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ABSTRACT

GaN is a semiconductor material with great potential for use in high power electronics and optoelectronics due to the high electron mobility, high breakdown voltage, high thermal stability, and large direct bandgap of GaN. Si is a desirable substrate material for GaN heteroepitaxy due to the low cost of production, large wafer sizes available, and current widespread use in the electronics industry. The growth of GaN/Si devices suffers from the lattice and CTE mismatches between GaN and Si and therefore multiple methods of strain reduction have been employed to counter these effects. In this work we presented two novel methods of substrate modification to promote the growth of device quality GaN on Si.

Initial work focused on the implantation of AlN/Si(111) substrates with N\textsuperscript{+} ions below the AlN/Si(111) interface. A reduction in the initial compressive stress in GaN films as well as the degree of tensile stress generation during growth was observed on implanted samples. Optical microscopy of the GaN surfaces showed reduced channeling crack density on implanted substrates. Transmission electron microscopy (TEM) studies showed a disordered layer in the Si substrate at the implantation depth which consisted of a mixture of polycrystalline and amorphous Si. Evidence was provided to suggest that the disordered layer at the implantation depth was acting as a compliant layer which decoupled the GaN film from the bulk Si substrate and partially accommodated the tensile stress formed during growth and cooling. A reduction in threading dislocation (TD) density on ion implanted substrates was also observed.
Additional studies showed that by increasing the lateral size of AlN islands, the
tensile growth stress and TD density in GaN films on ion implanted substrates could be
further reduced. XRD studies showed an expansion of the AlN lattice on implanted
substrates with larger lateral island sizes. The final tensile growth stress of films on
implanted substrates was further reduced by utilizing thinner buffer layers and increasing
the implantation depth of N\(^+\) ions.

Final studies were presented on a method of etching Si(001) substrates in order to
fabricate trenches with Si\{110\} sidewalls. It was shown in these studies that GaN could
be preferentially grown on Si\{110\} sidewalls such that GaN(0002)//Si\{110\}. The result
was non-polar GaN “fins” which vertically overgrew Si(001) ridges. Further studies
showed that high V/III, low temperature, and low pressure was required to promote the
lateral growth of the GaN(000\(\bar{2}\)) which was necessary to obtain a fully coalesced film.
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Chapter 1

Introduction

1.1 Motivation

The group III-nitrides are a class of materials that are of great interest in optoelectronic and electronic device research. This is due to the wide range of direct bandgaps encompassed by the binary III-nitride compounds which have values that span from the infrared (InN = 0.7 eV) to the deep UV (AlN = 6.2 eV) as shown in Figure 1-1 [1-3].

![Diagram of bandgap energy/wavelength vs. lattice constant of III-nitride binary compounds](image)

Figure 1-1. Bandgap energy/wavelength vs. lattice constant of III-nitride binary compounds [3].
With such a wide range of bandgaps, it is theoretically possible to compositionally control III-N ternary or quaternary compounds in order to tailor the wavelength of emitted light in optoelectronic devices over the full range of the visible spectrum. By mixing III-nitride-based blue and green LED’s with red LED’s, a full color display with the capability of forming white light may be created [4]. LED’s are desirable for lighting and display applications due to their compactness, long lifetime, and energy efficiency [4, 5].

Shuji Nakamura demonstrated the first high-brightness blue LED in 1994 which was based on an InGaN/AlGaN double heterostructure as shown in Figure 1-2 [6].

![Figure 1-2. The layer structure of an InGaN/AlGaN double-heterostructure blue LED[6].](image)

This work not only showed the possibilities for high-brightness blue LEDs from III-nitride based materials, it also opened the pathway to white light LEDs for displays and
lighting applications. White light LEDs can be fabricated in two main ways, depending on the application. One method is to mix III-nitride-based blue and green LEDs with red LEDs which allows for color mixing in the range of the visible spectrum [4]. This method allows for the development of LED displays with the capability to form a range of colors that encompasses the visible spectrum. The other main method for fabricating white-light LEDs involves combining GaN-based blue LEDs with a phosphor coating. The light emitted from the blue LED optically excites the phosphor coating, which then emits yellow light. The yellow and blue emitted light mix to create white light as shown in Figure 1-3 [3, 4]. This type of white-light LED is generally used for general lighting applications.

Figure 1-3. Diagram of a white-light LED made up of a blue LED and a phosphor coating [4].

GaN is an important base material for optoelectronic devices due to its direct bandgap and its ability to form ternary compounds with In and AlN for the fabrication of LEDs which emit in the blue and ultraviolet range, as discussed above. GaN is also of interest, however, in the field of high-power electronics due to its wide, direct bandgap.
The wide bandgap of GaN allows for higher voltage limits in power switching devices.
The high mobility and drift velocity of GaN as compared to SiC combine with its high 
breakdown field make GaN a promising candidate for high power applications such as 
high electron mobility transistors (HEMTs) [7]. The wide bandgap of GaN also allows 
for good electronic performance at high operating temperatures without device 
performance degradation [5, 8, 9].

1.2 Choice of Substrates for GaN Film Growth

GaN is an important material for the fabrication of optoelectronic devices such as 
LEDs. Defects in the material, however, can act to scatter charge carriers or result in 
non-radiative recombination of electron hole pairs. Therefore, the fabrication of single-
crystalline GaN films with a low density of defects has been studied extensively for the 
fabrication of GaN-based optoelectronic devices. GaN films are formed by epitaxial 
growth, which means that the film will grow with the same atomic arrangement as the 
underlying substrate. Since defects and dislocations can form due to mismatches in the 
lattice constant and thermal expansion coefficient between the substrate and the film, 
there is a desire to grow GaN homoepitaxially. Homoepitaxy is epitaxial growth that 
occurs when the substrate and film are the same material. Bulk GaN substrates are, 
however, still very expensive as compared to other available substrate materials. While 
there have been recent industrial pushes to make more affordable GaN substrates for 
GaN-on-GaN based devices, the fact remains that GaN is still an expensive substrate for 
the fabrication of GaN-based devices [10]. Therefore heteroepitaxy of GaN has been
heavily researched. Heteroepitaxy is the epitaxial deposition of a single crystalline material onto a different material substrate. The choice of substrate in the heteroepitaxial process is of the utmost importance to achieve GaN films with sufficiently low defect densities for device fabrication. A material with low lattice and thermal expansion mismatch with GaN is preferred so as to prevent formation of defects and cracking during film growth and cooling. Inexpensive substrates are also desirable in order to lower the final cost of the device being made.

Commercial GaN devices are commonly formed on sapphire and SiC substrates, but there is also a push for GaN device integration with Si substrates. Due to the widespread use of Si wafers for the fabrication of electronic devices, there is a wealth of research on Si fabrication, doping, and wafer preparation. Furthermore, Si is an abundant material in the earth’s crust which is relatively easy to refine into high purity wafers with large diameters. Si wafers with up to 300 mm (11.8 inch) diameters are currently available as compared to sapphire and SiC wafers which are only manufactured in 6 inch diameters [11-13]. The larger wafer size of Si further reduces the overall cost of manufacturing GaN-based devices on Si. All of these factors result in a base substrate material with versatility, high purity, and low-cost. The growth of GaN on Si is a benefit not only to GaN device fabrication, but may also lead to the incorporation of GaN-based high-power devices with current Si-based electronics resulting in novel device structures.

Despite the many benefits of GaN growth on Si, there are also several challenges associated with the epitaxial growth of GaN on Si. Si(001) is the substrate orientation of choice for current device technology, but the (001) plane lacks the 6-fold atomic
symmetry required for the growth of wurtzite GaN. The Si(111) face, however, has necessary hexagonal atomic arrangement necessary for the growth of GaN to that of the GaN(002) plane as shown in Figure 1-4 [14].

![Diagram showing lattice mismatch between GaN and (a) Si(111), (b) Sapphire, and (c) SiC [14].](image)

Due to this structural match, the majority of research performed on GaN heteroepitaxy on Si substrates has been performed on the Si(111) orientation. Si(111) still suffers from very large lattice (16.9%) and CTE (55.7%) mismatches with GaN as compared to sapphire and SiC [7]. The a-lattice constant of GaN is smaller than that of Si, which results in the GaN film undergoing a biaxial tensile stress as the GaN lattice strains to conform to the underlying Si lattice during growth. This tensile stress is normally relaxed via the formation of misfit dislocations in the film if the thickness exceeds a critical value [15]. Furthermore, the GaN CTE is larger than that of Si which results in further tensile stress in the film. Due to its larger CTE, free-standing GaN would contract more than Si when cooling from the temperatures used for GaN growth. For heteroepitaxial GaN films on Si, however, the GaN is constrained from full contraction.
by the Si substrate during the cooling process resulting in biaxial tensile stress in the film. This tensile stress is relaxed through the formation of channeling cracks in the GaN film. The formation of dislocations and channeling cracks in the GaN film are especially problematic for optoelectronic and electronic devices since they can act as non-radiative recombination centers and carrier scattering sites, which will lower the efficiency of devices [16]. Therefore, despite the benefits of Si as a substrate material for GaN heteroepitaxy, there is a need to overcome the issues arising from lattice and thermal expansion mismatch between the two materials.

A widespread research initiative to reduce these detrimental mismatch effects has arisen from the desire to form device quality GaN films on Si substrates. In order to gain the benefits of GaN heteroepitaxy on Si substrates, multiple methods for strain reduction have already been developed for GaN on Si including the use of AlN or AlGaN buffer layers [17-19], SiN_x buffer layers [20, 21], AlN/GaN superlattices [22, 23], AlN interlayers [24, 25]. Al-containing layers induce compressive stresses in the GaN film due to the lattice mismatch between AlN(0.311nm) and GaN(0.319nm). This compressive stress offsets the tensile stresses which normally form in GaN films due to lattice and CTE mismatch between the film and substrate. Furthermore the compressive strain caused by Al-containing layers can act to incline threading dislocations (TDs) such that they encounter neighboring TD’s and annihilate or form a single TD, thus reducing the overall TD density in the film [26].

Even though several techniques have been developed to grow low dislocation density, crack-free GaN on Si(111) there is still an interest in novel techniques to lower
the tensile stress and dislocations in GaN films on Si(111) substrates. One such technique that has been presented in the literature is the use of ion implanted AlN/Si(111) substrates for GaN film growth [27, 28]. This technique was developed by our collaborators at the University at Albany and has been shown to reduce the final tensile stress as well as the channeling crack density of GaN films. It was hypothesized in previous studies that the ion implantation process induced disorder in the Si lattice which decoupled the GaN film from the bulk substrate and thus lowered the stresses formed due to lattice and CTE mismatch [27, 28].

1.3 GaN growth on Si(100)

Polar GaN, with the c-axis oriented perpendicularly to the substrate surface, is the most commonly used orientation for GaN-based devices. Polar GaN, however, can result in the formation of piezoelectric polarization fields in the presence of stress in the GaN film as is the case of quantum well (QW) heterostructures [7, 29]. When GaN is polar along the growth direction, then these polarization fields act normal to the planes of quantum wells QWs in light emitting devices. These polarization fields act to separate the electron and hole wave functions, which reduces the likelihood of radiative recombination events and therefore reduces the efficiency of light emitting devices.

Therefore, the growth of non-polar or semi-polar GaN is desirable to reduce polarization effects in GaN devices. One method of forming semi-polar GaN is to grow on a semi-polar homoepitaxial substrate [30]. Unfortunately, due to the small wafer sizes and high cost associated with homoepitaxial substrates, there is a desire to grow GaN
heteroepitaxially. Therefore work has been performed which focused on growth of non-
polar and semi-polar GaN on a variety of heteroepitaxial substrates including r-plane
sapphire [31], γ-LiAlO₂ [32], and m-plane SiC [33]. Another method of growing semi-
polar GaN involves using anisotropic etchants in conjunction with pattern masks on
Si(001) substrates [29, 34]. The use of anisotropic etchants results in trenched or
pyramidal structures in the Si(001) surface with Si(111) facets [29, 34]. After the
fabrication of these Si(111) facets, the Si(001) facets can be masked with SiO₂ and GaN
can be grown off of the Si(111) facets such that GaN(0002)\(//\)Si(111). The resulting GaN
film has a semi-polar crystal orientation with respect to the Si(001) substrate.

Work has also been done focusing on utilizing isotropic etchants to form Si
structures such as pillars in Si wafers with various orientations [35]. It was shown that
GaN grows on Si(001) oriented pillars such that GaN(0002)\(//\)Si(110) with no observed
growth on the Si(001) plane. It was therefore hypothesized that non-polar GaN could be
fabricated on similar structures with Si\{110\} planes exposed on Si(001) substrates.
Furthermore, since dislocations propagate parallel to the growth direction, by growing
non-polar GaN off of facets that are perpendicular to the Si(001) substrate surface it may
be possible to lower the dislocation density in films grown by this method.

1.4 Scope of Dissertation

Many techniques have been developed to reduce tensile stresses in GaN films
grown on Si substrates, the most common of which are reported above. There is still a
desire to develop and understand new techniques to fabricate device quality GaN films on
Si substrates. Therefore in this work GaN growth will be studied on Si substrates that have undergone two different substrate modification techniques. The first method of substrate modification will be the ion implantation of AlN/Si(111) substrates as previously reported on by our collaborators at the University at Albany [27, 28]. The studies presented herein focused on furthering the understanding of the mechanism by which substrate implantation reduces tensile film stress. The studies presented here utilized in situ wafer curvature techniques in order to more closely study the stress evolution of the GaN film during the entire growth process. By combining in situ curvature measurements with additional ex situ characterization of the film and substrate, a more complete picture of the mechanisms through which ion implantation is lowering GaN film stress was obtained. Further studies were performed to determine the importance of buffer growth conditions and implantation variables on the implantation-induced stress reduction.

The second technique reported on was the fabrication of parallel trenches in Si(001) substrates. The trenches were formed with a deep reactive ion etching (DRIE) process and a patterned mask oriented such that the trench sidewalls belonged to the \{110\} family of planes. This technique was developed to draw on the results reported by Won et al. which showed a preference of GaN growth on pillars fabricated in Si(001) wafers such that GaN(0002)//Si{110} [35]. No growth was reported in prior studies on the Si(001) surface of the etched pillars. Therefore a trench structure was utilized in the following studies in an attempt to develop a maskless technique for the preferential growth of non-polar GaN. After the initial studies regarding the viability of this trench
structure to preferentially form non-polar GaN on Si\{110\} sidewalls further studies were performed in order to overgrow Si(001) trench structures in an attempt to form a fully coalesced, non-polar GaN film on Si(001) substrates.

1.5 Organization of Dissertation:

The work described in this work shall be divided into 8 chapters. Chapter 2 will focus on a review of the literature that has been deemed important to understand the main research presented in later chapters. An outline of common sources of stress reduction will be presented as well as a detailed overview of the literature related to implantation of AlN/Si(111) substrates, the growth of non-polar GaN, and etching of Si(001). Chapter 3 will provide an outline of the equipment and analysis techniques used in the presented research. Chapter 4 will present the results of preliminary studies of GaN growth on ion implanted AlN/Si(111) substrates. Chapter 5 will focus on the effect of the pre-growth annealing process on the curvature and AlN morphology of implanted AlN/Si(111) substrates. Chapter 6 will mainly focus on the effect of lateral AlN island size on growth stress in GaN films on ion implanted AlN/Si(111) substrates. Studies of the effect of AlN buffer thickness and ion implantation depth will also presented in Chapter 6. Chapter 7 will focus on preliminary studies of GaN growth on trenches etched into Si(001) substrates such that the trench sidewalls are Si\{110\} oriented. Chapter 8 will provide a summary of conclusions drawn regarding the work presented in this dissertation as well as plans for future research.
1.6 References:


Chapter 2

Literature Review

2.1 Introduction:

Several methods of strain reduction for GaN films grown on Si substrates have been developed to achieve device quality GaN epilayers. Initial studies presented in this work focused specifically on the ion implantation of AlN/Si(111) substrates as a method to reduce GaN film stress. In order to better understand the studies presented in this work, it is important to understand common methods of strain reduction and polarity control of GaN films and the mechanisms through which they work. The use of buffer layers, graded buffer layers, interlayers, superlattices, and substrate ion implantation will be reviewed. It is also important to understand the different mechanisms by which strain and dislocations are formed in the film. Therefore a discussion of threading dislocation (TD) formation and the effect of dislocation inclination on compressive stress relaxation and tensile stress generation in films will be presented. Later chapters of this work focused on the fabrication of vertical trenches as a method to obtain non-polar GaN on Si(001). Therefore, a discussion of prior research regarding the growth of non-polar GaN and GaN growth on etched Si(001), including common obstacles and solutions, will also be presented.
2.2 Advantages and disadvantages of GaN on Si heteroepitaxy

A major driving force for the use of Si as a substrate for GaN heteroepitaxy is the low cost as compared to other commonly used substrates such as SiC, sapphire, or GaN. Furthermore, due to silicon’s widespread use in current electronics, the fabrication of Si wafers and Si-based devices is a well-researched field. Large wafer sizes are available for Si, which allows for large scale device integration as well as reduced cost for fabrication of multiple devices on a single Si wafer with large diameter. The (111) plane of Si has a trigonal crystal symmetry which has a good epitaxial match with the atomic structure of the (0002) plane of wurtzite AlN and GaN as shown in Figure 2-1 [1]. Si also has a high thermal and electrical conductivity and mechanical hardness, which allow for better large scale device integration [2].
Despite the benefits that Si would provide as a substrate material for GaN devices, there are also several major issues that arise from the matching of the two materials. The first major issue arises from the reactivity of Si and Ga at the high temperatures necessary for growth [3]. This phenomenon is referred to as “meltback etching” and must be prevented through the use of chemically stable intermediary layers, such as AlN or AlGaN, between the GaN and Si. Another issue with the epitaxy of GaN on Si is the large lattice and CTE mismatch between the two materials. GaN has a smaller lattice constant (0.319nm) than Si(111) (0.384nm) which results in a biaxial tensile stress in the GaN as the lattice strains to accommodate the Si lattice. This tensile stress is relaxed through the formation of
misfit dislocations when the film grows above a critical thickness [4]. Threading dislocations can also form at the coalescence points of slightly misoriented 3-dimensional islands that form at the early stages of film growth in III-N films. The majority of threading dislocations in GaN are edge-type (Burgers vector, $\mathbf{b} = (1\bar{1}20)$) while screw dislocations ($\mathbf{b} = (0001)$) are present to a lesser extent [5]. Mixed-type dislocations are also present in these films. These dislocations can propagate throughout the film leading to large dislocation densities on the order of $\sim 10^{10}$ cm$^{-2}$ for GaN on Si(111). A schematic representation of this is presented in Figure 2-2 for the case of GaN on sapphire [6]. These threading dislocations (TDs) did not greatly affect the luminescence efficiency from GaN LEDs despite the density being four orders of magnitude higher than densities required for other semi-conductor materials of the time ($< 10^6$ cm$^{-2}$) [7]. For more complex device structures, such as laser diodes or devices operating at greater power density, the TDs found in GaN have been shown to lower the breakdown voltage of such devices leading to failure [7].

Figure 2-2. Diagram of TD formation during island coalescence [6].
The CTE of GaN ($5.59 \times 10^{-6} \text{K}^{-1}$) is larger than that of Si ($3.59 \times 10^{-6} \text{K}^{-1}$) which means that free-standing GaN contracts more than Si when cooling from the same temperature. Since the GaN film is constrained by the much thicker Si(111) substrate, however, the film lattice cannot contract fully. Therefore a biaxial tensile stress is formed in the GaN lattice during cooling from the growth temperature. The tensile stresses formed during cooling are relaxed primarily through the formation of channeling cracks in the GaN film, which are detrimental to device performance [8].

2.2 Common Stress and Dislocation Reduction Methods

In order to reduce the final crack and TD density in GaN films, several methods have been developed. The most commonly utilized methods involve the use of one or more intermediary layers before and/or during GaN growth. A brief overview of the most common methods used today will be the focus of this section.

2.2.1 Al-containing Buffer layers, Interlayers, and Superlattices

In order to prevent meltback etching of Si in the presence of Ga, several different buffer layer materials which are chemically inert with Si at typical GaN growth temperatures have been developed in order to isolate the GaN film from direct contact with the Si substrate. In the interest of simplicity, this section will forego an in-depth look at all the buffer materials currently available and will instead focus on commonly
used Al-containing nitride layers. Diagrams of the types of layer structures which will be discussed in this section are provided in Figure 2-3.

![Diagram of common stress reduction techniques for GaN growth on Si(111) including: (a) AlN buffer, (b) graded AlGaN buffer, (c) AlN interlayers, (d) AlN/GaN superlattices, and (e) substrate ion implantation.](image)

AlN buffer layers are commonly utilized for GaN growth on Si substrates because the AlN lattice constant is slightly smaller than that of GaN, as can be seen from Table 2-1 [2].
Table 2-1. Lattice Constants and Coefficients of Thermal Expansion for Common Substrate Materials [2]

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice Constant (nm)</th>
<th>CTE (10^-6 K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(111)</td>
<td>0.384</td>
<td>3.59</td>
</tr>
<tr>
<td>Sapphire</td>
<td>0.476</td>
<td>7.50</td>
</tr>
<tr>
<td>SiC (6H)</td>
<td>0.308</td>
<td>4.20</td>
</tr>
<tr>
<td>GaN</td>
<td>0.319</td>
<td>5.59</td>
</tr>
<tr>
<td>AlN</td>
<td>0.311</td>
<td>4.20</td>
</tr>
</tbody>
</table>

The lattice mismatch between AlN and GaN results in a biaxial compressive stress in the GaN film as opposed to the tensile stress that would be expected from the direct epitaxy of GaN on Si. This compressive stress can be used to counteract tensile stress formation during cooling due to CTE mismatch between GaN and Si(111), thus reducing the overall tensile stress in the final GaN film. The formation of tensile stress in the GaN film during cooling is due to the CTE mismatch between GaN and Si(111) as shown in Table 2-1 [2]. GaN has a larger CTE than Si, so it is constrained from full contraction by the Si(111) substrate on which it is grown during cooling, which induces a tensile stress. AlN also has improved wetting on Si as opposed to GaN [2].

For these reasons, AlN was first used as an intermediate layer for growth of high-quality GaN films on Si by Watanabe et al. [9]. In these studies, scanning electron microscopy (SEM) was used to show that GaN films grown with an AlN buffer had a smoother surface as compared to GaN grown directly on Si which had an island-like surface structure. This can be attributed to nucleation and lateral growth differences
caused by the lower lattice mismatch of the GaN film with the AlN buffer as well as the wetting differences of GaN on AlN versus GaN on Si(111). Watanabe also used double crystal x-ray diffraction (XRD) to study the full-width at half-maximum (FWHM) of the rocking curves for GaN films with AlN buffers grown at different temperatures. When the deposition temperature of the AlN buffer was below 900°C, large FWHMs of around 1300 arcsec were observed. At deposition temperatures above 1050°C, however, the FWHM was decreased to 900 arcsec which indicated an improvement in the GaN crystal quality [9].

