by depositing these pseudo-bulk films on PE and LEO templates respectively. Sapphire was used as the initial substrate in each study but it was not specified whether the self-separation occurred by fracture of template features or by delamination of the thick GaN layer.

### 6.3.2 FINITE ELEMENT MODEL

To verify the accuracy of the mechanics model, a finite element model of the cantilever epitaxy structure was constructed using ANSYS LS-DYNA Finite Element Analysis software [48]. The model consists of a silicon substrate, two silicon stripes, and a
GaN film. The edges are defined as symmetry planes. The input parameters for the model were chosen to be similar to the geometry used in Figs. 4 and 5 and are listed in Table I. Figure 7(a) is a vector plot of the deflection of a Si stripe. Each arrow pointing to the left in the figure represents the total deflection of the stripe from the corresponding original coordinate. Therefore, the final shape of the stripe after cooling to room temperature is represented by a line connecting the arrow heads in Fig. 7(a). Note the similarity between the shape in Fig. 7(a) and that calculated by the mechanics model in Fig. 4. The total net deflection of the stripe calculated by the FE model is 13.0 nm, which compares favorably with the value of 12.1 nm calculated by the mechanics model in section 2.2. The FE model also validated the assumption of the mechanics model that the curvature of the GaN and Si was negligible. Fig. 7(b) shows a close-up of the top left corner of the Si stripe. The white cell in the figure shows the location of the maximum tensile bending stress as calculated by the FE model, which has a value of 99.1 MPa and corresponds to the value of 76.8 MPa as determined by the mechanics model. Unlike the mechanics model, the bending stress is not perfectly symmetric about the center of the stripe, with a value of 38.5 MPa at the bottom right corner of the stripe. This may be due to the dissipation of stress in the thick GaN film and Si substrate, which was not accounted for in the mechanics model. As shown in Fig. 7(b), the GaN film around the Si stripe is under a small tensile stress. Due to the different mechanical properties of GaN and Si, the dissipated stress is different in the two materials. However, despite this discrepancy, the FE model and mechanics model agree in the shape and order of magnitude of the stripe deflection and the general distribution and order of magnitude of the bending stress.
6.4 EXPERIMENTAL PROCEDURE

6.4.1 SILICON PROCESSING AND III-NITRIDE GROWTH

Four-inch p-type (resistivity=3-6.6 Ω-cm) Si(111) wafers were used as substrates. The wafers were patterned using standard photolithographic techniques and etched using the Bosch process [49]. This process involves alternating etching and passivation cycles in an inductively coupled plasma etching chamber to achieve deep etch profiles with minimal undercut [50]. A representative image of the etched Si substrate is shown in the cross sectional scanning electron microscope (SEM) image Fig. 8. The scalloped pattern observed on the sidewalls of the Si stripe is a result of the etch/passivation cycles in the Bosch process, with each scallop corresponding to one cycle [50]. Each patterned and etched Si wafer contained stripes in the <112> direction with a full matrix of stripe widths and spacings of 1, 2, 5 µm and 5, 10, 15 µm respectively, resulting in nine different areas on each wafer. Etch depths (stripe heights) of 5, 10, and 20 µm were investigated. Following patterning and etching, the wafers were diced into separate regions and the photoresist removed with an H$_2$SO$_4$:H$_2$O$_2$ (5:1) solution at 150°C for 10 minutes. This resulted in an oxidized surface which was subsequently removed by dipping in HF:H$_2$O (1:10) for 10 minutes, leaving a hydrogen-terminated surface [51]. The wafer pieces were blown dry in N$_2$ and immediately loaded into the cold-walled vertical pancake-style MOVPE reactor. The chamber was evacuated to 10$^{-6}$ Torr prior to growth and held at 20 Torr for all growth steps. The temperature of the rotating SiC-coated graphite platter was measured using a single wavelength optical pyrometer. Trimethylaluminum (TMA), triethylgallium, (TEG) and ammonia (NH$_3$) were used as the precursors; hydrogen was used as both the carrier and the diluent. AlN buffer layers were deposited at 1120°C to a thickness of 100 nm using
optimized mass flow rates of 5.5 µmol/min and 0.14 mol/min for TMA and NH₃, respectively. GaN layers were deposited at temperatures ranging from 1015-1100°C with mass flow rates of 34-101 µmol/min and 0.14-0.42 mol/min for TEG and NH₃ respectively, resulting in V/III ratios from 1320-3970. The total gas flow into the reactor was held constant by adjusting the flow rate of the hydrogen diluent.

A thick GaN layer was grown on a selected cantilever-GaN template by iodine vapor phase growth (IVPG) following the method of Mecouch et al. [52].

6.4.2 CHARACTERIZATION

The microstructure of the III-Nitride surfaces and the morphology of the growth were determined using a JEOL 6400 field emission scanning electron microscope (SEM) and a Digital Instruments D3000 atomic force microscope (AFM) equipped with a silicon cantilever and tip operating in the tapping mode. The SEM was also used in determining lateral and vertical growth rates of the GaN layers. High resolution x-ray diffraction (HRXRD) was conducted using a Philips X’Pert Materials Research Diffractometer equipped with a copper x-ray source, fourfold Ge(220) monochromater, threefold Ge(220) analyzer and an Eulerian cradle. Rocking curves (ω-scans) and x-ray reciprocal space maps (ω vs. 2θ-ω) were acquired to examine dislocation-induced broadening and wing tilt respectively. Cathodoluminescence (CL) spectra, panchromatic images, and monochromatic images were acquired with an Oxford Instruments Mono-CL accessory on a second JEOL 6400 SEM. Cross-sectional samples for transmission electron microscopy (TEM) were prepared by focused ion beam (FIB) micromachining [53]. Structural analysis was subsequently performed along the <112> Si zone in a Topcon 002B TEM operating at 200 kV. Chemical
information was acquired from the bulk and the surface using energy dispersive spectroscopy (EDS) in a Hitachi S3200 SEM and a Riber LAS-3000 x-ray photoelectron spectroscopy (XPS) system equipped with a Mg anode source respectively. Additional chemical information was acquired from the bulk by examining the cross-sectional TEM samples in a Hitachi HD-2000 scanning transmission electron microscope (STEM) operating at 200 kV and equipped with an EDS detector.

6.5 RESULTS AND DISCUSSION

6.5.1 GROWTH RATE AND MORPHOLOGY OF GaN AS A FUNCTION OF GROWTH CONDITIONS AND Si STRIPE GEOMETRY

Cross sectional SEM micrographs of representative GaN layers grown on Si substrates with nominal etch depths of 5, 10 and 20 µm are shown in Fig. 9(a-c) respectively. In each case, the GaN deposited on top of the Si stripe, in the trenches between the Si stripes and on the sidewalls of the Si stripe. The latter deposition was not expected based on previously published results [19,20,21], yet it occurred for all samples in the current research. As shown in Fig. 9(d) and denoted by the arrow, the AlN buffer layer also deposits on the Si sidewalls. At the reactor pressures and flow rates employed in these experiments, the mean free path of the reactant species in the gas stream is expected to be on the order of the spacing for the Si stripes (5-15 µm) and convective transport into the trenches is expected to be minimal [54]. Therefore, the transport of the reactants into the trenches is expected to occur via a combination of gas phase diffusion through the relatively stagnant concentration boundary layer and molecular flow of the gaseous species between the Si stripes [55,56]. These mechanisms result in a decreasing supply of reactants along the height of the stripe...
due to reactant depletion and collisions of the molecules with the sidewalls, respectively. For 5 µm high Si stripes, the sidewall deposition is nearly symmetric between the parallel sidewalls, and the deposition thickness steadily decreases as a function of depth (i.e. the GaN on the sidewall is thickest at the top of the stripe). However, for taller stripes, two distinct profiles are observed. The sidewall which is the leading edge during the rotation of the substrate features a thicker GaN layer due to an increased number of collisions with the reactant species in the gas phase. The rotation direction is denoted by the arrows in Fig. 9(a-c). The GaN deposited on the trailing edge is generally thinner than that on the leading edge and decreases in thickness as a function of depth as for the case with shorter stripes.

In any lateral overgrowth technique, it is important to control the ratio of the lateral to vertical growth rates. It is desirable to have high lateral growth rates to achieve rapid coalescence but minimal vertical growth to avoid cracking of the thin film during cooling. The influence of growth temperature on the lateral and vertical growth rates of GaN grown on etched Si substrates is shown in Fig. 10. Profile view SEM micrographs of representative samples deposited at 1015, 1060 and 1100°C are shown in Fig. 10 (a)-(c), respectively, to observe both the cross section and surface. All samples were grown with TEG and NH₃ mass flow rates of 101 µmol/min and 0.14 mol/min respectively, resulting in a V/III ratio of 1320. For each sample, lateral GaN growth was preceded by a 100 nm thick AlN buffer layer and a 200 nm thick GaN “seed” layer using our optimized conditions for growth on planar substrates (T=1015°C, TEG=0.14 mol/min, NH₃=0.14 mol/min). The growth temperature was ramped over a period of 3 minutes for samples grown at elevated temperatures and the total time for the lateral growth step was 60 minutes in all cases.
As shown in the figure, the surfaces of the GaN films were smooth for all deposition temperatures. Spiral hillocks (not shown in this image) were occasionally observed in samples deposited at 1100°C, especially in the trenches and for 5 µm high stripes. These hillocks are the result of preferential growth at heterogeneous surface steps, which are pinned by threading dislocations having screw-character, as opposed to the homogeneous steps, which are due to the slight misorientation of the surface [57]. At temperatures above the optimum for step-flow growth the adatom diffusion length decreases due to the increased tendency for desorption, resulting in a subsequent decrease in the rate of homogeneous step advancement. However, the heterogeneous steps possess a double-step height and a greater concentration of dangling bonds; thus adatom incorporation is preferred at these sites. The combined effect of decreased homogeneous step advancement and preferential condensation at heterogeneous steps results in a spiraling growth mechanism and hillocks pervasive on the surface. Therefore, since the quoted growth temperature is the temperature of the sample platter, the hillocks were observed less frequently on the tops on tall stripes since the temperature at the surface is expected to decrease with an increase in stripe height due to radiative heat loss. Hillocks were observed more frequently in the trenches due to the higher temperature at this surface. The GaN deposited in the trenches is also believed to contain a higher density of screw-character TDs due to growth on the roughened surface of the dry-etched Si, resulting in a higher density of sites for hillock formation.

Unlike GaN grown by pendeo-epitaxy, where the laterally growing wings are typically bounded only by the (0001) top facet and \{1\overline{2}0\} sidewall facets [16], the GaN layers grown by cantilever epitaxy on Si featured numerous different facets on the sidewalls. Several of these facet geometries are shown in Fig. 10, where it is apparent that different
facets are observed even for the sidewalls of the same wing (Fig. 10(b)) and for the wings of neighboring stripes (Fig. 10(c)). The facets typically make angles of \(~53^\circ\), \(~58^\circ\), or \(~65^\circ\) relative to the surface and are therefore believed to correspond to the \{\overline{2}2\overline{4}5\}, \{\overline{1}1\overline{2}2\}, and \{\overline{2}2\overline{4}3\} planes, which make angles of 52.45\(^\circ\), 58.41\(^\circ\), and 65.24\(^\circ\), respectively, relative to the (0001) plane. As shown in Fig. 10(a), the facets forming the inclined sidewalls are not always smooth but sometimes break into narrow facets which are likely the \{\overline{1}0\overline{1}1\} pyramidal planes of GaN [57,58]. In general, lower growth temperatures tended to result in increased faceting and higher growth temperatures tended to result in the formation of \{\overline{1}1\overline{2}0\} facets but a definitive correlation, as described for ELO growth [58,59], could not be determined.

The average lateral and vertical growth rates are plotted as a function of GaN growth temperature in Fig. 10(d). The average rates were calculated by averaging over several stripes on several samples grown with the same conditions. For wings with only \{\overline{1}1\overline{2}0\} facets or a combination of \{\overline{1}1\overline{2}0\} and another plane, the lateral growth was measured from the stripe edge to the \{\overline{1}1\overline{2}0\} face of the laterally growing wing. For wings with \{\overline{1}1\overline{2}n\} facets (where \(n=1-2.5\)), the lateral growth was taken as the average between the top and bottom of the facet. As shown in the figure, increasing the GaN growth temperature from 1015\(^\circ\)C to 1100\(^\circ\)C results in a decrease of the vertical growth rate from 1.51 to 1.35 \(\mu\)m/hr and an increase in the lateral growth rate from 0.59 to 1.25 \(\mu\)m/hr.

The growth of III-Nitrides by MOVPE is typically reported to occur in the mass-transport limited regime in which the growth rate is controlled solely by the diffusion of the group III species across the concentration boundary layer [60]. Since the diffusion coefficient of the reactant species is fairly independent with temperature, the growth rate is
simplified as being constant with growth temperature. However, this simplification neglects
the influence of surface kinetics, which can influence the growth rates of different
crystallographic planes as the temperature changes. For an excellent review of the kinetics of
GaN(0001) surfaces during deposition, see Koleske et al. [61]. In general, GaN deposition is
a near-equilibrium competitive process between adatom incorporation, desorption into the
gas phase, and decomposition. The decomposition is postulated to occur by the desorption of
N atoms at the surface, diffusion of bulk N to the surface followed by N2 formation and
subsequent desorption, and the formation of Ga droplets on the surface [62,63]. At the
typical growth temperatures for GaN by MOVPE, the desorption rate of N is several orders
of magnitude larger than that of Ga. Therefore, large V/III ratios are employed to offset the
loss of N2 from the surface and to achieve essentially stoichiometric GaN [60].

The observed decrease in the vertical growth rate with constant V/III ratio as a
function of temperature is due to the increased desorption of Ga from the GaN(0001) surface.
The increased temperature also results in increased decomposition of NH3 [64] which
provides additional atomic hydrogen at the GaN surface. This atomic H, in turn, has been
reported to increase GaN decomposition by combining with N at the GaN surface to reform
NH3 and also to block sites for NH3 adsorption, thereby decreasing the growth rate [65].