Zamir et al expanded upon this work to study the effect of AlN buffer growth temperature on the final GaN film [10]. They grew GaN layers for short growth times to observe GaN islands forming atop AlN buffers grown with varying conditions. It was observed that by increasing the temperature at which the buffer was grown within the range of 700°C - 760°C, a sharp enhancement in the preferential growth of GaN(0002) crystallites was observed. Increasing the buffer growth temperature in the range of 760°C - 1100°C resulted in further improvement in the preferential orientation of the (0002) oriented GaN islands, but with a lesser rate of improvement with increasing temperature. SEM was used to observed the AlN crystallites which showed a reduced tilt and twist misorientation with respect to the Si(111) surface if annealed after growth. This in turn led to better GaN nuclei orientation. These results indicated that higher buffer layer growth temperatures led to improvement in the crystal quality of the GaN film and that a temperature above 760°C was necessary to achieve primarily (0002) oriented GaN films.
One of the benefits of using AlN as a buffer layer for GaN growth is the compressive stress formed due to lattice mismatch. If GaN on AlN grows past its critical thickness (≈1.3 nm), however, misfit dislocations can form to partially relieve the induced compressive stress [4]. Therefore a modified buffer layer approach was formed by gradually changing the group-III precursor gas flow rates in order to form a compositionally graded AlGaN layer [4, 11]. By grading the composition from pure AlN to pure GaN, the in-plane lattice constant was increased slowly which resulted in less compressive stress between atomic layers. This reduced compressive stress between layers resulted in a reduced formation of misfit dislocations which resulted in greater overall compressive stress formation in the GaN film. Able et al studied graded AlGaN buffers that consisted of a 100nm AlN layer followed by a 200-1000nm thick graded AlGaN layer [4]. A decrease in tensile film stress was observed via XRD and no cracking was found in 2.5 μm thick films when the graded buffers were grown for 35 minutes or longer. The prior studies by Able et al utilized ex situ characterization techniques and therefore the film stresses measured were due to lattice and CTE mismatch stresses. Raghavan et al. further studied the effect of a graded AlGaN layer on GaN growth stress by using an in situ laser reflectance wafer curvature measurement system to measure stress during buffer and film growth [12]. The stress in the graded buffer was observed to transition from tension to compression during growth. By increasing the thickness of the graded buffer, the thickness at which the GaN film transitioned from compressive to tensile stress increased and the final tensile stress decreased. In fact, GaN films grown on graded AlGaN buffers greater than 1μm in thickness did not transition to tensile stress at all within 1μm of film growth. Therefore,
the graded AlGaN layer acted to maximize the compressive stress formed within the film during growth. This in turn led to a higher critical thickness for cracking in the GaN films. It is noted, however, that beyond a 2μm thick graded buffer the tensile stress generated in the buffer with increasing thickness becomes greater than the compressive stress due to lattice mismatch. Later studies by Raghavan et al. studied the microstructure of GaN films grown on graded AlGaN buffer layers [13]. Cross-sectional transmission electron microscopy (XTEM) of GaN on AlGaN films showed a reduction in threading dislocation (TD) density with increasing film growth. Comparison with in situ wafer curvature measurements showed a correlation between relaxation of compressive stress in AlGaN layers and reduction of dislocation density. The reduction of TD density was found to be due to inclined dislocations with an edge-type component interacting with other TDs to annihilate and form dislocation loops. The relationship between inclined TDs and film stress will be discussed more fully in section 2.3.

Amano et al reported on the use of low temperature (LT) interlayers for the reduction of stress and threading dislocation (TD) densities in GaN films grown on sapphire [14]. The research showed that both LT-GaN and LT-AlN interlayers lowered the TD densities proportional to the number of interlayers in the final GaN films. The LT-GaN interlayers showed an increase in tensile stress with the number of interlayers up to ≈1 GPa. The mean tensile stress in GaN layers remained small and relatively constant when LT-AlN layers were employed, though. LT-AlN interlayers also resulted in no cracking in the final GaN film compared to the LT-GaN interlayers which reported extensive cracking. Dadgar et al used a similar interlayer schema to grow crack-free 1 μm GaN on Si(111) instead of sapphire [15]. They reported a lower crack density for
GaN grown on Si(111) by using LT-AlN interlayers compared to without interlayers. XRD rocking curve measurements for the film with interlayers showed a lower FWHM than for the film without interlayers. This indicated a lower tilt and twist misorientation between GaN grains in the film. Cracks and pits were observed in SEM studies of the GaN films without interlayers but not in those with interlayers. Raghavan et al studied the effect of AlN interlayers on the stress evolution of intermediate GaN layers [16]. It was observed that each GaN layer initiated growth under a compressive stress but that initial compressive stress relaxed during growth and transitioned to tensile stress. Due to this relaxation of compressive stress and transition to tensile stress, it was shown that AlN interlayers were required to periodically induce additional compressive stress in the GaN film. The final thickness and number of interlayers could also be tailored to induce a greater overall compressive stress in the final GaN layer and thereby delay the transition to tensile stress. A reduction in TD density in GaN layers was also observed due to the presence of AlN interlayers.

Another method of strain and threading dislocation density reduction in epitaxial GaN films was the use of AlN/GaN superlattices [17, 18]. Feltin et al demonstrated 2.5 μm thick, crack-free GaN grown via MOCVD through use of such superlattices [18]. In their method, multiple AlN/GaN superlattices were grown with ≈200 nm GaN layers separating each superlattice. The superlattice was used to induce a compressive strain in the film to counteract the normally observed tensile strain in the film. It was shown that the AlN and GaN layers in the superlattice must be approximately 3 nm and 4 nm thick, respectively. Thicker layers lowered the compressive strain induced by the superlattice. The number of AlN/GaN layers in the superlattice had little effect on the subsequent
strain above ten layers. TEM and atomic force microscopy (AFM) studies showed that the superlattices acted to block the propagation of TD’s in each subsequent GaN layer. The TD density decreased with an increasing number of superlattices used. The compressive strain and the crystalline quality of the final film also increased with increasing number of superlattices.

**2.3 Dislocation Inclination and Stress Formation**

Inclination of TDs in GaN and AlGaN films has been observed by several groups in the presence of compressive stress [13, 19] and in the presence of Si doping [20]. Cantu et al reported on Si doping-induced TD inclination, as shown in Figure 2-4, which relaxed compressive strain in the AlGaN films based on the angle of inclination with respect to the surface normal [20].
Romanov et al further investigated the observations made by Cantu and proposed a mechanism by which threading dislocation inclination relaxed compressive stresses in the film [21]. In this model, they projected the inclined edge dislocations onto the layer/substrate interface and equated the projected TD with sections of misfit dislocations. The biaxial stress gradient ($d\sigma_{xx}/dz$) throughout the thickness ($z$) of the film for a constant TD density ($\rho_{TD}$) was modeled as [22]:

$$\frac{d\sigma_{xx}}{dz} = M_f \frac{d\varepsilon_{xx}}{dz} = \frac{1}{2} M_f b \rho_{TD} \tan(\alpha)$$

where $\varepsilon_{xx}$ is the biaxial strain, $b$ is the magnitude of the dislocation Burger’s vector, $M_f$ is the biaxial modulus of the film, and $\alpha$ is the angle of inclination of dislocations with respect to the substrate normal. Romanov et al continued their studies of AlGaN layers.
and discovered that with further layer growth, inclined threading dislocations generated tensile stresses after the compressive stress was completely relaxed [22]. A critical thickness for cracking in Si-doped Al$_{0.49}$Ga$_{0.51}$N/Al$_{0.62}$Ga$_{0.38}$N films on c-plane sapphire substrates was calculated to be ≈303 nm based on the stress gradient caused by dislocation inclination. This value was consistent with optical microscopy studies of layers grown at varying thicknesses below and above 300 nm. Romanov et al. thereby proposed a thermodynamic model for dislocation inclination which states there is an energy barrier to dislocation inclination. It was further proposed in that work that dislocations may incline through an inclusion of adatoms at the intersection of TDs and the growth surface. Follstaedt et al. showed similar inclination of TDs in multilayer AlGaN structures without Si doping [19]. It was shown that TDs would also incline in undoped layers in the presence of a compressive stress resulting in the relaxation of that compressive stress. In their work, however, it was proposed that dislocations inclined by incorporating vacancies into dislocation cores at the growth surface [19]. Raghavan et al. proposed a kinetic theory for dislocation inclination in which the inclination of dislocations was determined by the transport of atoms to and from the dislocation cores [23]. There is still some debate as to the exact mechanism that leads to dislocation inclination, but several groups have confirmed the relationship between dislocation inclination and strain given above [24, 25].
2.4 Substrate Implantation as a Method of Film Crack Reduction

Ion implantation is an important process in semiconductor device fabrication. One benefit of ion implantation is that ionic species may be implanted at controlled depths with reasonable precision. Koh et al used ion implantation of Si(111) substrates prior to GaN film growth to induce a tensile stress in the Si(111) substrates and study how the substrate stress affected the stress in the subsequently grown film [26]. Implantation was performed with N\textsuperscript{+} ions at doses ranging from 2 \times 10^{14} – 2 \times 10^{16} cm\textsuperscript{-2} and energies of 60 and 100 keV. The substrates were annealed after implantation prior to buffer layer and GaN film growth. Raman spectroscopy was used to measure the stress state in the substrates and the subsequently grown GaN films. The stress in the substrate became more tensile with increasing ion implantation energy and dose after annealing. Raman studies performed after GaN growth showed that for samples with a single AlN buffer layer, an increase in the ion dose and energy led to a decrease in the biaxial tensile stress as well as an increase in crystal quality of the film.

Jamil et al subsequently developed a new method of substrate ion implantation to reduce stress in GaN films [27, 28]. Their method differs from that of Koh et al most noticeably in the sequence of steps in the implantation process. While Koh et al implanted the substrate with N\textsuperscript{+} ions before growing an AlN buffer layer, Jamil et al grew an AlN buffer on a Si(111) substrate and then implanted N\textsuperscript{+} ions at a set depth into the Si substrate. By doing this, N\textsuperscript{+} ions travelled through the AlN buffer layer as well as the surface of the Si. The AlN/Si(111) substrates were then annealed to remove excess ion damage in the AlN buffer and Si substrate. The substrates were implanted with an ion
energy of 60 keV and a dose of $2 \times 10^{16} \text{ cm}^{-2}$, comparable to values used by Koh. A lower tensile stress was observed in GaN films grown on ion implanted substrates than on unimplanted substrates which was similar to the result reported by Koh et al. Optical microscopy images also show a lower crack density for films grown on implanted substrates vs. unimplanted substrates after 2 μm of GaN growth. Since surface cracks are formed to reduce biaxial tensile stress in the film, the lower crack density indicated a lower tensile stress in the final film. Edge dislocation densities were $8.2 \times 10^8 \text{ cm}^{-2}$ for the unimplanted sample and $<8.0 \times 10^7 \text{ cm}^{-2}$ for the implanted sample. Screw dislocations for the unimplanted and implanted samples were, respectively: $2.6 \times 10^9 \text{ cm}^{-2}$ and $<3.3 \times 10^8 \text{ cm}^{-2}$. The near order of magnitude reduction in TD densities with implantation was measured with TEM and supported with high resolution (HR) XRD. XRD was also used to measure the FWHM of the (002) reflection of the AlN buffer layer before implantation, after implantation and after annealing. The FWHM was observed to decrease after implantation and annealing which indicated less crystallographic misorientation between AlN islands. The explanation put forth in the study was that the ion implantation induced disordered layer, which was observed in TEM studies, acted to decouple the AlN buffer from the Si substrate. This decoupling allowed the AlN islands to reorient with respect to one another during annealing and lower the misorientation between islands. This would lead to higher quality, less misoriented GaN film growth. It was also believed that this disordered layer played a role in lowering the tensile stress in the final GaN film.

The previous studies executed several ex situ characterization techniques in order to determine the effect of substrate ion implantation on the final GaN film. To fully
understand the mechanism by which tensile stress was reduced in the final GaN films on implanted substrates, it would be beneficial to understand how the stress evolves during the growth and cooling process. Therefore an in situ technique of stress measurement is brought forth in the studies performed in this work to better understand the stress-reducing mechanisms involved in the substrate ion implantation process.

2.5 GaN growth on Structured Substrates

While many stress and dislocation reduction techniques involve growing additional layers, there has also been work done on modifying the underlying Si substrate in order to reduce these detrimental effects. One common substrate modification technique is epitaxial lateral overgrowth (ELO). In the ELO process, a GaN seed layer is deposited and then growth is interrupted in order to mask or etch portions of the seed layer. Growth is then continued in order to promote lateral growth of GaN over the masked or etched regions of the initial GaN layer. Since TD’s propagate along the vertical growth direction the laterally overgrown regions of the GaN remain relatively free of dislocations, aside from those formed at the coalescence boundary, thus reducing the overall TD density of the final GaN films. This process has proven effective for GaN films grown by HVPE [29, 30] and MOCVD [31, 32]. Unfortunately this process usually requires an interruption of the growth process in order to deposit a masking layer or etch regions of the GaN seed layer and the TD density reduction only occurs in the laterally overgrown regions. In order to reduce the TD density further a secondary growth
interruption is required after the initial overgrowth step in order to etch or mask non-ELO regions of the film.

Linthicum et al. created a process of staggering silicon nitride masking regions and etched regions of the initially grown GaN seed layer in order to reduce TDs across the surface of the film with a single growth interruption [33]. In their method a GaN seed layer was deposited on SiC. Then a silicon nitride mask was deposited on top of the GaN seed layer followed by a patterned nickel etch mask. Inductively coupled plasma was used to etch the silicon nitride and GaN layers in the exposed regions defined by the patterned nickel mask. The resulting microstructure included alternating GaN ridges topped with a silicon nitride mask and etched trenches in the SiC. The V/III of the source gas was controlled to promote lateral growth of GaN from the sidewalls of the etched GaN seed layer. After the coalescence of GaN over the etched region of the SiC, growth was continued such that GaN then overgrew the silicon nitride mask. The outlined peendoepitaxy process resulted in a GaN film with reduced dislocation density due to the ELO over the etched trenches and silicon nitride masking layers.

Strittmatter et al. put forth a method of substrate modification that was similar to epitaxial lateral overgrowth but required no growth interruption by using a microstructured Si(111) substrate as shown in Figure 2-5 [34].
The substrates were structured with parallel trenches of various widths and GaN was grown on an AlN buffer on the top (111) surface of the Si ridges. GaN also grew on the bottom surface of the trenches, but the V/III ratio was varied to increase the lateral growth of the GaN on top of the ridge structures and overgrow the open trench area. AFM studies showed low roughness surface with clear steps present in the surface while the area over the Si ridge was noticeably rough with large pits indicating TDs in the film. Although no growth interruption was utilized in these studies, a reduction in TD density was only observed in the regions of GaN grown laterally over the etched Si trench.
2.6 Growth of Non-polar GaN and Semi-polar GaN:

Most GaN-based devices utilize GaN films in which the GaN(0002) plane is parallel to the substrate surface. Due to the wurtzite crystal structure of GaN, spontaneous and piezoelectric polarization can therefore occur in GaN-based heterostructures perpendicular to the substrate surface. Polarization of GaN results in a negative fixed polarization charge at the Ga-terminated interface and positive charges at the N-terminated interface, as shown schematically in Figure 2-6 [35].

Figure 2-6. Crystal structure of wurtzite GaN (top) and a schematic (bottom) of a slab of GaN showing negative and positive fixed polarization charges at Ga and N faces, respectively [35].
This spontaneous polarization field can be deleterious to optoelectronic devices such as LEDs or LDs. The polarization field can act to separate electrons and holes in multiple quantum well (MQW) layers, which can reduce the likelihood of radiative recombination of carriers and therefore reduce emission efficiency [2, 36]. Therefore the growth of semi-polar and non-polar GaN is desirable to reduce the effects of polarization along the GaN c-axis. Several common non-polar and semi-polar planes of interest are shown in Figure 2-7 [37].

Figure 2-7. Schematic depicting common polar (a), non-polar (b and c), and semi-polar (d and e) planes in wurtzite GaN [37].

Growth of non-polar a-plane (11̅20) has been reported on r-plane sapphire by several groups [38, 39]. Unfortunately, a-plane GaN grown on r-plane sapphire has poor crystal quality due to large densities of dislocations (>10⁹ cm⁻²) and stacking faults (~10⁵ cm⁻¹) [40]. Reductions in dislocation and stacking fault densities in non-polar GaN films have been reported through the use of masking layers and ELO processes, similar to those presented in previous sections [41, 42]. Similarly, m-plane (11̅00) GaN growth has been reported on m-plane SiC, but ELO processes were required to lower the density of stacking faults in non-polar films [43].
Semi-polar GaN growth has also been reported on Si(001) substrates by using an anisotropic etchant in conjunction with a patterned mask to fabricate microstructures in the Si(001) with exposed Si(111) facets [36, 44]. Then GaN can be grown off of the Si(111) facet while the Si(001) surface is masked with SiO$_2$ or SiN$_x$. Lee et al. showed an improved structural quality of the GaN films grown on exposed (111) facets using cathodoluminescence (CL) measurements [36]. In a separate study, Antwi et al. showed similar results for GaN grown on exposed Si(111) facets [44]. In their work TEM and AFM studies of GaN films grown on Si(001) and on Si(111) facets exposed on a Si(001) substrate showed that dislocations propagated along the c-axis direction of grown GaN and did not bend towards the exposed GaN(10-11) surface. Therefore an overall reduction in dislocations at the film surface was observed for films grown on patterned Si(001). This process resulted in semi-polar GaN films on cheap Si(001) substrates with a reduced dislocation density, however, photoluminescence studies showed a defect related peak associated with basal plane stacking faults [44].

2.7 Preferential Growth of GaN on Si Pillars

Won et al. reported on a growth of GaN on structured Si with different Si substrate orientations [45]. Si pillar arrays were formed by deep reactive ion etching (DRIE), as opposed to the more commonly used anisotropic KOH etching, in order to form arrays of vertical Si pillars in Si(111), Si(100), Si(112), and Si(110) substrates. It was observed that GaN grew on the Si pillar arrays with varying “fin” shapes radiating outward from the pillar sidewalls as seen in Figure 2-8 [45].
XTEM studies of the Si(111) pillar showed an epitaxial relationship of GaN growth on Si pillar sidewalls such that GaN[0001]//Si<-110>. From this the orientation of GaN on the other pillar orientations was determined from the respective Si wafer flats. A diagram showing the resulting orientations of GaN fins on Si pillars is given in Figure 2-9.
Figure 2-9. Schematic representation of orientation of GaN fins on pillars etched into (a) Si[111], (b) Si[110], (c) Si[112], and (d) Si[100] substrates [45].

The Si(100) wafer showed four GaN fins parallel to the Si<110> planes and no growth on the top (100) surface of the (100) pillar. Based on these results, it may be possible to use microstructured Si(100) substrates with exposed Si(110) sidewalls to obtain non-polar GaN on Si(100) substrates. In the studies presented later in this work a similar method
to that use by Won et al. was used to etch trenches into Si(100) wafers such that the trench sidewalls were <110> oriented. The studies were intended to develop a maskless method of forming non-polar GaN films on Si(001).
2.8 References:


Chapter 3
Experimental Methods

3.1 Introduction:

A wide variety of processing and characterization techniques were utilized in order to grow and study GaN films on modified silicon substrates. This chapter will focus on discussing the specific tools and equipment used in the experimental work described in later chapters. Particular care will be taken to illuminate the workings and intricacies of the in situ laser curvature measurement which will provide a large portion of the experimental basis for later chapters focusing on studies of growth stresses of films. The set-up of the MOCVD growth reactor used will be outlined as well. A brief description of additional ex situ characterization techniques used will then be presented.

3.2 Substrate Preparation:

The primary goal of the studies presented in later chapters was to determine the effect of substrate modification techniques on GaN film growth. In this section an overview of the modification techniques used will be provided. The first technique to be considered will be ion implantation of Si(111) substrates. The latter technique will involve the etching of trench structures on Si(100) substrates with Si(110) sidewall facets. Finally a review of pre-growth substrate cleaning techniques will be provided.
3.2.1 Ion Implantation of AlN/Si(111) Substrates:

Ion implanted substrates were prepared by Jeff Leathersich and Mihir Tungare, students in Dr. Fatemah Shahedipour-Sandvik’s research group at the University at Albany. Ion implantation of substrates used in this study was performed through a previously grown AlN buffer layer. Two MOCVD reactors were used for the growth of AlN buffer layers: a Veeco D75 and a Veeco D180 reactor, both equipped to grow on 2” Si(111) round substrates. Trimethylaluminum (TMA) and NH$_3$ were used as the source precursors for Al and N, respectively. Growth of AlN on all samples studied in this work was performed with standard conditions that had been developed at the University at Albany. For the Veeco D75 reactor the TMA and NH$_3$ flow rates were 29.3 µmol/min and 0.129 mol/min, respectively, unless otherwise specified. The standard flow rates for the D180 reactor were 43.5 µmol/min and 0.304 mol/min for TMA and NH$_3$, respectively. Regardless of the growth reactor used the AlN growth temperature was between 1000°C and 1010°C while the growth pressure was between 50 and 55 Torr. Implantation of substrates was performed after AlN buffer growth, as shown schematically in Figure 3-1 such that the N$^+$ ions were implanted through the AlN buffer into the Si substrate.
Figure 3-1. Schematic of ion implantation of AlN/Si(111) substrates.

The ion dose was $2-3 \times 10^{16}$ cm$^{-1}$ for all studies presented here. The energy of implanted ions could be adjusted to control the peak implantation depth with respect to the AlN/Si(111) interface. Implantation induced disorder in the Si lattice creating an amorphous region below the AlN/Si(111) interface which was recrystallized during substrate annealing. The substrate annealing process will be discussed in more detail in later chapters. Implantation was performed using an Extrion 400-10P ion implanter and Transport of Ions in Matter (TRIM) calculations were used to estimate the peak implantation depth of ions.
Later studies of ion implantation involved the use of different AlN buffer growth processes. The standard AlN growth process involved flowing TMA precursors into the reactor chamber for 6s prior to the addition of NH₃ in order to prevent nitridation of the Si(111) surface. NH₃ was then flowed into the reactor chamber while maintaining the TMA flow such that both precursors were flowing simultaneously as represented schematically in Figure 3-2a. Later studies necessitated the use of a pulsed precursor flow growth process to improve the lateral diffusion of Al adatoms. The pulsed growth scheme consisted of alternating 6 s pulses of TMA and NH₃ into the reactor as shown schematically in Figure 3-2b.

![Figure 3-2](image)

**Figure 3-2.** Schematic representation of continuous precursor flow and pulsed precursor flow AlN growth methods.

The number of repetition of these pulses (i.e. the overall buffer growth time) could be varied in order to control the thickness of the buffer layer grown. The pulsed growth
scheme allowed for greater lateral atomic diffusion at the growth surface which resulted in larger AlN island sizes and therefore further control of the AlN buffer morphology depending on the pulse length.

3.2.2 Fabrication of Si(100) Trenches:

The second type of modified substrate that was used in the studies presented here were Si(001) substrates with etched trenches. The trenches were fabricated on 4” Si(100) wafers using a deep reactive ion etching (DRIE) process in conjunction with a SiO$_2$ hard mask, fabricated with optical lithography, to define the trench arrays. The arrays were arranged in rectangular cells that were orientated with respect to the wafer such that the trench sidewalls were of the {110} family of planes. The fabrication of Si(100) trenches was performed by Yu Yuwen from Dr. Theresa Mayer’s research group at Penn State. The DRIE utilized an isotropic plasma etching process. After a short period of plasma etching, a passivation layer was deposited to prevent additional etching of trench sidewalls. Then plasma etching was performed again. This process was repeated until the desired feature depth was reached. Since the DRIE process consists of a series of repeated isotropic etches a roughness, or “scalloping” of the trench sidewalls is observed. This roughness and damage to the Si(110) sidewalls was reduced by incorporating two successive thermal oxidation and strip cycles. A schematic example of an etched Si(100) trench cross section is given in Figure 3-3 while an SEM image of residual sidewall roughness is provided in the inset.
To remove this residual sidewall roughness a pre-growth H$_2$ anneal at growth temperature was performed. The details of this anneal will be studied further in later chapters.

3.2.3 Substrate Cleaning:

All substrates used in these studies were diced into 10x10mm pieces using an ADT 7100 ProVectus dicing saw in order to ensure a proper fit into the MOCVD susceptor pocket used. In order to protect the growth surface from damage during the
dicing process, a protective tape was placed over the surface. Wafer pieces were then mechanically peeled off of the protective tape after dicing. Residue and particulates from wafer transport and the dicing tape had to be removed prior to film growth and therefore a cleaning cycle was performed on each substrate directly prior to growth. The substrates were ultrasonically cleaned in 20 ml of acetone for 15 minutes in order to remove any organics or particulates left over on the surface from dicing or transport. The substrates were then submitted to another ultrasonication step in isopropanol in order to remove any residue left over from the acetone cleaning step. Finally substrates were rinsed in 60ml of deionized (DI) water in order to remove any residue left over from the isopropanol step. The final rinse in DI water was repeated six times.

The Si(100) trench substrates were also submitted to a 10 minute immersion in a 10% solution of hydrofluoric acid (HF) after the organics removal step in order to remove any residual oxide from the DRIE process or native oxide that may have formed on Si trench sidewalls. After oxide removal the substrates were then rinsed in 60ml of water six times in order to remove any residual HF and ensure a clean surface for growth. Due to the presence of a pre-grown AlN layer on the implanted substrates, the oxide removal step was deemed unnecessary and therefore removed from the cleaning procedure for these samples. Directly prior to growth, substrates were removed from the rinse water and dried under a steady stream of $N_2$ before immediately moving the substrate to the MOCVD reactor vacuum chamber.
3.3 The MOCVD Reactor:

The studies presented within this work focus on the growth of GaN films via MOCVD. The following section will, therefore, discuss the specifics of the MOCVD reactor used for these studies.

3.3.1 The Gas Flow Delivery System:

The MOCVD reactor used in these studies consisted of a Thomas Swan CS0589 gas cabinet that was modified by CVD Equipment Corporation. The reactor was equipped with metalorganic bubblers of trimethylaluminum (TMA) and trimethylgallium (TMG) for use as Al and Ga precursors for growth studies. Trimethylindium (TMI), biscalclopentadienyl magnesium (CP₂Mg) and biscalclopentadienyl iron (CP₂Fe) were also attached to the system for use as In, Mg, and Fe sources but were not used in the studies discussed here. The metalorganic bubblers had to be temperature controlled in order to maintain the appropriate partial pressure of source gas above the liquid in the bubbler. Therefore each bubbler was immersed in a Lauda ECO RE 620S temperature controlled circulating bath in order to maintain the appropriate bath temperature. The TMA bubbler was kept at a temperature of 25°C and the TMG bubbler was kept at a temperature of -13°C. In order to maintain the sub-zero temperature of the TMG bath, a mixture of 50% Ethylene Glycol and 50% DI water was used to prevent the bath liquid from freezing. Pressure controllers were connected to the MO source lines and held at constant pressure so that the MO source flux could be controlled in appropriate ranges by varying the carrier gas flow through the bubblers. The reactor was connected to two
carrier gas sources. One was an in-house $\text{N}_2$ system while the other was an ultrahigh purity $\text{H}_2$ cylinder system. Both gas sources were flowed through purifiers prior to entering the system. The $\text{N}_2$ source gas was used for some thermal anneal studies and for purging the reactor prior to unloading or loading samples. $\text{H}_2$ was the primary source gas for film growth.

**3.3.2 The Reactor Chamber:**

The reactor chamber was a home-built system which a quartz chamber developed by CVD equipment corporation following designs provided by Dr. Joan Redwing. A schematic representation of the reactor is provided in Figure 3-4 alongside a picture of the actual reactor chamber.
Figure 3-4. Image (left) and diagram (right) of MOCVD reactor.

The reactor chamber was a double walled quartz bell jar with tubes connecting the interwall space to a water circulator in order to maintain a cold-wall system during growth. The top of the bell jar was sealed with a stainless steel end cap through which source gas flow lines were connected. The top end cap also included optical ports with quartz windows which allowed the laser from the in situ curvature measurement system to enter and leave the reactor for detection of substrate curvature changes. Carrier gases were purged through the optical ports in order to prevent deposition on the quartz windows during growth which would obstruct the detection laser. The lower stainless steel end cap was connected to a motor which allowed the end cap to be lowered for
bottom loading of samples. The bottom end cap also contained the quartz support shaft which was sealed using a suspended ferrofluid, thus allowing for rotation of the susceptor during growth to promote uniform surface coverage. Both end caps were sealed to the quartz bell jar through a system of two silicone o-rings. The space between the o-rings was connected to a roughing pump which evacuated the space between the o-rings in order to provide an additional vacuum seal at the quartz/stainless steel connection. This allowed for a leak-tight reactor chamber to prevent outside contamination during growth.

The heated graphite susceptor on which the substrate was placed during growth was coated in SiC in order to prevent degradation upon exposure to the gases used during our standard growth processes. Susceptor fabrication and coating were performed by Mersen-Midland, Inc. A Lepel radiofrequency (RF) generator was then used to apply an oscillating RF voltage signal to the coil around the quartz reactor chamber in order to inductively heat the graphite susceptor to the appropriate growth temperature. The temperature of the system was measured with a type K thermocouple placed inside the quartz support shaft such that it was in contact with the quartz at a distance of 2mm from the heated graphite susceptor.

The reactor chamber was connected to a Leybold Trivac BCS rotary vane pump. An MKS throttle valve was used in conjunction with a MKS Type 252A exhaust valve controller in order to control the reactor pressure during growth. Exhaust gases generated during growth were evacuated through a Misonix XGC-30M scrubber in order to neutralize harmful chemicals before exhausting the gases. All flow rates, reactor pressures, and temperature values were controlled with a computer running a CVD process control system software developed by the CVD Equipment Corporation.
Through this program all growth recipes—including gas flow rates, reactor temperatures, and pressures—could be edited and tailored to specific experimental purposes.

3.4 Characterization:

Characterization of the GaN films grown in this work was important in order to develop a fuller understanding of the mechanisms involved in the development of film stress and structure during growth. The major technique was in situ laser curvature measurements, which will be described in detail below. Several additional ex situ techniques will also be discussed.

3.4.1 In Situ Laser Curvature System:

The primary characterization technique used in our studies was in situ measurements of substrate curvature during all steps of the growth process. Due to this it is important for the reader to have a good understanding of the workings of the curvature measurement system to understand the results presented in later chapters.

3.4.1.1 Curvature Detection Equipment:

The laser curvature system used was a k-Space Associates multi-beam optical stress sensor (MOSS) and was equipped with mounting brackets above the main reactor chamber as shown in Figure 3-5a.
Figure 3-5. (a) Picture of MOSS laser reflectance system and (b) schematic representation of MOSS laser detection system.

The MOSS system was equipped with a 658 nm wavelength AlGaInP laser. An etalon then split the laser into four parallel beams. The four parallel beams entered the reactor through the left optical port and impinged upon the substrate as shown schematically in Figure 3-5b. The position of the MOSS laser on the substrate surface could be controlled, thus allowing for alignment of the MOSS onto the center of the substrate. The spacing between the parallel laser beams could also be adjusted if necessary by adjusting the degree of tilt of the etalon. For substrates of different thicknesses the laser had to be refocused on the substrate surface in order to properly track the reflected MOSS spots.

The laser beam then reflected off of the sample surface and exited the reactor through the right optical port and a mirror reflected the laser spots into a charge-coupled
device (CCD) camera. Due to the constantly rotating susceptor, an encoder was utilized so that the CCD camera only sent data to the computer at a particular point in the susceptor’s rotation. The k-space computer program then took the data from the CCD camera and plotted the curvature change of the sample based on the change in spot spacing. This is based on the geometry of the incident and reflected laser beams. Parallel incident laser beams will be reflected off of a curved sample surface in a non-parallel manner which will result in a change in spot spacing between the incident and reflected laser beams as shown schematically in Figure 3-6.

![Schematic representation of the effect of substrate curvature on reflected beam spacing.](image)

Therefore, by knowing the beam path length we can determine the curvature ($\kappa$) of the substrate during film growth using the following equation [1]:

$$
\kappa(t) = \frac{\cos(\alpha)}{2L} \left[ 1 - \frac{D(t)}{D_0} \right]
$$

(3.1)

where $\alpha$ is the angle of the incident beam as measured from the surface normal, $L$ is the length between the sample and the CCD detector, $D(t)$ is the spacing between spots at time $t$, and $D_0$ is the initial beam spacing.
3.4.1.2 Data Collected From MOSS:

The data collected from the MOSS can be split into two main categories for our purposes: Reflected laser intensity, and sample curvature. The reflected laser intensity is important as an *in situ* tool to determine the film thickness during growth as well as to determine the relative surface quality of the growing film. An example of reflected intensity data for a standard GaN/AlN/Si(111) growth is given in Figure 3-7.

![Graph showing reflected laser intensity vs. time for GaN growth on Si.]

Figure 3-7. Reflected laser intensity vs. time for GaN growth on Si.

It was observed that the reflected film intensity showed oscillations during GaN growth. These oscillations are caused by the change in the thickness of the film during growth and the peak-to-peak width of the oscillations is related to the thickness of the film. As
the MOSS laser reflects off of the film and the film/substrate interface, the reflected beams either constructively or destructively interfere with one another, depending on the thickness of the film. Therefore the thickness of the growing film can be estimated based on the following equation:

\[ d = \frac{m\lambda}{2n} \]  

(3.2)

where \( d \) is the peak-to-peak oscillation width, \( m \) is an integer, and \( n \) is the refractive index of the film (\( n_{\text{GaN}} = 2.37 \) and \( n_{\text{AlN}} = 2.06 \))[1, 2]. In Figure 3-7 we note that the initial oscillation for the GaN growth segment had a low initial amplitude due to the formation of GaN nuclei on the AlN surface. The presence of uncoalesced 3D GaN nuclei across the surface resulted in an increase in the effective roughness of the growth surface. This increase in roughness lowered the intensity of the reflected laser beam. The GaN nuclei laterally grew as film growth progressed which lowered the effective roughness of the surface and therefore increased the reflected beam intensity. This was observed in the increased oscillation intensity with continuing growth shown in Figure 3-7. When the GaN islands fully coalesced into a coherent film, the intensity oscillations reached a maximum amplitude. If the film were to roughen during growth due to etching or other chemical reactions, this roughening would be observed through a reduction in reflected laser intensity. Therefore the reflected laser intensity is also a useful tool for determining the relative surface quality of the growing film.

The other main use of the MOSS system in our experiments is to determine the change in curvature of the substrate during growth. As discussed previously, the change in curvature is measured based on the variation in reflected spot spacing observed by the
CCD camera. The change in film curvature during growth can be related to the biaxial stresses formed in the film due to heteroepitaxial growth as represented by the schematic in Figure 3-8.

Figure 3-8. Diagram of the effect of lattice strain on substrate curvature and reflected spot spacing.

If the film has a smaller lattice constant than the substrate parallel to the growth direction, then the film lattice experiences tensile strain which results in a concave change in curvature during growth. Similarly, if the film lattice is larger than that of the substrate, then the film experiences a compressive strain during epitaxial growth which results in a convex curvature change. This can be represented mathematically with Stoney’s equation [3]:
\[ \sigma_f h_f = \frac{\kappa_s M_s h_s^2}{6} \]  

(3.3)

where the stress thickness product \((\sigma_f h_f)\) of the film is represented as a function of sample curvature \((\kappa_s)\), the substrate thickness \((h_s)\) and the substrate biaxial modulus \((M_s)\). If the curvature of the substrate is calculated by MOSS and the substrate thickness and biaxial modulus are known then the stress evolution of the film during growth can be calculated.

An example of curvature data for GaN growth on Si(111) is presented in Figure 3-9a. The curvature change during the GaN growth step was converted to Stress-thickness data using the method outlined above. The resulting stress-thickness vs. thickness data is in Figure 3-9b. In the plot of stress-thickness vs. thickness the slope of the plot relates to the incremental stress of the film at that point during growth. A negative slope represents a compressive stress and a positive slope represents a tensile stress in the film. It is important to note in the stress-thickness data the sharp peaks observed periodically as indicated by the arrows in Figure 3-9. These peaks are artificially caused by non-uniformities in the film growth. As the intensity oscillations approach the minimum in intensity caused by destructive interference between the film and substrate surfaces the reflected beam intensity becomes so dim that the CCD camera can no longer detect the laser spot. This normally induces a short period where no data is collected. If the film growth is non-uniform, however, the four laser spots detected by MOSS may reach that extinction point at different times. This causes errors in the MOSS tracking of the reflected laser spots which leads to the sharp peaks observed in the stress-thickness data. These artifact peaks are ignored for the purposes of calculating incremental film stress.
Figure 3-9. Stress-Thickness vs. thickness of a GaN film grown on Si(111).

The incremental stress of the film during growth can be plotted by taking the instantaneous slope of the stress-thickness plot at various points along the curve. To accomplish this a trend line is drawn through the stress-thickness data. Engauge Digitizer Version 4.1, a point plotting software, is then used to plot the (x,y) coordinates of points...
along the curve. The linear slope of these data points is then calculated over short ranges (~5 data points) which results in the incremental stress of the film.

3.4.2 Ex Situ Characterization Techniques:

Several *ex situ* characterization techniques were also utilized during the course of the studies presented here. An Olympus MX50 optical microscope was initially used in order to determine the large scale surface quality of the grown films. The microscope was equipped with a Nomarski crystal for taking differential interference contrast mode images to observe slight changes in the film across the sample surface. Optical microscopy was also used to determine changes in crack and pit density between films and the degree of lateral growth on Si(100) trench samples. For smaller scale morphology studies a Veeco Dimension 3100 atomic force microscope (AFM) was used in conjunction with a NanoScope IIIa SPM controller. The main focus of AFM studies was to observe the small scale surface morphology and roughness of films and substrates before and after growth.

X-ray diffraction (XRD) was then performed using a Philips Pro MRD 4-circle diffractometer on select samples. X-ray rocking curves were performed in order to get a relative measure of film quality, particularly the on and off-axis mosaicity of GaN grains. Threading dislocation (TD) densities of films were also estimated from the full-width at half maximum (FWHM) of the GaN(0002) and (10\bar{1}0) peaks in select cases using the classical model for dislocations [4, 5].
GaN films on Si(100) trench samples were observed using a Hitachi S-3000H scanning electron microscope (SEM), a Hitachi S-3500N SEM, and a Led 1530 field emission scanning electron microscopes (FESEM). This technique was used to study the reduction of trench sidewall roughness based on growth conditions as well as the orientation and structure of GaN grown on Si(110) sidewalls.

Select samples were also submitted to cross-sectional transmission electron microscopy (XTEM) using a JEOL 2010F field emission microscope. XTEM samples were prepared by mechanical thinning and subsequent ion milling. XTEM studies and sample preparation were performed by Dr. Xiaojun Wang and Dr. Haoting Shen. TEM studies on ion implanted substrates focused on estimating TD density and GaN grain misorientation. The structure formed at the implantation depth in implanted AlN/Si substrates was also observed. TEM studies on trench samples focused on determining the orientation of GaN grown on Si(110) trench sidewalls.
3.5 References:

Chapter 4

The Effect of Substrate Ion Implantation on GaN Film Stress Evolution

4.1 Introduction:

Two methods of ion implantation induced stress reduction were presented in Chapter 2. Koh et al. presented a method where Si substrates were implanted prior to buffer or film growth[1]. Jamil et al. presented a modified implantation process where N\(^+\) ions were implanted through a pre-grown AlN buffer before GaN film growth[2]. Both studies showed a reduction in GaN film stress after cooling. Here we put forth a series of studies which utilize \textit{in situ} curvature measurements to provide further information on the GaN growth process in order to better understand how implantation of AlN/Si(111) substrates is resulting in the reduced crack and threading dislocation (TD) densities previously reported[2, 3]. The \textit{in situ} measurements were coupled with \textit{ex situ} studies of crack density, threading dislocation (TD) density, surface morphology, and film structure in order to investigate the mechanism through which substrate ion implantation affected the TD density and cracking of GaN films.

4.2 Effect of Substrate Ion Implantation on GaN Growth

The following studies were preliminary tests to observe how the stress evolution of GaN films varied between implanted and unimplanted AlN/Si(111) substrates when
submitted to our standard growth process. *In situ* characterization provided information on the incremental film stress of GaN films during growth while *ex situ* characterization was utilized to study the effects of implantation on crack and dislocation densities in GaN films.

### 4.2.1 In-Situ Stress Studies

The main goal of the studies discussed below was to use *in situ* measurements to determine how substrate ion implantation was affecting the growth stress evolution in GaN films. Therefore GaN growth was performed on AlN/Si(111) substrates with and without implantation while tracking curvature changes during growth to determine how the stress in the film was evolving during the growth process. The substrates used in these studies consisted of a 34nm AlN buffer layer grown on a 2” diameter Si (111) wafer. The AlN buffer was grown in a Veeco D75 MOCVD reactor using trimethylaluminum ((CH$_3$)$_3$Al, TMAI) and NH$_3$ at total gas flow rates of 1.23 mmol/min (27.5 sccm) and 134 mmol/min (3 slm), respectively. AlN growth was performed at 1050°C and 55 Torr. Implantation was performed on one piece of the 2” wafer at an ion dose of $2 \times 10^{16}$cm$^{-2}$ and energy of 65 keV, resulting in a peak implantation depth of $\approx 105$ nm below the AlN/Si interface. The implantation conditions used were chosen based on optimization of the implantation process that was discussed in previous work by our collaborators at the University at Albany[3]. The depth and range of implantation were estimated using transport of ions in matter (TRIM) calculations. The other piece of the substrate was left unimplanted for comparison. The AlN/Si substrates were then
further diced into 10 x 10 mm squares and ultrasonically cleaned in acetone and isopropanol followed by a deionized water rinse. There was no observable difference in the surface morphology or roughness of AlN/Si(111) before or after implantation as shown in Figure 4-1 and the average diameter of AlN islands was ~74nm.

Figure 4-1. AFM comparison of surface of (a) unimplanted and (b) implanted AlN/Si substrates.

GaN growth and \textit{in situ} stress characterization were performed using the reactor set up that was outlined in Chapter 3. The reactor pressure and temperature were 50 Torr and 1100°C, respectively. A 10 min H₂ anneal was performed directly before GaN growth in order to anneal out ion implantation induced damage in the AlN/Si(111) substrate before GaN growth was initiated. The total flow rate through the TMG mass flow controller (MFC) was 0.402 mmol/min (9 sccm) and the GaN growth rate was measured to be ≈0.56 nm/s using a V/III ratio of ≈12,000. A 1 µm thick GaN film was grown on both the implanted and unimplanted AlN/Si substrates using identical growth
conditions. After GaN growth, the samples were cooled at a rate of 1.6°C/s to a temperature of 750°C after which the susceptor heater was turned off and the samples were allowed to cool naturally to room temperature.

Curvature data collected during GaN growth on the implanted and unimplanted AlN/Si substrates is shown in Figure 4-2a. As shown in Figure 4-2a, both AlN/Si substrates initially exhibited negative curvature (convex) compared to the flat Si reference. The implanted sample exhibited a more negative initial curvature of \( \approx -0.12 \text{ m}^{-1} \) compared to \( \approx -0.08 \text{ m}^{-1} \) for the unimplanted sample. This difference in initial curvature between the two samples may have been due to structural/stress differences in the substrates due to the implantation, non-uniformity in the AlN buffer across the sample surface, or asymmetry in the bow of the initial Si(111) wafer.

![Figure 4-2. Comparison of (a) curvature change during entire growth process and (b) stress-thickness during growth segment for unimplanted and implanted substrates.](image)

The positive change in substrate curvature observed during heating was a commonly observed phenomenon on Si(111) substrates [4, 5]. Normally this increase in curvature
on bare Si(111) was due to thermal gradients across the substrate thickness caused by the direct contact between the bottom of the substrate and the top of the substrate being submitted to a flow of cooler carrier gasses. Due to the positive thermal expansion coefficient of Si, this thermal gradient normally caused greater expansion at the bottom of the sample than the top, resulting in positive change in curvature. The substrates used in these studies, however, consisted of an AlN layer on the Si(111) substrate and therefore the CTE mismatch between the AlN and the Si(111) would have affected the curvature change during heating. The change in curvature during heating was 0.0280 m$^{-1}$ for the unimplanted sample and 0.0479 m$^{-1}$ for the implanted sample. The origin of the greater increase in curvature during heating of the implanted substrate will be discussed further in Chapter 5. Despite the difference in initial curvature between the implanted and unimplanted substrates, both substrates had a similar curvature after the heating segment. The substrates were held at 1100°C in H$_2$ for ten minutes during which negligible curvature change was observed for both samples.