Unlike the vertical growth, the lateral growth rate is enhanced by increasing the
temperature. In ELO growth, this has previously been attributed to the increased diffusion
length of the Ga species as temperature increases [57] and/or an increased supply of active N
[58,66] as a result of the aforementioned enhancement of the NH3 decomposition process at
elevated temperature. This increased supply of active N is believed to result in an increased
probability of incorporation for the Ga species [58,65]. Furthermore, since the higher surface
energy facets of GaN such as \{1\bar{1}0\} and \{\bar{1}01\} are more stable at elevated temperature than 
the (0001) surface [67,68], the growth species which arrive on the faceted sidewalls are less 
likely to desorb than those on the (0001) surface. The increased Ga desorption from the 
(0001) surface at high temperatures is also believed to contribute to the lateral growth by 
diffusing to the sidewall and serving as a source of additional Ga [57].

Representative SEM micrographs of the surface and cross section of GaN layers 
deposited at different V/III ratios on etched Si substrates are shown in Fig. 11. All GaN 
layers were grown for a period of 60 minutes and preceded by a 100 nm thick AlN buffer 
layer and a 200 nm thick GaN seed layer, as mentioned previously. The growth temperature 
was fixed at 1060°C, as this temperature was shown above to result in the highest lateral 
growth rate while consistently maintaining a smooth surface. The control sample shown in 
Fig. 11(e) was grown at the standard V/III ratio of 1320 and thus featured the same growth 
sequence as the GaN layer shown in Fig. 10(b). For the layers shown in Fig. 11(a-d), the 
V/III ratio was increased to 2650 or 3970 by decreasing the flow rate of TEG ((a) and (c)) or 
increasing the flow rate of NH3 ((b) and (d)). The total gas flow into the reactor was fixed 
for all samples by adjusting the flow rate of the H₂ diluent.

The corresponding average lateral and vertical growth rates are shown in Fig. 11(f) as 
a function of V/III ratio for both methods of increasing the V/III ratio. As shown in the 
figure, increasing the V/III ratio from 1320 to 3970 by reducing the flow rate of TEG results 
in reductions of the vertical and lateral growth rates from 1.39 to 0.17 µm/hr and from 0.83 to 
0.45 µm/hr respectively. In each case, the growth rate decreases due to the decrease in the 
flux of the Ga species to the surface. However, despite that fact that the TEG flux decreased 
by a factor of 3, the cross sectional area of the GaN decreased by a factor of 9-11. Since the
complete pyrolysis of TEG has been observed to occur at temperatures greater than 625°C [69], the input flux of TEG should be completely dissociated into Ga atoms independent of V/III ratio or slight variations in growth temperature; yet the volume of grown material decreases more rapidly than the reduction in TEG flow rate, indicating that the incorporation rate of the rate-limiting Ga species seems to decrease for higher V/III ratios. As shown by the different slopes of the growth rate vs. V/III ratio curves, the incorporation rate on the (0001) surface was more dramatically affected than that on the \{11\overline{2}n\} \(n=0-2.5\) sidewalls. Therefore, at the expense of overall lateral growth rate, the ratio of lateral to vertical growth rate was increased from 0.6 to 2.6 by decreasing the flow rate of TEG.

For the GaN layers in which the V/III ratio was increased by increasing the flow rate of NH₃, the vertical growth rate decreased dramatically from 1.39 to 0.06 µm/hr. This reduction is likely due to the NH₃ site blocking mechanism proposed by Briot et al. [70,71]. These authors observed a reduction in the growth rate of GaN films by MOVPE when increasing the flow rate of NH₃ and proposed that the increased surface coverage by NH₃ and NHₓ fragments led to a reduction in the number of open surface sites for Ga adsorption and a subsequent decrease in the growth rate. Grandjean et al. [72] and Koleske et al. [64] have also observed a decrease in the decomposition rate of GaN as the flow rate of NH₃ was increased and proposed a similar site blocking mechanism in which the adsorbed NH₃ blocks sites for N₂ formation and desorption.

Increasing the NH₃ flow rate has a more complex effect on the lateral growth rate, as shown in Fig. 11(f). Changing the V/III ratio from 1320 to 2650 to 3970 results in corresponding lateral growth rates of 0.83, 1.61, and 1.37 µm/hr. Similarly to the increase in lateral growth rate as a function of temperature, the initial increase in lateral growth rate with
increasing NH₃ flow rate is believed to result from the additional supply of active N [65,73]. With a further increase in the NH₃ flow rate, the increasing supply of atomic surface H results in blocked sites for NH₃ and Ga adsorption and also aids in decomposition through the reformation of NH₃ [64].

With the exception of the GaN layer shown in Fig. 11(b), samples deposited at 1060°C with V/III ratios from 1320-3970 featured smooth surfaces and faceted sidewalls. The surfaces of the GaN layers deposited with a V/III ratio of 3970 at high NH₃ flow rates featured numerous spiral hillocks and a rough morphology. The vertical growth rate was near zero for these growth conditions and occurred nearly entirely via spiral hillocks. As discussed above, spiral hillock growth occurs via preferential incorporation of adatoms at heterogeneous steps. Under conditions of high temperature and high surface coverage of NH₃ species due to large NH₃ flow rates, the vertical growth rate is very low and the diffusion length for Ga is reduced because open lattice sites necessary for migration are blocked. The rate of advance of the homogeneous steps is therefore very low and nearly all growth occurs at the heterogeneous steps, resulting in high densities of spiral hillocks. Due to the absence of spiral hillocks and the high lateral growth rate, the optimum conditions for cantilever epitaxy of GaN on etched Si substrates were chosen as 1060°C growth temperature and V/III ratio of 2650 by increasing the NH₃ flow rate.

To determine the influence of the Si stripe geometry on the lateral and vertical growth rates of GaN, a dimensionless parameter termed the normalized surface length, Λ, is introduced and defined as:

\[
Λ = \frac{w + s}{w + 2h + s}
\]  

(15)
where \(w\), \(s\) and \(h\) are the width, space and height of the Si stripes respectively. The normalized surface length is essentially the ratio of the length of a planar surface to the corresponding effective length of the etched surface and is important to consider since the GaN deposits on the stripe surfaces, in the trenches and on the sidewalls. In Fig. 12(a) the lateral and vertical growth rates of GaN layers deposited with the aforementioned optimized conditions for cantilever epitaxy (1060°C, \(V/III=2650\) by increasing \(NH_3\)) are plotted for \(\Lambda\) values from 0.29-0.67. As shown in the figure, both the lateral and vertical growth rates tend to increase as \(\Lambda\) increases, i.e. as the substrate becomes more like that of a planar surface. Fitting the data to straight lines and extrapolating the vertical growth rate to the case for \(\Lambda=1\), which is the case for a planar substrate since \(h=0\), reveals reasonable agreement with the growth rate for GaN with these conditions on a planar substrate, indicated by the open symbol in the figure. Extrapolating the vertical growth rate toward \(\Lambda=0\), i.e. stripe height approaching infinity and stripe width approaching zero, reveals the expected result that the vertical growth rate will approach zero. Ideal \(\Lambda\) values based on the photolithographic mask and nominal etch depths range from 0.13 to 0.67. However, the actual values plotted in Fig. 12(a) vary due to variations in processing and etching which result in geometries different from the ideal. Small \(\Lambda\) values occurred for tall stripes spaced closely together, an example of which is shown in Fig. 12(b) where GaN has deposited on a portion of the sidewall which was the leading edge during rotation but the deposition has not occurred all the way to the base of the stripe. Therefore, data for \(\Lambda<0.29\) is excluded from Fig. 12(a) since GaN layers deposited with this stripe geometry do not feature complete coverage of the stripe sidewalls by the GaN. Despite the trends observed in growth rate as a function of stripe geometry, the scatter of the data is large due to variations in sidewall coverage. Normalizing the growth
rates based on Λ and examining them as a function of growth conditions reveals identical trends to those shown in Fig. 10(d) and Fig. 11(f), which are based on the average growth rates over several samples with varying geometry. However, consideration of Λ does help to account for the large error bars observed in these figures.

A comparison of the growth rates for GaN by cantilever epitaxy on Si to those for pendeo-epitaxy of GaN [66] on AlN/SiC substrates in the same MOVPE reactor reveals that, for the same growth conditions, the growth rates are a factor of 1.2-2.8 less in the former case. In lateral overgrowth techniques with a mask, there is a well-known growth rate enhancement in the unmasked areas of the template [74,75,76,77]. This enhancement is due to an additional supply of reactant species as a result of gas phase diffusion over the mask. This causes the total volume of deposited material to be constant for ELO vs. planar growth but the effective growth rates in the unmasked areas are greatly increased. A similar effect is believed to occur in pendeo-epitaxy since the exposed SiC substrate acts as a pseudo-mask in this growth technique. However, since the GaN grown by cantilever epitaxy in this study deposits over the entire exposed surface of the etched Si, a growth rate enhancement is not observed and the overall growth rates are low compared to other overgrowth techniques.

In an effort to increase the lateral growth rates, several attempts were made to minimize or eliminate the deposition on the stripe sidewalls. Theoretical simulations [54,55,78,79] for deposition into trenches indicate that the deposition will be minimized in the trench by increasing the chamber pressure during deposition, thereby decreasing the gas phase diffusion rate, or by increasing the sticking coefficient of the reactants to prevent them from reaching the sidewalls of the trenches. The authors suggest that a high sticking coefficient can be accomplished via a low surface coverage of reactants and/or an increased
deposition temperature. In the present research, higher reactor pressures, low reactant fluxes and high temperatures were all employed in an effort to minimize deposition on the sidewalls; however, none of these techniques were effective. Attempts were also made to mask the sidewalls with SiO₂ or Si₃N₄. However, the necessity of initiating growth on Si with an Al-containing buffer layer (i.e. AlN or AlₓGa₁₋ₓN) to minimize the melt-back etching reaction between Ga and Si [80] resulted in polycrystalline deposition on the mask material due to the strong Al-O and Al-N bonds. The extra processing steps required for mask deposition on the sidewalls and removal from the tops of the Si stripes prevented this technique from being worthwhile since the deposition on the sidewalls was only slightly reduced. Finally, it was theorized that the scalloped sidewalls of the Si stripes, as observed in Figs. 8 and 9(d), may serve as preferential nucleation sites for AlN and subsequently GaN. A wet etching process using KOH as a selective etchant was developed and was effective in eliminating the scallops and achieving smoother sidewalls. However, the deposition on the sidewalls was not affected. Various pre-growth cleaning procedures were also investigated, with little effect. Considering the multitude of attempted solutions, it was concluded that the sidewall deposition is affected by the MOVPE reactor itself or some other unknown parameter [81] since other researchers did not report this phenomenon [19,20,21].

6.5.2 CHARACTERIZATION OF CANTILEVER EPITAXY-GROWN GaN

6.5.2.1 HIGH RESOLUTION X-RAY DIFFRACTION

Typical HRXRD reciprocal space maps of the GaN (0002) reflection taken with the scattering plane parallel and perpendicular to the stripe direction are shown in Fig.13(a) and (b) respectively. When the incident X-ray beam is directed parallel to the Si stripes, a single
peak is observed and attributed to the GaN growing from the tops of the stripes. The peak also contains a broad shoulder, as shown in Fig. 13(a), due to the GaN which grows in the trenches. An X-ray beam directed perpendicular to the stripes results in three overlapping peaks separated in both the $\omega$ and $2\theta-\omega$ directions, as shown in Fig. 13(b). The central peak results from the GaN growing directly over the Si stripe and the two satellite peaks correspond to the two laterally growing GaN wings. The peak separation in the $2\theta-\omega$ direction is a result of a slight relaxation (~0.02%) of the c-axis lattice parameter of the GaN in the wings relative to that in the stripes. A similar trend has been observed in maskless pendeo-epitaxy [82].

The separation of the peaks in the $\omega$ direction is due to the crystallographic tilting of the c-axis in the wings relative to that over the stripe. For the GaN layer in Fig. 13, the tilt has a magnitude of 0.12°, which is typical for the samples measured in this research. In general, tilt values reported for maskless overgrowth techniques such as cantilever epitaxy (0.04-0.9° [22,83,84]) and pendeo-epitaxy (0.05-0.17° [81]) are less than those reported for overgrowth over a dielectric mask such as ELO and masked pendeo-epitaxy (~1° [12,85,86]). Therefore, the presence of a mask obviously influences the tilt of the laterally growing wings. However, the origin of the tilt in maskless overgrowth techniques is unclear. Finite element simulations supported by experimental results [81], indicate that the wing tilt is primarily due to the relaxation of the compressive stress in the GaN in the c-direction. This stress results from the mismatch in thermal expansion coefficients between the GaN and the substrate. However, temperature dependant measurements of the tilt revealed that residual tilt remains in the structure at the growth temperature, indicating that factors other than thermal strain also influence the tilt [66,83]. In the present research, as well as in previous studies [81], a
clear correlation between wing tilt and sample geometry or growth conditions could not be established.

Extracting single rocking curves (ω-scans) from the perpendicular-oriented reciprocal space plots such as Fig. 13(b) allowed for the comparison of the stripe and wing regions. The curves were separated and fitted to pseudovoight functions to evaluate the full-width-at-half-maximum (FWHM) of the (0002) reflection, which is sensitive to the density of screw-character threading dislocations in the film [87]. This analysis revealed average FWHM values of 648” and 517” for the stripe and wing regions respectively, indicative of a reduction in the dislocation density in the laterally-grown GaN wings.

6.5.2.2 CATHODOLUMINESCENCE

To assess the optical properties of the cantilever GaN layers, CL spectra of a sample grown with optimized conditions were acquired at room temperature (300K) and reduced temperature (100K) and plotted in Fig. 14(a). Each spectrum was obtained over a 11000 µm² area and thus the signal is averaged over approximately 25 stripes. The upper, room temperature, spectrum in Fig. 14(a) features an intense near-band-edge peak at 3.387 eV with a FWHM of 115 meV. The red shift of this peak relative to the position for relaxed GaN [88] indicates that the GaN layer is in tension in the growth plane, as predicted from the mismatch of the coefficients of thermal expansion and discussed in section 2. The spectrum also exhibits the commonly-observed yellow luminescence (YL) band centered at approximately 2.25 eV. This peak is believed to result from a transition involving a deep acceptor state, generally attributed to a complex between a Ga vacancy (V_{Ga}) and oxygen on a nitrogen site (O_N) [89,90], although other recent evidence [91] suggests that carbon impurities may be
responsible for this peak. The ratio of the near-band-edge to YL intensity is approximately 20:1, with high ratios generally considered an indicator of high purity and low defect density [47].

The low temperature spectrum in Fig. 14(a) demonstrates similar features to the spectrum at room temperature. The near-band-edge peak of the former is blue shifted relative to the room temperature value due to the change in the bandgap of GaN as a function of temperature. The FWHM at low temperature is reduced to 80 meV due to thermal effects and the YL band has decreased essentially to the background level. An additional peak also appears at 3.246 eV, which is commonly attributed to the zero phonon line of a donor-acceptor pair (DAP) transition [47]. The peak at 3.155 eV which comprises the shoulder of the broad DAP peak is therefore likely to be the first longitudinal optical phonon replica. The DAP transition and its associated replica are believed to be absent at room temperature do to the thermal ionization of the donor.

To examine the spatial variation of the luminescence in the GaN layers, CL maps were acquired for various photon energies. Fig. 14(b) shows a plan-view SEM image of the cantilever GaN sample from which the CL spectra were obtained. As shown in the figure, the lateral growth has been stopped prior to coalescence of the advancing wings. The wavy nature of the wing edges is an artifact of the instrument, as confirmed by images obtained in a separate microscope, which revealed straight and parallel wings. A panchromatic CL image of the same region from the SEM image is shown in Fig. 14(c). This imaging mode shows the integrated intensity of the entire CL emission spectrum. The laterally grown GaN wings, which appear as parallel white regions in the figure, exhibit the uniform and intense emission characteristic of a low density of threading dislocations [92,93], since these defects
have been shown to act as non-radiative recombination centers in GaN. Conversely, the GaN
over the Si stripes exhibits mottled and weak luminescence due to the high density of
threading dislocations in this area. TEM investigations of GaN grown on planar Si typically
yield threading dislocation densities of $10^{10}$ cm$^{-2}$, resulting in defects spaced so closely
together that the individual dislocations cannot be distinguished in the CL images. A
secondary feature noted in the GaN over the stripes is regions of increased and mottled
luminescence which extend for lengths of $\sim 10$ µm along a stripe and are bounded on each
side by the characteristic dark regions. A CL image of the band-edge luminescence from the
same region of the sample is shown in Fig. 14(d) and again reveals the intense luminescence
from the GaN wings and weaker luminescence over the stripes. However, close inspection of
the wings reveals areas of dark contrast with a one-to-one correspondence to the brighter
regions of the GaN over the stripe in the panchromatic image.

In an effort to determine the origin of the bright regions over the stripe in the
panchromatic image and the dark regions in the wings in the band-edge image, a CL image
was acquired at 3.246 eV and shown in Fig. 15(a). Clearly, the impurity or defect leading to
this transition is highly localized in the GaN layer rather than evenly distributed. The intense
regions in Fig. 15(a) extend from the stripe into the wing and correspond to the unexpected
features in Fig. 14(c) and (d). The donor level in the DAP transition can be attributed to Si
impurities. However, the acceptor state in this transition has been disputed and likely varies
from sample to sample. Numerous researchers [21,47,94,95,96] have observed a DAP
transition in GaN and attributed the acceptor to Mg$_{Ga}$, V$_{Ga}$, C$_N$ or structural defects (where
X$_Y$ denotes an X atom on a Y atom site and V is a vacancy). Due to the localized nature of
the emission, impurities such as Mg and C from the gas phase can be eliminated.
Furthermore, Mg is currently not used in the MOVPE reactor and C concentrations in GaN films deposited on planar substrates were below the detection limit of secondary ion mass spectroscopy (3x10^{17} \text{atoms/cm}^3). An additional possibility is the presence of Si_N possibly due to outdiffusion from the Si substrate. Silicon normally occupies the Ga sublattice in GaN and thus acts as a donor with a donor level 30 meV below the conduction band minimum. However, theoretical simulations [97,98] have shown that Si occupying a nitrogen site can act as an acceptor in GaN with a corresponding binding energy of 183-239 meV. Experimental results [99,100,101,102,103] have verified the validity of this phenomenon. The amphoteric behavior of Si is observed most frequently when the concentration is greater than 5x10^{18} \text{atoms/cm}^3. Fig 15(b) is an EDS image of the Si Kα x-ray line for the same cantilever GaN sample showing areas of elevated Si concentration with a size corresponding to the bright areas in Fig. 15(a). The Ga Lα1 EDS image of the same region is shown in Fig. 15(c) and reveals the constant Ga signal over the same area. While not quantified due to problems inherent with quantification in EDS, the Si signal detected in Fig. 15(b) was only slightly above the background and very long collection times had to be employed to observe the contrast in the figure. Since the detection limit for Si in GaN via EDS is on the order of 0.1 wt% (~1x10^{20} \text{cm}^{-3}) [104], the concentration of Si in the regions characterized by the DAP emission is believed to be close to this limit.

The influence of the localized high Si concentrations on the surface microstructure of cantilever GaN is shown in the 5x28 µm AFM image Fig. 15(d). The regions above and below the broken lines in the figure are the GaN wings and the region in the center corresponds to the GaN on top of the Si stripe. The areas labeled “A” in the figure correspond to the usual step and terrace structure of GaN deposited by MOVPE. However,
the areas labeled “B” correspond to a significantly rougher undulated surface. As with the EDS and CL images, the “B” regions observed in AFM randomly extend for 5-15 µm along the length of the stripes and are bounded on either side by the normal GaN surface. High Si concentrations in GaN are known to induce rough surfaces due to segregation of Si to the surface from the supersaturated bulk, thereby resulting in undulations [105] and the lack of step flow growth [106,107,108] due to a modification of the surface kinetics. Therefore, we believe that the DAP transition observed in the CL spectra and in the CL image Fig. 15(a) corresponds to a transition between SiGa and SiN due to a localized high concentration of Si as observed in Fig. 15(b) and (d). Additional details regarding the origin of the Si in the GaN layer will be presented in section 4.3.

6.5.2.3 TRANSMISSION ELECTRON MICROSCOPY

Cross sectional bright field transmission electron microscopy images of the GaN layer studied by CL above are shown in Fig. 16(a) and (b). The electron beam is directed along the stripe and aligned to the Si [112] zone axis. A carbon-based filler material was employed during the FIB preparation step and is denoted by black arrows in the figure. The selected area diffraction (SAD) pattern in Fig. 16(c) confirms the previously reported [109] epitaxial relationship between GaN/AlN(0001) and Si(111) to be \( \langle 0001 \rangle_{\text{GaN,AlN}} \parallel \langle 111 \rangle_{\text{Si}} \) and \( \langle 120 \rangle_{\text{GaN,AlN}} \parallel \langle 110 \rangle_{\text{Si}} \). Diffraction spots are observed for both GaN and AlN, indicating the single crystal nature of both layers.

The GaN deposited on top of the stripe features a high density of threading dislocations which appear to originate at the GaN/AlN and/or AlN/Si interfaces. Although plan-view images of this uncoalesced layer could not be obtained for verification, the
Dislocation density over the stripes is likely to be similar to that observed by other investigators when depositing GaN via MOVPE on Si(111) with AlN buffer layers. Values of $1 \times 10^9 - 1 \times 10^{10}$ cm$^{-2}$ are typically reported, with a distribution of ~2/3 pure edge, ~1/3 mixed, and very few pure screw dislocations [110,111,112]. In contrast to this high density over the stripes, no threading dislocations were observed in the laterally-grown GaN wings. A magnified view of a separate GaN wing is shown in Fig. 16(b) and again shows the absence of any threading dislocations in the lateral material. However, a small number of dislocations, examples of which are marked by black arrows, are seen to propagate along the basal plane into the wings. In most cases, these basal plane dislocations are seen to originate from the side of the AlN buffer layer (white arrow), as has been previously observed in the case of pendeo-epitaxy [17,113].

The lack of plan-view images, as well as the small volume of material, makes determination of the dislocation density in the wings difficult. Other researchers have reported densities between $5 \times 10^6$ and $1 \times 10^8$ cm$^{-2}$ for ELO [114,115], PE [112] and CE [22,23]. We believe this range to be a reasonable estimate of the density of threading dislocations in the GaN wings in the present research. The reduction in the density of threading dislocations as observed by cross sectional TEM is consistent with the reduced x-ray FWHM and increased luminescence for the GaN wings of cantilever epitaxy compared to that of the GaN over the Si stripe.

The GaN deposited on the sidewall of the above Si(111) stripe is shown in the cross sectional TEM image Fig. 17(a). As above, the electron beam is aligned to the Si [112] zone axis. AlN is also clearly observed on the scalloped Si sidewalls. The large white areas along the sidewall are voids due to penetration of the focused ion beam during sample preparation.
The SAD pattern from the sidewall GaN is shown superimposed with the Si pattern in Fig. 17(b). The spots due to diffraction from the GaN are surrounded by white circles in the figure and reveal that the GaN grows as crystalline cubic GaN (β-GaN) on the Si sidewalls. The pattern represents the β-GaN [223] zone axis with the [110] direction tilted approximately 7° relative to [111]$_{\text{Si}}$. The GaN diffraction spots are elongated rather than circular, indicative of stacking faults [116,117] in the film. High densities of stacking faults are commonly observed on {111} planes in β-GaN independent of the substrate and have been observed for films deposited on GaAs(001) [118], GaAs(311)$_{A}$ [119], Si(001) [120], MgO(001) [121], and β-SiC/Si [122]. The high density of planar defects observed in the TEM image, examples of which are arrowed, are believed to correspond to these stacking faults on {111} planes.

Fig. 17(c) is an SEM image of the GaN deposited on the sidewall of the Si stripe and shown in the TEM image in Fig. 17(a). A cross sectional SEM image of this layer was previously shown in Fig. 11(d). The black arrow in Fig. 17(c) indicates the interface between the GaN growing on the sidewall and the GaN growing laterally (out of the page) from the top of the stripe. As shown in the figure, the β-GaN does not grow as a smooth film on the Si sidewall but rather as an aligned, faceted structure. Also, due to the close spacing of the Si stripes in this sample, the GaN has not deposited all the way to the bottom of the stripe and distinct islands are observed to align along the scallops of the sidewall, as indicated by the white arrow.

To further examine the nucleation and growth on the Si sidewall, SEM images of sidewalls after 100 nm of AlN deposition (corresponding to the buffer layer of the sample in Fig. 17(a)) and 200 nm of GaN deposition (corresponding to the GaN seed layer) are shown
in Fig. 17(d) and (e) respectively and a schematic of the structural evolution is shown in Fig. 17(f). Widely spaced Si stripes were employed to observe the layer deposition over the entire sidewall. In Fig. 17(d), the arrows denoting the brightest features point to the location of the thickest AlN, which corresponds to the tops of the sidewall scallops. This preferential deposition on the scallop top surfaces can also be observed in Fig. 17(a) and is depicted in the schematic. The structure of the AlN on the sidewall is not known at the present time. As shown in Fig. 17(e), the GaN then deposits in linear strings along the scallops, with a thicker region, indicated by the arrows in the figure, on the top surface of the scallop and a thinner region on the underside of the scallop. The dark lines in the SEM image immediately above and below the thickest GaN correspond to the apex of the sidewall scallop, where GaN deposition does not immediately occur, and the coalescence region with the neighboring GaN string respectively. The GaN strings grow toward one another, as indicated by the arrows in the schematic and eventually coalesce. It is expected that the regions of coalescence, represented by the broken lines in the schematic, will have high defect densities and correspond to the areas of dark contrast emanating from the sidewalls in Fig. 17(a).

Interestingly, Lee et al. [123,124] have recently explored the deposition of GaN on Si(001) substrates in which arrays of triangular grooves were formed in the surface. They found that GaN nucleated in the wurtzite structure along the inclined sides of the grooves such that the direction of growth from the opposing faces intersected. When the two regions with different growth directions coalesced, the subsequently grown GaN grew in the zinc blende structure. This situation could be analogous to the growth of GaN on scalloped Si sidewalls, since two regions with different orientations coalesce as shown in Fig. 17. Further work remains to be done to determine if the GaN on the scalloped Si sidewalls behaves similarly to the
observations of Lee et al. by initially growing in the wurtzite crystal structure before coalescing and resulting in the subsequently deposited GaN adopting the cubic structure.

To further explore the growth of \( \beta \)-GaN, a series of films were deposited \[125\] on Si(110) substrates since this is the orientation of the sidewall in cantilever epitaxy. GaN film thicknesses of 0.25 and 0.5 µm with AlN buffer layer thicknesses of 25, 50 and 100 nm were deposited by MOVPE and examined by HRXRD and AFM. However, despite the lack of symmetry between the substrate surface and that of the wurtzite structure, all of the films were determined by HRXRD to consist of crystalline hexagonal GaN(0001), with rocking curve FWHM values only slightly higher than GaN films deposited on the usual Si(111) substrates. The cubic phase was undetectable within the limits of HRXRD. This study demonstrates the remarkable ability of the III-Nitrides to deposit in the wurtzite structure on a wide variety of substrates. Therefore, prior to further investigation, it is reasonable to expect that the GaN initially grows in the wurtzite structure on the scalloped sidewalls before coalescing and resulting in \( \beta \)-GaN deposition as observed by Lee \[122,123\].