The curvature change observed during GaN deposition was a result of growth-related stress generation and relaxation processes. The curvature data during this segment was converted to the product of the film stress and the film thickness via Stoney’s equation [6, 7]. The resulting stress-thickness data was plotted versus film thickness in Figure 4-2b. GaN initiated growth under an initial compressive stress (negative slope) for both samples which arose due to lattice mismatch between the GaN and AlN. Both samples relaxed the compressive stress with increasing layer thickness and transitioned to a small final tensile stress by the end of growth. This observed stress evolution was different from that reported for GaN grown on sapphire with an AlN
buffer, which has shown a constant tensile stress for the entire growth process [8]. In addition, previous studies of GaN growth on Si(111) with an AlN buffer observed a small initial compressive stress and a rapid transition to tensile stress [9]. The transition to tensile stress was faster and the final tensile stress was higher in the previous work, however, than was observed in these experiments. The curvature increased dramatically during cooling due to the difference in the thermal expansion coefficients between the GaN film and the Si substrate as shown in Figure 4-2a.

The incremental stress, or biaxial stress in the film, was calculated as a function of film thickness by using point plotting software as outlined in Section 3.4.1.2. The results are shown as a function of film thickness in Figure 4-3. It should be noted that the artifact peaks in the stress-thickness and curvature plots, whose origins have been detailed in Section 3.4.1.2, were removed from calculations of incremental film stress. It can be seen that the implanted sample had a lower initial compressive stress (-0.85 GPa) than the unimplanted sample (-1.44 GPa) which was a consistently observed trend in multiple experiments.
Figure 4-3. Incremental stress vs. thickness for GaN growth on implanted and unimplanted substrates.

The compressive stress in GaN at the beginning of growth arose from the 2.4% lattice mismatch between GaN and AlN which translates to an epitaxial stress of -11.3 GPa. The majority of the epitaxial stress was, however, relaxed by misfit dislocations within the first 10 Å of GaN growth which resulted in the lower values observed here [10, 11]. The reduced initial compressive stress in the ion implanted sample may have been due to an implantation-induced dilation, or swelling, of the AlN lattice, thus lowering the mismatch between AlN and GaN. It is also possible that the implantation-induced defective layer beneath the AlN/Si interface acted to decouple the GaN/AlN layers from the thick Si substrate, forming a semi-compliant layer which reduced the epitaxial stress.
Despite the difference in initial stress, both samples ended at similar tensile stress states of 0.098 GPa for the unimplanted sample and 0.125 GPa for the implanted sample as shown in Figure 4-3. This shows that the implanted sample relaxed the compressive stress more slowly than the unimplanted sample which would have led to a lower final tensile stress if the samples had similar initial stress states.

4.2.2 Threading Dislocation Bending as a Stress Reduction Mechanism

Compressive stress in GaN films is relaxed primarily via the inclination of edge-type threading dislocations [12-15]. Dislocation inclination gives rise to a biaxial stress gradient \( \frac{d\sigma_{xx}}{dz} \) throughout the thickness \( z \) of the film which, for a constant TD density \( \rho_{TD} \), can be modeled as [13]:

\[
\frac{d\sigma_{xx}}{dz} = M_f \frac{d\varepsilon_{xx}}{dz} = \frac{1}{2} M_f b \rho_{TD} \tan \alpha
\]

(4.1)

where \( \varepsilon_{xx} \) is the biaxial strain, \( M_f \) is the biaxial modulus, \( b \) is the magnitude of the Burger’s vector, and \( \alpha \) is the angle of inclination of the dislocations. The difference in the rates of compressive stress relaxation between the two samples may have, therefore, arisen from differences in TD density and/or the angle of dislocation inclination. In order to investigate this further, the TD densities in the films were estimated by XRD. The full width at half-maximum (FWHM) of the GaN (0002) and (1010) peaks obtained in an \( \omega \)-scan measurement correlate to the amount of tilt and twist in the film, respectively. In order to measure the FWHM of the (10\( \bar{1} \)0) peak, grazing incidence angle x-ray diffraction (GIXRD) is normally required. The FWHM of the (10\( \bar{1} \)0) peak can be
estimated, however, by measuring symmetric ω-scans in skew geometry. The inclination angle of the subsequent scans was increased and FWHMs obtained from the scans were plotted as a function of inclination angle as shown in Figure 4-4.

An empirical model involving a convolution of two Pseudo-Voigt functions, developed by Srikant et al. [16], was used to curve fit the FWHM vs. inclination angle data. The model fits are shown as solid lines in Figure 4-4. The expected FWHM at an inclination
angle of 90°, which corresponds to the (10\overline{1}0) reflection, was then estimated from this fit. The classical model for random dislocations was then used to estimate the screw and edge TD densities [17]:

$$\rho_{\text{screw}} = \frac{\Gamma_{\text{th}}}{4.36 \cdot b_{\text{screw}}^2}$$

$$\rho_{\text{edge}} = \frac{\Gamma_{\text{twist}}}{4.36 \cdot b_{\text{edge}}^2}$$

where $\rho$ represents the TD density, $\Gamma$ is the FWHM, and $b_{\text{screw}}$ is the burger’s vector of screw dislocations (5.1850Å), and $b_{\text{edge}}$ is the burger’s vector of edge dislocations (3.1888Å) in GaN [18, 19]. The subscripts tilt and twist correspond to the (0002) and (10\overline{1}0) reflections in GaN, respectively. The calculated total threading dislocation densities for the unimplanted and implanted samples were $1.53 \times 10^{10}$ cm$^{-2}$ and $1.37 \times 10^{10}$ cm$^{-2}$ respectively, as shown in Table 4-1.

<table>
<thead>
<tr>
<th></th>
<th>Total $\rho_{\text{TD}}$ (cm$^{-2}$)</th>
<th>Edge $\rho_{\text{TD}}$ (cm$^{-2}$)</th>
<th>Screw $\rho_{\text{TD}}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Implanted</strong></td>
<td>$1.37 \times 10^{10}$</td>
<td>$1.24 \times 10^{10}$</td>
<td>$1.29 \times 10^{9}$</td>
</tr>
<tr>
<td><strong>Unimplanted</strong></td>
<td>$1.53 \times 10^{10}$</td>
<td>$1.44 \times 10^{10}$</td>
<td>$9.13 \times 10^{8}$</td>
</tr>
</tbody>
</table>

The lower edge TD density of the implanted sample corresponds to a lower amount of twist misorientation between the GaN grains. While there were differences in the ratio of edge/screw dislocations between the samples, we observed only a small decrease in the total TD density in the ion implanted films in this study, compared to the order of
magnitude decrease observed by Jamil et al [2]. This is likely due to differences in the AlN thickness, implantation dosage and GaN growth reactor and process conditions used in the two studies. It is possible that the polycrystalline and amorphous Si layer that was formed during annealing of the Si substrate after ion implantation decoupled the AlN buffer from the bulk of the substrate, thus lowering the energy necessary for misoriented islands to reorient with respect to one another. This could lead to a lower edge TD density if the energy necessary for reorientation was smaller than that necessary for TD formation. The slightly lower density of edge-type dislocations in the ion implanted film may have also been responsible, in part, for the reduced stress gradient observed in Figure 4-3.

Transmission electron microscopy (TEM) studies were performed on unimplanted and implanted samples and are shown in Figure 4-5 and Figure 4-6, respectively. Figure 4-5a is a bright-field TEM image of the unimplanted sample that shows TDs with varying amounts of inclination near the GaN/AlN interface of the film. Selected area diffraction (SAD) of the unimplanted sample is shown in Figure 4-5b. From the SAD image, the sharp AlN spots indicated a buffer layer with relatively good crystal quality. A high-angle annular-dark-field (HAADF) scanning TEM (STEM) image of the unimplanted film (Figure 4-5c) showed TDs in the film as well as a lateral contrast variation between GaN grains.
Figure 4-5. (a) Bright-field TEM image of GaN/AlN/unimplanted Si(111) collected along [1\(\bar{1}\)00] zone axis under multibeam diffraction conditions. (b) SAD pattern collected from a region consisting of GaN, AlN, and Si. (c) High-angle annular dark-field (HAADF) scanning TEM (STEM) image.

This contrast variation indicated that the GaN grains were misoriented with respect to one another which was consistent with the increased twist as compared to the implanted sample measured in the XRD.

The TEM images and SAD pattern obtained from the implanted sample are shown in Figure 4-6.
Figure 4-6. (a) Bright-field TEM image of GaN/AlN/implanted Si(111) collected along [1\(\overline{1}00\)] zone axis under multibeam diffraction conditions. Arrows indicated short edge dislocation segments. (b) SAD pattern collected from a region consisting of GaN, AlN, and Si. (c) High-angle annular dark-field (HAADF) scanning TEM (STEM) image. Arrow indicates lateral cracking in substrate polycrystalline layer.

In addition to TDs, bright-field TEM of the implanted sample (Figure 4-6a) showed short edge dislocation segments, of unknown origin, which were nearly parallel to the basal plane as indicated by the arrows in Figure 4-6a. A SAD pattern of the implanted sample
collected near the GaN/AlN/Si interface is shown in Figure 4-6b. The reflections from the AlN buffer layer were diffuse compared to those in the unimplanted sample which indicated a degraded AlN crystal quality due to ion implantation. In addition, polycrystalline Si diffraction rings were present in the SAD pattern of the implanted sample. These rings were from the ≈130 nm thick polycrystalline Si layer immediately below the AlN layer, which was presumably formed by the recrystallization of the amorphous Si created by the ion implantation. A ≈60 nm Si layer consisting of a high density of planar defects was also observed between the polycrystalline Si layer and the single crystalline Si substrate, which likely formed through a solid phase epitaxial growth (SPEG) process. The SPEG Si layer was observed in the HAADF STEM image (Figure 4-6c) as a brighter layer directly above the bulk crystalline Si substrate. The higher brightness of this layer arose from strain induced by the high density of defects in this layer [20]. HAADF STEM also revealed that there was less lateral contrast in the GaN film for the implanted sample as compared to the unimplanted sample. This indicated lower misorientation of the GaN grains which was consistent with the lower edge TD density measured by XRD. The reduced GaN misorientation suggested that the AlN islands on which they were epitaxially grown may have also had a reduced misorientation. In order to test this theory, cross-sectional STEM studies of AlN buffers before and after implantation and annealing were performed by our collaborators concurrently with this work [21]. The resulting HAADF scanning TEM of the AlN buffer layer showed that the AlN had reduced misorientation between neighboring islands after implantation and annealing. This reduced misorientation of AlN islands may have resulted in the lower twist misorientation between neighboring GaN grains, and
therefore the reduced edge TD density observed on implanted samples presented in this study. Inclined TDs were also present in the implanted sample and were particularly prominent at the early stages of growth. As shown in Figure 4-3, the implanted sample relaxed approximately 82% of the initial compressive stress within the first 400 nm of growth. The majority of the TDs either annihilated or reoriented to the substrate normal after approximately 360 nm of growth as shown in Figure 4-6c. The similarity of these thickness values indicates that the dislocation inclination and annihilation was playing a dominant role in the relaxation of the compressive stress in these samples.

In spite of the fact that the GaN films grew on the ion implanted AlN/Si substrates under a reduced initial compressive stress compared to the unimplanted case and the stress was essentially fully relaxed by the end of 1.0 μm of GaN growth for both samples, the films grown on the implanted substrates consistently exhibited a lower density of channeling cracks as shown in Figure 4-7.

![Figure 4-7](image)

Figure 4-7. Optical microscopy images of surface cracking in GaN films grown on (a) unimplanted and (b) implanted substrates.
In these samples, horizontal cracks within the polycrystalline Si layer were occasionally observed as indicated by the arrow in Figure 4-6c. The cracks in the polycrystalline Si layer suggested that the polycrystalline region may have partially accommodated the stress formed during growth and cooling due to the epitaxial and thermal expansion mismatches between the film and substrate. It is likely, therefore, that the polycrystalline Si acted as a weakened layer beneath the AlN/Si interface which decoupled the GaN films from the Si substrate and thereby reduced the tensile stress in the GaN due to CTE mismatch. This would have resulted in the decreased density of channeling cracks observed in the GaN film. This decoupling effect would have also led to the lower initial compressive stress observed in the GaN film on the implanted sample. These horizontal cracks were not observed by Jamil et al [3]. This could be attributed to the differences in annealing, growth conditions, and the MOCVD reactor used. It is also possible that the horizontal cracks were not evenly distributed throughout the substrate and were therefore not present in the specific cross-sections studied by Jamil et al. Differences in annealing may also explain the diffused AlN spots of the implanted buffer layer as seen in the SAD pattern. The small scale surface morphology of the GaN films was studied with atomic force microscopy as shown in Figure 4-8. Substrate ion implantation seemed to have had little effect on the GaN surface morphology. RMS roughness measurements of a 2 x 2 μm area showed similar values of 0.197 ± 0.003 nm and 0.281 ± 0.045 nm for unimplanted and implanted samples, respectively.
4.3 Conclusions

Substrate ion implantation resulted in a reduction in the initial compressive stress in the GaN film, which arose due to epitaxial mismatch with the AlN buffer layer, as compared to unimplanted samples. In addition, the films grown on the ion implanted substrates exhibited reduced twist and therefore had a lower density of edge-type threading dislocations. Inclined threading dislocations were present in all of the GaN films in the initial 300-400 nm of growth which corresponded to the region where the majority of the compressive stress relaxation was observed to occur. In summary, ion implantation was found to reduce the initial compressive stress and the degree of compressive stress relaxation and tensile stress generation in GaN films.

Implanted samples consistently exhibited a lower density of surface cracks due to thermal mismatch stress despite the reduced initial compressive stress in these films. Cross-sectional TEM images of the ion implanted samples revealed a polycrystalline Si
layer between the AlN buffer layer and the SPEG Si layer. Horizontal cracks observed in the polycrystalline Si suggested that this layer provided a weakened interface between the GaN/AlN films and the Si substrate which partially accommodated the tensile stress due to thermal expansion mismatch and thereby reduced the density of channeling cracks in the GaN film. This implanted region may also have accommodated the growth stress in the GaN film, resulting in a lower stress reduction during film growth than was observed on unimplanted samples.

Implanted substrates were observed to undergo a greater increase in curvature during heating than unimplanted samples. The pre-growth annealing step was necessary to remove ion channeling damage from the film as well as to recrystallize the amorphous Si at the implantation depth, yet no studies have been performed on these substrates to optimize the annealing process. Therefore studies of how factors such as the annealing time, temperature, and ambient gas affect the substrate curvature, AlN buffer morphology, and GaN stress evolution will be performed.

Further studies of substrate ion implantation must also be performed in order to understand and optimize the important parameters to stress reduction via this method. Studies performed by the University at Albany have indicated that the ion implantation process induces AlN grain reorientation in the buffer layer which acts to reduce misorientation between neighboring grains [21]. Further studies into the effect of the AlN buffer layer conditions (i.e. island size, thickness) will be performed in order to better understand which variables affect implantation induced stress and dislocation density reduction.
4.4 References:


Chapter 5

The Effects of Annealing on Implanted Substrate Curvature

5.1 Introduction

Ion implantation is a widely used process in semiconductor processing. It is a well-known feature of ion implantation that the channeling of ions through the target lattice results in damage to the lattice structure [1]. Prior studies of GaN growth on ion implanted AlN/Si(111) substrates have therefore taken care to anneal the ion implanted substrates prior to growth in order to remove the residual channeling damage present in the AlN buffer after implantation. The importance of this pre-growth annealing step must not be understated and therefore a study of the effects of annealing conditions on the implanted AlN/Si(111) substrate and subsequently grown film was performed. Initial studies compared the effect of annealing on substrate curvature change for implanted and unimplanted substrates. Later studies focused on how annealing variables such as the anneal length, ambient gas, and anneal temperature affected the AlN/Si(111) substrates.

In situ curvature measurements were utilized to determine how ion implantation was affecting the initial curvature of AlN/Si(111) substrates. The curvature measurements were also used to track how the curvature change during heating, annealing at high temperature, and cooling varied between implanted and unimplanted substrates which could be related to structural or stress changes in the substrate occurring during the annealing process. Studies of the AlN morphology were utilized to determine
if substrate implantation or annealing affected the grain size or surface roughness of the buffer prior to growth. Later studies involved growth of a GaN film on implanted substrates to determine if the annealing variables were affecting the GaN stress evolution in ways that could not be anticipated solely from substrate curvature and morphology studies.

5.2 Preliminary Annealing Studies

Preliminary studies focused the effect of the pre-growth annealing process on substrate curvature for implanted and unimplanted samples. The samples used in preliminary annealing studies consisted of 2” round Si wafers onto which an approximately 60 nm AlN buffer layer had been grown. The AlN buffer layers were grown by our collaborators at the University at Albany in a Veeco D75 MOCVD reactor using the growth conditions outlined in chapter 3. After AlN buffer growth the wafers were cleaved and one piece was submitted to the ion implantation process while another was left unimplanted. N⁺ ions were implanted into the AlN/Si substrate at a dose of 3 x 10¹⁶ cm⁻² and a range of 75 nm below the AlN/Si interface using an Extrion 400-10P ion implanter. The 2” round pieces that were received were diced into 10 x 10 mm squares prior to growth in order to match the size of the substrate pocket in the graphite susceptor. The substrates were loaded into the MOCVD reactor that was outlined in chapter 3 and the reactor chamber was pumped down to 50 Torr. The substrates were then heated in a N₂ ambient to a temperature of 1100°C, and held for 30 minutes in order
to mimic the annealing conditions used previously by our collaborators at the University of Albany. The MOSS was used to track curvature changes during the annealing process.

The effect of annealing on the substrate curvature was initially investigated for AlN/Si substrates prepared with and without ion implantation. A bare Si(111) wafer was also submitted to identical annealing conditions to be used as a baseline for comparison. Figure 5-1a shows the curvature change during the anneal of the bare Si(111) wafer.

Figure 5-1a shows the curvature change during the anneal of the bare Si(111) wafer.

Figure 5-1. Curvature change as a function of time for 30 minute N$_2$ anneals of (a) bare Si(111), (b) unimplanted AlN/Si(111), and (c) implanted AlN/Si(111).
The sample started at an initial curvature of \( \sim 0.038 \text{ m}^{-1} \). The curvature increased (became more concave) as the temperature was heated to 1100°C as was commonly observed during the growth of GaN on Si(111) substrates [2, 3]. The curvature remained at a steady value of \( 0.073 \text{ m}^{-1} \) during the 1100°C hold segment resulting in an overall increase in curvature of \( 0.035 \text{ m}^{-1} \) during the heating process. The sample was cooled to a value of \( \sim 200°C \) after the high temperature hold and returned to a curvature value of \( 0.040 \text{ m}^{-1} \) which was similar to its starting value. Due to this and the extensive times required for the reactor to naturally cool from 200°C to room temperature (>1.5hours) MOSS tracking was ended at \( \sim 200°C \). The overall change in curvature of the bare Si(111) substrate was \( 0.002 \text{ m}^{-1} \). This indicated that there was no change in the stress state of the Si substrate during the annealing process.

The curvature change of the unimplanted AlN/Si(111) sample can be seen in Figure 5-1b. A negative, or convex, initial curvature of \( -0.007 \text{ m}^{-1} \) was present in the AlN/Si substrate prior to annealing. This indicated that the AlN/Si(111) substrate had a more negative initial curvature than the bare Si(111) wafer. AlN has a smaller lattice constant and a larger coefficient of thermal expansion (CTE) than the Si(111) substrate; both of which would induce a tensile stress in the AlN after growth. This tensile film stress would lead to a more positive curvature in the AlN/Si(111) substrate as compared to the bare Si(111) substrate which is opposite the trend observed in these studies. The origin of the observed negative initial curvature of the unimplanted AlN/Si(111) substrate is unknown, but it is possible that non-uniformities in the thickness of the AlN buffer where the MOSS laser reflected off of the surface led to an observed negative curvature of the substrate. It is also possible that difference in initial curvature between the
AlN/Si(111) and Si(111) was due to variations in the curvature of the starting substrate. The curvature increased to a concave value of 0.018 m\(^{-1}\) during the heating process, which resulted in a curvature change of 0.025 m\(^{-1}\) during heating, and remained relatively constant during the anneal at 1100°C. The AlN/Si(111) substrate showed a smaller increase in curvature during heating than the bare Si(111) substrate (0.035 m\(^{-1}\)). This was due to the fact that the thermal gradient was not the only factor affecting the curvature of the AlN/Si(111) substrate during heating. The mismatch in CTEs between AlN and Si would have also played a role in the curvature change during heating. A greater expansion would be observed in free-standing AlN than Si(111) due to its larger CTE (4.20x10\(^{-6}\)K\(^{-1}\)) as compared to Si (3.59x10\(^{-6}\)K\(^{-1}\)) [4]. Since the AlN is constrained by atomic bonding on the Si(111) substrate, however, the result is a bending moment in the wafer due to stresses from the thermal expansion mismatch [2]. This mismatch would result in a negative curvature in the substrate during heating which would have acted against the positive curvature change due to the thermal gradient across the sample thickness. The would have resulted in the smaller increase in curvature that was observed during heating of the AlN/Si(111) as compared to the bare Si(111) wafer. The sample was cooled down to approximately 200°C after the 30 minute hold at 1100°C. The sample stabilized at a curvature of -0.006 m\(^{-1}\), which was similar to its starting value, by this temperature. The resulting curvature change in the sample from pre-anneal to post-anneal states was 0.001 m\(^{-1}\). This indicated that there was no change in the stress state of the unimplanted AlN/Si(111) substrate due to the annealing process.

In Figure 5-1c the curvature change for an equivalent anneal of the implanted AlN/Si(111) sample is shown. The implanted sample started with a slightly concave
curvature value of 0.007 m$^{-1}$. The difference in the initial sample curvature between unimplanted and implanted samples may have been dependent on the uniformity of the AlN grown across the original 2” wafer, slight variations in the position of the sample in the susceptor pocket, or stresses in the substrate caused by the implantation process. Previous studies have shown that ion implantation of Si(111) substrates resulted in biaxial tensile stress in the Si lattice due to the additional N$^+$ ions that had been added to the surface of the substrate [5]. If a tensile stress was similarly observed in the AlN buffer of the AlN/Si(111) substrates used in this study, a negative change in curvature would be expected with implantation. This is opposite the trend observed. Therefore the difference in curvature was possibly due to another factor, such as the uniformity of the AlN buffer across the original 2” wafer. An increase in curvature during the heating process was again observed. The curvature at the anneal temperature was measured to be 0.046 m$^{-1}$ for the implanted sample. The resulting curvature change during heating was 0.039 m$^{-1}$, which was larger than that of its unimplanted counterpart. This may have been due to several factors including the decoupling of the AlN from the Si(111) substrate due to implantation, an increase in the thermal gradient across the substrate thickness, or structural changes in the implanted region due to recrystallization of the amorphous implanted region. There was no observable change in curvature at the anneal temperature which may have indicated that recrystallization due to annealing did not affect the curvature of the substrate, or that recrystallization occurred at temperatures below 1100°C during the heating step. The curvature decreased to a value of 0.016 m$^{-1}$ during cooling which resulted in an overall change in curvature of 0.009 m$^{-1}$ during the annealing process.
The implanted sample showed a greater increase in curvature during heating (0.039 m\(^{-1}\)) than its unimplanted counterpart (0.025 m\(^{-1}\)). Evidence was given in Chapter 4 that suggested that ion implantation was acting to decouple the GaN film from the Si(111) substrate. It is possible that the AlN was decoupled from the Si(111) substrate due to the presence of the implanted region. If this were the case, the effect of thermal expansion mismatch between AlN and Si(111) on the curvature change during heating would be reduced. As mentioned previously, the thermal expansion mismatch between AlN and Si(111) acts against the increase in curvature observed due to thermal gradients across the substrate thickness. It is therefore possible that the decoupling of the AlN from the Si(111) would result in an increase in the curvature change during heating to a value closer to that of bare Si(111). This could explain the similar curvature changes observed on bare Si(111) and implanted AlN/Si(111) substrates.