6.5.3 GROWTH INSTABILITY DUE TO Si OUTDIFFUSION

Since the process flow design requires GaN wings on neighboring stripes to be brought close to coalescence by MOVPE prior to HVPE deposition, and due to the comparatively slow lateral growth rates in cantilever epitaxy as discussed in section 4.1, long growth times were required to cover appreciable spaces between stripes. However, for growth at 1060°C, deposition times exceeding 120 min resulted in localized areas with very rough surfaces. An example of this surface roughening is shown for two stripes in the plan-view SEM image shown in Fig. 18(a). The GaN layer on the left-hand stripe in the image
features the typical smooth surface observed for these growth conditions, yet the surface on
the right-hand stripe is very rough and islanded. The fraction of the surface covered by these
rough areas increased with time, eventually consuming the entire surface for growth times
exceeding four hours. A similar surface degradation in ELO-GaN on Si(111) substrates as a
function of growth time was briefly mentioned by Marchand et al. [92] but neither details nor
analysis was given. A profile-view SEM image of a GaN layer featuring the surface
degradation is given in Fig. 18(b) and appears to show the presence of a void in the Si stripe
beneath the rough surface.

To assess the elements present in the degraded surface, EDS spectra and maps of the
constituent elements were acquired and are presented in Fig. 18(c-e). An electron beam
energy of 5 keV was employed to prevent signal generation from the Si substrate and
analysis at beam energies up to 15 keV did not reveal the presence of species in addition to
those observed at the lower beam energy. Electron penetration depths in GaN are expected
to be less than 200 nm at 5 keV [126]. The spectrum in Fig. 18(c) reveals the presence of N,
Ga, Al and Si in the layers; however the maps of the Ga L\alpha and Si K\alpha peaks, shown in Fig.
18(d) and (e) respectively, reveal very different distributions of the elements in the two GaN
stripes. Specifically, the roughened layer contains areas of locally higher Si concentration
while the Si content in the smooth layer is within the noise-limited resolution of the EDS
detector. Furthermore, the areas of high Si concentration in the rough layer seem to
correspond to regions of decreased Ga concentration, as observed in Fig. 18(d).

Further chemical analysis of the smooth vs. rough layers was performed by STEM in
conjunction with EDS. Cross-sectional STEM images of a smooth and rough layer are
shown in Fig. 19(a) and (b), respectively. The contrast observed in the smooth GaN grown
over the Si stripe can be attributed to defects and/or mosaic structure. The lack of contrast in the wings is further evidence of the low defect density in these regions. An EDS spectrum acquired from the GaN layer in Fig. 19(a) is shown in Fig. 19(c) and reveals the major constituents to be Ga and N. The intensity of the N peak is low due to an absorption edge characteristic of the detector. The detected C and F are due to contamination from the pump oil in the FIB and the Cu is due to the Cu grid in the STEM. Si was not detectable by EDS in this region.

The STEM image in Fig. 19(b) reveals a very different structure. In addition to the rough surface, alternating layers of light and dark contrast roughly parallel to the stripe surface are observed. A selected area diffraction pattern acquired from a region comprising both light and dark phases is shown in the inset of Fig. 19(b). The rings observed around the central spot in the pattern indicate the presence of an amorphous structure while the high density of asymmetric spots indicates the presence of multiple crystalline phases of varying orientation. EDS spectra from the dark and light phases, denoted “A” and “B”, respectively, are shown in Fig. 19(d). The darker phase is comprised entirely of Si and N with no detectable Ga while the lighter phase contains Ga, N, and a much lower concentration of Si. The distributions of these species are shown in the EDS maps Fig. 19(f-h) with the corresponding STEM image shown in Fig. 19(e). The Ga and Si signals demonstrate clear anti-correlation while the nitrogen signal is fairly uniform.

XPS studies were conducted to further characterize the different phases in the rough areas. Since the probe diameter in XPS is much larger than the electron beam in STEM, a separate series of samples was investigated to eliminate any potential Si signal from exposed areas of the etched Si substrate. Rather than an etched substrate, the GaN control film
consisted of a 0.5 µm thick film deposited on a conventional Si(111) substrate with the previously optimized conditions for growth by cantilever epitaxy. As with the cantilever epitaxy samples, GaN deposition was preceded by a 100 nm thick AlN buffer layer. This thickness of GaN was sufficient to result in cracks extending from the edges of the wafer for several millimeters in length, thus allowing for examination of cracked and un-cracked areas of the film. A cracked region of the control sample is shown in the SEM image Fig. 20(a) where the cracks extend between the white arrows in the image. The second GaN layer examined by XPS consisted of a portion of the control sample which was subsequently annealed for 1 hr at 1060°C in flowing NH₃. A region of this annealed sample which contains cracks is shown in the SEM image in Fig. 20(b) and reveals a roughened surface in the vicinity of each crack. The final sample examined by XPS consisted of a third portion of the control sample which was heated to 1060°C in flowing NH₃ and subsequently coated with additional GaN using the optimized CE growth conditions for 1 hr. As shown in the SEM image Fig. 20(c), this sample again featured linear rough areas believed to correspond to the cracks in the original template layer. Fig. 20(d) is an SEM image revealing both the surface and cross-section of the re-grown sample. The cracks are emphasized by broken lines in the image and voids observed to occur exclusively beneath the cracks are indicated by arrows. For all three sample types, the GaN surface in regions without cracks was smooth and featureless. It is believed that the rough areas observed in Fig. 20(b-d) correspond to the rough areas in Figs. 18 and 19 since EDS maps (not shown) of the samples in Fig. 20 reveal similar features, i.e. the rough areas contain high Si concentrations and low Ga concentrations while Si is undetectable in the smooth areas.
XPS analysis of specimens that contain both Si and Ga can be difficult due to peak overlap problems since the Si 2p and Ga 3p$_{3/2}$ photoelectron peaks possess binding energies of 99.3 and 104 eV respectively while the Si 2s peak at 151 eV can be occluded by an x-ray satellite of the Ga 3s peak [127]. The Si 2p photoelectron peak was chose for this analysis due to the greater peak separation and the spectra acquired from each of the samples in Fig. 20(a-c) are shown in Fig. 20(e). The spectra were normalized based on the location of the adventitious C peak. Each spectrum was acquired from a region of the sample featuring cracks and thus rough surfaces for the annealed and re-grown samples. The as-grown spectrum features only the low-energy side of the Ga 3p$_{3/2}$ peak and Si was undetectable by XPS. However, the spectrum for the annealed sample features a pronounced shoulder to the Ga peak centered at ~101.5 eV. The Ga 3p$_{3/2}$ peak also decreased in intensity. After re-growth, the shoulder of the Ga peak decreased in intensity and shifted to slightly higher energy but was still present. In addition to the peak positions commonly cited for Si and SiO$_2$ [126], Fig. 20(e) also shows the range of values reported for the Si 2p photoelectron peak of Si$_x$N$_y$ [128,129,130].

Based on the evidence presented in Figs. 18-20, it is concluded that after long deposition times, the surface of the GaN is roughening due to the presence of Si$_x$N$_y$. The N source for the formation of this compound is most certainly the NH$_3$ growth species, since it is present in excess. Si present in the quantity observed by EDS can only result from the Si substrate but the transport could occur by different routes. A gas phase transport mechanism has been observed to result in increased Si incorporation in GaAs films deposited on Si substrates [131]. Due to the low vapor pressure of Si at the GaAs growth temperature, the process is believed to involve reactions between the gaseous species and the Si substrate and
subsequent diffusion through the boundary layer rather than simple evaporation of Si. While this mechanism could be operative in the present research, it is unlikely to serve as the primary source of Si, since the roughness is localized over finite lengths in cantilever epitaxy and only occurs near cracks in planar growth. Therefore, it is far more likely that the Si reaches the surface by diffusion through the AlN and GaN films. The voids present in Figs. 18(b), 19(b) and 20(d) are therefore believed to result from transport of the Si to the growth surface and subsequent reaction with NH₃ to form SiₓNᵧ. Similar voids as a result of outdiffusion of the substrate have been observed in the deposition of 3C-SiC [132,133], AlN [132], and GaN [111] on Si substrates.

Cracks obviously served as the pathway for Si diffusion in Figs. 20(b-d). These cracks were previously formed in the template layer while cooling from the growth temperature and, in the case of cantilever epitaxy, only one growth step is employed. Therefore, for the latter case, diffusion along cracks would require cracking at the growth temperature. This process has been thoroughly reviewed by Etzkorn and Clarke [134] for GaN deposition on sapphire and attributed to tensile stresses generated during island coalescence. However, neither open cracks due to cooling nor closed or healed cracks due to cracking at growth temperature and subsequent burial by continued growth have been observed in the GaN layers deposited on etched Si substrates. Therefore, we do not believe that cracks serve as a diffusion pathway for Si. Instead, it is far more likely that defect-enhanced diffusion is the operative mechanism for Si transport since both the GaN and AlN over the Si stripe contain a high density of threading dislocations and low angle grain boundaries. Outdiffusion from the Si substrate has previously been observed for GaAs
[135,136], AlN [137] and GaN [138] epilayers and was enhanced in films with high dislocation density and/or small grain size.

A schematic of the Si diffusion and Si$_{x}$N$_{y}$ formation process is given in Fig. 21(a-d). The first diagram shows the cross section of a GaN layer growing laterally and vertically off of a Si stripe. As shown in Fig. 21(b), as the GaN continues to grow, Si is also diffusing through the AlN and then GaN films. The vertical diffusion occurs by a defect-enhanced mechanism and is thus more rapid while the lateral diffusion occurs more slowly through the lattice. The temperature dependence of the diffusion coefficient of Si in GaN is not known and the only value reported in the literature is 4x10$^{-18}$ cm$^{2}$/s at 800°C [106]. This lateral diffusion of Si into the surrounding GaN is believed to be the source of the Si resulting in the DAP emission observed in the CL measurements. As the Si diffuses into the overlying layer, a void begins to form at the film/substrate interface. Continued growth and diffusion results in Si present on the surface of the GaN and the subsequent reaction with NH$_{3}$ to form the Si$_{x}$N$_{y}$ observed in Figs. 18-20. The Si$_{x}$N$_{y}$ is believed to be amorphous, resulting in the rings observed in the diffraction pattern of Fig. 19(b). The arrival of the Si at the surface may result entirely from diffusion along defects or may result from rejection of the Si from the supersaturated GaN to the surface when the Si concentration exceeds 3x10$^{20}$ cm$^{-3}$, as observed by Munkholm et al. [106]. Eventually the pathway of Si to the surface is closed by the Si$_{x}$N$_{y}$ layer on the surface as shown in Fig. 21(c). The GaN then overgrows the Si$_{x}$N$_{y}$, as depicted in Fig. 21(d) and evidenced by the XPS spectra in Fig. 20(e), resulting in a rough surface with many crystallographic orientations as observed in the SAD pattern in Fig. 19(b). Meanwhile, Si continues to diffuse along other pathways, eventually reaching the surface and
forming Si₃N₅. The repeated process of diffusion, nitridation, and overgrowth results in the layered structure observed in Fig. 19(b,e-h).

Visual evidence of the process detailed above is presented in Fig. 21(e) and (f). Figure 21(e) is a 1 µm² AFM height image of a GaN surface over a Si stripe. The white islands observed in the image form at the terminations of heterogeneous steps on the GaN surface, which are known to occur at the intersection of screw-character threading dislocations with the surface [139]. Due to the correlation between the islands and the step terminations, it was concluded that these islands are real surface features rather than contamination and that they correspond to the early stages of Si₃N₅ formation on the GaN surface. The cores of the threading dislocations are thus believed to serve as the pathway for Si diffusion through the GaN. Diffusion along grain boundaries is also likely to occur, especially through the AlN buffer layer, although this mechanism was not observable. An SEM image of a GaN layer which has partially overgrown the Si₃N₅ on the surface is shown in Fig. 21(e). Numerous tilt and twist alignments of the GaN islands can be observed in the figure, thereby resulting in the multiple diffraction patterns observed in the SAD in Fig. 19(b).

Since the onset of Si₃N₅ formation on the surface is initially delayed but then rapidly progresses, it is believed that the rate limiting step in the arrival of Si on the surface is the diffusion through the AlN buffer layer. Once this layer is penetrated, the Si diffuses rapidly through the GaN. To test this hypothesis, AlN buffer layer thicknesses of 50, 100 and 200 nm were investigated. The AlN layer was followed by the standard 200 nm GaN seed layer and GaN was subsequently deposited in 30 minute increments using the optimized conditions for CE growth. Plan-view SEM images were acquired for each sample after each growth
step and the percentage of the surface roughened by Si$_3$N$_x$ formation was estimated based on these images. The results of this study are present in Fig. 22, which shows the percentage of the surface degraded as a function of total GaN growth time for each of the three AlN thicknesses. Clearly, the thinnest AlN buffer layer resulted in the most rapid degradation of the surface while the thickest AlN buffer layer delayed the onset. The improvement of the AlN buffer layer as a diffusion barrier was thus of critical importance. A secondary approach to that of using thicker AlN buffer layers was employed. This technique, as detailed in Appendix 1 [140], initiated AlN growth by pre-covering the Si(111) substrate with a thin Al layer. This resulted in a larger AlN grain size and decreased dislocation density in the GaN films as evidenced by AFM and HRXRD measurements respectively. The application of this technique to cantilever epitaxy resulted in a further delay of the onset of surface roughening due to Si$_3$N$_x$ formation as compared to the 200 nm thick AlN buffer layer. The larger AlN grain size and resulting decrease in the length of grain boundaries in the AlN is believed to result in a longer diffusion time across the buffer layer. Examples of GaN layers grown close to coalescence are shown in the plan-view images Fig. 23. The GaN over the Si stripe is labeled with an “s” in each image and the broken lines represent the edges of the stripes.