It is also possible that the increase in curvature change during the heating process was caused by an increase in the thermal gradient across the substrate thickness due to the presence of the implanted region. The thermal gradient across a material is determined by the thermal resistance (\(R_{th}\)) of the material, which can be given by [6]:

\[
R_{th} = \frac{t}{Ak}
\]  

(5.1)

where \(t\) is the thickness of the material, \(A\) is the cross-sectional area perpendicular to the flow of heat, and \(k\) is the thermal conductivity of the material. For multiple layers in series the total thermal resistance is represented by:

\[
R_{total} = \sum R_i = \frac{t_1}{Ak_1} + \frac{t_2}{Ak_2} + \cdots + \frac{t_n}{Ak_n}
\]  

(5.2)
where the total thermal resistance is the summation of the individual thermal resistances of each layer. The AlN/Si(111) substrates used in these studies consisted of AlN buffers which were several orders of magnitude thinner than the Si substrate. Furthermore the thermal conductivity of AlN at 300K (285 W m$^{-1}$K$^{-1}$) is on the same order as that of Si(111) (142 Wm$^{-1}$K$^{-1}$) [7, 8]. The temperature gradient across the substrate thickness would therefore be dominated by the Si substrate and the effect of the AlN buffer can be ignored. The implanted sample however had an amorphous silicon (a-Si) layer at the implantation depth which has a thermal conductivity that is 100x lower than that of Si (1.5Wm$^{-1}$K$^{-1}$) [9]. Based on these values the thermal resistance of unimplanted AlN/Si(111) was 2.11x10$^{-2}$ K·W$^{-1}$. By estimating the thickness of the amorphous implanted region to be equivalent to the peak implantation depth the implanted AlN/Si(111) sample was expected to have a thermal resistance of 2.16x10$^{-2}$ K·W$^{-1}$. It is therefore possible that the amorphous implanted region induced a slightly larger thermal gradient across the thickness of the implanted AlN/Si(111) substrate resulting in a slightly increased curvature change during heating.

The amorphous implanted region has been shown to recrystallize during the annealing segment. It has been shown that recrystallization of implantation induced amorphous Si films can occur over a scale of minutes at temperatures above 700°C [10]. Furthermore, there was no observed change in curvature during the high temperature hold for the implanted sample. It is therefore possible that annealing of the amorphous region of the implanted sample was occurring during the heating segment and that the recrystallization process was resulting in stresses in the substrate which increased the
curvature change in the substrate during heating. Further studies are presented in section 5.3 to test this hypothesis.

The implanted sample also showed a greater overall change in curvature (0.009 m\(^{-1}\)) between pre-anneal and post-anneal states than the unimplanted sample (0.001 m\(^{-1}\)). The unimplanted sample curvature returned to the pre-anneal curvature as the temperature gradient across the substrate thickness was reduced. The implanted sample, however, did not return to its original curvature value after cooling indicating that some change in the room temperature stress state of the implanted substrate had occurred during the annealing process. It was reported in section 4.3.2 that the implanted region below the AlN buffer layer recrystallized during the annealing process into a SPEG Si layer and a layer that was a mixture of amorphous and polycrystalline Si. The polycrystalline Si layer at the implantation depth after annealing would have a different CTE than the amorphous Si layer at the implantation depth prior to annealing. This difference in CTE mismatch between the implanted region and the substrate may have led to the observed difference in room temperature curvature of the sample between pre-anneal and post-anneal states. It was also possible that the recrystallization of the implanted layer induced stresses in the substrate during the annealing process which affected the stress of the substrate at high temperatures and resulted in a different post-anneal curvature. No change in curvature was observed, however, during the annealing process. This is either because there was no change in the stress state of the substrate due to recrystallization at high temperature, or because the annealing process occurred primarily during the heating segment. A series of short annealing cycles at temperatures
below 1100°C were therefore proposed in order to study if annealing effects at lower temperature were affecting the substrate curvature during heating.

### 5.3 Effect of Anneal Temperature on Substrate Curvature

The focus of the studies outlined below was to determine if structural changes due to annealing at temperatures below 1100°C were affecting the substrate curvature change previously observed for implanted samples during heating to 1100°C. A series of short (10 min) anneals at temperatures below 1100°C were performed in order to observe if any changes in curvature of the implanted substrate occurred during lower temperature holds. Due to a lack of implanted substrates used in the previous study, new implanted substrates were fabricated. A different growth reactor was used than for the previous series of samples. An approximately 60 nm thick AlN buffer was grown in a Veeco D180 reactor at the University at Albany using the growth conditions outlined in chapter 3. Implantation was performed with conditions identical to the previous studies in order to create a similar implantation structure. Unimplanted and implanted substrates were submitted to 10 minute holds at increasing temperatures (200°C, 400°C, 600°C, 800°C, 1000°C, 1100°C) during the heating process. Heating was performed in between holds at a rate of 1.1°C/s. The sample was cooled to ~200°C after the final hold segment at 1100°C, similarly to initial annealing studies. Sample curvature was tracked *in situ* throughout the process in order to observe changes in curvature during the heating and hold segments.
Curvature data for both implanted and unimplanted substrates was compiled into the plot given in Figure 5-2.

![Curvature vs. time comparison for unimplanted and implanted samples during annealing at multiple temperatures.](image)

Figure 5-2. Curvature vs. time comparison for unimplanted and implanted samples during annealing at multiple temperatures.

The initial curvature of the implanted sample was ≈-0.038 m⁻¹ while the unimplanted sample began with a curvature of ≈-0.042 m⁻¹. A greater overall increase in curvature from 0 to 1100°C was observed for the implanted sample than for the unimplanted sample, which was similar to the trend observed for samples studied in section 5.2. No change in curvature was observed during the temperature hold segments which indicated that recrystallization of the implantation induced amorphous region, if occurring at
temperatures below 1100°C, did not affect the substrate curvature. The curvature change for each heating segment is given in Table 5-1.

**Table 5-1. Curvature Values for Implanted and Unimplanted Samples During Heating**

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Unimplanted (m⁻¹)</th>
<th>Implanted (m⁻¹)</th>
<th>Implanted/Unimplanted</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-200</td>
<td>3.24E-04</td>
<td>4.34E-03</td>
<td>13.41</td>
</tr>
<tr>
<td>200-400</td>
<td>4.89E-04</td>
<td>4.18E-03</td>
<td>8.54</td>
</tr>
<tr>
<td>400-600</td>
<td>1.60E-03</td>
<td>2.30E-03</td>
<td>1.43</td>
</tr>
<tr>
<td>600-800</td>
<td>5.07E-03</td>
<td>7.78E-03</td>
<td>1.53</td>
</tr>
<tr>
<td>800-1000</td>
<td>9.72E-03</td>
<td>1.71E-02</td>
<td>1.76</td>
</tr>
<tr>
<td>1000-1100</td>
<td>5.57E-03</td>
<td>8.81E-03</td>
<td>1.58</td>
</tr>
</tbody>
</table>

The implanted sample curvature increased more than that of the unimplanted sample during each heating step. At temperatures below 400°C the implanted sample curvature increase was noticeably larger than the unimplanted sample. At temperatures above 400°C the magnitude of the curvature change for the implanted sample was roughly 1.5x that of the unimplanted sample. After cooling from the 1100°C hold, the unimplanted sample returned to a curvature value similar to its pre-anneal state with an overall curvature change of 0.005 m⁻¹, while the implanted sample had a noticeably larger overall curvature change of 0.023 m⁻¹. Based on these results, it was suggested that the greater increase in curvature during heating that was observed on implanted samples was unrelated to structural changes in the implanted layer due to annealing. Instead the greater change in curvature was likely due to the implanted layer affecting the thermal gradient across the substrate as well as decoupling the AlN buffer from the Si(111) substrate.
Atomic force microscopy (AFM) studies of the samples were also performed before and after the annealing process. This was done to determine if there was a variation in the AlN surface morphology or roughness after annealing. The resulting AFM images of each sample are shown in Figure 5-3.

![AFM images](image)

Figure 5-3. AFM images of AlN buffers on unimplanted (a and b) and implanted substrates (c and d). Scans were taken before (a and c) and after (b and d) annealing. All images are 2µm wide.

There was negligible change in the surface morphology or roughness with annealing for either unimplanted or implanted substrates. It was therefore concluded that implantation
and annealing had no observable effect on the surface morphology of the underlying AlN buffer layer.

5.4 Effect of Anneal Time on Substrate Curvature

The previous series of studies showed that an overall change in curvature was observed for implanted AlN/Si(111) samples after annealing. It was suggested that this difference in curvature may have been due to recrystallization of the implanted region of the Si(111) substrate resulting in stresses formed in the substrate during the cooling process. A series of studies was therefore performed to determine if the length of the N$_2$ anneal had an effect on the overall change in curvature of implanted substrates. Initial experiments of anneal length consisted of three implanted substrates from the same 2” wafer being submitted to N$_2$ anneals of varying lengths. The curvature change during the annealing process was observed to see if any difference arose due to anneal length. The samples used in this study had 35 nm AlN layers grown in a Veeco D180 reactor. Ion implantation was performed at an ion dose and range of $2 \times 10^{16}$ cm$^{-2}$ and 74 nm below the AlN/Si interface, respectively.

The anneal lengths used were 10, 30, and 60 minutes and the substrate curvature change for each sample is shown in Figure 5-4a.
Figure 5-4. (a) Curvature comparison of implanted AlN/Si(111) substrates during anneals of various lengths. (b) Curvature comparison of implanted substrates during GaN growth with varying pre-growth anneal lengths.

The starting curvature for each sample in this set of experiments was zeroed in order to more easily compare the change in curvature from the pre-anneal to post-anneal states. No difference in the curvature change during the high temperature hold was observed. The overall curvature change from pre-anneal to post-anneal states was the same regardless of anneal time. This suggested that anneal times as short at 10 minutes at 1100°C were sufficient to recrystallize the amorphous implanted region of the substrates.

In order to prove the theory that anneal times as short as 10 minutes were sufficient to remove ion channeling damage and recrystallize the implanted region of AlN/Si(111) substrates, a second set of experiments was performed. GaN films were grown on identical ion implanted substrates with varying pre-growth anneal lengths in order to determine if the anneal length affected the curvature change during GaN growth. This was important to ensure that the pre-growth anneal time did not affect the stress evolution during GaN growth for implanted samples, which was the main focus of study.
for the experiments presented in this work. The substrates used in this study were grown and implanted with the same conditions as those used in the previous study. Each sample was heated in a N\textsubscript{2} ambient up to a temperature of 1100°C and held for a set period of time prior to GaN growth. The carrier gas was switched to H\textsubscript{2} after the 1100°C hold and the flows were allowed to stabilize for 10 minutes prior to growth. Trimethylgallium and NH\textsubscript{3} were used as the Ga and N precursors for growth and were flowed through the reactor with a V/III of \textasciitilde 12000. The reactor was held at 50 Torr and growth was performed at 1100°C. The curvature, which was directly related to the stress-thickness product of the film, is given in Figure 5-4b for samples with a 10 min and 60 min pre-growth N\textsubscript{2} anneal time. The curvature evolution during GaN growth was nearly identical between the two samples which indicated that the length of the pre-growth anneal had a negligible effect on the stress in the subsequently grown GaN films. This further indicated that an anneal length of 10 minutes was sufficient to recrystallize the ion implanted region of the substrate.

It is worth noting, however, that the curvature evolution during GaN growth for these samples, which is directly linked to the film stress evolution, was different from the samples studied in chapter 4. Previous studies showed an initial compressive growth stress which relaxed over \textasciitilde 400 nm of growth. Little tensile stress was generated after the initial stress relaxation. The initially negative slope (compressive stress) observed in the samples in Figure 5-4b, however, transitioned to a positive slope (tensile stress) after only 300 s of growth (<200 nm). This indicated that the compressive stress relaxation and compressive stress generation in these samples occurred more quickly in these samples than in those studied in chapter 4. AFM studies of these samples showed a noticeably
smaller diameter of AlN islands (≈45 nm) than those observed in the substrates studied in chapter 4 (≈74 nm). The effect of island size on film stress evolution on ion implantation substrates will be discussed further in Chapter 6.

5.5 Effect of Ambient Anneal Gas

All prior annealing studies had been performed in a N₂ ambient while the standard GaN growth process in our reactor was performed entirely in a H₂ ambient. Previous studies of the effects of anneal length indicated that a 10 minute N₂ anneal at high temperature was sufficient to recrystallize the implanted region of the substrate. Our standard growth process included a 10min H₂ hold prior to growth and therefore it was desirable to determine if heating and annealing in a H₂ ambient using our standard growth process would be detrimental to the growth stress or morphology of the final GaN film.

To ensure that the heating in a H₂ ambient had no effect on the implanted samples stress evolution, we performed two growths on identical implanted substrates. One growth consisted of our standard H₂ heating segment to the growth temperature (1100°C) and a 10 minute hold in H₂ prior to growth to ensure annealing had completely occurred. The second growth mimicked the conditions performed at the University at Albany and consisted of heating the substrate to the growth temperature in N₂ and then performing a 30 minute N₂ anneal. The carrier gas was then switched to H₂ and growth was performed. MOSS was used to track the curvature change during growth to determine if any differences in stress evolution occurred due to the heating ambient. The substrates used in this study were identical to those used previously in chapter 5.3.
Figure 5-5 shows the *in situ* curvature change during the GaN growth segment for both samples (H\textsubscript{2} anneal and N\textsubscript{2} anneal).

![Curvature comparison during GaN growth on implanted AlN/Si(111) with pre-growth H\textsubscript{2} and N\textsubscript{2} anneals.](image)

There was no observable difference in the curvature evolution during GaN growth between the sample with the 30 minute N\textsubscript{2} anneal and the 10 minute H\textsubscript{2} anneal. Further AFM studies of the GaN surface, as shown in Figure 5-6, showed that there was also little difference in the morphology of the GaN films that were grown.
The sample with the 30 min $N_2$ anneal had a GaN RMS surface roughness of $0.639 \pm 0.16$ nm and the sample with the 10 min $H_2$ anneal showed a similar RMS roughness of $0.61 \pm 0.076$ nm. The use of a 10 min high-temperature hold in $H_2$ was therefore deemed sufficient for the pre-growth anneal of implanted substrates. Due to the similarities of this anneal with our standard growth process, these conditions were used for the continued studies of ion implanted substrates.

5.6 Conclusions

In conclusion, studies of the pre-growth anneal and its effect on the curvature of unimplanted and implanted AlN/Si(111) substrates was performed. Initial studies into the importance of the pre-growth anneal showed that implanted samples underwent a larger increase in curvature during heating than unimplanted samples. The overall
curvature change during heating for implanted substrates was similar to that of bare Si(111). This indicated that implantation may have been decoupling the AlN buffer from the silicon substrate, thus resulting in a greater increase in curvature due to the reduced stresses from CTE mismatch between the AlN and Si. It was also suggested, however, that the amorphous Si at the implantation depth may have been acting to increase the thermal gradient across the substrate thickness, which could have also played a role in the larger increase in curvature during heating. Low temperature anneals were performed in order to determine if structural changes due to annealing below 1100°C could be affecting the curvature of the substrate. No change in curvature was observed during any hold segment which indicated that the recrystallization of the implanted region did not affect the substrate curvature. Implanted samples were also observed to have a larger overall change in curvature between pre-anneal and post-anneal states. This may have been due to formation of the SPEG layer at the implantation depth, annealing of ion channeling damage from implantation, or reorientation of AlN islands.

A series of studies was also performed to determine the effect of anneal time and ambient on the substrate curvature. No difference in curvature was observed for anneals over 10 minutes. Furthermore, no difference in curvature evolution was observed during GaN growth for samples with anneals longer than 10 minutes. These results indicated that a 10 minute anneal was sufficient to recrystallize the implanted region of AlN/Si(111) substrates and remove any ion damage which may affect the subsequent GaN growth.
5.7 References:


Chapter 6

The Effect of AlN Buffer Conditions on Implantation Induced Stress Reduction

6.1 Introduction

The preliminary studies presented in chapter 4 showed evidence that ion implantation of an AlN/Si(111) substrate affected the growth stress, threading dislocation density and crack density in GaN films. It was suggested that the reduction of both the crack density and initial GaN growth stress observed on the implanted substrates was related to a decoupling of the film from the bulk Si through the formation of a polycrystalline/amorphous Si layer at the implantation depth. A reduction in edge TD density was also observed in GaN films with implantation, which was related to the stress gradient in the film during growth. This reduction in TD density was partially attributed to the reorientation of AlN islands in the buffer layer during the post-implantation annealing process. Later studies of GaN growth on ion implanted substrates presented in chapter 5.4 showed a noticeably quicker reduction in initial stress of the GaN film, within the first 200 nm of growth, as compared to the preliminary studies. The substrates used in preliminary studies had a noticeably larger AlN island diameter (74 nm) than those used in the later studies (45 nm). The smaller AlN island size may have led to more TDs formed at island coalescence points in the GaN film. Since compressive stress relaxation and tensile stress generation in GaN films has been linked to TD density and inclination,
it was hypothesized that the lateral size of AlN islands affected the growth stress evolution of implanted films by affecting the density of TDs formed.

In order to test this hypothesis, several studies were proposed. Initial studies involved growing a thin layer of additional AlN after the implantation and annealing processes in order to promote lateral growth of the reoriented AlN islands prior to GaN growth. Secondary studies focused instead on the use of a pulsed precursor flow method for initial AlN growth on Si(111) in order to promote larger island size prior to implantation.

A further understanding of the effect of certain ion implantation and AlN buffer variables on the implantation induced stress reduction of GaN films was also desired. Therefore, additional studies were performed in order to determine the effect of the peak implantation depth and the AlN buffer thickness on stress reduction in GaN films on ion implanted substrates.

6.2 Increased AlN Island Size Through Post-Implantation AlN Growth

Previous results showed distinctly different GaN growth stress evolution between substrate sets. It was observed that the substrates studied in chapter 5 had noticeably smaller AlN islands. It was therefore hypothesized that increasing the lateral AlN island size of implanted substrates could reduce the compressive stress relaxation and tensile stress generation in GaN films. Preliminary studies to test this theory consisted of growing an additional thin (~20 nm) AlN layer on the pre-grown AlN buffer prior to GaN growth. By varying the V/III of the pre-grown AlN it was expected that the lateral
growth of AlN islands could be promoted prior to GaN growth. The effect of the V/III of additionally grown AlN on the stress evolution of subsequently grown GaN films was studied.

6.2.1 Experimental Setup

The experiments herein described were conducted on implanted substrate pieces from 2” Si(111) rounds that underwent MOCVD growth of a ~40 nm AlN buffer prior to implantation. AlN buffer growth and ion implantation were performed using the conditions outlined in chapter 3.2.1. An implantation energy of 50 keV was used, resulting in a peak implantation depth of 74 nm below the AlN/Si(111) interface. AlN/Si(111) samples were diced into 10 x 10 mm wafers and submitted to an organics cleaning process, outlined in chapter 3, prior to growth. Substrates were heated in a hydrogen ambient and annealed for 10 minutes prior to growth. Three different growths were then performed different substrates. The baseline substrate was submitted to an identical growth process as was used in Chapter 4 for comparison. The second substrate was submitted to growth of a thin (~20 nm) AlN layer with a V/III of 8450 followed by 1µm of GaN growth. A third substrate was submitted to the growth of an additional ~20 nm AlN layer with a V/III of 4300 followed by a 1µm GaN layer. To achieve these V/IIIs the NH$_3$ flow was held constant at 89 mmol/min and the TMA flow was held at 2.01 mmol/min and 1.03 mmol/min for V/IIIs of 4300 and 8450, respectively. The additional AlN layers were grown after the H$_2$ anneal step in order to allow recrystallization of the amorphous implanted region and AlN island reorientation to
occur. The samples with additional AlN V/III’s of 4300 and 8450 will be respectively referred to as “low V/III” and “high V/III” samples from this point forward. The GaN growth conditions for all samples were identical to those used in Chapter 4. MOSS was used \textit{in situ} to track stress changes in the GaN film during the growth process.

\textbf{6.2.2 The Effect of Post-Annealing AlN Growth}

The surface morphology and roughness of the AlN/Si(111) substrates used in these studies were characterized prior to growth, as shown in Figure 6-1.

![AFM of implanted AlN/Si(111) surface morphology prior to annealing and growth.](image)

Figure 6-1. AFM of implanted AlN/Si(111) surface morphology prior to annealing and growth.
It is worth noting that the AlN island size observed on these substrates was noticeably smaller than was observed on previous substrates shown in Figure 4-1. This may have been due to the fact that the two sets of AlN/Si(111) substrates had AlN growth performed in two different reactors at the University at Albany. This may have resulted in the variation in AlN island size observed here. The curvature change observed during GaN growth was translated into stress-thickness data via Stoney’s equation and plotted as a function of thickness for each sample as shown in Figure 6-2.

Figure 6-2. Stress-thickness vs. thickness plot for samples with varying additional AlN growth conditions.
All three samples initiated growth under a similar initial compressive stress as indicated by the negative slope of the stress-thickness vs. thickness plot. The standard and high V/III samples relaxed the initial compressive stress after approximately 100 nm of growth, while the low V/III sample relaxed the initial compressive stress after approximately 200 nm of growth. All three samples then transitioned to a constant incremental tensile stress for the remainder of growth. The final tensile stresses for each sample are given in Table 6-1. The stress evolution of the samples presented in Figure 6-2 was similar to the commonly observed stress evolution for GaN on Si(111) reported in literature [1]. The relaxation of compressive stress and generation of tensile stress occurred much earlier during growth than was observed for the samples shown in Figure 4-2b. As discussed in Chapter 4.3.2 the compressive stress relaxation and tensile stress generation in GaN films is affected by the inclination and density of TDs in the film. Furthermore TDs can form due to lattice mismatch between the film and substrate, or at the coalescence point of 3-dimensional nuclei early in growth. It was therefore hypothesized that the larger stress gradient (i.e. faster compressive stress relaxation and greater tensile stress generation) observed in these films as compared to those studied in chapter 4 was due to a higher density of TDs in the GaN film. It was further suggested that a higher density of TDs in the films in this study may have arisen from the smaller AlN island size leading to a higher density of coalescence points in the GaN film. The sample with an additional low V/III AlN layer was observed to have the lowest final tensile growth stress of all three samples. The V/III ratio of precursor gases can distinctly affect the growth mode of the AlN film in MOCVD. It is well understood that lowering
the V/III ratio during AlN growth results in increased Al atomic diffusion, and therefore more 2-dimensional growth of the film [2]. This occurs because as the V/III ratio is decreased, there are fewer reactions between Al and N at the substrate surface. Therefore Al atoms have a longer time on the surface before NH₃ dissociates at the surface and reacts to form AlN. This results in longer diffusion lengths of group-III metal atoms on the substrate surface before reacting with N atoms. Longer diffusion lengths increase the probability that a group-III atom will diffuse to an existing AlN nuclei sidewall as opposed to forming a new nuclei. Therefore greater lateral growth of AlN islands is observed at lower V/IIIs. Therefore by growing an additional AlN layer with low V/III the lateral growth of the pre-existing AlN islands was expected to increase, resulting in increased coalescence and larger lateral size of AlN islands. Furthermore, the implantation induced reorientation of AlN islands would have resulted in lower misorientation between AlN islands and therefore reduced TD formation at island boundaries during coalescence. Therefore it was expected that the reduction in final tensile stress observed with the growth of additional low V/III AlN was due to reduced TD density in the GaN films.

In order to determine if the expected TD reduction on low V/III samples was observed, we performed X-ray rocking curve measurements of the off-axis (1011) peak. The FWHM of off-axis GaN peaks is related to the degree of misorientation of GaN grains. By comparing the FWHM of off-axis peaks with high inclination angles such as the (1011) peak (inclination angle = 62°), we can qualitatively compare the twist misorientation, and therefore the edge-type TD density of GaN films on the different substrates. Increased misorientation (edge TD density) should be observed as a widening
of the FWHM of the (10\overline{1}1) peak in GaN films. The FWHM’s of the (10\overline{1}1) peak for each sample are included in Table 6-1.

Table 6-1. Comparison of Final Growth Stress and Off-Axis Rocking Curve FWHM for GaN Films on Ion Implanted AlN/Si(111) with Additionally Growth AlN

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final Incremental Stress (GPa)</th>
<th>(10-11) FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>0.6707</td>
<td>0.7063°</td>
</tr>
<tr>
<td>Low V/III AlN</td>
<td>0.4921</td>
<td>0.6744°</td>
</tr>
<tr>
<td>High V/III AlN</td>
<td>0.7141</td>
<td>0.7729°</td>
</tr>
</tbody>
</table>

A decrease in FWHM of the GaN(10\overline{1}1) peak was observed to follow the decrease in final tensile stress for GaN films. This supported the hypothesis of reduced TD density due to the growth of additional AlN with low V/III. It is also worth noting that the sample with high V/III AlN showed a larger FWHM and final tensile stress than the standard sample. This was possibly due to the high V/III of the additionally grown AlN resulting in more 3D growth. If the degree of 3D growth in the additionally grown AlN was large enough, the buffer may have had smaller exposed AlN islands than the standard buffer. This would have led to more island coalescence points and therefore a higher TD density in the GaN film. Unfortunately the AlN island size of the low V/III and high V/III buffers could not be compared since the GaN film was grown directly after the growth of additional AlN. Therefore no AFM studies of the AlN surface were obtained. Due to lack of further substrates, additional studies to observe the effect of additional AlN growth on AlN island size could not be performed.
AFM studies of the morphology of GaN grown on each substrate were performed in order to determine how the post-anneal AlN growth affected the GaN surface morphology. The results are presented in Figure 6-3.

The sample with no additional AlN growth shows clear step edges, which is indicative of a step-flow growth mode and has a similar morphology to previous studies of GaN on implanted AlN/Si(111). The samples with additional AlN growth, however, had a noticeably rougher surface with a high number of pits present and no distinct step-edges.
This may have been due to a lack of optimization of the additionally grown AlN film. It is also possible that the growth of additional AlN is more sensitive to implantation damage present in the AlN after annealing than GaN growth. This could have led to a rougher surface of the additionally grown AlN as compared to the standard buffer which could have then resulted in a rougher surface morphology in the subsequent GaN film.

It was shown that the growth of additional AlN with a low precursor V/III resulted in a decrease of the final tensile stress generated during GaN growth. The high V/III additional AlN showed a slightly increased final tensile stresses in the GaN films, however, indicating that the conditions of the additional AlN growth were important to the stress evolution observed during GaN growth. It was proposed that the reduction in tensile growth stress for the low V/III sample was caused by increased lateral growth of post-annealed AlN islands resulting in fewer dislocations from the coalescence of misoriented islands. X-ray rocking curves of off-axis peaks showed a decrease in FWHM as the final tensile GaN growth stress was decreased, which indicated decreased edge TD density. A distinctly rougher surface was observed in the GaN grown on samples with post-anneal AlN growth. This could have been due to the additional AlN layer being more sensitive to implantation damage in the AlN/Si(111) substrate than the GaN or to the unoptimized growth of additional AlN. It may be possible to optimize the post-implantation AlN layer to reduce or prevent the roughening of the GaN surface on implanted samples with additionally grown AlN. Previous studies of GaN on implanted AlN/Si(111) substrates without additional AlN growth, however, have shown no change in the GaN morphology with implantation. Another possible solution would therefore be to increase the lateral size of AlN islands prior to implantation of AlN/Si(111) substrates.
6.3 The Effect of AlN Island Size/Coalescence on Implantation Induced Stress Reduction

It was observed in the previous study that additional growth of AlN with low V/III ratios resulted in a lower final tensile growth stress in GaN on implanted substrates. This was hypothesized to be due to the increased lateral diffusion of AlN at low V/III’s which could have resulted in larger AlN island sizes. The actual AlN island size in the previous studies was not, however, observed. Furthermore, the growth of additional AlN on implanted samples resulted in poor GaN surface morphology. Therefore, the following studies were performed on AlN buffers grown with varying island sizes prior to substrate implantation in order to more closely study the effects of increased AlN island size on implantation induced stress reduction in GaN films. It was hypothesized that by increasing the lateral island size in AlN prior to implantation, a greater reduction in TD density and tensile growth stress in GaN films on implanted substrates would be observed without roughening the GaN surface morphology.

6.3.1 Experimental Set-Up

The substrates used in this study consisted of 55 nm thick AlN buffers grown using a Veeco D180 reactor. Two types of AlN buffer layer growth processes were used in this study. The first, designated as the “standard” buffer layer, was performed following the process outlined in chapter 3.2.1. with both TMA and NH$_3$ source precursors flowing into the reactor simultaneously. The second growth process, hereby designated as the “pulsed” buffer layer, utilized TMA and NH$_3$ pulses which were
alternately introduced into the reactor with each pulse lasting 6 s. This alternating precursor process was repeated 100 times in order to achieve a 55 nm thick AlN buffer. The AlN buffer layer grown with the pulsed technique exhibited increased film coalescence and grain size compared to the standard AlN buffer layer as shown in Figure 6-4.

![AFM of standard and pulsed AlN buffer layers on Si(111)](image)

Figure 6-4. AFM of standard and pulsed AlN buffer layers on Si(111).

The AlN growth temperature was 1040°C for the pulsed buffer and approximately 1000°C for the standard buffer. Implantation of N⁺ ions into the AlN/Si(111) substrates was performed with an energy of 60 keV/atom which resulting in a peak ion depth of 73 nm below the AlN/Si(111) depth. Additional AlN/Si(111) samples with each buffer type were left unimplanted for comparison. The implanted and unimplanted AlN/Si(111) samples were then used as substrates for the growth of ~1µm thick GaN layers using the growth conditions outlined in Chapter 4.
6.3.2 Results and Discussion

The MOSS system was used to monitor the change in the sample curvature during the entire GaN growth process for films grown on Si substrates prepared with the standard (Figure 6-5(a)) and the pulsed (Figure 6-5(b)) AlN buffer layers.

Figure 6-5. Sample curvature during entire GaN growth process on unimplanted and implanted samples prepared with (a) standard and (b) pulsed AlN buffers.

In the curvature data shown in Figure 6-5, a positive value indicated a concave curvature and a negative value indicated a convex curvature. The samples started off at an initial curvature value based on the residual stress in the AlN/Si substrate. The unimplanted samples exhibited concave curvatures of 0.022 m⁻¹ and 0.032 m⁻¹ for the standard and pulsed buffer layers, respectively, which is consistent with the presence of tensile biaxial stress in the AlN layers as commonly observed for AlN films grown on Si(111) [1]. After implantation, the curvature of the standard buffer layer sample increased to 0.032 m⁻¹ while the pulsed buffer layer sample became convex (-0.015 m⁻¹).
The substrates were then heated under H\textsubscript{2} to the GaN growth temperature of 1100\textdegree C and held at this temperature for 10 minutes. As shown in Figure 6-5, the curvature of each sample became more positive during this heating step. The origin of this increase in curvature during heating was discussed in detail in Chapter 5.2. The change in curvature during heating for the standard and pulsed samples without implantation was 0.014 m\textsuperscript{-1} and 0.021 m\textsuperscript{-1}, respectively. This was noticeably less than what was observed for the implanted samples which had a curvature change of 0.042 m\textsuperscript{-1} for the standard buffer and 0.044 m\textsuperscript{-1} for the pulsed buffer. The larger change in curvature during heating of implanted samples followed the trend observed in previous studies discussed in chapters 4 and 5.

Prior studies have reported an observed swelling in the lattices of thin films that had been implanted with ions due to the presence of residual ions in the lattice [3-5]. The initial compressive stress in GaN films on AlN is induced by the lattice mismatch between AlN and GaN. It is therefore possible that the swelling of the AlN lattice due to implantation may have affected the initial strains in the subsequently grown GaN films. Therefore, to determine if there was a correlation between AlN lattice strain and initial GaN growth stress, X-ray diffraction studies were performed on the AlN buffer layer for all samples. The reflected intensity of the AlN(002) peak is shown in Figure 6-6 for samples before and after annealing.
Figure 6-6. X-ray of AlN(0002) peaks of standard and pulsed buffers with and without implantation before (left) and after (right) annealing.

The AlN(002) peak position was used to calculate the c-axis lattice parameters which are included in Table 6-2. The intensities of the asymmetric reflections of AlN were not sufficiently strong in this measurement configuration to enable accurate determination of the a-axis lattice parameters. The unimplanted samples exhibited a positive shift in XRD peak position as compared to that of relaxed AlN was observed in Figure 6-6 which indicated a contraction of the c-lattice [6]. Due to the epitaxial nature of AlN growth, this c-lattice contraction would be expected to correlate to a biaxial tensile strain in the buffer. The c-lattice parameters for the standard and pulsed AlN buffer layers are 4.973 Å and 4.974 Å, respectively, compared to 4.981Å for relaxed AlN. The XRD peaks shift to the left of that expected for a relaxed layer after implantation indicating an expansion of the AlN c-lattice. The corresponding c-lattice parameters for the implanted standard and pulsed AlN buffer layers are 5.002 Å and 5.004 Å, respectively. Since the expansion of the c-lattice with implantation was related to the presence of residual N+ ions in the
buffer, it is expected that the a-lattice would also undergo a similar tensile strain due to implantation. Similar levels of tensile strain were observed in the AlN buffers grown with the standard and pulsed conditions indicating that the degree of AlN coalescence does not greatly impact the effects of ion implantation on the AlN lattice.

After annealing at 1100°C and cooling to room temperature, significant relaxation of the tensile stress in the AlN films on implanted substrates was observed as evidenced by the shift in the AlN(002) peak position (Figure 6-6) and the change in the c-lattice constants to 4.979Å (standard) and 4.987Å (pulsed) which are close to that of relaxed AlN. The slight difference in the post-annealing lattice constants indicate that the tensile strain in the pulsed buffer was not relaxed to the same extent as that of the standard buffer. In contrast, there was only a small change in the c-lattice parameter of the unimplanted samples post-annealing (Table 6-2). Since the a-lattice constant of GaN (0.319 nm) is larger than that of AlN(0.311 nm), the residual tensile strain in the pulsed AlN lattice due to residual ions in the lattice would have led to a lower mismatch between the AlN and GaN lattices on the implanted pulsed sample than on the standard sample. This reduced lattice mismatch would have resulted in a lower initial compressive stress during GaN growth on the implanted, pulsed buffer which was observed in Table 6-2.
Table 6-2. $c$-Axis Lattice Parameters of AlN Buffer Layer and Film Stress and TD Density of GaN Films Prepared With Standard and Pulsed Buffer Layer With and Without Implantation

<table>
<thead>
<tr>
<th></th>
<th>AlN</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c-lattice Parameter (Å)</td>
<td>Film Stress (GPa)</td>
</tr>
<tr>
<td></td>
<td>Pre-anneal</td>
<td>Post anneal</td>
</tr>
<tr>
<td>Standard, unimplanted</td>
<td>4.973</td>
<td>4.971</td>
</tr>
<tr>
<td>Standard, implanted</td>
<td>5.002</td>
<td>4.979</td>
</tr>
<tr>
<td>Pulsed, unimplanted</td>
<td>4.974</td>
<td>4.977</td>
</tr>
<tr>
<td>Pulsed, implanted</td>
<td>5.004</td>
<td>4.987</td>
</tr>
</tbody>
</table>
In-situ wafer curvature measurements provided a means to measure stress in the GaN film at the initial stages of growth on the AlN buffer layers and monitor how it evolved with increasing layer thickness. The curvature data obtained during GaN growth (Figure 6-5) was used to calculate the incremental stress in the GaN layers as a function of layer thickness (Figure 6-7) using the procedure outlined in chapter 3.4.1.2. Values for the initial and final incremental stress during GaN growth are included in Table 6-2.

Figure 6-7. Incremental stress in GaN films as a function of film thickness for layers grown on standard and pulsed AlN buffer layer samples with and without implantation.
In all cases, the GaN initiated growth on the AlN buffer layer under a compressive stress which arose due to the heteroepitaxial mismatch. The compressive stress relaxed with increasing layer thickness and evolved to a constant tensile stress as was commonly observed in GaN on Si epitaxy as discussed in chapter 4. In the case of the standard buffer layer samples and the unimplanted pulsed buffer layer, the initial compressive stress was fully relaxed within the first 150 nm of growth and reached a steady-state tensile stress on the order of 0.2-0.3 GPa after ~200 nm. In contrast, the GaN grown on the implanted pulsed buffer layer initiated growth under a small compressive stress (-0.088 GPa) which slowly evolved to a small, constant tensile stress (0.045 GPa) after several hundred nanometers of growth. The results demonstrated a significant overall reduction in growth stress for GaN films grown on the implanted pulsed buffer layer compared to the other samples. It is interesting to note that for both the standard and pulsed buffer layer samples, implantation resulted in a reduction in the initial compressive stress in the GaN epilayers. The initial compressive stress on the pulsed buffered sample, however, was lower than that of the standard sample after implantation. It was proposed that this reduced initial compressive stress was due to ion implantation induced swelling of the AlN lattice that remained after annealing in the pulsed buffer.

High resolution X-ray diffraction was used to analyze the TD density of the GaN layers post-growth. The TD densities can be estimated from the full-width at half maximum (FWHM) of the GaN (0002) and (1010) XRD peaks using the method discussed in chapter 4.3.2. The FWHMs of x-ray rocking curves of GaN planes with
Increasing inclination angle were used to estimate the FWHM at an inclination angle of 90°, the angle of the (10\bar{1}0) plane. The results are shown in Figure 6-8.

![Figure 6-8. FWHM vs. inclination angle for x-ray rocking curves of GaN grown on AlN/Si(111) grown with pulsed and standard growth methods with and without ion implantation.](image)

The density of screw, edge and total TDs for each of the samples estimated from the XRD analysis are included in Table 6-2. There was an observed reduction in TD density with implantation for both buffer layer types. The amount of TD reduction was, however, greater for the pulsed buffer (63%) than for the standard buffer (16%). The reduction in TD’s arose primarily from a reduction in edge-type threading dislocations in
both cases. Threading dislocations in GaN arise from misorientation of the islands at the beginning of growth. It has been previously suggested that the reduction in TD density with implantation results from reorientation of the AlN islands during the annealing process. The larger AlN islands formed during the pulsed growth process resulted in a reduced density of coalescence points between AlN islands, and therefore a greater reduction in TD density after AlN island reorientation. Furthermore, the larger AlN islands with less misorientation after implantation may have also resulted in decreased misorientation between the GaN nuclei, resulting in fewer TDs generated due to the coalescence of misoriented GaN.

The lower TD density and the low initial compressive stress in the GaN film grown on the pulsed implanted AlN/Si(111) substrate are likely responsible for the overall low growth stress observed in this sample compared to the others (Figure 6-7). As discussed in chapter 4 the strain gradient in GaN films is related to the inclination of edge-type threading dislocations [7]. The magnitude of the strain gradient is proportional to the density of edge-type TDs as well as the inclination angle of the dislocations. The GaN epilayers grown on the standard buffer layer and the unimplanted pulsed buffer layer exhibited a higher initial compressive stress and higher TD density. The higher initial compressive stress would serve to promote the bending of TDs and the higher TD density would give rise to an increased strain gradient. These effects are responsible for the rapid change in incremental stress in the first ~150 nm of GaN growth as shown in Figure 6-7. In contrast, the low initial compressive stress in the GaN film on the pulsed implanted buffer layer would lead to reduced TD inclination which, when combined with
the lower TD density, would lead to the significantly reduced strain gradient shown in Figure 6-7.

Channeling cracks in GaN films grown on Si form due to tensile stress in the film that arises due to CTE mismatch as well as growth-related stress. Consequently, the low overall growth stress measured in the GaN epilayer grown on the pulsed, implanted AlN/Si(111) substrate would be expected to yield reduced film cracking as compared to the standard buffer layer and unimplanted samples which exhibited a higher tensile growth stress. The density of channeling cracks on the implanted pulsed buffer, however, was larger than that observed on the unimplanted substrate as shown in Figure 6-9.

Figure 6-9. Dark-field optical microscopy images of GaN on AlN/Si(111) with pulsed and standard buffer with and without implantation.
The GaN films grown on the implanted pulsed buffer also exhibited large surface pits which may have acted as nucleation sites for crack formation. Aside from the presence of large surface pits, the small-scale surface morphology of the GaN films showed little difference based on the buffer type used as shown in Figure 6-10. Further studies are required to investigate the origin of surface pits and channeling cracks in these samples.

Figure 6-10. AFM of GaN grown on standard (a and c) and pulsed (b and d) buffer layers without (a and b) and with (c and d) implantation.
6.4 The Effect of Buffer Layer Thickness and Implantation Depth

It has been shown that the substrate ion implantation and annealing process affected the growth and cooling stresses of the GaN film in two main ways. One way is the reorientation of AlN islands with respect to one another which reduces the twist misorientation between neighboring grains. The AlN island reorientation resulted in lower edge TD density in the GaN film, which reduces the tensile growth stress generated due to dislocation bending. Substrate ion implantation also resulted in the formation of an amorphous/polycrystalline layer which decouples the GaN film from the bulk Si substrate and acts as a compliant layer to accommodate some of the stresses formed during growth and cooling. Therefore it was important to understand how variables related to the buffer layer and the implantation layer affected the GaN film stress. The following series of studies give a preliminary look at how the AlN buffer thickness and implantation energy, which relates to the depth of implanted ions, affected the GaN growth stresses on implanted samples.

6.4.1 Experimental Set-Up

Four substrates were fabricated for these studies with varying AlN buffer thickness and implantation depth. The AlN buffers for each substrate were grown via MOCVD in a VEECO D180 reactor at the University at Albany using the standard growth procedure outlined in chapter 3. The AlN growth time was varied in order to obtain two sets of substrates with 40 nm and 61 nm thick AlN buffers. Two different implantation depths were studied with each buffer thickness. The 40nm AlN buffer
substrates were submitted to implantation energies of 50 keV and 62 keV in order to achieve peak implantation depths of \( \approx 75 \) nm and \( \approx 100 \) nm below the AlN/Si(111) interface, respectively. The substrates with 61 nm thick AlN layers were submitted to implantation energies of 63 keV and 75 keV, to achieve similar peak implantation depths of \( \approx 75 \) nm and \( \approx 100 \) nm below the AlN/Si(111) interface, respectively. TRIM calculations of the four samples are given in Figure 6-11 showing the estimated peak implantation depth of ions below the AlN/Si(111).

Figure 6-11. TRIM calculations of substrates with varying buffer thicknesses and implantation energies showing estimated peak implantation depth.
The ion implantation energies were chosen such that the effect of implantation depth (75 nm vs. 100 nm) on GaN stress evolution could be studied simultaneously with the effect of AlN buffer thickness (40nm vs. 61nm).

Implanted AlN/Si(111) substrates were annealed in a H$_2$ ambient at 1100°C directly prior to MOCVD growth of GaN films. Annealing and GaN growth were performed using identical conditions to the previous studies outlined in chapter 4. Curvature changes were tracked in situ during growth to determine the effect of buffer thickness and implantation depth on GaN growth stresses. These results were coupled with ex situ AFM and optical microscopy to study changes in GaN surface morphology and crack density.

**6.4.2 Results and Discussion**

Curvature data collected during GaN growth for the four samples studied was converted to stress-thickness data as shown in Figure 6-12. It was observed that all four samples, regardless of buffer thickness or implantation depth, started at similar initial compressive stresses of roughly -0.40 GPa·µm which relaxed within the first ~200 nm of growth.
The films then transitioned to a constant tensile incremental stress, the value of which varied depending on buffer thickness and implantation depth. The final tensile stresses for each film are compiled in Table 6-3.
Table 6-3. Tensile Stress and Pit Density of Films with Varying Buffer Thickness and Implantation Depth

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final Stress</th>
<th>Estimated Pit Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>40nm AlN; 75nm implantation depth</td>
<td>0.8142</td>
<td>89.5</td>
</tr>
<tr>
<td>40nm AlN; 100nm implantation depth</td>
<td>0.4433</td>
<td>49.5</td>
</tr>
<tr>
<td>61nm AlN; 75nm implantation depth</td>
<td>1.1057</td>
<td>138.5</td>
</tr>
<tr>
<td>61nm AlN; 100nm implantation depth</td>
<td>0.7044</td>
<td>109</td>
</tr>
</tbody>
</table>

It was observed that AlN/Si(111) substrates with a 40 nm buffer layer showed noticeably lower final tensile stresses than those with a 70 nm buffer layer, regardless of implantation depth. It was also observed that the substrates with an implantation depth of ≈100 nm below the AlN/Si interface resulted in lower final tensile stress than those with an implantation depth of ≈75 nm. This was true for both buffer thicknesses. These results indicated that a thinner buffer layer and a larger implantation depth resulted in reduced tensile stress generation during film growth. There was no clear trend in crack density with buffer thickness or implantation depth. This may indicate that buffer thickness and implantation depth have minimal effects on the reduction of thermal mismatch stresses due to decoupling of the film from the substrate.