6.5.4 THICK GaN LAYERS DEPOSITED BY HVPE ON CANTILEVER GaN TEMPLATES

An initial attempt at depositing thick GaN by IVPG on a cantilever GaN template is shown in the SEM micrographs in Fig. 24. The GaN template layer was deposited on the improved AlN buffer layer achieved by pre-covering the substrate with Al as discussed above and is shown in Fig. 24(a). The optimized conditions for CE growth were used for a
growth time of two hours and the nominal Si stripe width, spacing, and height were 5, 5, and 10 µm, respectively. The thick GaN layer was grown for one hour to a thickness of 130 µm.

As shown in Fig. 24(b), the thick GaN layer spontaneously separated from the Si substrate after cooling to room temperature, leaving a freestanding GaN layer. The substrate was initially located at the bottom of the layer as it is oriented in the figure. A magnified view of the bottom of the freestanding layer is shown in Fig. 24(c) and reveals that the separation did not occur due to fracture of the Si stripes but rather because the Si stripes completely diffused into the overgrown GaN during the IVPG growth. Therefore separation occurred by the delamination of the GaN from the substrate. The large amount of Si present in the GaN may lead to the rough surface observed in Fig. 24(b), although rough surfaces are often observed by this growth technique [52] due to the relative infancy of the process as compared to chloride-based GaN deposition.

6.6 SUMMARY

Cantilever epitaxy of GaN on Si(111) substrates was explored as a means of achieving a low dislocation density through lateral overgrowth as well as serving as a template for the deposition of thick GaN pseudo-bulk substrates by HVPE. A mechanics model based on the bending of cantilever beams suggested that significant tensile stress develops in the Si stripes as a result of the mismatch in the coefficients of thermal expansion of GaN and Si. The effect of the stripe geometry was evaluated and it was determined that short, wide Si stripes spaced far apart would be most likely to result in fracture. The findings of the mechanics model were validated by a finite element model.
The effect of growth temperature and V/III ratio during GaN deposition were evaluated to arrive at high lateral growth rates, reduced vertical growth rates and smooth surfaces. Increasing the growth temperature for GaN decreased the vertical growth rate due to increased desorption of Ga from the GaN(0001) surface. The lateral growth rate increased as a function of temperature over the range investigated due to the increased diffusion length of the Ga species and/or an increased supply of active N as a result of more complete NH₃ decomposition at elevated temperature. Similar effects on the growth rates were observed by increasing the V/III ratio via an increase in the NH₃ flow rate. In this case the vertical growth rate decreased due to the blocking of surface sites by NH₃. The lateral growth rate initially increased as a result of an increased supply of active N and subsequently decreased due to the high concentration of atomic surface H resulting from NH₃ decomposition. Increasing the V/III ratio by decreasing the flow rate of TEG resulted in decreased vertical and lateral growth rates as a result of the decreased flux of the minority growth species. However, the vertical growth rate decreased more rapidly than the lateral growth rate indicating that the incorporation rate of the Ga species on the (0001) surface decreased at high V/III ratios. In consideration of the vertical and lateral growth rates as well as the smoothness of the GaN surface, the optimized conditions for CE growth were determined to be a growth temperature of 1060°C and a V/III ratio increased to 2650 by increasing the flow rate of NH₃. Despite several attempts to minimize or eliminate it, deposition occurred on the sidewalls of the Si stripes for all geometries and growth conditions employed. This undesired deposition resulted in decreased growth rates relative to other overgrowth techniques since the deposition did not occur selectively and therefore did not have an additional source of reactant species.
Characterization of GaN layers grown with the optimized conditions for CE revealed dramatically reduced densities of threading dislocations in the laterally grown GaN wings. This was evidenced by a reduction in the FWHM of the x-ray rocking curves for the wing relative to the stripe and increased band-edge luminescence intensity in CL measurements from the wings. The latter also provided evidence of a localized DAP transition in which the acceptor was attributed to Si on a N site. The microstructure of the GaN layers was also investigated by cross sectional TEM. While a high density of threading dislocations was observed over the Si stripe, no threading dislocations were observed in the GaN wings. TEM also provided evidence that the GaN unintentionally deposited on the Si sidewalls grew in the zinc-blende cubic polytype.

The long deposition times required to cover appreciable spaces between Si stripes resulted in a roughened surface as observed by SEM. EDS analysis in SEM and STEM, as well as XPS spectra, provided evidence for the defect enhanced outdiffusion of Si from the substrate and subsequent reaction with NH₃ to form amorphous SiₓNᵧ on the GaN surface. The GaN subsequently overgrew this amorphous layer but resulted in a layered GaN-SiₓNᵧ microstructure and a rough surface. The rate limiting step in this diffusional process was shown to be diffusion of Si through the AlN buffer layer and was minimized through the use of thicker AlN films or pre-coverage of the Si with a very thin Al layer to result in larger AlN grains.

Despite the improvement in the AlN buffer layers, the outdiffusion of the Si substrate continued during the deposition of a thick GaN layer by IVPG. Although the thick layer spontaneously separated from the substrate after cooling to room temperature, its surface was rough and the Si stripes completely diffused into the overlying layer. Separation therefore
occurred by delamination at the interface between the Si substrate and the GaN deposited in the trenches between the Si stripes. Future success of this technique for achieving freestanding GaN layers will require further improvements in the AlN buffer layer to suppress outdiffusion of the Si substrate.
6.7 REFERENCES


[48] ANSYS LS-DYNA Finite Element Analysis, Mallett Technology Inc.

[49] Integrated Sensing Systems, Inc. (ISSYS), Ypsilanti, MI.


[53] Materials Analytical Services, Inc., Raleigh, NC.


[57] Roskowski AM, Miraglia PQ, Preble EA, Einfeldt S, Davis RF, J Cryst Growth 2002;241:141.


[81] Strittmatter A, private communication, revealed that sidewall deposition sometimes occurred but unpredictably and for unknown reasons.


[125] Reitmeier ZJ, Davis RF, unpublished.


### Table I  Input parameters for the finite element model of the cantilever GaN/Si structure.

<table>
<thead>
<tr>
<th>Parameter</th>
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<td>Average CTE</td>
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<td>Maskless pendeo-epitaxy (PE)</td>
<td>Cantilever epitaxy (CE)</td>
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<td>-----------------------------------</td>
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<td>-------------------------</td>
</tr>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
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<td>Template</td>
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<td>Intermediate stage of overgrowth</td>
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<tr>
<td>(d)</td>
<td>(e)</td>
<td>(f)</td>
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<tr>
<td>(g)</td>
<td>(h)</td>
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<td>Si</td>
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**Figure 1** Schematics of epitaxial lateral overgrowth (a,d,g), pendeo-epitaxy(b,e,h) and cantilever epitaxy (c,f,i). Each process is shown for a typical substrate material starting with the template structure and proceeding to coalescence. The arrows in (d-f) indicate the directions of growth as both lateral and vertical.
Figure 2  Process flow for a proposed route towards freestanding GaN substrates produced by HVPE growth and separation from a Si(111) substrate. Note that (c) is at the HVPE growth temperature and (d) is at room temperature. The arrow in (d) denotes a crack in the silicon stripe which may form during cooling from the growth temperature. Note that the Si stripes are expected to bend due to the 57% mismatch in the coefficients of thermal expansion between GaN and Si.
**Figure 3** Mechanics model for determination of the displacement of Si stripes and bending stress in the stripes. The structure is shown at the growth temperature in (a) and at room temperature in (b) and (c).
Figure 4  Deflection of a Si stripe in cantilever epitaxy due to the mismatch in the coefficients of thermal expansion between GaN and Si, as described by equation (9). The Si stripe is 2 µm wide, 10 µm high, and separated from its neighboring stripe by 5 µm. The thick GaN film and Si substrate are at the top and bottom of the figure respectively. The total deflection, i.e. the separation of the top and bottom of the stripe in the x-direction, is 12.1 nm for this stripe geometry.
**Figure 5** Contour plot of the bending stress in a Si stripe following HVPE GaN growth and cooling to room temperature. The thick GaN film is at the top and the Si substrate is at the bottom. Positive values of stress indicate tension.
Figure 6  Maximum bending stress in a silicon stripe at room temperature calculated from equation (14) as a function of stripe width for (a) three different stripe spacings and (b) three different stripe heights. The stripe height and stripe spacing are fixed at 10 µm in (a) and (b) respectively. The horizontal broken line in (b) represents the average fracture stress for Si microcantilevers as measured by Wilson and Beck [44].
Figure 7 Outputs of the finite element model of the cantilever GaN/Si structure. The stripe geometry is the same as for Figs. 4 and 5. (a) is a vector plot in which the arrows show the deflection of the stripe from the original location, resulting in a total stripe deflection of 13 nm. (b) is a close-up of the top left corner of the righthand stripe and shows the bending stress at each cell in the model. The white cell denotes the position of the maximum tensile bending stress, which has a magnitude of 99.1 MPa.
Figure 8  Cross sectional SEM image of a Si stripe after patterning and dry etching. The photoresist mask is still present on the top of the stripe. Note the scalloping on the sidewalls as a result of the alternating etch/passivation cycles.
Figure 9  Cross-sectional SEM micrographs of GaN grown on Si by the cantilever epitaxy technique. The nominal stripe heights (etch depths) are 5, 10, and 20 µm for (a-c) respectively. The arrows in (a-c) point in the direction of rotation during growth, indicating that the leading edge of the rotation features increased deposition on the Si sidewall. The arrow in (d) denotes the presence of AlN on the sidewall.
Figure 10  (a-c) SEM micrographs of GaN grown on etched Si substrates at growth temperatures of 1015°, 1060°, and 1100°C respectively. The images are profile views so that both the cross section and surface are observed. The corresponding lateral and vertical growth rates are plotted as a function of temperature in (d).
Figure 11  (a-e) profile-view SEM micrographs of GaN layers deposited on etched Si substrates. The layers were grown at a constant temperature of 1060°C and the V/III ratio was varied from the standard condition shown in (e). In (a) and (c), the V/III ratio was increased by decreasing the TEG flow rate while holding the NH₃ flow rate constant. In (b) and (d) the NH₃ flow rate was varied. The V/III ratio and method of increase relative to (e) are shown in the upper left corner of each image and the corresponding lateral and vertical growth rates are plotted as a function of V/III ratio in (f).
Figure 12 (a) Growth rates of GaN in cantilever epitaxy on Si as a function of the normalized surface length, $\Lambda$, as defined in equation (15). All samples were deposited at 1060°C and V/III=2650 by increasing the flow rate of NH$_3$. Dashed lines are linear least squares fits. The open data point for $\Lambda=1$ represents the vertical growth rate of GaN for these growth conditions on planar Si substrates. (b) is a cross sectional SEM micrograph of a GaN layer deposited on an etched Si template with $\Lambda=0.23$ showing that the GaN does not deposit along the entire sidewall when the space between stripes is small.
Figure 13  HRXRD triple axis reciprocal space plots of the GaN(0002) reflection for GaN grown by cantilever epitaxy on Si. The incident x-ray beam is directed parallel and perpendicular to the Si stripe direction in (a) and (b) respectively.
Figure 14 Cathodoluminescence of GaN films grown by cantilever epitaxy on Si substrates. Room and reduced temperature spectra are given in (a) and panchromatic and band-edge CL maps are shown in (c) and (d) respectively. The region from which the CL maps were acquired is shown in the plan view SEM image (b).
Figure 15  The presence of regions of locally higher Si concentration as evidenced by a CL map of the donor-acceptor-pair peak, EDS map of the Si Kα peak, and xxx µm AFM height image in (a), (b) and (d) respectively. (d) represents the EDS map of the Ga Lα1 peak.
Figure 16  (a) Cross sectional bright field transmission electron microscopy image of GaN grown by cantilever epitaxy on Si substrates and aligned to the [112] zone axis of Si. The black arrows indicate a carbon-based filler material employed during sample preparation.  (b) A magnified TEM image of a GaN wing, where the black arrows indicate dislocations on the GaN basal plane and the white arrow indicates the edge of the AlN buffer layer from which the GaN has grown laterally.  (c) Selected area diffraction pattern from the GaN/AlN/Si interface.
Figure 17 Deposition of GaN/AlN on the sidewall of an etched Si substrate. (a) A cross sectional bright field TEM image along the Si [112] zone axis with arrows indicating planar defects believed to correspond to stacking faults. (b) Selected area diffraction pattern from the GaN on the sidewall superimposed over the Si pattern. (c) SEM image of the sidewall shown in cross section in (a). (d and e) SEM images of the sidewall 100 nm of AlN and 200 nm of GaN deposition respectively. (f) Schematic of the growth process occurring on the sidewall.
Figure 18  (a) Plan-view SEM image of two Si stripes, one of which features a roughened surface. (b) Profile view SEM image showing the presence of a void in the Si substrate beneath an area featuring the rough surface. (c) EDS spectrum acquired from the region in (a). (d and e) EDS maps of the Ga Lα and Si Kα signals as acquired from the region shown in (a).
Figure 19  (a and b) STEM images of GaN layers featuring smooth and rough surfaces respectively. The inset of (b) is a selected area diffraction pattern observed from the deposit on top of the Si stripe. (c and d) EDS spectra acquired from the GaN layer in (a) and regions “A” and “B” in (b) respectively. (f-h) EDS maps of the Ga Lα, Si Kα, and N Kα signals acquired from the region shown in the STEM image (e).
Figure 20  (a-c) SEM images of a cracked GaN film on a planar Si substrate, a subsequently annealed cracked GaN film, and a GaN layer re-grown on a cracked GaN template respectively. The arrows in (a) indicate the ends of cracks traversing the GaN surface. (d) Profile view SEM image of the sample in (c) showing voids in the Si substrate beneath the cracks. (e) XPS spectra acquired from the layers shown in (a-c).
Figure 21  (a-d) Schematic showing the process by which Si diffuses from the substrate to the GaN surface resulting in the formation of $\text{Si}_x\text{N}_y$ and subsequent GaN overgrowth. (e) 1x1 µm AFM height image of GaN deposited over a Si stripe. The white islands occur at the termination of heterogeneous steps and are believed to correspond to the early stages of $\text{Si}_x\text{N}_y$ formation on the surface. (f) SEM image showing GaN overgrowing the $\text{Si}_x\text{N}_y$ on the surface.
Figure 22  The percentage of the cantilever GaN surface degraded due to Si₃N₄ formation as a function of GaN growth time for three different AlN buffer layer thicknesses. The lines are guides to the eye.
Figure 23  Plan view SEM images of two cantilever GaN samples near coalescence. The “s” denotes the regions of deposition over the Si stripe and the broken lines indicate the boundary between the GaN over the stripe and the laterally grown GaN wings.
Figure 24  a) Plan-view SEM micrograph of CE-GaN template.  b) SEM micrograph showing the surface and cross-section of a GaN layer grown by IVPG which spontaneously separated from the Si substrate during cooling. The original substrate was located toward the bottom of the layer as it is oriented in (b).  c) Magnified view of the former interface between GaN/AlN and Si showing that the Si stripes have completely diffused into the growing film, leaving surface voids in their former location.
7. **In-situ cleaning of GaN(0001) surfaces in an MOVPE environment**

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7.1 ABSTRACT

The presence of ammonia in a metalorganic vapor phase epitaxy (MOVPE) system configured for the growth of GaN films is necessary and sufficient to remove adsorbed O- and C-containing species from the (0001) surface of this compound without measurable decomposition of this surface. Chemical and microstructural evidence in support of this statement has been obtained from investigations concerned with the extension of a previously developed in-situ process route for cleaning heated GaN(0001) surfaces in a molecular beam epitaxy environment using flowing ammonia to the higher pressure regime of MOVPE. Thin films of GaN were deposited under 20 torr total pressure on GaN templates, previously exposed to the laboratory ambient, and heated in either a nitrogen/hydrogen or an ammonia/hydrogen mixture to the deposition temperature of 1020°C. Secondary ion mass spectroscopy of these samples revealed significant concentrations of carbon and oxygen at the GaN/GaN interface in the former and the absence of these contaminants above the detection limits of the instrument in the latter. The surfaces of the templates heated in the nitrogen/hydrogen atmosphere also decomposed sufficiently to form a very thin liquid Ga layer that reacted with ammonia to form a GaN-containing film either at the outset of film growth or on cooling in an ammonia/nitrogen atmosphere. Atomic force microscopy (AFM) showed a smoother surface for the GaN films deposited on templates heated and cleaned in the ammonia/hydrogen mixture relative to films deposited on templates heated in the nitrogen/hydrogen mixture. The latter surface contained both a higher density of step terminations, indicative of a higher density of threading dislocations having screw and mixed character, and pits.
7.2 INTRODUCTION

The surfaces of GaN films and GaN wafers, the latter derived, e.g., via laser lift-off [1], exposed to the ambient acquire a contamination layer containing carbon and oxygen [2,3]. These impurities have a deleterious effect on the properties of films [4] and of metal contacts [5,6] subsequently deposited on the contaminated surface. Ex-situ cleaning techniques including wet chemistry [2] and ultraviolet/ozone [7], and in-situ ultrahigh vacuum techniques such as nitrogen ion sputtering and vacuum annealing [8] do not yield a stoichiometric GaN surface free of C and O contamination. By contrast, Tracy et. al. [9] achieved O- and C-free, stoichiometric (0001) surfaces of n- and p-type GaN, within the detection limits of ultraviolet and x-ray photoelectron spectroscopies, via in-situ exposure at 860°C to flowing ammonia at 10^{-4} torr in a gas source molecular beam epitaxy (GSMBE) system. Atomic force microscopy (AFM) and low energy electron diffraction measurements showed that the surface microstructure of these GaN films remained unchanged. A corresponding in-situ technique for the higher pressure regimes normally employed in metalorganic vapor phase epitaxy (MOVPE) has not been reported. The advantages of such a technique would be the removal of contamination prior to (i) homoepitaxial growth on either thick pseudo-bulk GaN substrates or the initial GaN template layers preceding either lateral epitaxial overgrowth [10] or pendeo-epitaxy [11] and ii) growth of the second nitride layer in any device requiring two growth sequences. The current investigation borrows from the process route developed by Tracy et. al. [9] and extends it to an MOVPE environment by incorporating flowing ammonia into the gas stream during heating to the deposition temperature of GaN of 1020°C. The cleaned GaN surface is capped with a homoepitaxial GaN film and the GaN/GaN interface is probed via depth-profile secondary ion mass
spectroscopy. The surface microstructure of the homoepitaxial films was also investigated to verify the preservation of the GaN surface during the cleaning procedure and assess the effect of different heating ambients on the microstructure of the homoepitaxial film.

7.3 EXPERIMENTAL PROCEDURES

Unintentionally doped, 1 µm thick, GaN(0001) template layers were deposited via MOVPE on 0.1 µm thick AlN buffer layers deposited in the same growth run on 6H-SiC(0001) substrates in a vertical, resistively heated, cold wall, pancake-style system. Details regarding the growth and characterization of these layers are reported elsewhere [12]. The GaN templates were stored in Teflon®-based containers. Each template surface was cleaned ex-situ in an HCl:DI H2O (1:1) solution at 75°C for 10 minutes immediately prior to loading into the MOVPE system for homoepitaxial growth or annealing. Previous studies have shown that this procedure removes some contamination from the GaN surface; however, residual C and O remain [2]. The chamber was then evacuated to 10⁻⁶ torr and selected templates were heated individually at a rate of 90°C/minute to 1020°C within different flowing ambients at a constant total pressure of 20 torr. The ambients included i) 3 slm N₂ + 4 slm H₂, hereafter simplified as nitrogen/hydrogen heating, and ii) 3 slm NH₃ + 4 slm H₂, hereafter referred to as ammonia/hydrogen heating. A ~0.25 µm thick, homoepitaxial GaN film was deposited on each template. Each thin film assembly was then cooled under 3 slm NH₃ + 4 slm H₂. Selected templates were also heated, annealed and cooled according to the parameters in Table I.

The GaN/GaN interface of the homoepitaxial films was quantitatively chemically analyzed using a Cameca 6F SIMS in tandem with ion implanted GaN standards of known C
and O concentration profiles. The nominal background concentrations for oxygen and carbon in this instrument are $\sim 1 \times 10^{17} \text{ cm}^{-3}$ and $\sim 3 \times 10^{17} \text{ cm}^{-3}$, respectively. The surface microstructure of the annealed templates and the homoepitaxial films were determined using a Digital Instruments D3000 AFM equipped with a Si cantilever and tip operating in tapping mode and a JEOL 6400F field emission scanning electron microscope (SEM).

7.4 RESULTS AND DISCUSSION
7.4.1 Profiles of impurity concentrations

SIMS profiles of hydrogen, carbon and oxygen concentrations as a function of depth within two GaN film/GaN template assemblies and their associated interfaces are shown in figures 1(a) and (b). The templates on which the films were deposited were previously exposed to the laboratory ambient and then heated in the MOVPE chamber to 1020°C in either a nitrogen/hydrogen or an ammonia/hydrogen mixture. Figure 1(a) shows marked increases in the concentrations of carbon and oxygen at a depth of approximately 0.22 µm below the sample surface. This depth corresponds well to the expected thickness of 0.25 µm for the film and indicates that these species were present on the surface of the associated template prior to the initiation of the homoepitaxial growth. An increase in the hydrogen concentration at this depth was not observed.

Evidence that heating the GaN template layer in ammonia results in a cleaner surface for homoepitaxy is shown in figure 1(b) by the essentially constant concentrations of carbon and hydrogen over most of the thickness of the sample. Additionally, these concentrations were found to be at or near the aforementioned detection limits for these species. SIMS profiles acquired from additional samples in which the GaN templates were heated in
ammonia/hydrogen and held at the growth temperature for ten minutes prior to film growth were identical to figure 1(b). These results show that (1) heating as-loaded GaN(0001) surfaces containing adsorbed O- and C-containing species to at least 1020°C irrespective of the atmosphere is not sufficient to remove these species and (2) heating the same surface in the presence of ammonia is sufficient to remove these species.

The results of X-ray photoelectron spectroscopy studies by King et. al. [2] revealed that the adsorbed oxygen-and carbon-containing species on as-loaded GaN(0001) surfaces exposed to a laboratory environment consisted of OH− and O2− bonded to Ga and C-H and C-O, respectively. The carbon in these species originated from the pyrolysis reaction of the triethylgallium [13] and/or from the graphite heater employed in the growth reactor and/or from the hydrocarbons in the laboratory environment. Ammonia has been shown to be an excellent scavenger of hydrocarbons [14] and has been observed to chemisorb dissociatively on GaN (0001) surfaces to form NH2 and H species [15]. As such, the removal of the C- and O-containing contaminants during heating in this gas is believed to occur via reactions with the ammonia fragments and the atomic hydrogen.

A second explanation regarding the absence of contaminants at the GaN/GaN interface is that the surface of the template layer decomposed upon heating to the growth temperature. However, ammonia has been observed to inhibit or dramatically decrease the decomposition of GaN as compared to heating in vacuum, hydrogen, nitrogen or various nitrogen/hydrogen mixtures [16,17]. It has been postulated that the ammonia blocks sites for N2 formation and desorption [18]. To confirm or deny the preservation of the GaN surface, a template was heated, annealed for 5 minutes and cooled in our ammonia/hydrogen mixture. Representative 5x5 µm AFM images of the resultant surface before (a) and after (b) heating.
and annealing are shown in figure 2. The RMS roughness of the respective images is 0.24 nm and 0.30 nm. The images clearly reveal that the surface of a GaN template layer heated, annealed, and cooled in our ammonia/hydrogen mixture does not undergo observable decomposition. By contrast, it will be shown below that the surfaces of GaN templates heated to 1020°C in the nitrogen/hydrogen ambient do decompose. Therefore, the cleaning effect deduced from the SIMS measurements cannot be attributed to decomposition of the surface during heating.

7.4.2 AFM of homoepitaxial GaN films

Figure 3 shows 5x5 µm AFM images of the (0001) surfaces of the homoepitaxial GaN films deposited after heating the underlying template surfaces in nitrogen/hydrogen (a) and ammonia/hydrogen (b). The respective RMS roughness values for the two films are 1.04 nm and 0.36 nm over a 25 µm² area and 4.13 nm and 1.09 nm for a 400 µm² area. The microstructures of the surfaces of both films show that they grew via the dislocation-mediated step-flow growth mode typical of GaN deposited by MOVPE [19]; however, there are two marked differences in these microstructures. Firstly, the surface of the film deposited on the template heated in nitrogen/hydrogen contained 600-800 nm diameter pits having a density of ~7x10⁶ cm⁻². An example of these pits is shown in the lower right corner of figure 3 (a). These pits were not observed in the film deposited on the template heated in ammonia/hydrogen. Secondly, the surface of the film shown in figure 3 (a) contains a larger number of step terminations that are the ends of threading dislocations having screw or mixed character [19] than are observed in the film shown in figure 3 (b). Circles in these figures surround selected terminations. Thus, the homoepitaxial film deposited on the GaN
template heated in nitrogen/hydrogen contains a higher density of threading dislocations relative to the film deposited on a similar template heated in ammonia/hydrogen. Moreover, the density of step terminations in the surface of a homoepitaxial film deposited after heating the GaN template in ammonia and annealing for ten minutes yielded no discernible differences relative to that observed on the surface of a film deposited on a template heated in ammonia/hydrogen without annealing. We believe that the density of these defects is correlated with the concentrations of impurities on the template surfaces. Support for this statement is found in the results of several previous studies (see e.g., Refs. 4,20,21) that have shown that the removal of contaminants from the surfaces of silicon-and gallium arsenide-based substrates decreases markedly the concentration of growth related zero- and one-dimensional defects in the subsequently deposited epitaxial films. These results correlate well with the SIMS measurements of the interfaces of similarly processed samples.

7.4.3 SEM and AFM of GaN templates.

Previous studies by Koleske et. al. [22] showed that GaN decomposes in the presence of hydrogen and nitrogen over the range of pressures employed in MOVPE. This results in the formation of Ga droplets on the remaining GaN surface, since the rate of GaN decomposition is greater than the rate of Ga evaporation. Additionally, they observed that the onset of measurable GaN decomposition occurred in the range of 800-900°C and varied with the reactor pressure and the nitrogen/hydrogen ratio. Since the temperature for homoepitaxial growth of GaN in this study exceeds this temperature window for decomposition and decomposition increases exponentially with an increase in temperature, it is expected that the GaN surfaces of our templates decompose during heating in the
nitrogen/hydrogen ambient. The effect of heating ambient and anneal time on template decomposition is shown in figures 4 (a-d) for templates A-D listed in table I, respectively.

The GaN template heated in nitrogen/hydrogen and immediately cooled in ammonia/hydrogen maintains a relatively smooth surface microstructure, comparable to that of the as-grown material, as shown in Figure 4 (a). However, annealing the template for 5 minutes in the former ambient resulted in marked decomposition that is revealed by the hexagonal pits in figure 4 (b). A comparison of either figures 4 (a) and 4 (c) or 4 (b) and 4 (d) shows the effect of cooling the template in an ammonia/hydrogen ambient rather than in a nitrogen/hydrogen ambient. Cooling under the latter results in the continued decomposition of the template surface. The surfaces that were annealed and cooled in the absence of ammonia also contained droplets, an example of which is shown in the center of the hexagonal pit in the lower right corner of figure 4 (d). Energy dispersive x-ray spectroscopy confirmed these droplets to be Ga, in agreement with the results of Koleske et. al. [22]

These droplets were not observed on the surfaces of the templates cooled in ammonia/hydrogen. This provides additional, though indirect, evidence that the droplets are Ga, since any Ga present on the surface when ammonia was introduced would have reacted to form GaN.