Since the compressive stress relaxation and tensile stress generation of GaN films is related to the TD density, as discussed previously in chapter 4 it is possible that decreasing the buffer thickness and increasing the implantation depth may act to reduce the TD density in overgrown GaN films. In previous studies, implantation reduced the TD’s formed at coalescence boundaries by inducing reorientation of AlN islands during the annealing process. It has been previously suggested that thinner buffer layers allow for a greater reorientation of AlN islands due to the smaller vertical island size required.
to reorient during annealing [8]. Furthermore, greater implantation depth was shown to reduce the stress gradients of GaN films even further. It is possible that the reorientation of AlN islands is related to the implanted region decoupling the AlN film from the Si substrate, thus making it more thermodynamically favorable to reorient AlN islands. The substrates implanted at 100 nm would have had a thicker implanted region below the AlN/Si(111) interface which may have led to greater decoupling of the film from the substrate thus resulting in greater AlN island reorientation during annealing.

AFM studies were performed on GaN films grown on the above substrates in order to estimate TD densities in the GaN films. Pits can be seen in small-scale AFM scans which relate to the presence of TDs which propagated to the GaN surface [9]. Commonly the pits observed in AFM are found at step-edge terminations and are associated with screw or mixed-type dislocations. Small pits that are not associated with step-edge terminations can sometimes also be observed which relate to the presence of edge-type dislocations. Therefore an estimation of relative densities of screw and mixed-type dislocations can be made based on these pit densities. The pit densities and final stresses of GaN films are compared in Table 6-3. Here it can be seen that the reduction of GaN final stress follows the reduction of pits in GaN films as was expected based on previous studies. Additional studies are, however, required to estimate the edge-type TD density in GaN films specifically.

While these preliminary studies show the importance of AlN buffer thickness and implantation energy/depth to the optimization of substrate implantation as a film stress reduction method, there is still a need for further studies to completely understand the mechanisms at play. It was proposed that the thinner AlN buffer layer and greater
implantation depth allowed for greater reorientation of AlN islands after annealing. Further studies should be performed to specifically study the edge-type TD density of the grown films as well as to study the effect of buffer thickness and implantation depth on the twist misorientation of AlN islands.

6.5 Conclusions

Prior studies have suggested that ion implantation induces a reorientation of AlN islands and a reduction of atomic disorder at the AlN/Si(111) interface. These two effects have been proposed to result in the lower TD densities observed in GaN films grown on implanted AlN/Si substrates. Studies provided here have shown that by increasing the AlN island size, the threading dislocation density can be reduced in GaN films grown on ion implanted substrates. Initial studies involved growing additional AlN after annealing of implanted substrates in order to promote lateral growth of AlN islands before GaN film growth. These studies showed a reduced stress gradient during GaN film growth, but the growth of additional AlN led to high pit density and surface roughness poor in GaN films.

Subsequent studies utilized a pulsed precursor growth method for pre-implantation AlN buffers which resulted in a noticeably larger AlN size. In situ curvature measurements and ex situ XRD showed that the larger island size induced by the pulsed buffer growth scheme resulted in significant reduction in tensile growth stress and threading dislocation densities in GaN films with implantation. The pulsed buffer scheme did not affect the small-scale GaN surface morphology, but large pits were
present across the surface of the implanted sample. Furthermore there was an increase in channeling crack density with implantation on pulsed buffers which was opposite the trend observed on standard buffer samples. The origin of these effects is still unclear, but it is possible that the large pits observed in GaN on the implanted pulsed buffer acted as crack nucleation sites. Further studies must be performed in order to elucidate the origin of the large pits and increased crack density in GaN films on implanted pulsed buffer substrates. It was shown, however, that increasing AlN island size resulted in lower tensile growth stress on implanted substrates. This was suggested to be due to fewer island coalescence points and lower misorientation between AlN islands after implantation and annealing. Furthermore the reduced initial compressive stress on the pulsed implanted buffer was proposed to have led to reduced TD bending in the film which would have further lowered the generation of tensile stress during GaN growth.

Preliminary studies were also put forth which showed that the generation of tensile growth stress could be reduced by utilizing thinner AlN buffer layers and increased peak ion implantation depths. It was suggested that thinner buffers allowed for greater AlN reorientation and therefore lower TD density in the final GaN films. Increasing the ion implantation depth was proposed to induce greater decoupling of the buffer from the Si substrate, which was hypothesized to result in greater AlN island reorientation. Although further studies must be performed to better understand these issues, it has been shown in this work that substrate ion implantation is a viable method for GaN stress reduction with promise of further benefit with optimization of the implantation and growth processes.
6.6 References:

Chapter 7

Preferential Growth of Non-Polar GaN on Si\{110\} Sidewalls of Trenches Etched in Si(100) Substrates

7.1 Introduction:

The growth of non-polar GaN is an area of interest in the III-nitride semiconductor community as discussed previously in Chapter 1. Furthermore, Si is a well-researched and inexpensive substrate material. Due to this, there is a desire to incorporate GaN devices on Si substrates. Previous studies presented by Won et al. showed that GaN preferentially grows on the sidewalls of pillars etched into a Si(001) substrate such that GaN(0002)//Si\{110\}[1]. It is therefore possible, that a similar structure may be used for the growth of GaN which consists of parallel trenches etched in Si(001) substrates such that the trench sidewalls were Si\{110\} oriented as shown in Figure 7-1a. It was hypothesized based on previous results on Si pillars that GaN would preferentially nucleate with the GaN(0002) plane parallel to the Si\{110\} sidewalls of Si(001) trenches as shown in Figure 7-1c. Figure 7-1d shows the proposed continuation of the growth process in which the GaN growth conditions may be controlled to vertically and laterally overgrow the Si(001) trenches and the tops of Si(001) ridges in order to achieve a fully coalesced non-polar GaN film with respect to the Si(001) substrate surface.
Figure 7-1. Schematic showing Si trench structure and proposed growth process. Si trench sidewalls are of the Si\{110\} family of planes and the top trench surface is Si(001).

7.2 Preliminary growths of GaN on Si(001) trenches

The following studies show the results of preliminary growths of GaN on etched Si(001) trenches. The objective of this preliminary work was to experimentally show that GaN would grow preferentially on Si\{110\} sidewalls of etched Si trenches such that GaN(0002)//Si\{110\}. 
7.2.1 Initial growth of GaN on Si<110> trench sidewalls

The trench structures were formed in Si(001) substrates using the DRIE etching process outlined in Chapter 2. A SEM image is given in Figure 7-2 which shows a cross-section of a bare Si(001) trench after the hydrofluoric acid oxide removal step.

Figure 7-2. Cross-sectional SEM image of an etched Si ridge.

Scalloping of the Si{110} sidewalls was caused by the anisotropic etch steps of the DRIE process and had to be removed prior to growth through the use of a high-temperature H₂ annealing step. Initial studies were performed in order to prove the
viability of the Si(001) trench structure as a method to obtain preferential growth of GaN from Si{110} sidewalls.

A 10x10mm Si(001) wafer piece with etched trenches was submitted to a short GaN growth process. The substrate was cleaned prior to growth using the cleaning process outlined in Chapter 2. After oxide removal in hydrofluoric acid, the substrate was loaded into the MOCVD reactor and heated to the growth temperature (1100°C) in a H₂ ambient. A 10min H₂ hold was performed at 1100°C prior to growth in order to reduce the roughness of the Si{110} sidewalls caused by DRIE as well as to remove any residual oxide left on the Si trench surfaces after the HF cleaning. A thin AlN layer (~90nm) was then grown on the substrate before GaN growth. TMA and NH₃ were used as Al and N source precursors with flow rates of 15 sccm and 1.41 slm, respectively. GaN was grown after the AlN buffer with TMG and NH₃ flow rates of 9.4 sccm and 1.41 slm. A reactor pressure of 50 Torr was used throughout the entire growth process. These growth conditions were chosen based on the conditions used in the previous study of GaN growth on Si(001) pillars[1]. Normally the in situ MOSS system was used on planar samples in order to determine the thickness of the GaN film during growth, but such a measurement was unusable on the trench substrates. The trench structures scattered the reflected laser light, resulting in weak intensity for tracking of the reflected laser spots. The trench structures, however, did not span the entire surface area of the wafer piece and therefore the MOSS laser was aligned on a planar region of the wafer away from the etched trenches initially in an attempt to get analogous growth rates of GaN and AlN on the planar Si. The reflected laser intensity was tracked by the MOSS computer during AlN growth in order to get the AlN thickness, but the intensity dropped
early on during the GaN growth due to the rough surface of polycrystalline GaN in the planar region scattering the reflected laser light. Therefore GaN growth was stopped after the reflected laser intensity reached zero. The overall growth time was ~17 min.

The sample was cooled to room temperature after growth and cleaved perpendicular to the trench direction in order to observe the cross-section of GaN growth on Si trenches in the scanning electron microscope (SEM).

A cross-sectional SEM image showing initial GaN growth on Si(001) trenches is shown in Figure 7-3a. GaN was observed to grow preferentially on the Si{110} sidewalls of the trench, while no growth was observed on the Si(001) surface of the ridge. A top down image of the trenches, given in Figure 7-3b, however showed the presence of GaN islands that appeared to be forming at the interface between the Si trench and the GaN sidewall growth.

![Figure 7-3. (a) Cross-sectional and (b) Top-down SEM images of short (~17 min) GaN growth on Si(001) trench structures.](image)

The origin of these islands was unknown. Aside from the GaN islands of unknown origin, there was little GaN growth observed on the Si(001) face of the ridges which supported
the hypothesis that GaN would preferentially grow on Si\{110\} trench sidewalls as opposed to the top surface of the Si(001) ridge. The GaN grown on Si\{110\} sidewalls showed no vertical overgrowth of the Si(001) ridge, which may have been linked to the presence of the GaN islands at the trench corners or due to the short growth time. Therefore, a longer growth (90 minutes) was performed with the same growth conditions in an attempt to grow GaN vertically over the Si(001) ridge surface as well as to study the evolution of the GaN islands observed in top-down SEM images.

### 7.2.2 Extended GaN growth times for the overgrowth of Si(001) ridges

Cross-sectional SEM of the 90 min GaN growth is shown in Figure 7-4a. GaN was observed to have grown vertically above the Si(001) ridge as well as laterally over the Si(001) ridge surface forming a “fin” structure.

![Cross-sectional and Top-down SEM images](image)

Figure 7-4. (a) Cross-sectional and (b) Top-down SEM images of long (~90 min) GaN growth on Si(001) trench structures.
While the region of the GaN fin near the Si\{110\} sidewall had similar faceting and shape as that observed in Figure 7-3a, the GaN region that overgrew the Si(001) surface did not appear to follow the shape of the sidewall GaN growth. Top-down SEM of the overgrown GaN fins is given in Figure 7-4b. The shape of the overgrown GaN fin is similar to the shape of the GaN islands observed in Figure 7-3b. It was therefore possible that the majority of the overgrown GaN did not originate from the sidewall nucleation, but instead originated from the GaN islands observed in Figure 7-3b. This would have resulted in a different orientation of GaN overgrowing the Si(001) ridge than that which nucleated on the Si\{110\} sidewall. In order to prove of this hypothesis, however, the crystallographic orientation of the GaN fin structure must be measured.

Previous work by Won et al. showed the relationship GaN(0002)//Si\{110\} on etched Si pillars. It was assumed that this relationship held true on the Si trenches used in this study. In order to test this assumption, as well as determine the crystallographic orientation of the overgrown GaN fins, TEM was performed by Haoting Shen on cross-sections of the GaN fins shown in Figure 7-4. Cross-sectional high-resolution TEM (HR-TEM) of the interface between the Si\{110\} sidewall and the GaN as well as diffraction patterns of the two regions are given in Figure 7-5.
From the diffraction patterns, it was shown that GaN on the Si\{110\} trench sidewalls is growing such that GaN(0002)//Si\{110\} as was predicted based on the work by Won \textit{et al.} This resulted in GaN growing on Si\{110\} sidewalls such that the crystal structure of the GaN was non-polar with respect to the Si(001) substrate surface. Cross-sectional bright-field (BF) TEM of the entire overgrown GaN fin is given in Figure 7-6.
Aside from the growth originating from the Si{110} sidewall, two distinct crystallographic regions were observed in the overgrown GaN. All three regions had different crystallographic orientations as indicated by the diffraction patterns included in Figure 7-6. The arrows in Figure 7-6 correspond to the GaN(0002) growth direction in each region. The crystallographic orientation of regions (b) and (c) were semi-polar with respect to the Si(001) substrate surface and appeared to block the vertical propagation of...
the desired non-polar sidewall GaN (region a). In the interest of simplicity, the terms “non-polar” and “semi-polar” in this work shall henceforth be used to reference the orientation of the GaN crystal structure with respect to the Si(001) substrate surface.

Control of the orientation of overgrown GaN is of the utmost importance to the ultimate goal of forming a single-crystalline, non-polar GaN film on Si(001). The preferential growth of GaN on Si{110} sidewalls was shown to be a viable method to form non-polar GaN (region a) with respect to the Si(001) substrate, however the additional semi-polar orientations (regions b and c) of GaN observed in Figure 7-6 acted to block the vertical propagation of non-polar sidewall GaN. Therefore the origin of the semi-polar orientations of GaN, as well as how to suppress them, must be understood. The presence of GaN islands at ridge corners shown in Figure 7-3b were likely the origins of the semi-polar regions observed in Figure 7-6. Based on this, it seemed that semi-polar GaN was originating from the corner of the Si(001) ridges. H\textsubscript{2} annealing was used to remove any residual oxide left on the surface of the wafer as well as smooth the scalloping of the Si trench sidewalls caused by the DRIE process. Si etching can occur in the presence of H\textsubscript{2} at high temperatures [2]. It was therefore possible that during the pre-growth H\textsubscript{2} anneal the Si ridge corners were being etched which resulted in the exposure of additional Si planes which were preferential for growth. If this was the case, then Ga ad-atoms diffusing from the Si(001) surface to the Si{110} sidewall may have formed nuclei at the exposed facet at the trench corners instead of diffusing all the way to the Si{110} sidewall, resulting in the semi-polar GaN regions observed in Figure 7-6. It was therefore proposed that the nucleation and growth of semi-polar GaN occurred due to the presence of another preferential plane for GaN growth at the corners of etched Si ridges.
7.3 The Origin of Non-Sidewall GaN Fins

It was hypothesized that the semi-polar orientations of GaN observed in the previous set of samples were forming at Si facets at the trench corners that were exposed due to H\(_2\) etching during the pre-growth H\(_2\) anneal. A schematic representation of this hypothesis is given in Figure 7-7.

![Figure 7-7. Schematic representation of hypothesized origin of semi-polar GaN fin growth.](image)

The proposed additional Si facets were believed to act as preferential growth planes for GaN. As GaN nucleated and grew on the expose Si facets, the vertical propagation of GaN nuclei on Si\{1\10\} sidewalls was blocked. Two different methods were developed to test this theory: increase the lateral diffusion of Ga atoms and decrease the etching of
Si trench corners. By increasing the lateral diffusion of Ga atoms more Ga atoms may overcome the exposed planes at the Si trench corners, thereby improving the degree of Ga growth on the Si\{110\} and reducing the nucleation and growth of GaN at the trench corners. If the origin of the semi-polar GaN is exposed Si planes at trench corners, it should also be possible to suppress the formation of semi-polar GaN by reducing the formation of Si facets at the trench corners. In order to do this, the length of the pre-growth H\textsubscript{2} could be reduced. The first series of studies focused on increasing the lateral diffusion of Ga ad-atoms.

7.3.1 Variation of Lateral Diffusion of Ga atoms Via Two Methods:

Two methods of increasing the lateral diffusion of surface atoms are presented here. The first method reported on focused on lowering the V/III of the precursor gas flows while the second method was to increase the temperature of the growth substrate.

7.3.1.1 Decreasing precursor V/III to improve lateral atomic diffusion

One method of increasing lateral diffusion of Ga ad-atoms is to decrease the V/III ratio of the Ga and N source precursors. Lowering the V/III ratio of Ga and N precursors allows for longer lateral atomic diffusion lengths due to the increased residence time of Ga ad-atoms on the surface before reacting with NH\textsubscript{3}. This was discussed more fully in section 6.2.2 for AlN films. A series of studies was therefore developed to grow GaN on Si(001) trenches using the same conditions as outlined in section 7.2.2 except for the NH\textsubscript{3}
flow rate, which was varied in order to test the effect of V/III on GaN fin structure. Each sample was grown for 90 minutes so as to be comparable to the previous work and variations in the observed GaN fin structure were studied. For this series of studies the NH$_3$ flow rate was varied in the range of 0.2 – 2.1 slm in order to test V/III’s over a range of 1100-12000. SEM studies were performed on the samples after growth in order to observe variations in the GaN fin structure with V/III. The results of GaN growths with varying V/III are shown via cross-sectional SEM images given in Figure 7-8.

![Figure 7-8](image.png)

Figure 7-8. Cross-sectional (top) and tilted (bottom) SEM images of GaN growth on Si trenches with varying precursor V/III ratios.

It can be seen for V/III of 5600 and 12000 the GaN fin structure is similar to that of the previous sample grown at 8000, indicating that there are multiple semi-polar orientations of GaN present at the trench corners. However a V/III of 1100 showed triangular fins that appeared to have similar faceting as the non-polar GaN sidewall growth and vertically overgrew the Si(001) ridge. Tilted SEM images showed that the top facet of the GaN fins at V/III of 5600 and 1200 were very rough due to the presence of multiple
orientations of GaN. The sample with a V/III of 1100, however, showed a single, smooth top GaN facet along the length of the trench. This top GaN fin facet at low V/IIIs was likely the (10\overline{1}2) facet based on previous studies of GaN growth originating from Si\{110\} sidewalls. These results indicated that the GaN fins grown with a lower V/III were likely a single orientation of GaN that grew from the initial GaN nucleation on Si(110) sidewalls.

Rough deposition with no clear crystallographic orientation or faceting was also observed on top of the GaN fins grown at a V/III of 1100 as indicated by the arrow in Figure 7-8. The origin of this deposition was unknown, but it was observed on top of the grown GaN fins as well as at the bottom of the Si(001) trenches and it was only present at low V/IIIs. Varying the V/III alters the chemistry of the precursor gas reactions at the substrate surface in the MOCVD system, which can result in increased lateral diffusion of adsorbed atoms on the Si surface. The V/III ratio and the precursor gas flow rates can also affect the likelihood of gas-phase reactions between source precursors. It has been shown in prior work that TMG and NH\textsubscript{3} react to form (TMG:NH\textsubscript{3})-based adducts which then decompose at the growth surface to form GaN at the surface [3]. However, by decreasing the flow rate of the NH\textsubscript{3} precursor in these studies, the residence time of the NH\textsubscript{3} molecules in the gas-phase has been increased. This increased residence time allows for increased parasitic gas-phase reactions between TMG and NH\textsubscript{3} as well as adducts in the gas-phase. Furthermore, the lower flow rates of the low V/III sample may have resulted in greater temperatures present upstream, which could have further increased the likelihood of parasitic gas-phase reactions. These reactions may result in the formation of particulates in the gas phase. Due to the non-crystallographic nature of this rough
deposition and the fact that it appeared to grow on top of as well as below GaN fins, it was hypothesized that the lower V/III was resulting in greater gas-phase reactions during growth and the products of these reactions were then depositing on the Si substrate and GaN fins during growth. Since the rough deposition only occurred at a V/III of 1100 and the range of tested V/IIIs was wide, it may be possible to reduce the presence of the rough deposition while maintaining the single orientation GaN fins by increasing the V/III slightly.

Therefore a series of further studies of the precursor V/III was performed in an attempt to reduce this parasitic GaN deposition while maintaining the single orientation GaN fin growth. An additional benefit of these studies was the ability to observe more closely the transition point from multiple orientation GaN to single orientation GaN fins as the V/III was decreased. Based on the previous results, samples were grown at varying V/III’s in a narrower range between 5600 and 1100. The growths used in this study were performed with NH₃ flow rates of 0.4 slm and 0.6 slm while all other growth conditions were held constant. The resulting V/IIIs were 2300 and 3400, respectively. This series of samples was grown several months after the previous set. Over that course of time the thermocouple in the reactor had been replaced and the base reactor temperature had shifted. After recalibrating the system growth parameters, it was determined that a baseline growth temperature of 1150°C would be required instead of the previously used 1100°C in order to get comparable results.

Tilted trench images of trench cross sections with varying V/III’s are given in Figure 7-9.
Figure 7-9. Tilted cross-sectional SEM images of GaN grown on Si trenches with varying precursor V/IIIs.

It was observed that as the V/III was changed from 5600 to 3400 the presence of multiple orientations disappeared and only single orientation GaN fins were left. At 3400, however, the facets of GaN fins were noticeably rougher than previous samples. The observed facet roughness was decreased by reducing the V/III ratio further to a value of 2300. This may have indicated that the rough facets of GaN fins at a V/III of 3400 were due to poor lateral diffusion along the Si{110} sidewall and that increasing the lateral atomic diffusion by decreasing the V/III to 2300 resulted in smoother sidewall facets.

Some nucleation on the top of the Si(001) trenches was also observed at a V/III of 2300, but it did not appear to have an effect on the GaN sidewall growth. The exact origin of this top of the trench growth is still unknown. No rough deposition, as seen previously at a V/III of 1100, was observed on either sample in this study. Based on these results, the optimal V/III for GaN growth on Si(001) trenches would appear to be between 3400 and 2300 in order to achieve single orientation GaN fins with clean faceting while preventing the deposition on the top of Si(001) trenches observed at lower V/IIIs.
The shape and faceting of GaN fins grown at lower V/III is similar to GaN initially nucleated on the Si\{110\} sidewalls of Si(001) trenches as observed previously in Figure 7-3. Based on this observation it was proposed that the lower V/III samples had single orientation GaN fins that were oriented such that GaN(0002)//Si\{110\}. Cross-sectional BF TEM was performed on the sample grown with a V/III of 2300 in order to determine that the GaN fin was a single orientation originating from the Si\{110\} sidewall as opposed to multiple orientations as observed previously in Figure 7-6. TEM results are presented in Figure 7-10.