Figure 5 shows 5x5µm AFM images of templates A-D denoted in table I and shown in the SEM images of figure 4. For templates in which significant decomposition occurred, the AFM images were acquired from regions between the hexagonal pits. The surfaces of the templates heated in nitrogen/hydrogen show a much rougher microstructure, with RMS roughness values of 3.09, 3.15, 3.52, and 19.0 nm for figures 5 (a-d), respectively, compared to the surfaces of the templates processed only in ammonia/hydrogen and shown in figure 2.
Moreover, the former surfaces no longer exhibit the step and terrace microstructure typically observed for MOVPE-grown GaN, but instead contain numerous islands. The areas of these islands increased as the time above the decomposition temperature without the presence of ammonia increased. We propose that for templates A and B, i.e., those cooled in the ammonia/hydrogen mixture, the observed surface features are due to a thin GaN-containing layer that formed via reaction of ammonia with liquid Ga which was on the surface as a result of decomposition during heating. For templates C and D, i.e., those cooled in nitrogen/hydrogen mixture, we propose that the observed surface features are roughened GaN as a result of decomposition of the template. We did not observe decomposition in a step-flow mode, as has been previously reported [22].

To confirm that the island-like surface features observed in figures 5 (a-d) were GaN and not, for example, small Ga droplets, templates B and C, which were within the window for decomposition for approximately the same time despite their different cooling ambients, were exposed to a 30% HNO₃ solution for 10 minutes. This solution is known to remove Ga droplets from GaN surfaces [22]. Representative 5x5µm AFM images of the surfaces of templates B and C after the acid dip are shown in figures 6 (a) and (b), respectively. The nitric acid had a significant effect on template B (compare figure 6 (a) with figure 5 (b) and note the change in island size) but little-to-no effect on template C (compare figure 6 (b) with figure 5 (c)) It is expected that if a GaN-containing layer formed on the surface of template B during cooling, it would be either polycrystalline or a two-phase mixture of Ga and GaN and thus easily removed in the HNO₃ solution to reveal a surface microstructure very similar to that of template C prior to the exposure to the HNO₃. The similarity of the microstructures of the surfaces of templates B and C after HNO₃ exposure supports the hypothesis that the
surface features formed during cooling in the nitrogen/hydrogen mixture are roughened GaN as a result of decomposition, and the features formed during cooling in ammonia are GaN or a mixture of Ga and GaN.

Based on the evidence from figures 2-6, we propose the following sequences for the homoepitaxial growth on GaN templates after heating the latter in ammonia/hydrogen or nitrogen/hydrogen mixtures. The original step-and-terrace microstructure of the GaN surface remains unchanged when the template is heated in ammonia/hydrogen, as shown by a comparison of figures 2 (a) and 2 (b), and the carbon- and oxygen-containing species are removed from the surface via reaction with ammonia and/or ammonia fragments and hydrogen. Subsequent homoepitaxial growth occurs via step-flow mechanism, as has been previously shown for GaN deposited on Al$_x$Ga$_{1-x}$N [12]. The resultant film is smooth and the contaminants are below the detection limits of SIMS at the GaN/GaN interface. For the templates heated in nitrogen/hydrogen, the GaN surface decomposes, leaving a thin layer of liquid Ga on the surface prior to the initiation of homoepitaxial growth. However, the decomposition is insufficient to remove the contaminants from the GaN/GaN interface, as shown in the SIMS profiles in figure 1 (a). In this latter case, the initial growth of the homoepitaxial layer consists of both the immediate reaction of ammonia with the Ga on the surface of the template, the microstructure of which should be similar to that shown in figure 5 (a), and the homoepitaxial growth of GaN via the reaction of ammonia and TEG. The resultant surface microstructure of the subsequently deposited 250 nm GaN film still features step-flow growth but the surface is rougher and pitted, as compared to the film deposited on the template heated in ammonia/hydrogen.
7.5 SUMMARY

A previously established ammonia-based process for cleaning GaN surfaces in a high vacuum GSMBE environment has been extended to an MOVPE environment at 20 torr. Incorporation of ammonia into the gas flow during the heating of [0001]-oriented GaN templates to 1020°C reduces the concentrations of carbon- and oxygen-containing species on this surface below the detection limits of SIMS, as shown by depth profiles through a GaN film/GaN template assembly. Templates heated in nitrogen/hydrogen mixtures continue to show relatively high concentrations of these contaminants at the GaN/GaN interface. It is believed that the carbon and oxygen are removed from the surface via reaction with ammonia and/or ammonia fragments and hydrogen. AFM revealed a smoother surface microstructure for the homoepitaxial GaN films deposited after ammonia cleaning. The presence of ammonia during heating and cooling of template layers also prevents GaN decomposition prior to further growth. Conversely, heating the template layers in a nitrogen/hydrogen mixture results in the decomposition of the surface and the formation of a thin layer of Ga. The surfaces of homoepitaxial films grown on GaN templates heated in the absence of ammonia contained both pits and a higher density of step terminations. This rougher surface microstructure is a consequence of the reaction between the liquid Ga and ammonia to form a thin GaN-containing layer on the surface of the template at the outset of homoepitaxial growth. The higher density of step terminations is indicative of a higher density of threading dislocations having screw and mixed character.
7.6 REFERENCES


7.7 TABLES AND FIGURES

Table I  Annealing conditions for GaN/AlN/SiC templates heated to 1020°C in an MOVPE system.  N₂/H₂ refers to an ambient composed of 4 slm N₂ + 3 slm H₂.  NH₃/H₂ refers to an ambient composed of 4 slm NH₃ + 3 slm H₂.

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<th>Cooling</th>
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<td>D</td>
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Figure 1 SIMS depth profiles of H, C, and O acquired from [0001]-oriented GaN-film/GaN-template heterostructures in which the template was heated to 1020°C in a mixture of either (a) nitrogen and hydrogen or (b) ammonia and hydrogen prior to the homoepitaxial growth of the films having a nominal thickness of 0.22 µm.
Figure 2  AFM images acquired using 5 x 5 µm scans of the (0001) surface of a GaN template (a) before and (b) after being heated, annealed for 5 minutes and cooled in an ammonia/hydrogen atmosphere. The Z range is 4 nm in each case.
Figure 3  AFM images acquired using 5 x 5 µm scans of the (0001) surfaces of homoeptaxial GaN films deposited on GaN templates previously heated to 1020°C in (a) nitrogen and hydrogen and (b) ammonia and hydrogen. The Z range is 5 nm in each case.
Figure 4  SEM images showing both the surface and cross section of GaN templates subjected to the following heat treatments: (a) heating in nitrogen/hydrogen to 1020°C and cooling in ammonia/hydrogen, (b) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, (c) heating in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen, (d) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in nitrogen/hydrogen. The hexagonal pits are the result of GaN decomposition. Note the Ga droplets within pits shown in (d).
Figure 5  5x5 µm AFM scans of GaN templates after (a) heating in nitrogen/hydrogen to 1020°C and cooling in ammonia/hydrogen, (b) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, (c) heating in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen, (d) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in nitrogen/hydrogen. The Z ranges are 15, 15, 30, and 100 nm for the respective images. (a) and (b) show a thin GaN-containing layer formed via reaction of liquid Ga with ammonia. (c) and (d) show a decomposed roughened GaN surface.
Figure 6 5x5 μm AFM scans of GaN templates exposed to 30% HNO₃ for 10 minutes following (a) heating in nitrogen/hydrogen to 1020°C, annealing 5 minutes, and cooling in ammonia/hydrogen, and (b) in nitrogen/hydrogen to 1020°C and cooling in nitrogen/hydrogen. The Z ranges are 15 and 30 nm respectively. (a) reveals the roughened GaN surface after removal of the thin GaN-containing layer observed in figure 5 (b). (b) shows that the roughened surface formed upon heating in the absence of ammonia is unaffected by exposure to HNO₃.
8. Summary
As stated in the introduction, the goals of this dissertation were to obtain an improved understanding of the evolution of strain and defects in III-nitride heterostructures grown by metalorganic vapor phase epitaxy and to explore techniques for lateral overgrowth, pseudo-bulk substrate formation and in-situ surface cleaning. In chapter 2 it was demonstrated that AlN initially grew on as-received SiC substrates in the form of flat-topped islands which coalesced and subsequently grew in the dislocation-mediated step-flow mode. Complex misfit dislocation networks were observed on terraces for thin AlN films and polishing scratches in the substrate resulted in undulations in the thicker AlN films. Defects in the mechanically-polished SiC substrates and/or condensation of point defects were proposed to explain the highly defective regions present at the AlN/SiC interface. The deposition of GaN on these AlN layers resulted in growth by the Stranksi-Krastanov mode, with an initial 2D wetting layer followed by island nucleation in the undulations of the AlN. The majority of the threading dislocations (TDs) in the GaN layers were seen to originate from the TDs present in the AlN buffer layer. Increasing the thickness of the GaN resulted in a reduction of the TD density due to annihilation mechanisms.

In chapter 3, the thickness of the GaN layer as well as the composition of the buffer layer (i.e. AlN or Al\textsubscript{15}Ga\textsubscript{85}N) was shown to influence the biaxial strain in the layer. GaN layers were determined to be under compression in the growth plane when deposited on either buffer layer due to incomplete relaxation of the coherent strain. As the thickness of the GaN layer increased, this strain gradually decreased, following an exponential dependence. The strain was also observed to be inhomogeneous through the GaN layer, with the region near the GaN/AlN interface being under increased compression relative to the surface.
The growth of Al\textsubscript{x}Ga\textsubscript{1-x}N directly on SiC was further explored in chapter 4 using atomic force microscopy, X-ray diffraction, and transmission electron microscopy (TEM) in conjunction with finite element simulations. The presence of strain at the initial growth of these layers is believed to be the cause of the inhomogeneous Al distribution observed at the Al\textsubscript{x}Ga\textsubscript{1-x}N/SiC interface. Narrow, irregular trenches formed in the surface as the phase-separated Al-rich and Al-deficient islands coalesced and grew. Further growth resulted in a second layer of Al-rich and Al-poor regions, this time shifted relative to the original domains at the interface due to growth kinetics.

In an effort to reduce the defect density in III-Nitride films as well as gain further insight into the formation of defects, growth of AlN and GaN/AlN on hydrogen-etched SiC was explored in chapter 5. The process of hydrogen etching was shown to remove the polishing scratches from the SiC surface and produce unit-cell-height steps. AlN layers nucleated both at the step edges and on the terraces of these substrates due to the low surface mobility of the Al species at the growth temperature. The undulations present on AlN surfaces with conventionally polished substrates were absent in the case of hydrogen-etched substrates and the pit density decreased. Irregular networks of misfit dislocations, some of which traversed the steps from one terrace to another, were observed in 15 nm thick AlN layers. The majority of the TDs observed in these films were \( a \) type. Similar to growth on the conventional as-received SiC substrates, GaN grew in the Stranski-Krastanov mode on AlN/hydrogen-etched-SiC substrates, with the initial islands forming on hillocks present on the AlN surface. High resolution X-ray diffraction analysis revealed that the GaN deposited on hydrogen-etched SiC substrates was under less compressive strain than when deposited on as-received substrates and that the full-width-at-half-maximum of the X-ray rocking curves
yielded statistically similar results, indicative of comparable TD densities. This conclusion was supported by TEM images which showed only a slight reduction in the TD density from 3.5- to 1.4x10^9 cm^-2 for 1000 nm thick GaN films deposited on 100 nm buffer layers on as-received and hydrogen-etched SiC substrates respectively. The TDs in the GaN were again observed to be predominantly a type and to form as a result of propagation of TDs in the AlN across the GaN/AlN interface.

Chapter 6 explored the technique of cantilever epitaxy of GaN on stripe-patterned Si substrates as a means of achieving reduced TD densities through lateral overgrowth as well as free-standing pseudo-bulk GaN substrates through spontaneous separation. Mechanics and finite element models predicted the generation of significant tensile stresses in the Si stripes as a result of the mismatch in thermal expansion coefficients between GaN and Si.

The effect of growth temperature and V/III ratio during GaN deposition were evaluated to arrive at high lateral growth rates, reduced vertical growth rates and smooth surfaces. Increasing the growth temperature for GaN decreased the vertical growth rate due to increased desorption of Ga from the GaN(0001) surface. The lateral growth rate increased as a function of temperature over the range investigated due to the increased diffusion length of the Ga species and/or an increased supply of active N as a result of more complete NH₃ decomposition at elevated temperature. Similar effects on the growth rates were observed by increasing the V/III ratio via an increase in the NH₃ flow rate. In this case the vertical growth rate decreased due to the blocking of surface sites by NH₃. The lateral growth rate initially increased as a result of an increased supply of active N and subsequently decreased due to the high concentration of atomic surface H resulting from NH₃ decomposition. Increasing the V/III ratio by decreasing the flow rate of TEG resulted in decreased vertical
and lateral growth rates as a result of the decreased flux of the minority growth species. However, the vertical growth rate decreased more rapidly than the lateral growth rate indicating that the incorporation rate of the Ga species on the (0001) surface decreased at high V/III ratios. Characterization of the GaN layers grown by cantilever epitaxy with optimized conditions revealed dramatically reduced TD densities in the laterally-grown GaN wings compared to the film deposited over the Si stripes, as evidenced by X-ray diffraction, cathodoluminescence and TEM.

Problems arose for long deposition times of GaN due to diffusion of Si through the AlN buffer layer to the surface of the GaN and subsequent formation of Si$_x$N$_y$ on the growth surface. This Si$_x$N$_y$ was observed with X-ray photoelectron spectroscopy and energy dispersive spectroscopy in conjunction with both a scanning electron microscope and a scanning transmission electron microscope. The amorphous Si$_x$N$_y$ resulted in roughening of the subsequently deposited GaN layers. Increasing the thickness of the AlN buffer layer and/or changing its microstructure through growth condition modifications were shown to delay the outdiffusion of Si from the substrate. Despite the improvement in the AlN buffer layers, the outdiffusion of the Si substrate continued during the deposition of a thick GaN layer by IVPG. Although the thick layer spontaneously separated from the substrate after cooling to room temperature, its surface was rough and the Si stripes completely diffused into the overlying layer. Separation therefore occurred by delamination at the interface between the Si substrate and the GaN deposited in the trenches between the Si stripes.

Finally, in chapter 7, a previously established ammonia-based process for cleaning GaN surfaces in a high vacuum environment was extended to the higher pressure environment of MOVPE. Analysis by secondary ion mass spectroscopy revealed a reduction
in the concentration of C and O impurities at the GaN/GaN interface of a homoepitaxial GaN film when growth was preceded by heating in an ammonia atmosphere. It is believed that the C and O are removed from the surface via reaction with ammonia and/or ammonia fragments and hydrogen. The GaN layers deposited after the ammonia cleaning procedure also demonstrated a smoother surface than those layers heated to the growth temperature in a mixed hydrogen/nitrogen atmosphere. The rougher surface is believed to be the result of the reaction between liquid Ga, present due to surface decomposition, and ammonia to form a thin GaN-containing layer at the outset of homoepitaxial growth.
Appendix 1.

Growth and Characterization of AlN and GaN Thin Films Deposited on Si(111) Substrates Containing a Very Thin Al Layer

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A1.1 ABSTRACT

AlN films and GaN films with AlN buffer layers were deposited via metalorganic vapor phase epitaxy on Si(111) substrates previously exposed to trimethylaluminum for increasing times. Atomic force microscopy (AFM) was used to determine the influence of Al pre-flow time on the nucleation and surface morphology of the AlN and GaN films. When preceded by a 10 second Al pre-flow, AlN films feature an increased and more uniform nucleation density as compared to films deposited without Al pre-flows. Ten second Al pre-flows were also found to result in a reduction of the RMS roughness for 100 nm thick AlN films from 3.6 nm to 1.0 nm. AFM of 0.5 µm thick GaN films deposited on AlN buffers with varying pre-flow times showed reduced roughness and decreased pit density when using Al pre-flows of 10 or 20 seconds. High resolution x-ray diffraction of the GaN films showed a reduction in the average full-width half-maximum (FWHM) of the GaN (00.2) reflection from 1076 arcsec to 914 arcsec when the AlN buffer layer was initiated with a 10 second Al pre-flow. Increasing the pre-flow time to 20 seconds and 30 seconds resulted in average (00.2) FWHM values of 925 arcsec and 928 arcsec, respectively. Similar behavior of the peak widths was observed for the (30.2) and (10.3) reflections when the pre-flow times were varied from 0 to 30 seconds.

A1.2 INTRODUCTION

Silicon (111) represents an attractive alternative to sapphire and silicon carbide for III-nitride heteroepitaxy due to its low cost, nearly defect free microstructure over large areas, wide range of available resistivities, and the possibility for integration of III-nitride based devices with Si-based devices on one chip. Due to the meltback etching of Si by Ga, it is
necessary to employ a buffer layer of another material for deposition of GaN [1]. Some materials which have been employed as buffer layers include GaAs [2], oxidized AlAs [3], 3C-SiC [4], and AlN [5,6]. This work will focus on the use of an AlN buffer layer since the lattice mismatch induces a compressive stress in the GaN, which can partially compensate for the thermally induced tensile stress [7] between GaN and Si, and is easily deposited in a conventional III-nitride metalorganic vapor phase epitaxy system (MOVPE) system. In using AlN as a buffer layer, numerous researchers have reported the formation of an amorphous 1-4 nm thick Si$_x$N$_y$ layer at the Si/AlN interface [5,8,9,10], purportedly due to the thermal nitridation of the Si surface in an ammonia atmosphere. This amorphous layer is reported to be discontinuous or of varying thickness across the interface. Indeed, in studying the nitridation of Si(111) in various nitriding agents, Wang et. al. observed Si$_x$N$_y$ forming at temperatures above 800°C and saturating at a thickness of 2 nm [11]. It is theorized that this amorphous layer, although still allowing AlN nucleation and subsequent single crystal GaN epi-layers, can lead to excessive tilting and twisting of the AlN subgrains which compose the buffer layer, thereby leading to an increased dislocation density. In an attempt to prevent this nitridation, a few investigators have explored the effect of initiating the AlN buffer layer with an exposure of Al without the presence of ammonia, hereafter referred to as an Al pre-flow, rather than the usual simultaneous introduction of Al and N species. Some have reported improvements when using pre-flows [12,13,14], and others have reported no significant difference [15]. However, the use of Al pre-flows has yet to be studied in detail. In this work, AlN films and GaN films with AlN buffer layers were investigated to determine the effect of various Al pre-flow times. The goal was to deposit a thin layer of Al on the Si surface in order to prevent the nitridation of the substrate. Atomic force microscopy was
used to determine the influence of Al pre-flows on the surface morphology of AlN and GaN films. High resolution x-ray diffraction (HRXRD) was used to investigate the effect of the Al pre-flow time on the microstructure of GaN films on AlN buffer layers by examining both on- and off-axis rocking curves. The samples with varying pre-flow times were compared to reference samples in which the Al and N species were introduced simultaneously.

A1.3 EXPERIMENTAL PROCEDURE

Two inch n-type (resistivity=1-20Ω-cm) Si (111) wafers were used as substrates. The wafers were cleaned sequentially in H₂O₂: H₂SO₄ (1:5) for 10 minutes to oxidize the surface and in HF:H₂O (1:10) for 10 minutes to remove the oxide and leave a hydrogen-terminated surface [16] prior to loading into a vertical, cold-walled, resistively-heated, pancake-style MOVPE system. The chamber was evacuated to ~2x10⁻⁶ torr prior to growth and was held at 20 torr during all growth steps. Following an additional cleaning step at 1100°C in hydrogen to ensure the removal of all oxide from the Si surface, Al pre-flows were performed with 5.5 µmol/min trimethylaluminum for 10, 20, and 30 seconds. A fourth sample set was grown without any Al pre-flow. Three samples of each type were grown for statistical significance. The 100 nm thick AlN buffer layer was grown via the addition of 3.0 slm of ammonia at the aforementioned temperature and Al flow. For AlN films, the samples were then cooled to room temperature in flowing NH₃ to prevent significant decomposition of the surface. For GaN films, the temperature was lowered to 1015°C and the GaN was grown to a thickness of 0.5 µm. Triethylgallium at 100 µmol/min and ammonia at 3 slm were employed as the source gases for GaN. Hydrogen served as the carrier and diluent gas during all growth steps. The growth rates for AlN and GaN were 300 nm/hr and 1700 nm/hr, respectively.
Atomic force microscopy images were acquired with a Dimension D3000 SPM equipped with a Si tip operating in the tapping mode. Double axis on- and off-axis HRXRD rocking curve measurements were performed using a Philips X’Pert Materials Research Diffractometer with a copper x-ray source at a power setting of 40 kV and 45 mA and an open slit on the detector side. Off-axis rocking curves were acquired in skew-symmetric diffraction geometry.

A1.4 RESULTS

AFM height images of 100 nm AlN films deposited with 0, 10, 20 and 30 second Al pre-flows are shown in Figure 1. The respective average RMS roughness values are 3.6, 1.0, 4.9 and 3.4 nm. As shown in the figure, all AlN films exhibit a grain-like morphology, although Figure 1b seems to show the beginning of a step-flow growth mode, albeit one mediated by a very high density of threading dislocations and limited by the fact that the film is only 100 nm thick.

The reason for the different surface morphologies of the AlN with 0 and 10 second pre-flows may lie in the difference in initial nucleation of the two samples. Figure 2 shows AFM surface plots after 30 seconds of AlN deposition. As shown in the figure, when growth is initiated with a 10 second Al pre-flow, the nucleation density is higher and more uniform. The Al pre-flow may result in a uniformly Al-covered surface rather than a discontinuous Si₃N₄ as mentioned previously. This would, in turn, result in more uniform nucleation of AlN and promote more rapid coalescence of the growing film. In comparison to Figure 1b, Figure 1(c) and (d) show rougher surfaces and apparent clustering of smaller grains separated
by deeper voids. The reason for this rougher surface is unclear as of this writing but may result from too long of an Al pre-flow and subsequent reaction at the Al-Si interface.

Figure 3 shows representative AFM height images for the GaN films deposited on AlN buffer layers similar to those shown in Figure 1. The associated average RMS roughness values for the four sample sets are plotted vs. Al pre-flow time in Figure 4. All samples show the commonly observed dislocation-mediated step-flow growth mode commonly observed for GaN deposited via MOVPE [17]. In addition to the dislocations which are observed as small pits pinning the steps, larger black pits are also observed on the surface. The density of these larger pits is greatest for the sample with no pre-flow and smallest for the samples with 10 and 20 second pre-flows. Following the convention of Lilienthal-Weber et. al.[18], it is unclear whether these large pits are nanotubes, which extend deep into the GaN, or pinholes, which have a finite depth, since AFM cannot provide depth information for such a small feature. As shown in the figures, the roughness decreases with increasing pre-flow time up to 20 seconds and then increases slightly for 30 seconds. The difference in the surface morphology of the GaN films is likely a result of the different surface morphologies of the AlN buffer layers. It is clear that the smoother buffer layer resulting from the 10 second Al-pre-flow would result in a smoother GaN epi-layer as compared to the buffer layer grown without an Al pre-flow. However, it is unclear why the roughest buffer layer, that which was achieved with a 20 second Al pre-flow, resulted in the smoothest GaN film.

Figure 5 shows the FWHM of the rocking curves for three GaN reflections, namely (00.2), (10.3) and (30.2), plotted vs. the Al pre-flow time. The plotted data points represent mean values from multiple measurement points on multiple samples and the error bars
represent plus and minus one standard deviation. As shown in the figure, the FWHM of the rocking curves decreases for all Al pre-flow times compared to using a simultaneous introduction of Al and ammonia. This trend is consistent for on-axis (00.2) and both off-axis reflections. Considering the GaN film to be composed of mosaic blocks which are both tilted and twisted against one another, the (00.2) reflection is indicative of the out of plane tilt in the sample, which can be correlated to the density of threading dislocations with screw character [19]. Therefore, the use of Al pre-flows is shown to result in decreased FWHM values and thus lower dislocation densities in the subsequently grown GaN films. However, Follstaedt et al. [20] have shown that the most prevalent threading dislocation in GaN films with an AlN buffer layer on Si substrates are edge type. Estimation of pure edge threading dislocations, or in-plane twist of the mosaic blocks, via HRXRD would require the incident x-ray beam to be perpendicular to the basal plane of the film, an impossible measurement with the employed HRXRD hardware. Alternatively, one may examine the FWHM of increasingly off-axis reflections and extrapolate to the perpendicular case. Figure 6 shows such a plot of GaN FWHM vs. increasing inclination angle for the cases of 0 and 10 second pre-flows. Since the FWHM values for 20 and 30 second pre-flows are statistically similar to the 10 second case, these curves are excluded from Figure 6 for clarity. Various models have been proposed to fit the data of these plots [21,22] but here the fits are simply empirical polynomial fits extrapolated to the perpendicular case. Empirical fits were performed since a widespread consensus does not exist in the literature as to the best manner in which to fit the data, especially when the relative populations of dislocation types are not as well studied as the case for GaN on sapphire substrates. However, by extrapolating to the case for a 90° inclination angle, or by simply taking the (30.2) reflection as a good indicator of the out of
plane twist [23], it is shown that the use of Al pre-flows decreases the density of edge type threading dislocations in epitaxial GaN films on Si substrates. The decreased dislocation density observed by HRXRD may result from the increased AlN grain size, as shown in Figure 1, since it has been observed that many of the dislocations in GaN deposited with AlN buffer layers on Si substrates originate at the edges of AlN grains [20].

A1.5 CONCLUSIONS

The use of Al pre-flows prior to deposition of AlN layers on Si (111) substrates has been demonstrated to result in dramatically decreased film RMS roughness for 10 second pre-flows as compared to 0, 20 and 30 second pre-flows. This may result from coverage of the Si surface by a thin layer of Al, thus preventing thermal nitridation of the substrate. AFM images also show that a 10 second Al pre-flow resulted in an increased and more uniform initial nucleation of AlN. GaN films deposited on 100 nm AlN films initiated with 10, 20 and 30 second Al pre-flows exhibit smoother surface morphologies, as evidenced by AFM, as well as decreased HRXRD rocking curve FWHM values, indicative of decreased dislocation densities.
A1.6 REFERENCES


Figure 1 2x2 µm AFM height images of 100 nm AlN films deposited on Si(111) previously exposed to Al pre-flows of 0 (a), 10 (b), 20 (c) and 30 seconds (d). Respective RMS roughness values are 3.6, 1.0, 4.9 and 3.4 nm.
**Figure 2** 500x500 nm AFM surface plots of 30 seconds AlN deposition on Si(111) previously exposed to Al pre-flows of 0 (a) and 10 seconds (b).
Figure 3 5x5 \( \mu m \) AFM height images of 0.5 \( \mu m \) GaN films deposited on 100 nm AlN buffer layers previously initiated with 0 (a), 10 (b), 20 (c) and 30 second (d) Al pre-flows.
Figure 4  RMS roughness of GaN films from Figure 3 vs. Al pre-flow time. Dashed line is a guide to the eye.
**Figure 5** XRD rocking curve FWHM for three GaN reflections vs. Al pre-flow time.

Dashed lines are a guide to the eye. Error bars represent plus and minus one standard deviation from the mean.
**Figure 6** FWHM of GaN HRXRD rocking curves for three inclination angles for the cases of no Al pre-flow and 10 second Al pre-flow. Dashed lines are a guide to the eye.