Figure 7-10. Cross-sectional BF TEM of GaN fin on Si trench grown with a V/III of 2300.Selected area diffraction (SAD) patterns on the left correspond to regions a and b in the bright-field TEM image.
The cross-section of the GaN fin shows no grain boundary throughout the GaN fin, which indicated that the fin was a single orientation of GaN. Furthermore, diffraction patterns of the GaN fin were taken near the Si{110} sidewall and in the vertically overgrown region of the fin as shown in insets a and b. These diffraction patterns indicate that the both regions of the GaN fin are oriented such that GaN(0002)//Si{110}. Therefore the lowering of the V/III of GaN fin growth did indeed result in the suppression of semi-polar GaN orientations, resulting in a vertically overgrown non-polar GaN fin with respect to the Si(001) substrate surface. It is worth noting the presence of defects in the overgrown region of the GaN fin. The type and origin of these defects are, as of yet, unknown. However, TDs generally propagate normal to the growth direction which for these samples would be perpendicular to the Si(001) surface. Furthermore, growth of non-polar and semi-polar GaN has been reported to be susceptible to high density of stacking faults [4, 5]. It was therefore hypothesized that the defects present in the overgrown GaN were stacking faults, but further studies are required in order to accurately characterize these defects and their origin.

7.3.1.2 Increasing growth temperature to improve lateral atomic diffusion

It was hypothesized that the increased lateral diffusion caused by decreasing precursor V/III allowed Ga ad-atoms to overcome exposed planes at the Si trench corners, thus resulting in the reduction of semi-polar GaN growth. Varying the V/III also affects the surface and gas-phase chemistry during growth. Therefore in order to isolate the increased lateral atomic diffusion of surface atoms as the cause of reduction semi-
polar GaN fin orientations, we put forth a series of experiments which use another method to vary lateral atomic diffusion, namely the growth temperature. Increased growth temperature increases the surface diffusion length of Ga ad-atoms during the growth process. Two samples were grown for this series of studies with precursor gas flows of 9.4 sccm for TMG and 1.41 slm for NH₃. The resulting V/III was 8000, which previously resulted in the formation of semi-polar GaN fins. One sample was grown with a GaN growth temperature of 1150°C, which was the baseline temperature for these studies, while a second sample was grown with a GaN growth temperature of 1170°C. The GaN growth time was 70 minutes. All other growth parameters were held constant using the same conditions outlined in section 7.2.1. Increasing growth temperature will increase the lateral diffusion of surface atoms without greatly varying the chemistry of the system. Therefore by increasing the growth temperature we tested the increased lateral atomic diffusion as the source of the reduction of non-sidewall GaN orientations on Si trenches.

Tilted images of SEM cross-sections of both growths are given in Figure 7-11.
Figure 7-11. Tilted cross-sectional SEM of GaN growth on Si(001) trenches with varying growth temperatures.

Multiple orientations of GaN were observed at Si(001) trench corners for the growth at 1150°C which was similar to previous studies. For the growth at 1170°C, however, only a single orientation of GaN originating from the Si\{110\} sidewalls is present which was similar to the previous samples grown at lower V/III's. Therefore a clear reduction in semi-polar GaN orientations was observed with a 20°C increase in growth temperature. These results supported the hypothesis that the increased lateral diffusion of surface atoms resulted in the observed reduction in semi-polar GaN instead of variations in the gas-phase or surface chemistry of the system.

7.3.2. The reduction of multiple GaN fin orientations through reduced H₂ hold time

The previous studies showed evidence that increasing the lateral diffusion of Ga surface atoms resulted in the reduction of semi-polar GaN orientations at the corners of
Si(100) trenches. This was hypothesized to be due to the increased lateral diffusion allowing Ga atoms to overcome preferential Si planes at trench corners that were exposed due to H₂ etching during the pre-growth anneal. A series of studies was proposed to test the theory that semi-polar GaN was originating at exposed Si planes at trench corners. In this series of studies the pre-growth H₂ anneal time was decreased. It was hypothesized that decreasing the H₂ hold time would result in less etching of Si trench corners and therefore fewer exposed Si planes for the nucleation of semi-polar GaN.

A V/III of 8000 was used for this series of studies by controlling TMG and NH₃ flows at 9.4 sccm and 1.41 slm, respectively. This was done in order to ensure the presence of semi-polar GaN in the baseline growths. The pre-growth H₂ hold time was decreased within the range of 10 min to 2 min between growths while all other conditions were held at constant values as used in previous studies (T = 1150°C, P = 50 Torr, etc.). Trench samples were removed from the reactor after growth and SEM was used to analyze the effect of pre-growth H₂ hold time on GaN fin structure. The results are presented in Figure 7-12.
Figure 7-12. Tilted cross-sectional (a, b, c) and top-down (d, e, f) SEM images of GaN growth on Si(100) trenches with pre-growth H$_2$ anneal times of 10 (a and d), 5 (b and e), and 2 (c and f) minutes.
It was observed that for a H\textsubscript{2} hold time of 10 min multiple GaN orientations are observed, similar to previous studies, as well as some GaN nuclei on the top of the Si(001) trench. As the H\textsubscript{2} hold was decreased to 5 minutes, however, the presence of multiple GaN orientations was suppressed and single orientation GaN fins originating from the Si sidewalls were observed to vertically overgrow the Si(001) ridge. The top-down SEM image of the 5 min hold sample showed small GaN “islands” along the edge of the sidewall GaN as indicated by the arrows in Figure 7-12e. It was believed that these GaN islands were the beginning of semi-polar GaN nuclei at the trench corner. The presence of these additional GaN islands was decreased further by decreasing the H\textsubscript{2} hold time to 2 min as shown by the arrows in Figure 7-12f. It is also worth noting that the 2 min H\textsubscript{2} annealing step was still sufficient to remove the scalloping of the Si sidewall left behind by DRIE etching. These results showed that the presence of semi-polar GaN orientations on Si(001) trenches were directly related to the length of the H\textsubscript{2} hold time. This supported the hypothesis that semi-polar GaN growth initiated at Si facets at the trench corners which were exposed during the pre-growth H\textsubscript{2} anneal.

The series of studies reported on above have presented evidence linking the presence of semi-polar GaN orientations to the lateral diffusion of surface atoms and the length of the pre-growth H\textsubscript{2} hold. It was suggested based on these results that the origin of semi-polar GaN orientations was due to the exposure of additional facets at the Si trench corners due to H\textsubscript{2} etching of the Si at elevated temperatures. It was also shown that the semi-polar regions of GaN fins could be suppressed through a number of methods including: lowering precursor V/III, increasing growth temperature, and decreasing pre-growth anneal length. Vertical overgrowth of non-polar GaN films was
achieved through these methods. The overall goal of the studies presented in this chapter was, however, to demonstrate the feasibility of using this approach to achieve overgrowth of Si(001) trench structures resulting in a fully-coalesced, non-polar GaN film. Therefore, the following series of studies focused on improving the degree of lateral overgrowth of non-polar GaN fins.

7.4 2-step GaN fin growth to improve lateral trench overgrowth

To promote the lateral overgrowth of non-polar GaN fins, it was necessary to understand how GaN growth conditions affected the growth rates of fin facets. Common variables related to the growth rate of individual GaN facets are the precursor V/III, the growth temperature, and the growth pressure. Studies presented in previous sections have shown, however, that the precursor V/III and the growth temperature can result in the formation of semi-polar GaN fins which prevent the vertical propagation of non-polar sidewall growth. Evidence has also been provided, however, to indicate that the origin of semi-polar GaN growth was exposed Si facets at the trench corners. Therefore, in order to test how the above variables affected the growth rate of GaN fin facets, a two-step growth method was proposed to study the effect of V/III, growth temperature, and growth pressure on facet growth rates while suppressing the formation of semi-polar GaN. The first growth step was performed with optimized conditions to suppress the formation of semi-polar GaN and to overgrow the Si trench corners in order to prevent the formation of semi-polar GaN as the growth conditions were varied in the second growth step. The
growth rates of the GaN(0002) and GaN(000\bar{2}) facets were studied in particular in order to promote the lateral overgrowth of Si(001) trenches and ridges.

A series of optimization studies were performed to determine the optimal growth conditions for the initial growth step to obtain non-polar GaN fins which had overgrown the Si trench corners. It was determined from the optimization studies that the TMG and NH\textsubscript{3} precursor flow rates would be 9.4 sccm and 0.4 slm, respectively, resulting in a V/III of 2300. A growth temperature of 1170°C and a growth pressure of 50 Torr were used for the GaN segment. Prior to growth, a 2 minute H\textsubscript{2} clean segment was utilized. A growth time of 45 min was determined to be sufficient for the non-polar GaN fins to overgrow the Si trench corners and therefore would be used as the time for the initial growth step. The second growth step was 30 minutes and the growth temperature, growth pressure, and V/III were varied individually in order to determine the effect of each variable on facet growth rate. The growth rates were determined by measuring the distance between the Si\{110\} sidewall and the GaN(0002) and (000\bar{2}) faces for each sample in cross-sectional SEM images. The distances measured in the single-step baseline were subtracted from the distances measured for two-step samples in order to determine the amount of growth of each facet during the second growth step. The resulting value was divided by the growth time for the second step (30 min) in order to determine the growth rate. The goal was to determine which conditions were the best for promoting lateral GaN growth in order to coalesce opposing GaN fins over the surface of the Si(001) trench region. The calculated growth rates for varying samples is included in Table 7-1 and representative SEM images of trench cross-sections are given for each sample in Figure 7-13.
Table 7-1. Comparison of Facet Growth Rates with Varying GaN Growth Conditions

<table>
<thead>
<tr>
<th>Sample Information</th>
<th>Facet Growth Rates (nm/s)</th>
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<tr>
<td>Sample ID</td>
<td>Temp (°C)</td>
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<td>A</td>
<td>1170</td>
</tr>
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<td>B</td>
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<td>D</td>
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Figure 7-13. Cross-sectional SEM of GaN grown on Si(001) trenches with varying GaN growth conditions. Image letters (A-E) correspond to sample ID given in Table 7-1.

The sample ID in Table 7-1 corresponds to the letters given in Figure 7-13. All growth rates were based on the average distances measured from 5 - 10 GaN fins across the sample surface.
The first growth variable to be tested was the V/III of source gas precursors. In previous experiments it was observed that increasing the V/III during GaN growth greatly affected the GaN fin structure by promoting the formation of semi-polar GaN fins. It can be observed from Figure 7-13 that using the first GaN growth step to overgrow the Si(001) trench corners partially suppressed the formation of non-sidewall GaN even with a V/III of 8000 during the second step. There were still non-sidewall orientations of GaN present on the top of the Si(001) trench, however, as indicated by the arrow in Figure 7-13B. Despite the presence GaN growth on the top of the Si(001) ridge, it was observed that increasing the V/III from 2300 to 8000 improved the growth rate of the GaN(000$\bar{2}$) face by a factor of 2 as shown in Table 7-1. The growth rate of the GaN(0002) face, however, decreased slightly with increasing V/III. Sun et al. showed in previous studies of GaN growth through a patterned mask that the growth rate of the GaN(0002) face decreased with increasing V/III and reactor pressure, which was similar to the results obtained in these studies [6]. Little increase was observed in the growth rate of the GaN(000$\bar{2}$) face in the studies reported by Sun. This may have been due to the fact that the V/III and pressure were increased simultaneously in their studies. Based on the results presented here, it may be possible to adjust the V/III to a value between 2300 and 8000 in order to improve the GaN(000$\bar{2}$) facet growth rate while suppressing the nucleation and growth of GaN on Si(001) surfaces.

The second growth variable to be studied was temperature. The growth temperature for this study was decreased from 1170°C to 1150°C and the resulting GaN fin structures are shown in Figures 7-12A and 7-12C, respectively. A faster growth rate was observed for the GaN(000$\bar{2}$) facet at the lower growth temperature of 1150°C as
compared to 1170°C. A slight reduction in the growth rate of the GaN(0002) facet was observed as well as a significant increase in growth rate of the inclined GaN(10\overline{1}1) facet of GaN fins. This facet, which was also observed in previous work studying the growth of m-plane GaN by Ni et al., was a slow growth facet which defined the initial shape of the GaN fins [7]. Therefore, in order to form a fully coalesced GaN film with a smooth m-plane surface, the growth rate of the GaN(10\overline{1}1) facet must be increased. No GaN growth nucleation was observed on the top of the Si(001) ridges.

The final growth condition tested was the reactor pressure. Three reactor pressures were studied: 25, 50, and 100 Torr. It was observed that the GaN(000\overline{2}) facet growth rate increased with decreasing pressure. The GaN(0002) facet, however, had a maximum growth rate at a reactor pressure of 50 Torr. These results indicated that higher V/III, lower temperature, and lower pressure were necessary to promote the growth of the GaN(000\overline{2}) facet, which was necessary to overgrow the Si(001) ridges. Lower V/III and lower temperature, however, were required to improve the growth rate of the GaN(10\overline{1}1) facet, which is required to obtain a smooth m-plane GaN film. Due to the slow growth rate of the GaN(000\overline{2}) facet, however, it would be beneficial to consider narrower Si(001) ridges to promote earlier coalescence of opposing GaN fin structures.

7.5 Conclusions

The growth of GaN on Si(001) trenches with Si{110} sidewalls fabricated by DRIE was studied. Initial growths showed the capability of the DRIE structures as a method for selective growth of GaN on Si{110} sidewalls. TEM studies showed that the
sidewall GaN was non-polar with respect to the Si(001) substrate surface. Upon further growth, however, semi-polar orientations of GaN were observed which blocked the vertical propagation of non-polar GaN on the Si{110} sidewall. A series of studies of the effect of precursor V/III, growth temperature, and the length of the pre-growth H₂ anneal gave evidence that the semi-polar orientations of GaN were originating from exposed Si planes formed at the corners of Si(001) trenches due to H₂ etching of the Si during the pre-growth anneal. By increasing the lateral diffusion of Ga ad-atoms and decreasing the length of the pre-growth H₂ anneal, it was possible to suppress the formation of semi-polar GaN at Si trench corners.

A series of preliminary studies of 2-step GaN growths was also performed. The initial GaN growth was performed in order to overgrow the Si(001) trench corners to prevent the formation of semi-polar GaN during the second growth step. The temperature, pressure, and precursor V/III were varied individually during the second growth step in order to determine how these growth variables affected the growth rate of GaN facets, particularly the GaN(000\(\bar{2}\)) facet. It was determined that a lower temperature and pressure as well as an increased V/III were necessary to increase the growth rate of the GaN(000\(\bar{2}\)) plane of GaN fins. Despite the improvements in GaN(000\(\bar{2}\)) facet growth rate, none of the GaN fins coalesced over the Si(001) ridge after 90 minutes of total growth. Therefore, in order to reduce the required growth time for complete GaN overgrowth, it would be beneficial to decrease the width of the Si(001) ridge in etched substrates. Further studies are still necessary to accomplish complete GaN overgrowth of Si(001) trench structures as well as to study the quality and defect density of fully
coalesced non-polar GaN films. The studies presented here, however, have shown the viability of this method to achieve non-polar GaN on Si(001).
7.6 References:

8.1 Summary of Work

Growth of heteroepitaxial GaN films on Si substrates is desirable due to the low cost and large available wafer sizes of Si as compared to other common substrates such as sapphire and SiC. Device quality GaN growth on Si substrates is currently achieved through the use of Al-containing buffer layers and interlayers to reduce the final tensile stress of GaN films. Additionally, most GaN research has been performed on polar c-plane GaN films. Due to the spontaneous and piezoelectric polarization that can occur in c-plane GaN films, there is a desire to grow non-polar GaN as well. In this work we have presented two types of modified Si substrate for the growth of GaN.

The first method of substrate modification involved ion-implanting AlN/Si(111) substrates directly below the AlN/Si(111) interface in order to form a defective region below the AlN to mitigate stress in the GaN film during growth and cooling. In situ stress measurements showed that GaN films on ion-implanted substrates initiated growth under a reduced initial compressive stress as compared to unimplanted samples with identical AlN buffer layers. Implanted and unimplanted samples relaxed the initial compressive stress and generated little tensile stress by the end of growth. The relaxation of compressive stress and generation of tensile stress in GaN films was linked to the inclination and density of edge-type threading dislocations. The edge-type TD density of
unimplanted samples was measured to be $1.44 \times 10^{10}$ cm$^{-2}$ while the density of edge-type TDs for implanted samples was $1.24 \times 10^{10}$ cm$^{-2}$. Therefore, little reduction in TD density was observed on implanted samples. The density of channeling cracks in the GaN surface decreased with substrate implantation. TEM studies showed the presence of a defective SPEG region in the Si substrate at the implantation depth as well as a polycrystalline Si layer between the SPEG Si and the AlN buffer. Horizontal cracks were observed in the implantation induced polycrystalline layer. These cracks, as well as the lower initial compressive stress, provided evidence that the implanted region was acting to partially accommodate stresses formed in the GaN film during growth and cooling.

Ion implanted substrates were annealed prior to growth in order to recrystallize the amorphous Si region below the AlN buffer formed by implantation. A series of studies were performed in order to observe the effect of annealing conditions on the curvature of ion implanted substrates. The curvature of both unimplanted and implanted substrates increased during heating to the annealing temperature. This was commonly observed for bare Si(111) samples and was due to the thermal gradient across the substrate thickness. The presence of a pre-grown AlN buffer on the samples used in this study also affected the substrate curvature due to the CTE mismatch between AlN and Si(111). The implanted samples underwent a greater increase in curvature during heating than unimplanted samples. This was hypothesized to be due to a number of factors including: structural changes in the sample as the amorphous implanted region recrystallized, an increased temperature gradient across the substrate due to the inclusion of the amorphous region at the implantation depth, and decoupling of the AlN buffer from the Si substrate due to the implanted region. Since AlN has a greater CTE than Si,
the buffer layer would normally expand more than the Si substrate, thus acting against the positive change in curvature during heating. Therefore decoupling the AlN from the Si may have lowered this effect, resulting in a greater positive curvature change during heating.

An overall change in curvature from pre-anneal to post-anneal was also observed. The unimplanted sample returned to its original curvature while the implanted sample showed a positive overall change in curvature from pre- to post-anneal. It was hypothesized that this curvature change was due to the recrystallization of the amorphous Si region below the AlN/Si(111) interface, annealing of ion channeling damage in the AlN film, and the reorientation of AlN islands during annealing. No curvature change was observed during anneals of implanted samples ranging from 10 to 60 minutes. The overall change in curvature from pre-anneal to post-anneal did not vary with the length of high-temperature anneal segment. These results indicated that anneal lengths of 10 minutes were sufficient to completely recrystallize the implantation-induced amorphous region. Further studies showed that there was no observable difference in substrate curvature or GaN film stress based on what ambient gas was used during annealing (H$_2$ or N$_2$).

Follow up studies showed a noticeably different stress evolution during GaN growth. Preliminary studies showed a relatively large initial compressive stress in both unimplanted (~1.44 GPa) and implanted (~0.85 GPa) samples which relaxed within the first ~400nm of growth, after which little tensile stress (~0.1GPa) was formed. Later studies, however, showed a smaller initial compressive stress in GaN films which quickly relaxed within the first 100nm of growth and then transitioned to a relatively large tensile
stress (0.67 GPa) later in the growth process. The origin of this difference in film stress evolution was hypothesized to be a result of the smaller AlN island size resulting in a larger dislocation density in the GaN films. The effect of AlN buffer layer island size on stress evolution in the GaN film was investigated using an AlN buffer layer grown using a pulsed-precursor method that led to increased AlN island size as compared to standard continuous flow buffers. In situ curvature measurements showed a significantly reduced final GaN growth stress, as well as reduced initial compressive stresses, on pulsed buffers that had undergone ion implantation. Furthermore, a greater reduction in threading dislocation density with substrate implantation was observed on the pulsed buffers (63% reduction) as compared to standard buffers (16%). These results indicated that the increased lateral island size of pulsed AlN buffer layers reduced the TD density on implanted substrates. The lower observed tensile stress generation in GaN films on implanted, pulsed buffer layers was proposed to be a result of the reduced TD density and reduced initial compressive film stress present in those samples. It was also shown that the thinner AlN buffers and greater implantation depths resulted in lower TD densities, which may have been linked to the degree of AlN island reorientation.

A series of preliminary studies using a different method of Si substrate modification were also performed. The growth of GaN on etched Si(001) trenches with Si{110} sidewalls were performed to obtain non-polar GaN films with respect to the Si(001) substrate. Preliminary studies showed that GaN grew preferentially on Si{110} sidewalls such that GaN(0002)//Si{110} for short GaN growth segments (<20 min). This resulted in non-polar GaN with respect to the Si(001) substrate. As growth times were extended, however, additional orientations of GaN that were semi-polar with respect to
the Si(001) substrate were formed at the corners of Si ridges. These semi-polar GaN orientations blocked the vertical propagation of GaN that had originated at the Si trench sidewall. A series of studies showed that the presence of semi-polar GaN at Si ridge corners could be suppressed by lowering the precursor V/III, increasing the GaN growth temperature, or lowering the length of the pre-growth H₂ anneal. These results indicated that semi-polar GaN was originating from etched facets at the corners of Si ridges. A series of 2-step GaN studies also showed that the growth rate of the GaN(000\bar{2}) facet could be increased by lowering the growth temperature and pressure, or increasing the V/III. This pointed the way towards achieving a fully coalesced GaN film on Si(001) substrates.

8.2 Future Work:

Studies of ion implanted AlN/Si(111) substrates have shown the viability of this method to reduce stress in GaN films caused by lattice and CTE mismatch between GaN and Si. The effects of several different parameters have been studied including: lateral AlN island size, buffer thickness, anneal length, anneal ambient, and implantation energy/depth. It would also be worthwhile to test the effect of implantation dose on GaN growth stress. Leathersich et al. have shown that the implantation dose has a large effect on the structure of the implanted region after annealing [1]. Since it has been proposed that this implanted region is acting to partially decouple the GaN/AlN/ from the bulk Si substrate, it is likely that variations in the post-annealing structure of the film may affect the degree of stress relaxation in subsequently grown GaN films.
It was shown that GaN would grow preferentially on the Si\{110\} sidewalls of DRIE etched trenches on Si(001) substrates. Single orientation GaN fins which vertically overgrew the Si(001) ridge surface were obtained and the conditions to promote growth of the GaN(00\bar{2}) facet were discussed. A fully coalesced, non-polar GaN film was not obtained. Therefore further studies are required to obtain and study fully coalesced GaN films on Si(001) trench structures. In order to do this a two-step growth method is recommend, as reported in Chapter 7.4 with the second step utilizing the optimal growth conditions from previous studies: temperature of 1150°C, pressure of 25 Torr, and V/III \sim 5000. The width of the Si(001) ridges should also be decreased to promote earlier coalescence of GaN(00\bar{2}) planes. When a fully coalesced GaN film is obtained, X-ray should be performed in order to determine the GaN orientation. Due to the GaN originating at the Si\{110\} sidewalls, it is expected that the density of TDs should be reduced in these films as well. Therefore cross-sectional TEM of the non-polar GaN films should be performed in order to observe the dislocations in the film as well as to determine what other defects (i.e. stacking faults) might be present in the film.
8.3 References:

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